Part 4

Non-metallic materials

Ceramics

Useful structural materials

Useful functional properties (electrical, optical)

Useful thermal properties

What are Ceramics?

Named form the Greek for “burnt stuff”

Inorganic non-metallic materials

Ionic ceramics – ionic compounds of metals (Mg, Ti) and non-metals (O, N)

Covalent ceramics – single element diamond) or compound of 2 non-metals

Examples

- Traditional ceramics – clay based
- Engineering ceramics
  - Carbides
  - Nitrides
- Cement and concrete
- Minerals and rocks
  - Iron oxide
  - Chalk
  - Silica

Examples of uses

- Structural
  - Bricks, tiles, cement
- Cutting/Grinding
  - Carbides, Nitrides, Diamond
- Optical
  - Window glass, optical fibres
- Electrical
  - Capacitors, insulators, piezoelectrics
- Thermal
  - Engine components, space shuttle tiles

Properties

- Mechanical
  - Hard, brittle, hard wearing, stiff
- Thermal
  - High melting point
  - Low thermal expansion
  - Low or high thermal conductivity (diamond)
- Electrical
  - Low electrical conduction
  - High capacitance
  - Special ceramics have ionic conductivity
- Optical
  - Often transparent or coloured

Bonding

Material	Percentage Ionic Character
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Crystal Structures

- r_c – radius of cation (positive ion)
- r_a – radius of anion (negative ion)
- In ionic crystals the crystal structure depends on r_c/r_a
- Stable structures form when anions surrounding a cation are all in contact with the cation
- Large r_c/r_a lead to large coordination numbers

Coordination Numbers

Coordination number	r_c/r_a
2	<0.155
3	0.155-0.225
4	0.225-0.414
6	0.414-0.732
8	0.732-1.0
12	>1.0

Most common are coordination numbers of 4, 6, 8

Ionic Radii

Cation	Ionic radius (nm)	Anion	Ionic radius (nm)
Al^{3+}	0.053	Br^-	0.196
Ba^{2+}	0.135	Cl^-	0.181
Ca^{2+}	0.100	F^-	0.133
Fe^{2+}	0.077	I^-	0.220
Fe^{3+}	0.069	O^{2-}	0.140
Na^+	0.102	S^{2-}	0.184
Si^{4+}	0.040		
Ti^{4+}	0.061		

Common Crystal Structures

- AX type – equal numbers of cations and anions
  - Rocksalt - coordination numbers of cations and anions both 6
  - Cesium Chloride – Cl on cube edge, Cs in cube centre (not bcc)
  - Zinc Blende (ZnS) – S on FCC, Zn in tetrahedral holes – common in highly covalent materials

- A_mX_p – m $\neq 1$ or p$\neq 1$
  - Fluorite CaF_2 - $r_c/r_a = 0.8$ – coordination number 8
  - F on cube edge Ca in centre
  - Only 50% cubes occupied by Ca
  - Also UO_2

- $A_mB_nX_p$
  - Perovskite
  - $BaTiO_3$ – Ba on cell corners, Ti cell centres, O face centres

Crystal Structures from anion packing

- Ceramic crystal structures can often be considered as close-packed anion structures with cations in interstitial holes
- 2 types of hole –Tetrahedral or Octahedral (larger)
- 2 types of packing – FCC or HCP
- Examples
  - NaCl – FCC anion packing, cations in octahedral holes
  - ZnS – FCC anion packing with cations in tetrahedral holes
  - Al_2O_3 – HCP anion packing with Al in 2/3 octahedral sites

Silicates

- Si , O are two most abundant elements in earths crust – most soils, rocks and clays are silicates
- Characterised by arrangement of SiO_4^{4-} tetrahedra
- Silica – pure SiO_2 –low density and open structures, polymorphic (allotropic)
  - Quartz
  - Cristobalite
  - Tridymite
- Silicates – 1,2 or 3 tetrahedral are shared to form complex structures
  - SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_9^{8-}$

Silicates

- Simple silicates
  - Isolated tetrahedral associated with divalent cation eg Fosterite Mg_2SiO_4
  - Double tetrahedral associated with 3 divalent cations eg Akermanite $Ca_2MgSi_2O_7$

- Layered Silicates - clays
  - 2-d sheet of silicate formed by sharing 3 O ions in each tetrahedron
  - Unbonded O projects out of plane
  - 2nd plane has excess cations
  - $Al_2(Si_2O_5)(OH)_4$ - kaolinite

Carbon

- Allotropic
  - Diamond – ZnS structure
    - Extremely hard
    - Unusually high thermal conductivity
    - Optically transparent in visible and IR
  - Graphite
    - Weak interplanar bonds
    - Relatively high electrical conductivity
    - High thermal conductivity
    - Low coefficient of thermal expansion
    - Used for electrical contacts, brushes, electrodes
  - Fullerene
    - C_{60} molecule
    - Nano tubes

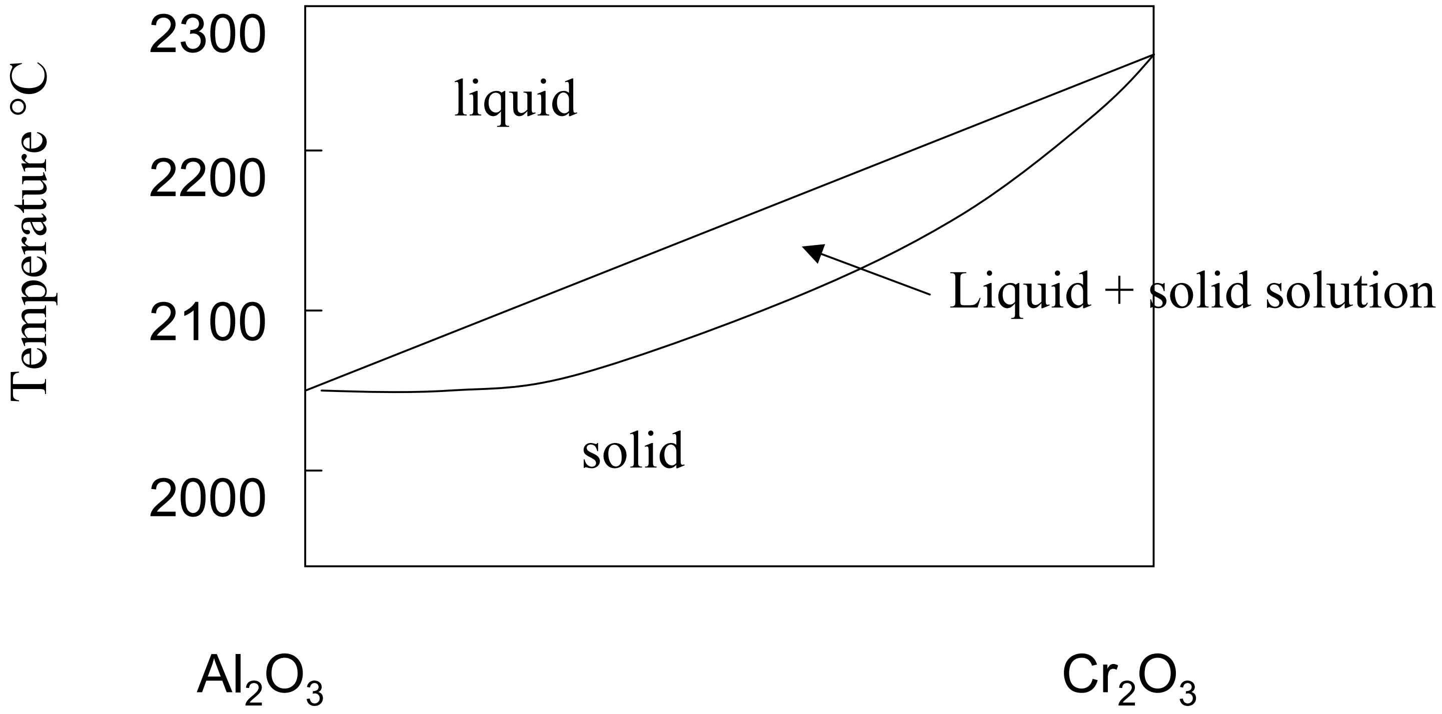
Point Defects

- Defects must be electrically neutral – defects do not occurs alone
- Frenkel Defect – ion moves from lattice site to interstitial position
- Schottky Defect – Neutral combination of anion vacancies and cation vacancies
- Charge compensation also attained by changing charge state of metal (eg Fe^{2+} to Fe^{3+} in FeO) or by trapping electrons (colour centres)

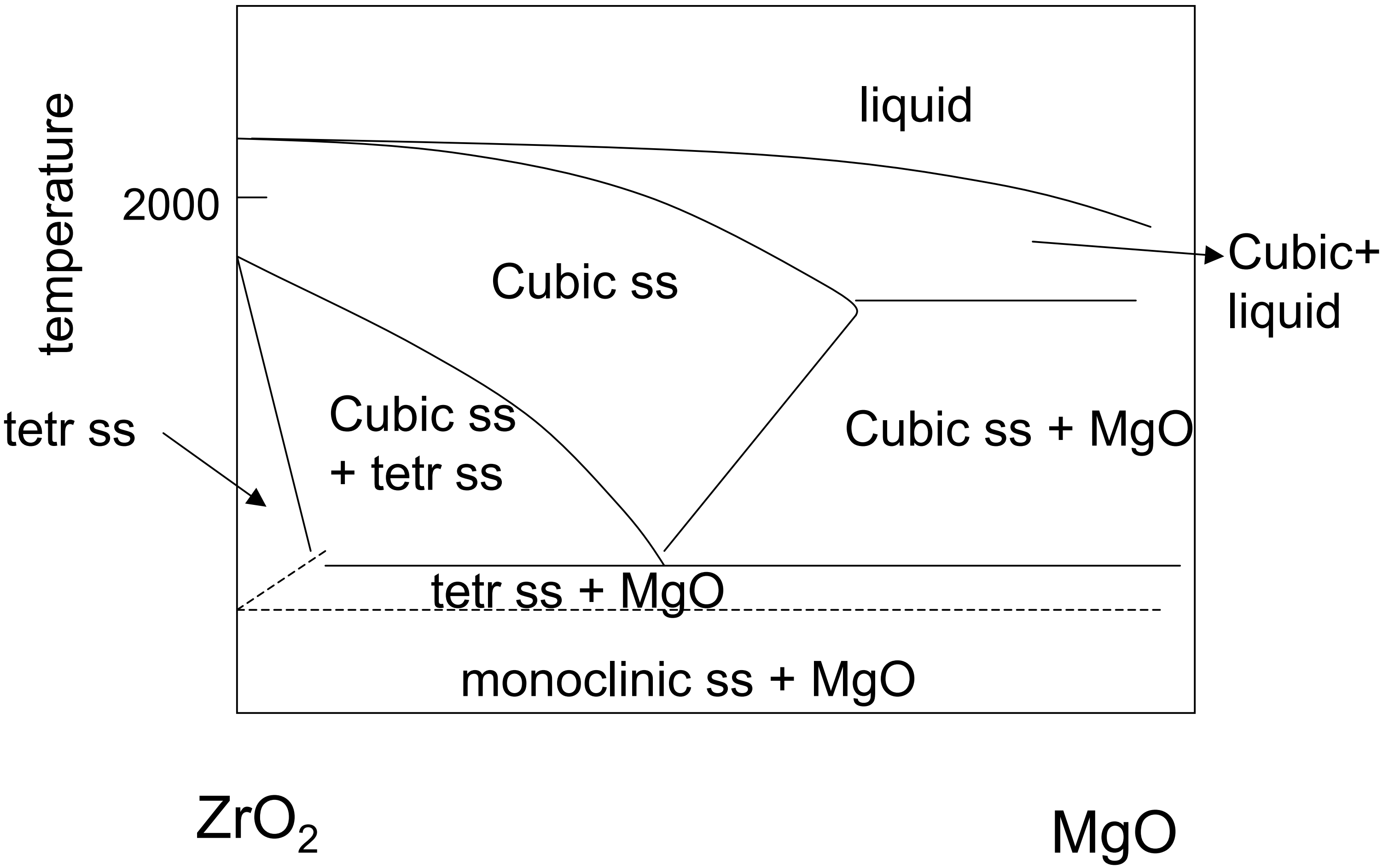
Phase diagrams

Al_2O_3 / Cr_2O_3 – Solid solution at all compositions

Isomorphic



Phase diagram



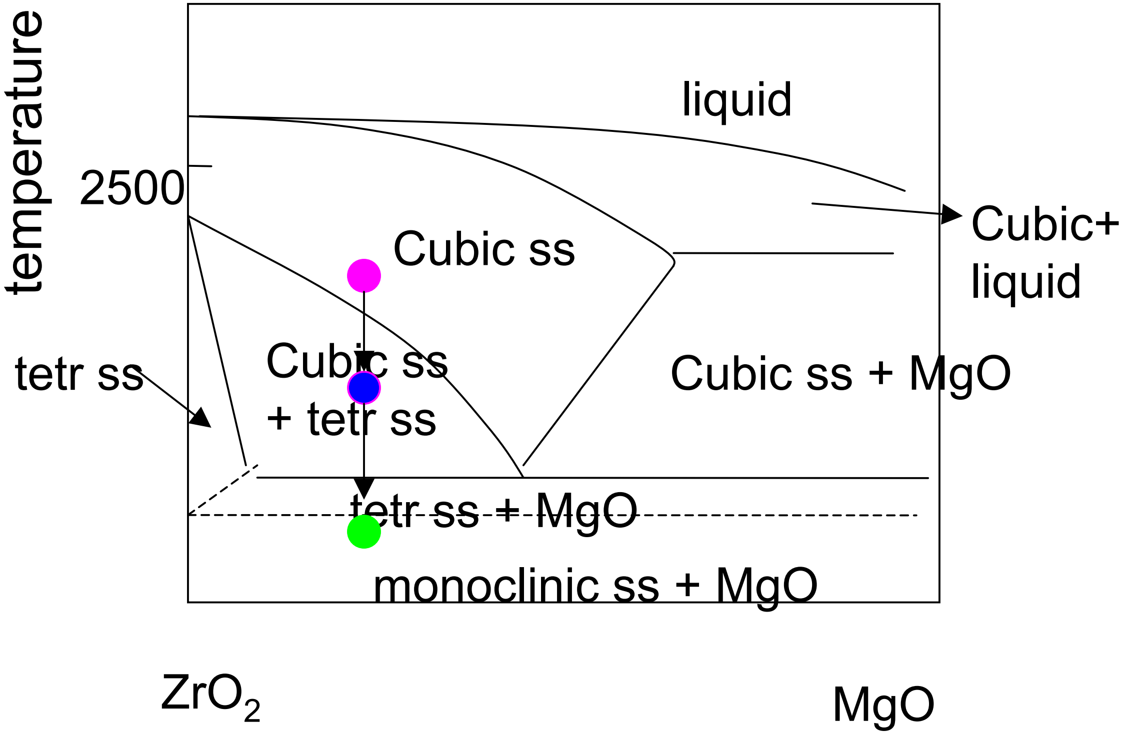
Partially Stabilised Zirconia (PSZ)

Add 10% MgO

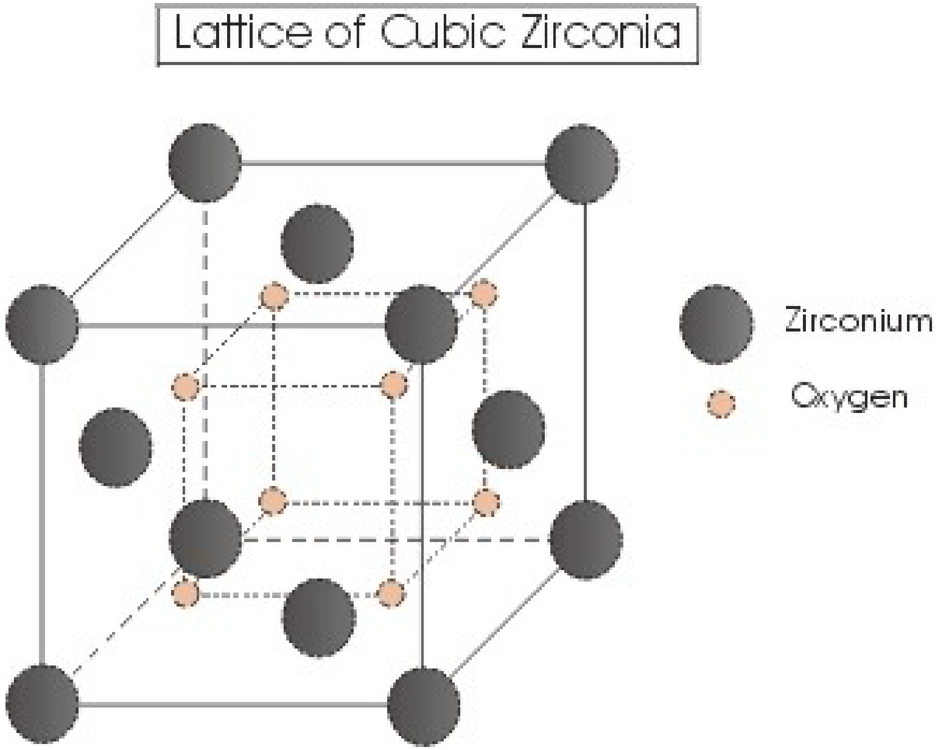
Sinter in cubic phase

Lower temperature and age to nucleate particles of t phase

Cool to room temperature – remaining C phase does not get time to transform



Cubic Zirconia – Crystal Structure



Cubic Zirconia (coloured)

Mechanical Properties

- Mechanical properties of ceramics are dominated by the microstructure
- Microcrystalline with grains separated by grain boundaries or amorphous regions
- Often formed from powders therefore microporous
- Pores may have a deleterious effect on properties

Elastic Modulus

- High elastic modulus
  - Higher than metals
  - Due to strong bonding (covalent or ionic)

- Usually have low density
  - High specific modulus (E/ρ)

- Modulus decreases with increasing porosity

$$E = E_0(1 - 1.9P + 0.9P^2)$$

Fluctuations in Mechanical Properties

- Structure insensitive properties
  - Melting point
  - Fracture toughness

- Structure sensitive properties – depends on manufacturer
  - Tensile strength
  - Thermal conductivity
  - Thermal expansion coefficient
  - Density
  - Elastic modulus

Elastic Modulus

Material	Modulus E(GPa)	Density ρ(Mg m^{-3})	E/ρ
Steels	210	7.8	27
Al alloys	70	2.7	26
Al_2O_3	390	3.9	100
SiO_2	69	2.6	27
Cement	45	2.4	19

$E = E0(1 – 1.9 P + 0.9 P^2)$ P is the porosity

Hardness

- Very high hardness due to difficult dislocation motion
  - strong bonding in covalent materials
  - Few slip systems in ionic crystals

- Engineering ceramics have been developed to be fully dense
  - Abrasives
  - Cutting tools
  - Body armour

- Examples
  - Al_2O_3
  - SiC – sealing rings and
  - Si_3N_4 – Turbine blades for helicopter engine
  - ZrO_2 – Hip joints

Hardness - Knoop

Diamond	7000
B_4C	2800
SiC	2500
WC	2100
Al_2O_3	2100
SiO_2 (Quartz)	800
SiO_2 (Glass)	550

Strength

- Strength depends on cracks and flaws in material
- Usually measure flexural strength $\sigma_{FS} \sim 1.7\ \sigma_{TS}$
- Very strong under compression $\sigma_c \sim 15\ \sigma_{TS}$
- Porosity also reduces flexural strength
  - $\sigma_{FS} = \sigma_0 \exp(-nP)$

Material	Flexural strength (MPa)
Si_3N_4	250-1000
ZrO_2	800-1500
SiC	100-820
Al_2O_3	275-900

Strong under compression

A Kung Fu expert balances on his head on a beer bottle in Jiangsu province in China yesterday. The pressure on the bottle was nearly 2million pascal – more than a steel pipe can stand

Picture:MAXPPP

Fracture

- Penalty of having hard material (large lattice resistance) is brittleness

- Strength of ceramics strongly dependent on flaws (weakest link – largest flaw)

- Fracture toughness $K_{Ic} = Y\sigma_{Ts}\sqrt{\pi a}$
  - □ $\sigma_{TS} = K_{Ic}/Y\sqrt{\pi a}$
  - – Typical toughness ~ 2 MPa $m^{1/2}$
  - – Fracture occurs when largest crack reaches a critical size

Statistics of Fracture - Weibull

- Probability of survival (P) for a material with volume (V_0) depends on applied stress σ
  - – $P(V_0) = \exp\{-(\sigma/\sigma_0)^m\}$
  - – m, σ_0 found from experiment
  - – High m – low variability (m~100 for steel)
  - – Low m – high variability (m~10 for engineering ceramics; m~5 for pottery)

- Volume dependence
  - – Increase volume to $V=nV_0$
  - – $P(V) = \exp\{-V/V_0(\sigma/\sigma_0)^m\}$

Ceramics – Production and Shaping

High melting temperatures means ceramics cannot be moulded

Brittle nature means they cannot be machined

Method of preparation has large effect on properties – porosity , flaws

Clay Products

- When mixed with water clays become plastic and highly formable
- Mixture must have correct consistency (water/clay ratio)
- Plastic mixture can be extruded or cast
- Shaped ceramic then dried slowly to control shrinkage
- Dried (green) ceramic fired between 900 and 1400 C - vitrification

Sintering

- Sintering is the process of heat treatment of powder compacts at elevated temperatures
- Sintering is carried out at T > 0.5 Tm
- Successful sintering results in a dense polycrystalline solid
- The driving force - the reduction in surface free energy – replacing solid vapour interfaces with solid sold interfaces
- The mechanism is diffusion $d\rho/dt = C/a^n \exp(-Q/kT)$

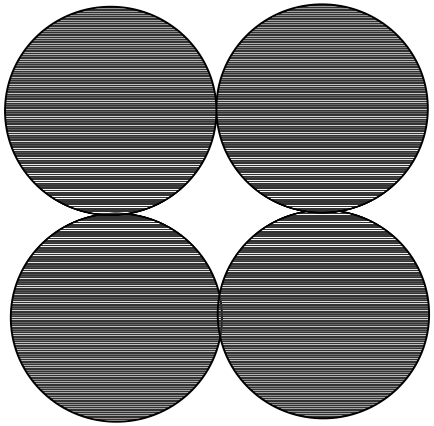
Sintering – key steps

- Powder synthesis (0.5 – 5 μm)
- Powder handling –liquid suspension followed by drying
- Green body formation – formed by compacting dry powder – can be formed in shapes or moulds
- Green body sintering – form into solid body by heating
- Final machining and assembly

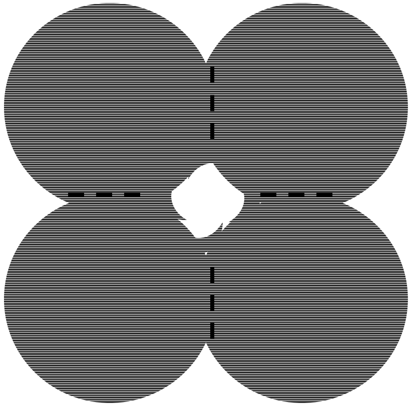
Green body sintering

- Atoms leave grain boundaries in neck between particles and diffuse into pore (thermally activated diffusion)
- Driving force is reduction in surface area and surface curvature
- Final state generally has small spherical pores at intersection of grains
- Diffusion of atoms from grain boundaries to pores leads to densification (shrinkage may be as much as 30%)
- Diffusion along pore surfaces leads to reduction in curvature

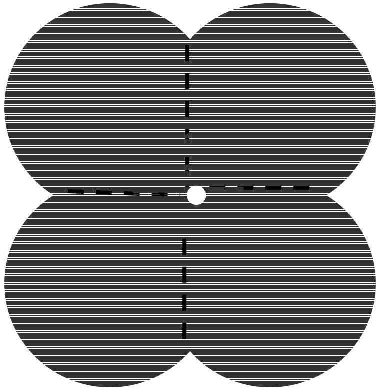
Sintering - Mechanisms



Diffusion from necks between grains into pores



Diffusion along grain boundaries to reduce curvature of pores



Final configuration

Small spherical pores

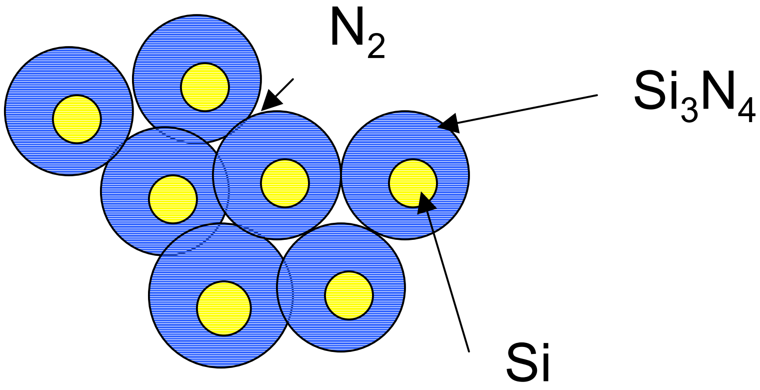
Increasing Sintering rates

- Sintering can be speeded up by
  - Hot pressing ie applying pressure (SiC)

- Adding sintering aids
  - Materials which coat particles and increase diffusion
  - Glassy or liquid additives (eg SiO_2 in Al_2O_3)

Reaction Bonding

- SiN formed by direct interaction of Si with N
- Si powder is heated in N_2 gas
  - $3\ Si + 2N_2 = Si_3N_4$
- As reaction proceeds the production and bonding occur simultaneously
- Little shrinkage because ceramic grows into pores
- Porous because of restricted access to N_2



Property changes during sintering

- Strength, elastic modulus
- Hardness
- Electrical and thermal conductivity
- Permeability to gases and liquids
- Distribution of grain size and shape
- Distribution of pore size and shape
- Chemical composition and crystal structures

Improving performance

- Reduce flaw size
  - Produce powder of controlled small size and sinter under carefully controlled conditions
- Introduce a dispersion of a second phase
  - Slows crack advancement
- Transformation toughening
  - ZrO_2
- Fibre toughening
  - Glass fibres in cement
  - Straw in mud
  - Horse-hair in plaster

Applications of high performance ceramics

Application	Property	Material
Cutting tools	Hardness, toughness	Alumina, Sialon
Bearing, liners, seals	Wear resistance	Alumina, zirconia
Agricultural machinery	Wear resistance	Aluminia, zirconia
Engine and turbine parts Burner nozzles	Heat, wear resistance	SiC, Alumina, Si_3N_4
Shielding, armour	Hardness, toughness	Alumina, Boron Carbide
High performance windows	Translucence, strength	Alumina, magnesia
Artificial bones, teeth	Wear resistance, strength	Zirconia, aluminia

Alumina (Al_2O_3)

- The most important engineering ceramic

- Gemstones (sapphire, ruby, emerald, topaz) are Al_2O_3

- Properties
  - Chemically stable
  - High electrical resistivity and dielectric constant
  - Very hard / hard wearing

- Sinter impure alumina at 1400-1550 C – additives melt and increase densification

Alumina - Uses

- Insulators – thermal and electrical
- Wear resistant linings for pipes and vessels
- Spark plugs
- Biomedical implants
- High T engineering components
- Abrasive
- Cutting tools

Microstructure

96% Al_2O_3 with MgO,CaO and SiO_2

Additives melt and aid densification

Zirconia –ZrO_2

- 3 crystal structure
  - Monoclinic at low temperature
  - Tetragonal at intermediate temperatures
  - Cubic at high temperatures

- Adding MgO stabilises cubic phase to lower temperatures (room temperature)

- Cubic tetragonal transformation is diffusional

- Tetragonal to monoclinic transformation is displacive and associated with 6% increase in volume

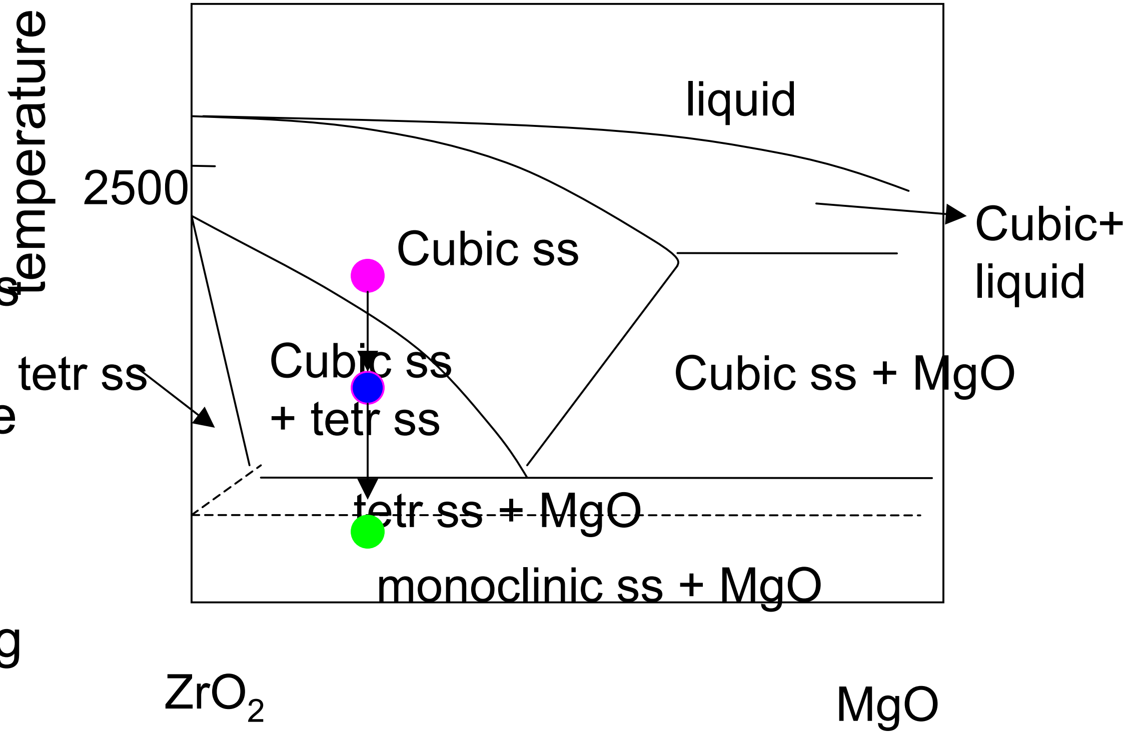
Partially Stabilised Zirconia (PSZ)

Add 10% MgO

Sinter in cubic phase

Lower temperature and age to nucleate particles of t phase – stopped before reach critical size for t-m transformation

Cool to room temperature – remaining C phase does not get time to transform



Precipitation

- PSZ microstructure analogous to precipitation hardening in metals (Duralumin)

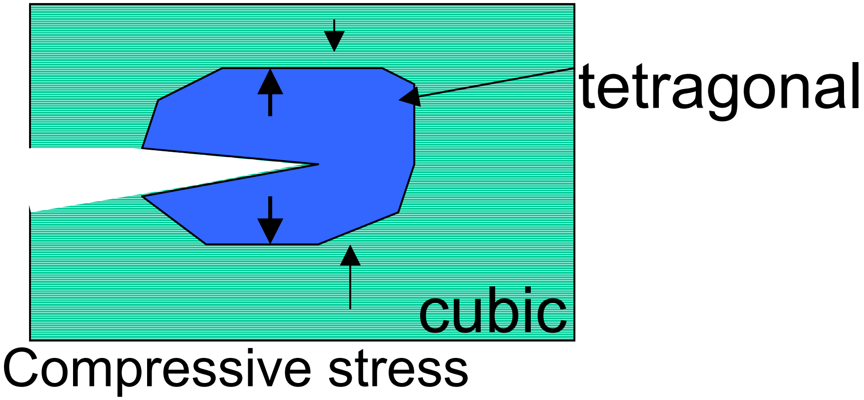
- Too much stabiliser tends to precipitate at grain boundaries and give particles too large to remain in tetragonal phase

- Too little stabiliser means firing T is too high

- Age at 1400 C for 4-5 hours
  - T particles grow as coherent spheroids along (001) cube planes
  - Below critical size of 200 nm t is retained on quenching
  - Optimum microstructure has 25%-30% t-phase

PCZ – Microstructure and Toughening

- Small tetragonal particles in cubic matrix
- Tetragonal to monoclinic transformation takes place spontaneously on expansion with a 6% volume increase
- When crack reaches the particle
  - the expansion behind the crack causes the transformation to occur
  - The expansion on transformation causes a compressive stress in front of crack



PSZ - Properties

Optimise particle size by adjusting aging time

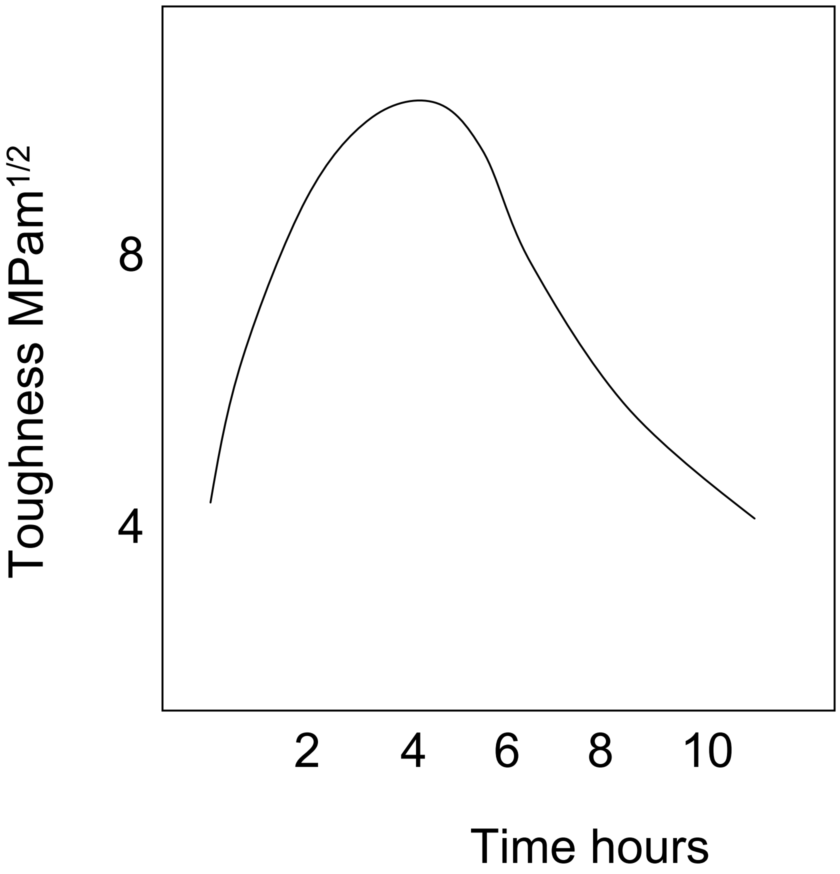
Mg stabilised PSZ

Hardness 10-14 GPa

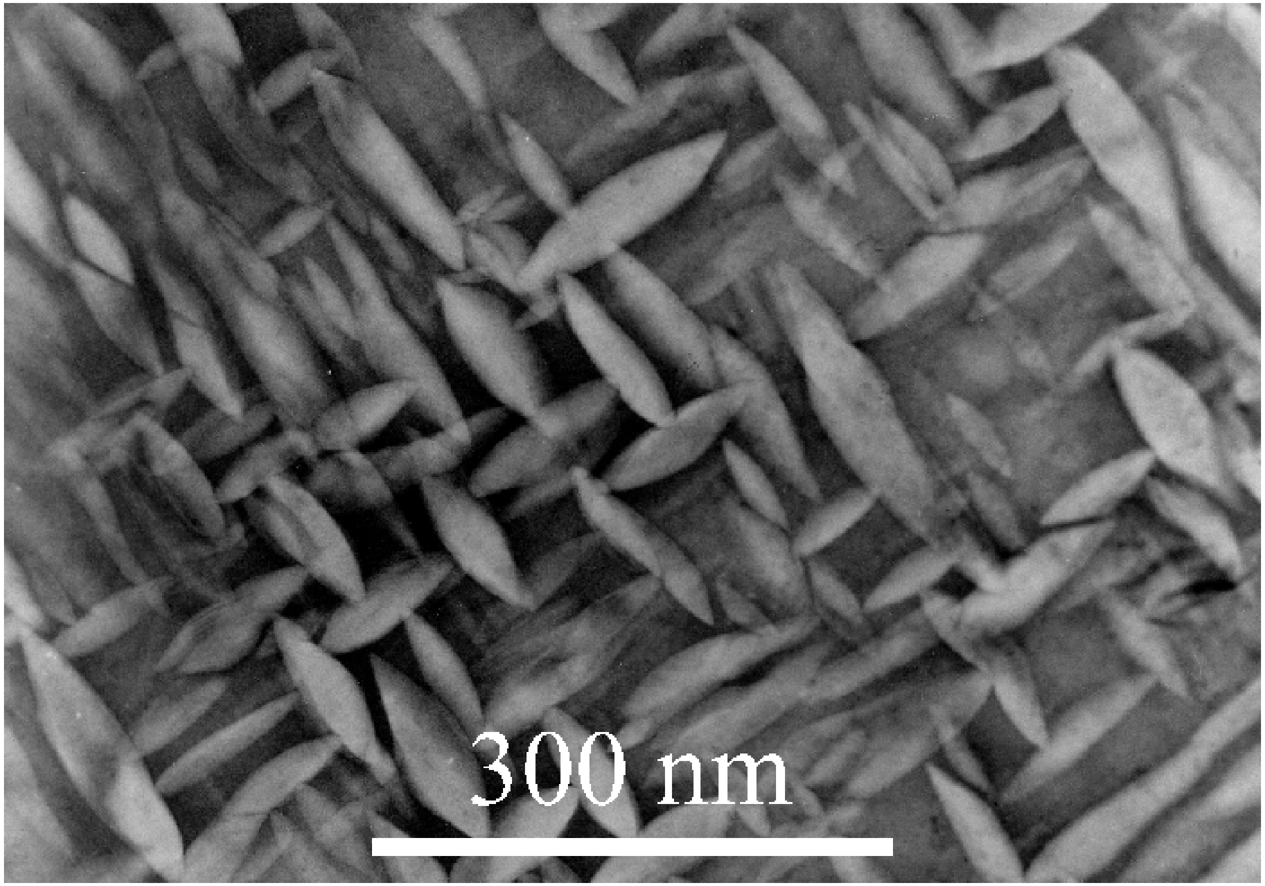
Modulus 170-210 GPa

Strength 440-720 MPa

Toughness 6-20 MPa $m^{1/2}$



PSZ Microstructure



PSZ - Uses

- Artificial hips
- Thermal barrier coatings
- Wear liners for metal components
- Bearings
- Ball valves

Silicon Carbide – SiC (Carborundum)

- Most widely used non-oxide ceramic
- Mostly used as an abrasive
- Very high melting point – difficult to sinter
- With sintering aids (B,C and Al) can sinter around 2000 C
- Structure similar to diamond and silicon

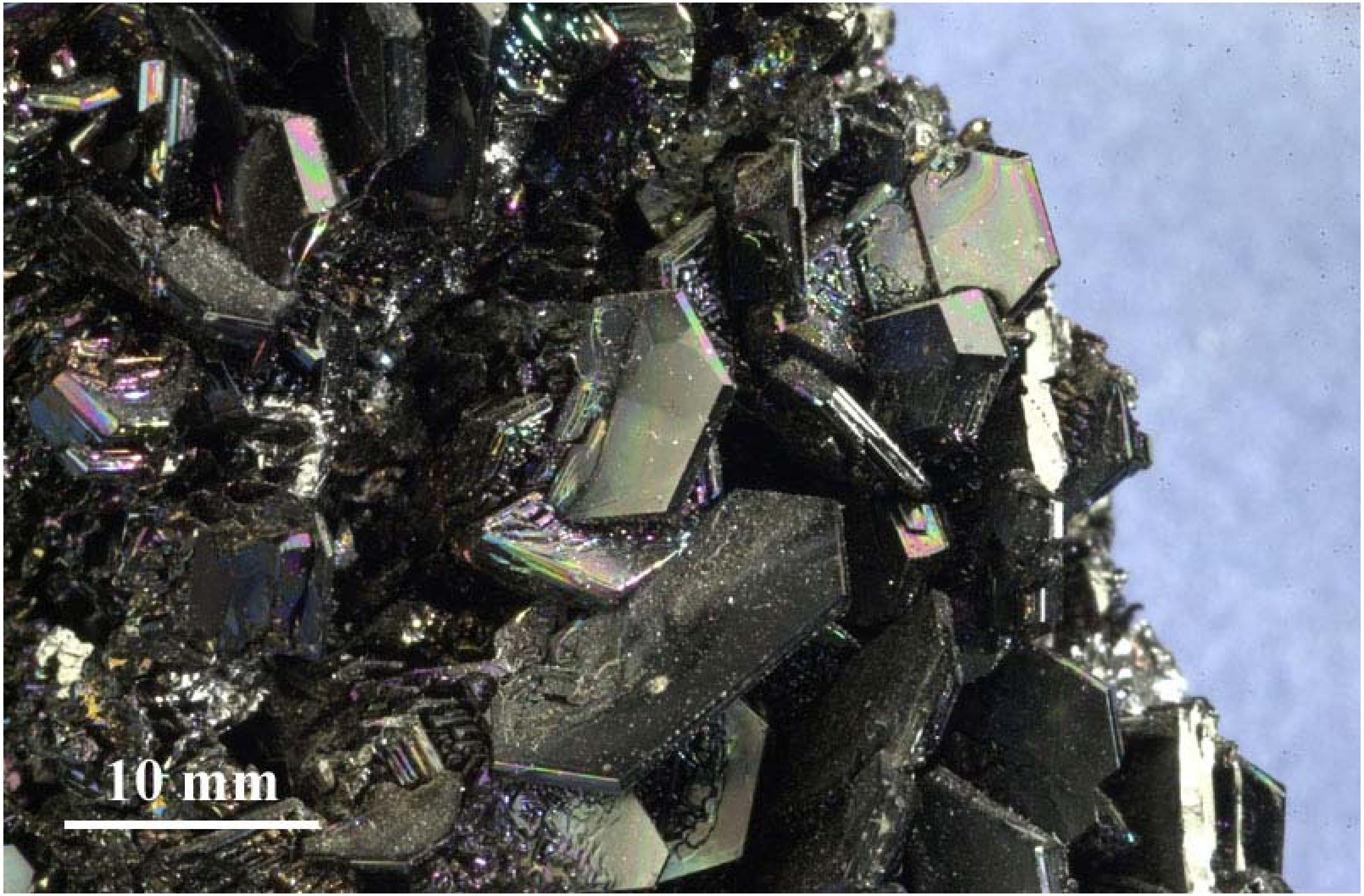
SiC - Properties

- Decomposes at 2700 C
- Hard – very good wear resistance
- Stiff – E = 300-400 GPa
- Good high temperature strength
- Oxidation and corrosion resistant
- Very good thermal shock resistance – high thermal conductivity and low thermal expansion

Reaction bonded SiC

- Mix SiC grains with C and liquid Si at 1500 C
- Si + C -> SiC – binds with original SiC
- Any remaining liquid Si fuses particles together
- Minimal shrinkage – very good dimensional control

SiC



Cements

- Form a paste when mixed with water – subsequently sets and hardens

- Principle components are tricalcium silicate ($3CaO\text{-}SiO_2$) and dicalcium silicate ($2CaO\text{-}SiO_2$)

- Setting and hardening result from complex hydration reactions
  - $2CaO\text{-}SiO_2 + xH_2O = 2CaO\text{-}SiO_2\text{-}xH_2O$

- Not drying – chemical reaction

Glasses

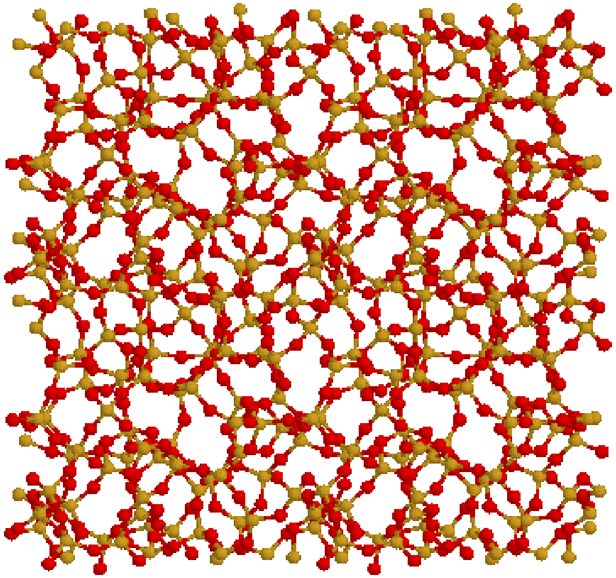
- Glasses are characterised by the absence of long range order
- When a liquid cools below freezing point it usually transforms to crystalline state (phase transformation)
- Most liquids crystallise easily on cooling – eg metals and molten salts
- Some liquids - with complex molecular structures or slow molecular transport - do not crystallise. They form a rigid disordered network
- Crystallisation depends on cooling rate (TTT curve)
- The glassy state is meta-stable

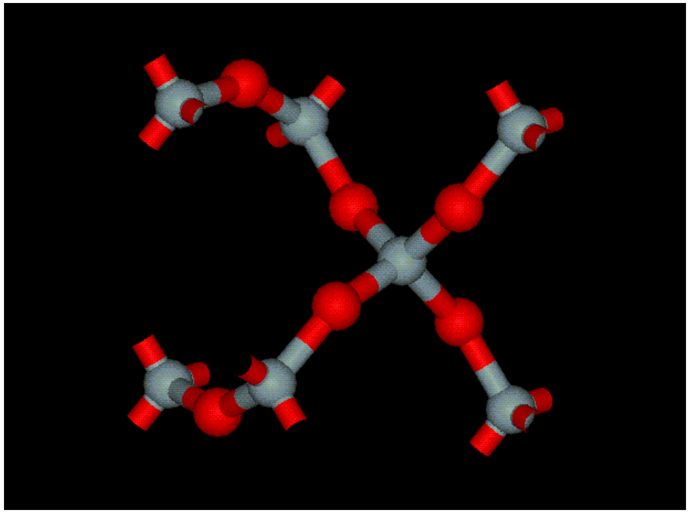
Silicate Glasses

- Most commercial glasses are bases on Silica
- SiO_4 form rigid tetrahedra
- The molten state consists of strings and rings of tetrahedra continually breaking up and reforming
- The disordered liquid cannot flow easily (highly viscous) and fluidity decreases rapidly with temperature
- As temperature is lowered the tetrahedra get stuck in a continuous random network

Structure of Silicate Glasses

- The silica (SiO_2) tetrahedral are linked together by corner sharing O atoms
- 4,5,6,7 membered rings (cf quartz with only 6 membered rings)
- Structure resembles that of a frozen liquid

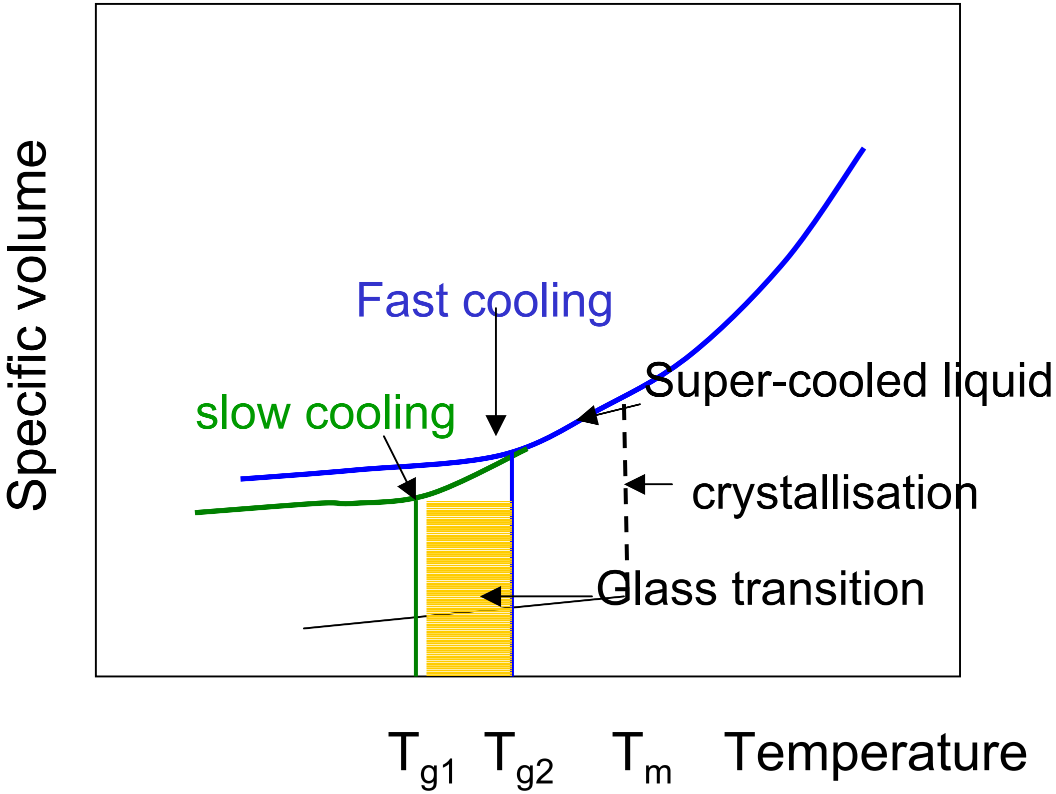




Properties of Silicate glasses

- Optically transparent
  - Large band gap
- Chemically inert
  - May be attacked by HF and strong alkalis
- Poor conductor of electricity
  - Large band gap
- Low thermal conductivity
- Hard and brittle
  - No slip planes
  - Cannot define a dislocation

The Glass transition



Crystallisation and melting occur at a well-defined temperature

The glass transition temperature depends on the rate of cooling.

Slow cooling gives tetrahedra more time to reorganise

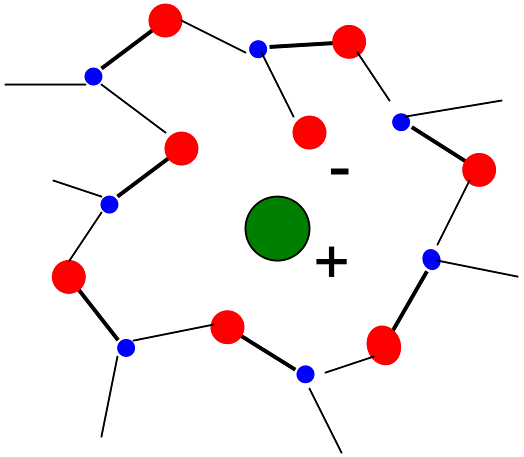
There is no sudden volume change at T_g but there is a change in slope

Viscosity of Glass

- Viscosity increases continuously on cooling
  - Melting point (η~ 10 Pa s) – temperature at which glass is fluid enough to be considered a liquid
  - Working point (η~ 10^3 Pa s) – glass is easily formed
  - Softening point (η~ 4×10^6 Pa s) – glass may be handled without causing significant distortion
  - Annealing point (η~ 10^{12} Pa s) – stress removed by rapid diffusion
  - Glass transition temperature – discontinuity in gradient of density/temperature curve (depends on cooling rate)
  - Strain point (η~ 10^{13} Pa s) – below this point fracture will occur before plastic deformation

Network Modifiers

- The properties of glass are controlled by the addition of network modifiers (metal oxides)
  - Eg Na_2O, K_2O, Li_2O, CaO, MgO, PbO
- The positive ions of the network modifiers interrupt the network by bonding to O atoms
- Network modifiers reduce the viscosity and enable working at lower temperatures



Types of Glass

Type of Glass	% Composition SiO_2	Na_2O	CaO	MgO	B_2O_3	Uses
Soda-lime	72	14	9	4	0	Window glass
Silica glass	99.5	0	0	0	0	High T applications low coefficient of expansion
Borosilicate	81	4	1	0	13	Resistant to heat and chemicals

Glass Forming

- Glass is produced by heating the raw materials above melting point
- For optical transparency must be homogenous and pore free
- Forming methods
  - Pressing – thick walled pieces
  - Blowing – bottles, jars
  - Drawing – fibres, rods, tubes, sheets and plates

Heat Treatment

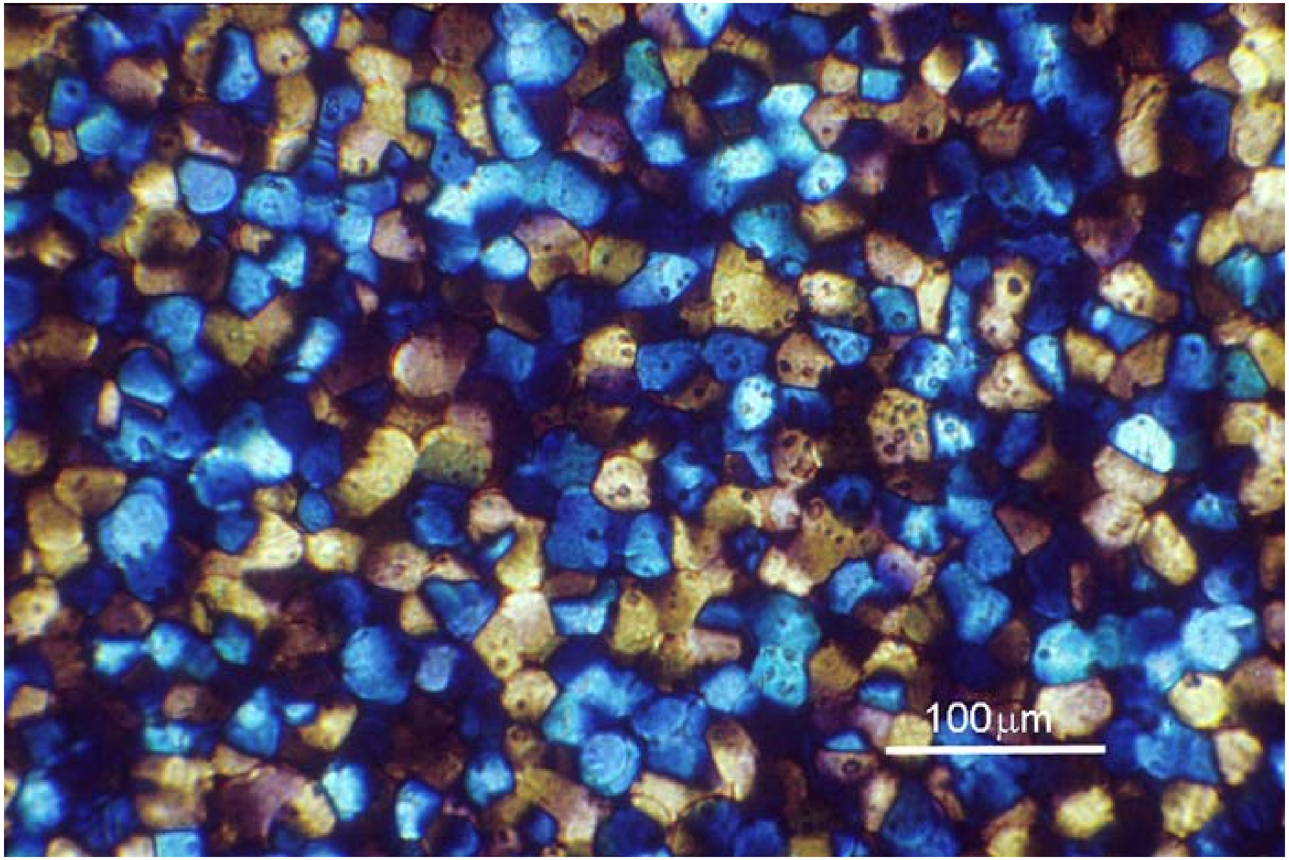
- Annealing
  - Heat to annealing point and cool slowly
  - Reduces internal stresses introduced by differential cooling

- Tempering
  - Heat to a temperature above glass transition temperature but below softening point
  - Cool to room T with a jet of air
  - Surface becomes rigid while interior still plastic
  - Interior cools and contracts
  - Introduces compressive stresses to surface

Devitrification – Glass ceramics

- Inorganic glasses can be made to crystallise by high temperature heat treatment
- Transformation to microcrystalline state by introducing a nucleating agent (TiO_2)
- Very fine grain microcrystalline material results (glass ceramic)
  - Very high impact strength, hardness and thermal shock resistance
  - Used for oven ware and cooker hobs

Li_2O-Al_2O_3-SiO_2 Glass Ceramic



Ceramics - Summary

- Traditional ceramics – clays, glasses
  - Al_2O_3, SiO_2
  - Artware, tableware, construction, refractory uses
- High performance ceramics
  - Al_2O_3, SiC, Si_3N_4, ZrO_2
  - Cutting tools, bearings, medical implants, engine and turbine parts
- Cements and concrete
  - $CaO + SiO_2 + Al_2O_3$
  - General construction

Polymers

Natural polymers have been used for centuries

Wood, Rubber, leather, Silk

Materials science has been revolutionized by synthetic polymers

Plastics, nylon, PTFE, Perspex

What are polymers?

- Polymers are made up of large covalently bonded molecules

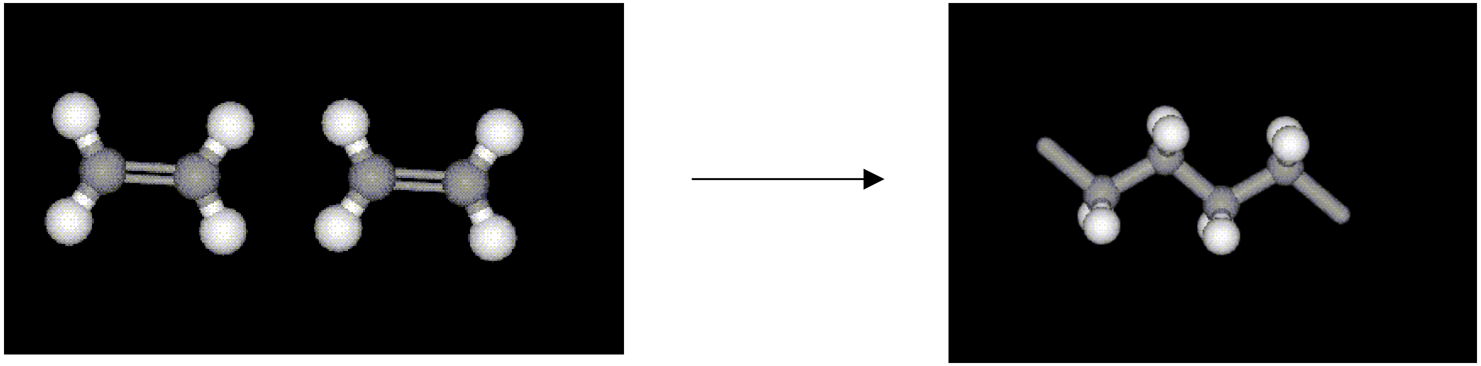
- The large molecules are held together by weak (secondary) van der Waals or hydrogen bonds

- The weak bonds are close to melting point at room temperature - creep is significant

- Elastic properties vary enormously depending on molecular structure

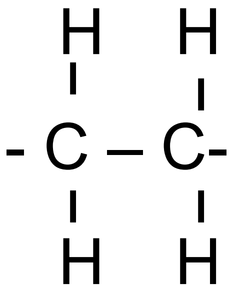
How are polymers made?

- Polymers are made from small organic molecules such as ethylene (C_2H_4) or acetylene (C_2H_2)
- The process begins with an initiator or catalyst breaking the double bond and attaching the molecule
- The number of active bonds in the molecule determines the structure of the polymer
  - Double bonds lead to linear chains
  - Triple bonds lead to branched chains



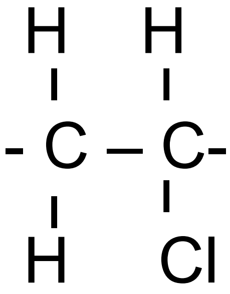
Examples

Polyethylene (PE)



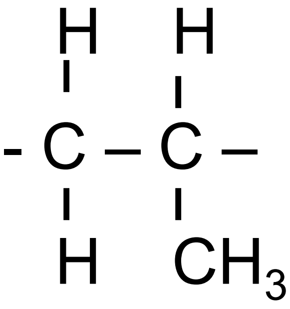
$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

Polyvinyl chloride (PVC)



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$$

Polypropylene

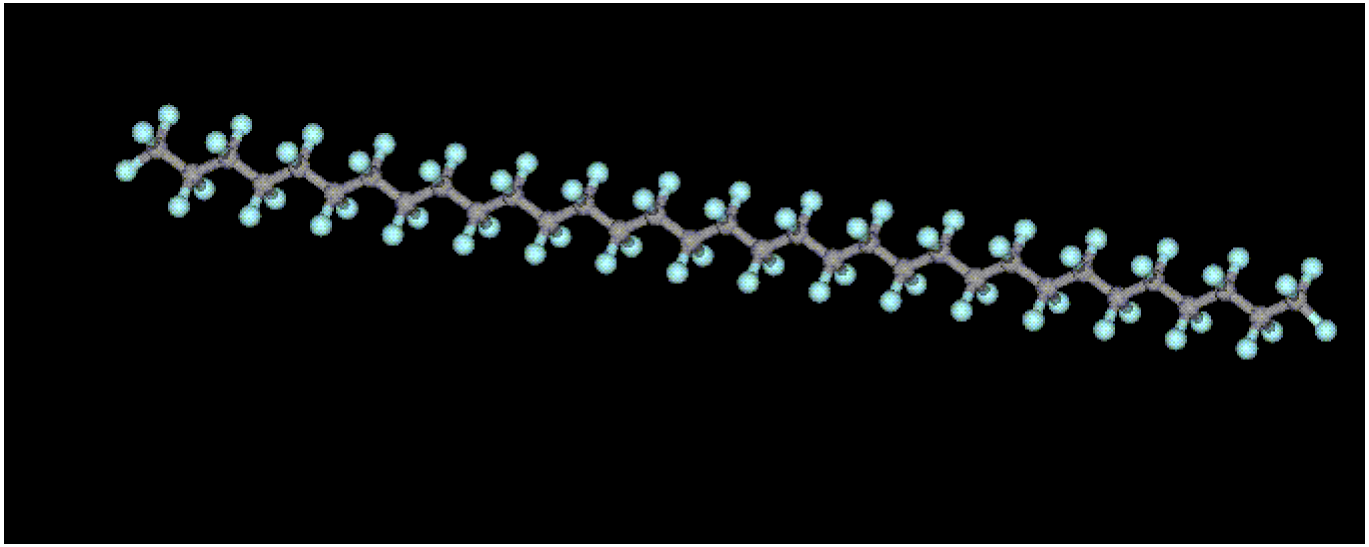


$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$$

Polymers - Example

PTFE (polytetrafluoroethylene) Teflon

Non stick frying pans, bearings, seals



Properties Depend on:

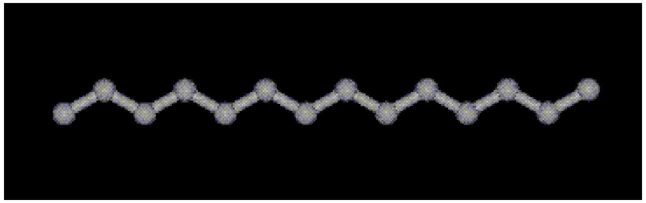
- Chemistry
  - Size of side groups
  - Reactivity
  - bonding
- Molecular weight
  - Length of molecules
- Molecular structure
  - Branching
  - Crosslinking

Molecular Weight

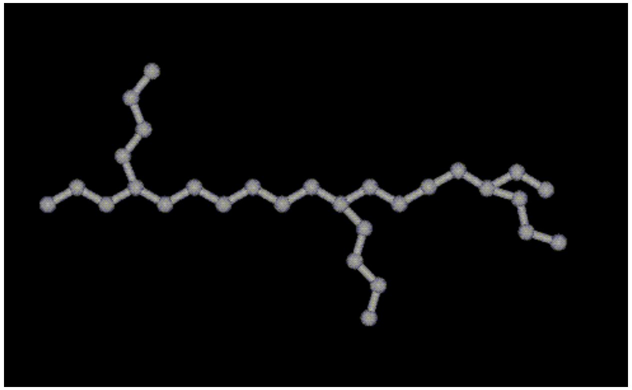
- Not all chains grow to the same length
- Average molecular weight determined by measurement of physical properties
- Number average molecular weight
  - $M_n = \Sigma x_i M_i$
- Weight average molecular weight
  - $M_w = \Sigma w_i M_i$

Properties of Polymer Molecules

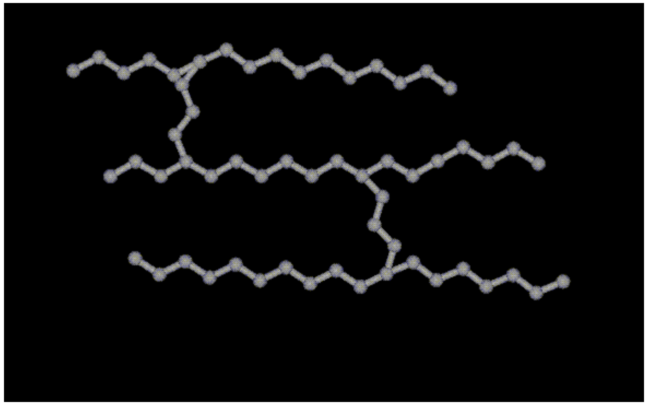
- Molecular Shape
  - Linear – Molecules rotate freely to form bends and twists



  - Branched – packing efficiency reduced



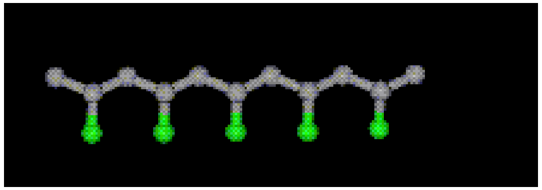
  - Cross-linked – chains linked by side-branches
  - Network – 3-d network of monomers



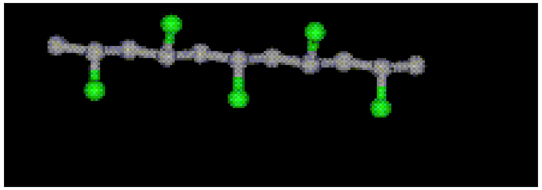
Properties of chains

Tacticity – position of side-groups on chain

- Isotactic
  - All sidegroups on same side of chain
  - High crystallinity and high density



- Syndiotactic
  - Sidegroups on alternating side of chain



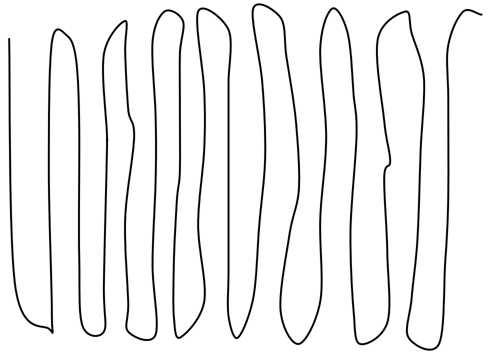
- Atactic
  - Sidegroups randomly placed on chain

Co-polymers

- Copolymers are polymers with more than one type of basic unit
  - Random copolymer
    - The units are distributed randomly along chain
  - Alternating copolymer
    - The basic units alternate along chain
  - Block copolymer
    - The basic units are positioned in blocks of the same type along chain
  - Graft
    - Homopolymer side branches on a main chain of a second type of homopolymer

Crystallinity

- Crystalline
  - Long chain polymers with few cross links can fold into regular ordered arrays



- Semi-crystalline
  - Polymers are often semi-crystalline with region with crystalline regions separated by regions of disorder
- Amorphous
  - Rapidly cooled polymers and highly branched polymers do not crystallise but remain as a tangled bundle of molecules
- Degree of crystallinity can be determined from density
  - %cryst = $\rho_c(\rho_s-\rho_a)/\rho_s(\rho_c-\rho_a)$ x100

Crystallinity

- Degree of crystallinity depends on
  - Chemistry
    - Hydrogen bonding
  - Chain structure
    - Size of side groups
    - Number of branches
    - Degree of cross-linking
    - Number of double bonds
  - Molecular weight
  - Tacticity

Types of Polymer

- Thermoplastic (PE, PP, PS, PVC, nylon)
  - Chains not cross-linked (may be branched)
  - Amorphous or partially crystalline
  - No sharp melting point- viscosity falls gradually with decreasing T (cf glass)

- Thermosets or resins (Epoxy, polyester)
  - 2 components mixed which react and harden
  - Heavily cross-linked (network polymers)

- Elastomers (natural or synthetic rubber)
  - Almost linear polymers with occasional cross-links
  - Cross-links provide shape-memory

Polymers – Properties and Processing

Polymers can be designed to obtain a vast range of properties by varying

the chemistry (basic units)

the molecular structure

General

- Secondary (van der Waals) bonds melt at around room temperature

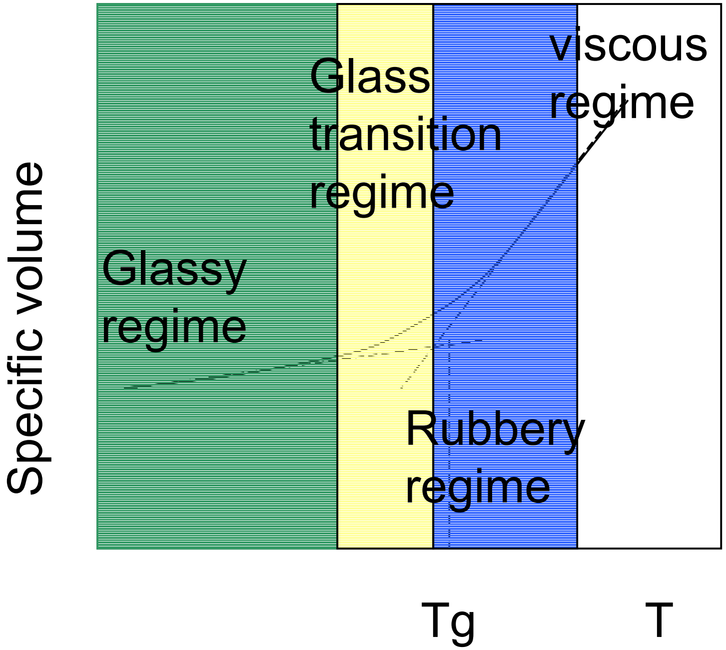
- Mechanical properties depend on the degree of cross-linking

Typical glass transition temperatures

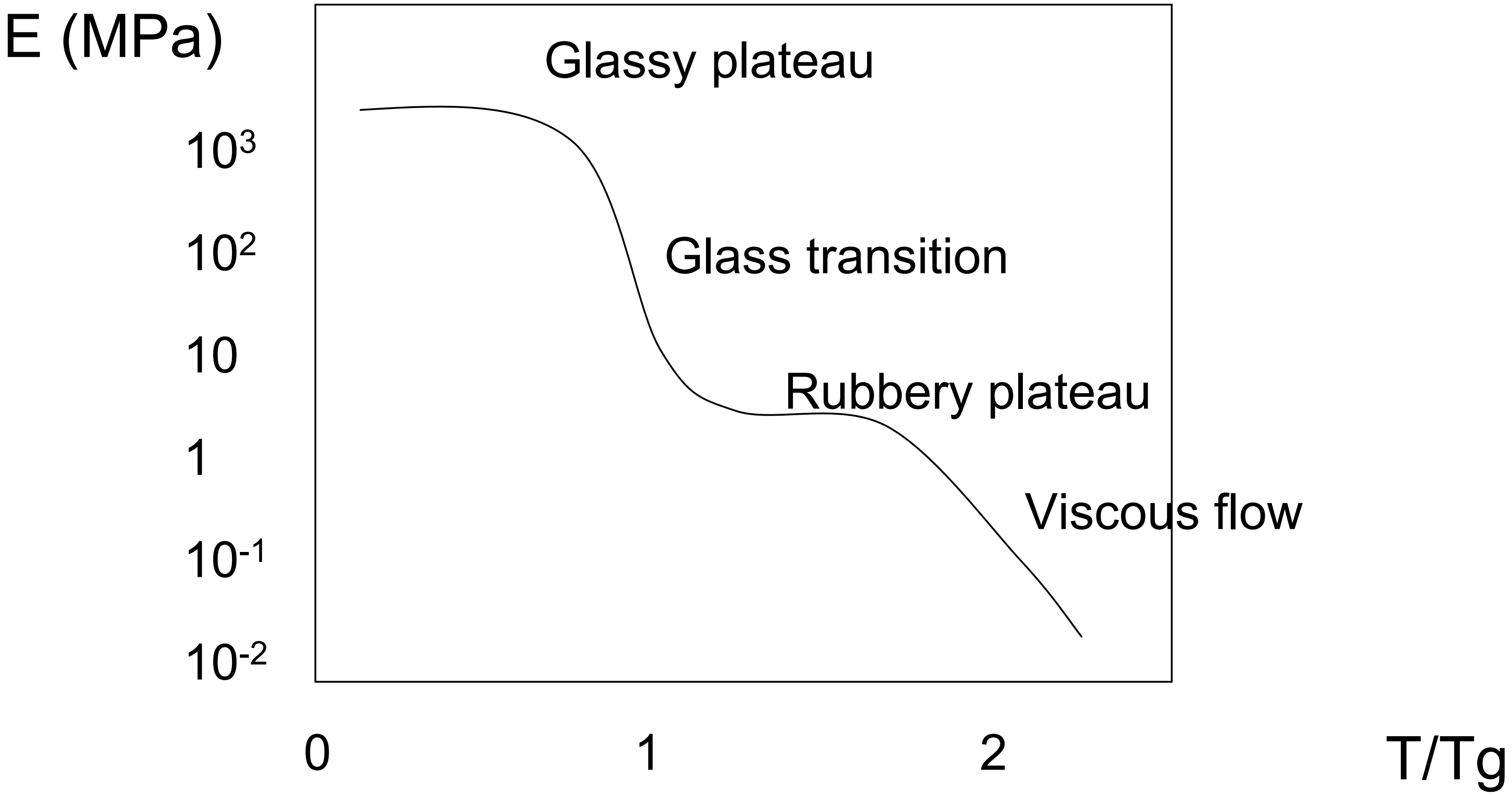
	Glass transition temperature	Softening temperature
PE (low density)	270 K	355 K
PE (high density)	300 K	390 K
PP	253 K	310 K
PVC	350 K	370 K
Nylon	340 K	400 K

Mechanical properties

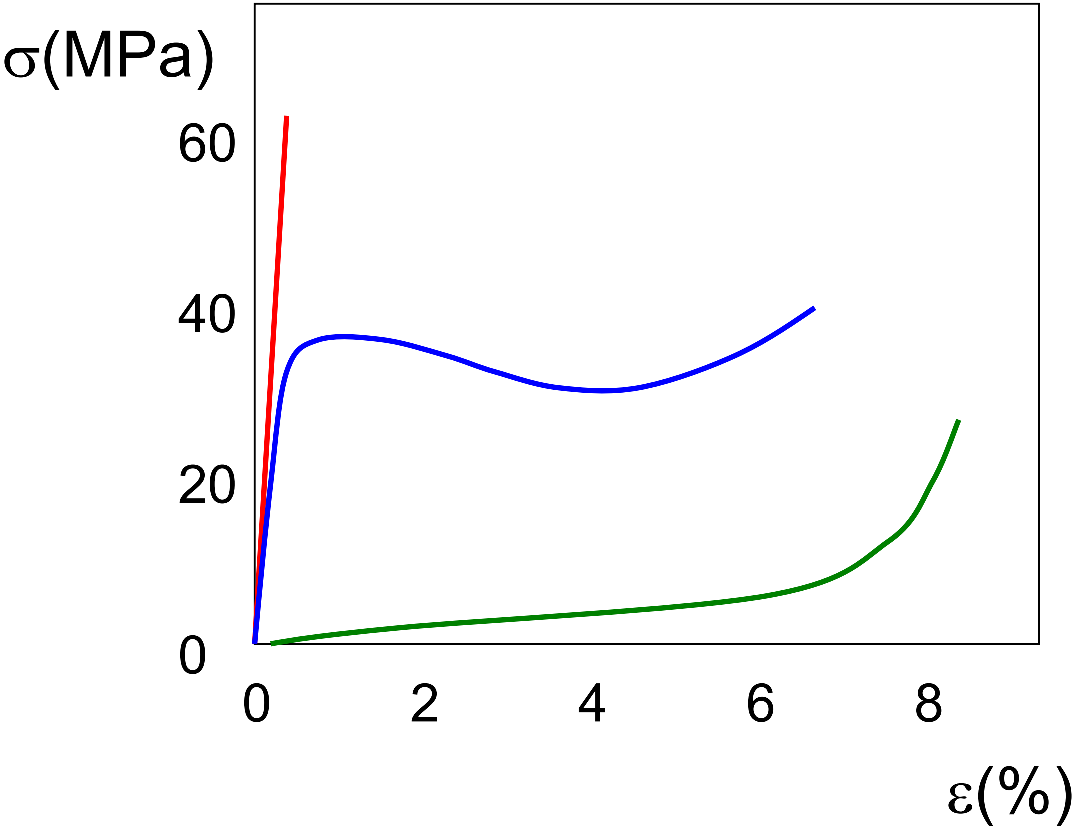
- The mechanical properties are temperature dependent
- 4 main temperature regimes
  - Glassy regime
    - Up to 0.8 Tg
  - Glass transition regime
    - 0.8 < T < Tg
  - Rubbery regime
    - Tg < T < 1.4 Tg
  - Viscous flow
    - T>1.4 Tg



Elastic Modulus (constant loading time)



Stress- Strain Curves



Elastic

Plastic

Elastomeric

Deformation depends on -

temperature

strain rate

degree of cross-linking

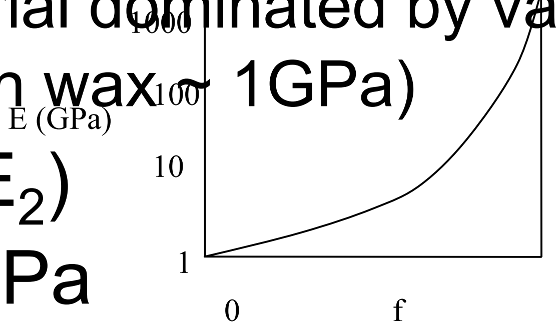
crystallinity

Elastic Deformation/ Glassy regime

- Low temperature (<0.8Tg) and high strain rate
- Elongation of molecules from their stable configuration
- Some displacement of adjacent molecules – resisted by relatively weak van der Waals interactions

Elastic Modulus

- Polymers have 2 types of bond
  - Intermolecular covalent bonds – strong and stiff
  - Intramolecular van der Waals forces – weak
- Strain is the weighted sum from the 2 types of bond
  - For fraction f of covalent bonds: $\varepsilon = f\,\sigma/E_1 + (1-f)\,\sigma/E_2$
  - E_1 is modulus of a totally covalent material (eg diamond ~1000 GPa)
  - E_2 is the modulus of a material dominated by van der Waals forces (eg paraffin wax ~ 1GPa)
  - $Ec = \sigma/\varepsilon = 1/(f/E_1+(1-f)/E_2)$
  - $E = (f/1000 + (1 – f))^{-1}$ GPa



- E is temperature dependent
  - Local arrangement of bonds

Glass Transition Regime

- $0.8T_g < T < T_g$
- Plastic deformation
- Viscoelastic properties
- Elastic modulus varies rapidly with temperaure

Plastic deformation – amorphous

- At higher temperatures the Van der Waals bonds weaken
- Moderate stresses cause molecules to slide past each other
- On removal of stress the molecules relax to new (elongated) conformation

Plastic deformation – semi-crystalline

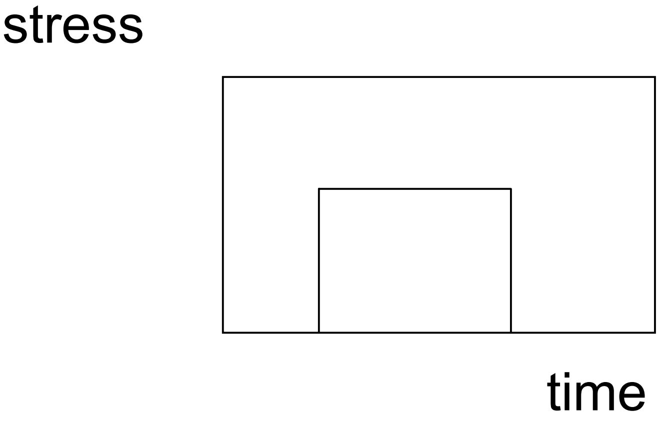
- Crystalline regions separated by amorphous regions
- On application of stress amorphous regions elongate – crystalline regions remain unchanged
- Further stress causes crystalline regions to deform to align molecules with tensile stress
- Crystalline regions separate into blocks
- Final structure – oriented crystalline blocks and elongated amorphous regions

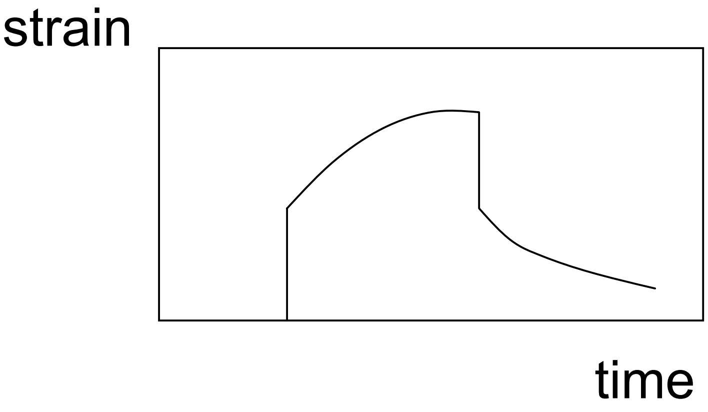
Macroscopic Deformation – semi-crystalline

- Initial uniform elongation
- Small neck forms
- Within neck chains become oriented – localised strengthening
- Neck region propagates
- Contrast to metals

Glass Transition Regime (viscoelastic)

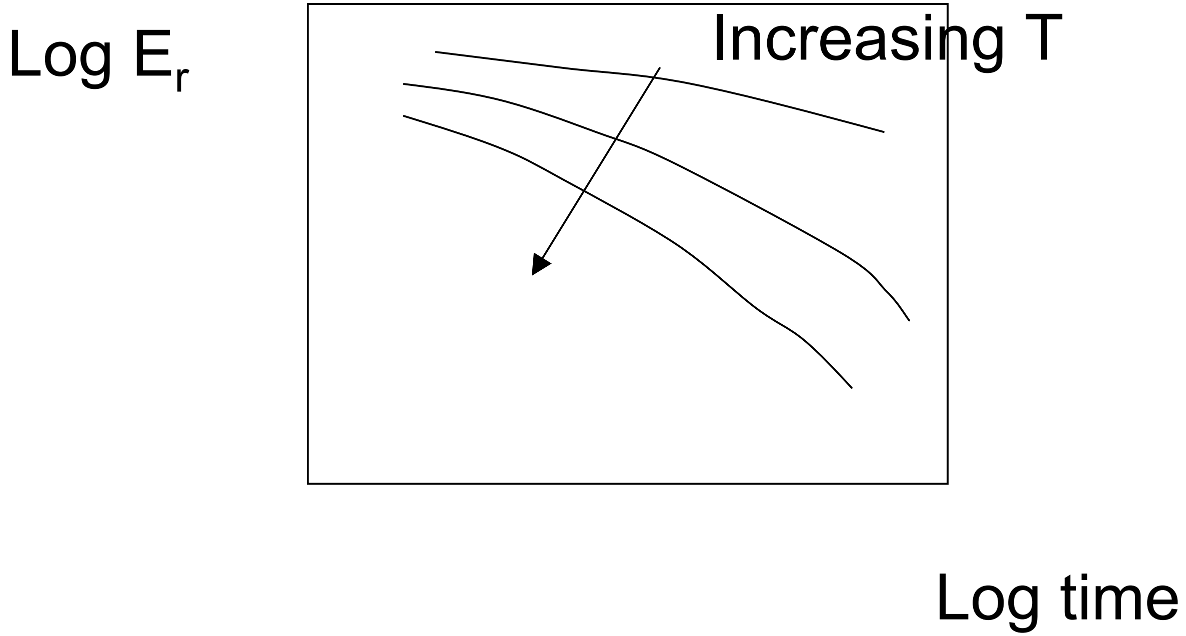
- As temperature increases van der Waals bonds melt
- Chains slip relative to each other
- Chains can be thought of as being in a tube
- Part of crystal still elastic
- After release of stress the elastic regions pull crystal back to original shape but this takes time





Relaxation Modulus

- Apply constant strain ε_0
- Measure time dependent stress required to maintain strain
- $E_r(t) = \sigma(t)/\varepsilon_0$
- Temperature dependent (cf creep)



Viscoelastic Creep

- Time dependent deformation at constant stress
- Significant at room temperature and for low stress
- Time-dependent relaxation (creep) modulus
  - $E_r(t) = \sigma_0/\varepsilon(t)$
- Susceptibility to creep decreases as degree of crystallinity increases

Rubbery regime (Tg<T<1.4Tg)

- Very long chain polymers pass through a rubbery state
- Molecules become entangled and knotted
- On loading molecules slide past each other
- On unloading the entanglement pulls material back to original shape
- Low density of cross-links has the same effect (elastomers, rubber)

Characteristics of elastomers

- The elastomeric (rubbery) state occurs above Tg

- Highly amorphous with high density of twists and coils

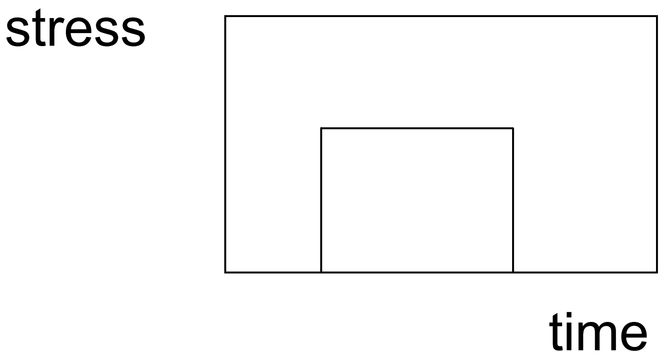
- Flexible (freely rotating) chains respond easily to applied stress

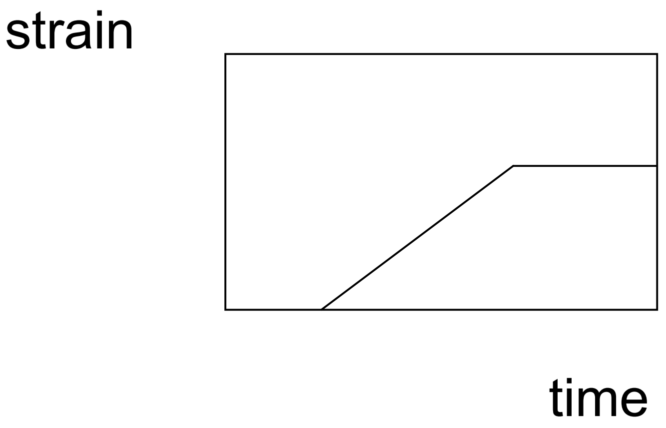
- Entanglements and cross-links inhibit plastic deformation

- Driving force is increase in entropy (disorder)

Viscous Flow (T>1.4Tg)

- When the temperature is greater than 1.4Tg the secondary bonds melt completely and entanglement points slip
- The polymer becomes a viscous liquid with a temperature dependent viscosity
- Cross-linked polymers do not melt – they decompose at high temperatures





Factors influencing mechanical properties

- Molecular weight
  - Tensile strength increases
  - Modulus less affected
- Degree of crystallinity
  - Secondary bonding increased in crystalline regions
  - PE modulus increases by factor of 10 on increasing crystallinity from 0.3 to 0.6
  - Enhances strength and brittleness
- Pre-deformation by drawing (fibres)
  - Orient molecules along one direction
  - Increase strength by factor of 2-5
  - Increase modulus by factor of 3

Factors influencing Tg and Tm

- Chain stiffness
  - Size and type of side groups

- Molecular weight
  - Higher molecular weight give higher Tg and Tm

- Degree of branching
  - Branching increases disorder and decreases packing – lowers Tg
  - HDPE has higher Tg than LDPE

- Degree of cross-linking

Strength

- Below 0.75 T_g polymers are brittle – flaws or cracks may lead to failure
- Cold drawing – in the plastic regime pulling the polymer results in the chains unfolding and drawing out of the amorphous tangle
  - Used to strengthen fibres
- Crazing occurs when local regions of drawn material are linked with regions with microcracks
- Shear banding occurs in compression

Fracture

- Fracture strength low compared to metals and ceramics

- Thermosetting polymers experience brittle fracture
  - Covalent bonds break

- Thermoplastic polymers experience ductile to brittle transition
  - Type of fracture influenced by temperature, strain rate and presence of flaws

Crazing

- Frequently precedes fracture
- Regions of very localised yielding with small interconnected microvoids
- Molecules in bridges between microvoids orient leading to strengthening
- Bridges eventually break and voids coalesce
- A craze can support a load across its face

Applications - thermoplastics

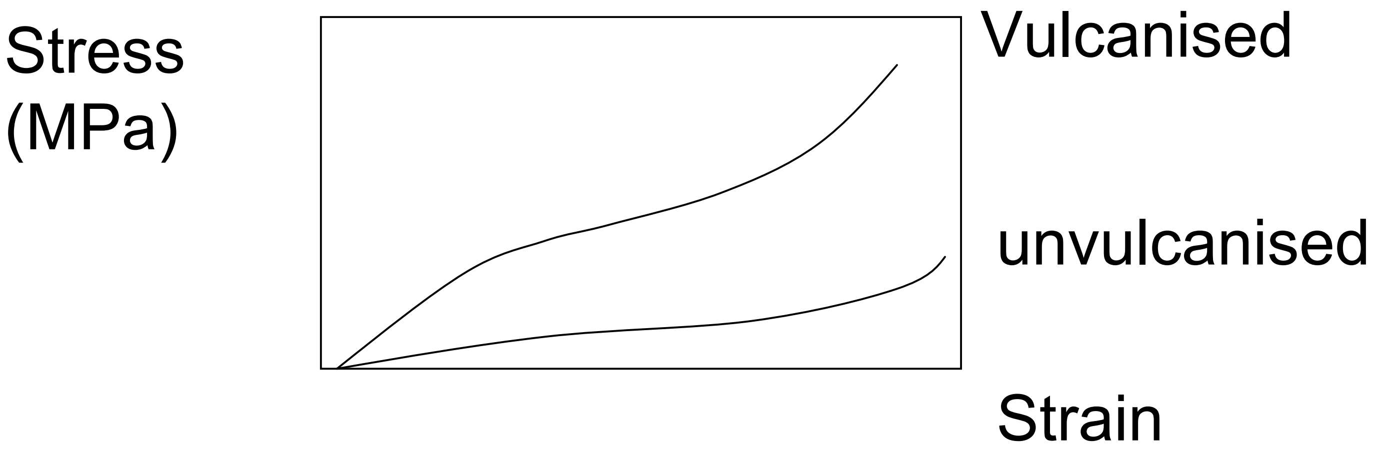
- Most important and versatile plastic is polyethylene
  - Low density PE (LDPE) has branched chains
    - Used for plastic bags, electric insulation, packaging
  - High density PE (HDPE) has few branches
    - Used for plastic tubing, bottles and bottle tops
  - High molecular weight PE has very long chains
    - Used when very tough and resilient materials required
  - UHMWPE – M_w ~4 x 10^6 g/mol
    - Extremely high impact resistance
    - Outstanding resistance to wear and abrasion
    - Very low coefficient of friction
    - Self lubricating, non-stick surface
    - Applications include bullet proof vests, bowling alley surfaces, ski bottoms, fishing lines

Applications -Elastomers

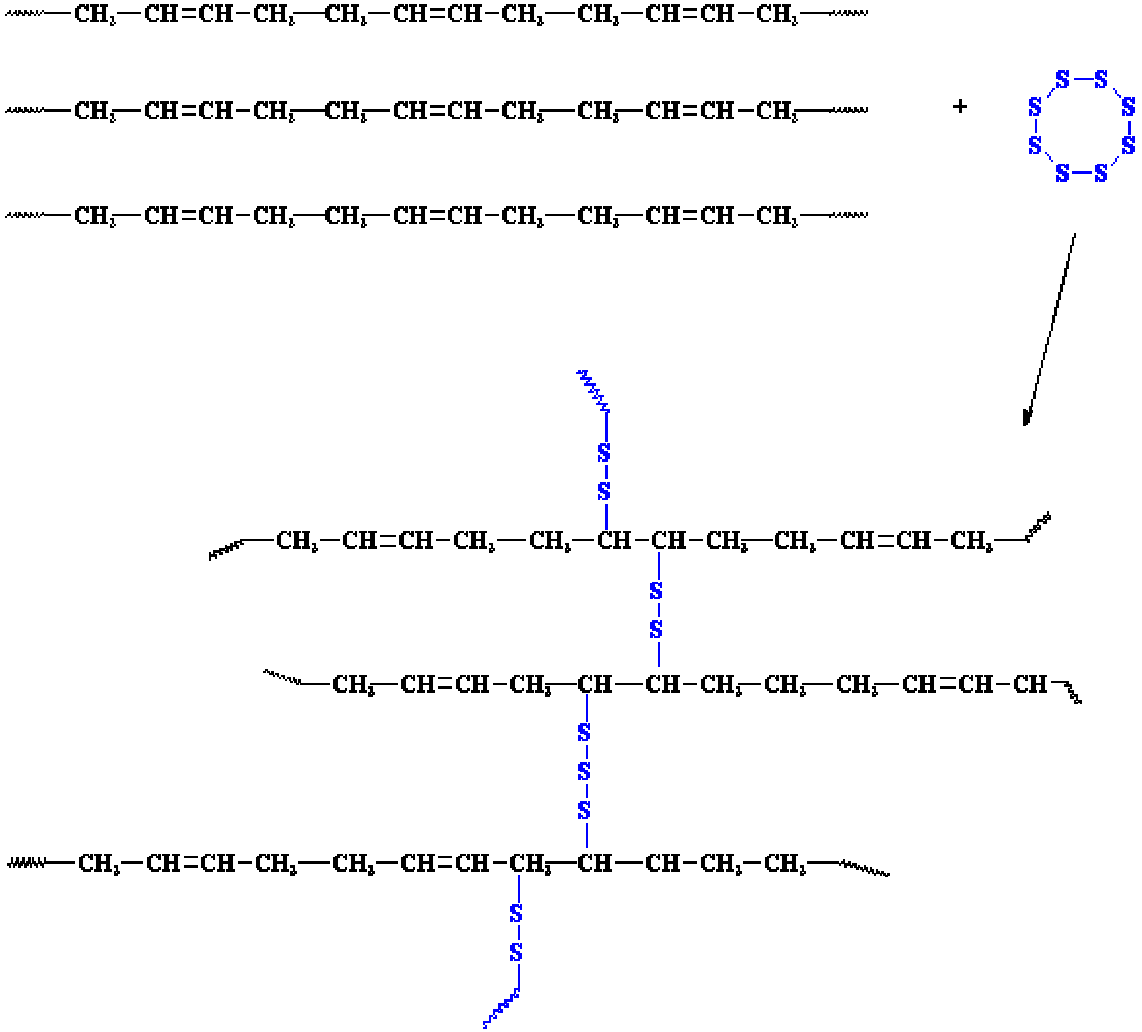
- Elastomers can experience large deformations and return to original shape
- Rubber is the most important elastomer
- Elastomers are formed by vulcanisation
  - causes cross-inking of the polymer chains
  - Double bonds in the chains break and link to neighbouring chains with sulphur chains
- Uses
  - Tyres
  - Petrol hoses
  - Heels and soles of shoes

Vulcanisation

- Elastomeric behaviour - light cross-linking
- S added – bonds with adjacent polymer chains and forms cross-links
- Modulus of elasticity, tensile strength, resistance to degradation enhanced by vulcanisation



Vulcanisation



polyisoprene

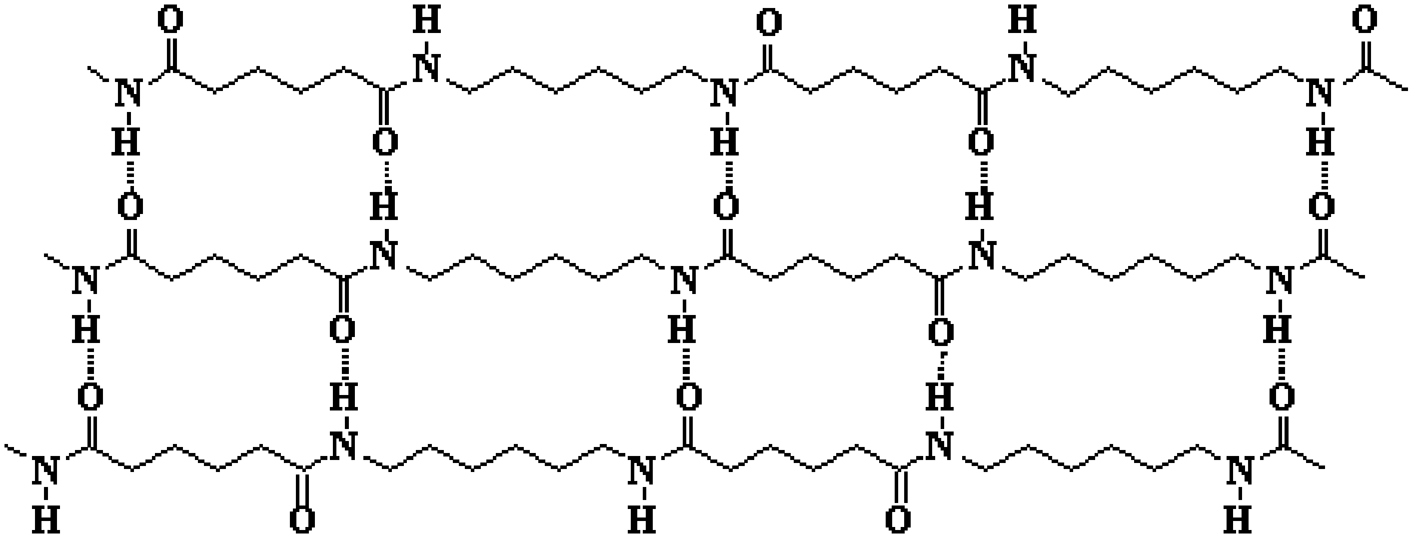
sulphur

Fibres

- Natural fibres (cotton , wool, silk) have been used by humans for centuries
- Man-made fibres include nylon, polyester, rayon and acrylic
  - Good strength to weight ratio
  - Good durability
  - Good chemical stability
- Nylon is very elastic and has a very high electrical resistance
  - Static charge build up on clothes and carpets
- Drawn fibres have good tensile strength in axial direction

Nylon –6,6

www.psrc.usm.edu/macrog



In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

Shaping and Forming Polymers

- Thermoplastics – softening when heated
  - Extrusion
  - Injection moulding
  - Vacuum or blow forming
  - Compression moulding
  - Films and fibres
  - Foams

- Thermosets
  - Heated formed and cured simultaneously

Summary

- Polymers either brittle plastic or highly elastic
- Mechanical properties sensitive to temperature changes
- Viscoelasticity displayed over certain temperature range
- Properties depend on
  - Chemistry
  - Chain length
  - Degree of crystallinity
  - Degree of cross-linking
- Less strong and stiff than metals and ceramics

Composite Materials

Combinations of 2 or more materials which generally have superior properties to the single components

Examples

Wood and bone are natural composites

Glass fibre

Multiphase metal alloys

Terminology

- Matrix
  - The continuous phase
  - Purpose of the matrix is to
    - Transfer stress to other phases
    - Protect other phases form the environment
  - Matrix can be a metal, ceramic or a polymer
- Dispersed phase
  - The material that is added to the matrix
  - Purpose is to enhance the properties of the matrix
  - Dispersed phase can be particles, fibres or lamellae

Types of Composites

- Composites
  - Particle-reinforced
    - Large particle
    - Dispersion strengthened
  - Fibre reinforced
    - Continuous (aligned)
    - Discontinuous (short)
      - aligned
      - Randomly oriented
  - Structural
    - Laminates
    - Sandwich

Large-Particle Reinforced Composites

- Reinforcing particles harder and stiffer than matrix
- Matrix transfers some applied stress to particles
- Examples
  - Concrete
    - cement matrix
    - sand and gravel particulates
  - Cermets used for cutting tools
    - Metal (W, Ni) matrix
    - Ceramic (TiC, WC) particulates
  - Polymers often reinforced with particles (fillers) to reduce cost and improve performance
    - Carbon black used as a filler for tyres (15-30%)
    - Enhances strength, toughness and abrasion resistance

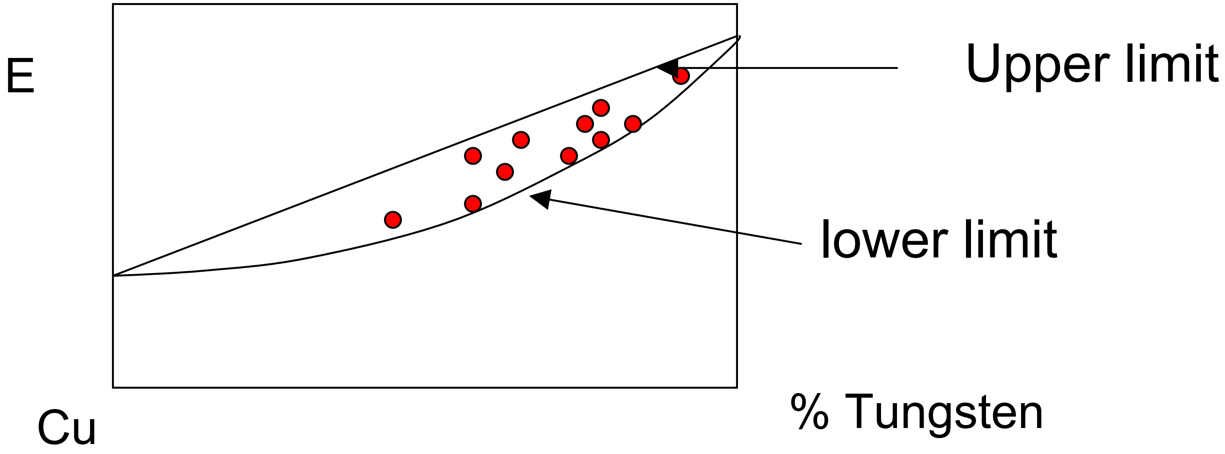
Properties

- Rule of mixtures
  - V_m volume of matrix; V_p volume of particles
  - E_m modulus of matrix; E_p modulus of particles
  - Elastic modulus lies between an upper limit

$$E_c(u) = E_m V_m + E_p V_p$$

  - And a lower limit

$$E_c(l) = E_m E_p / (E_m V_m + E_p V_p)$$



Dispersion-strengthened Composites

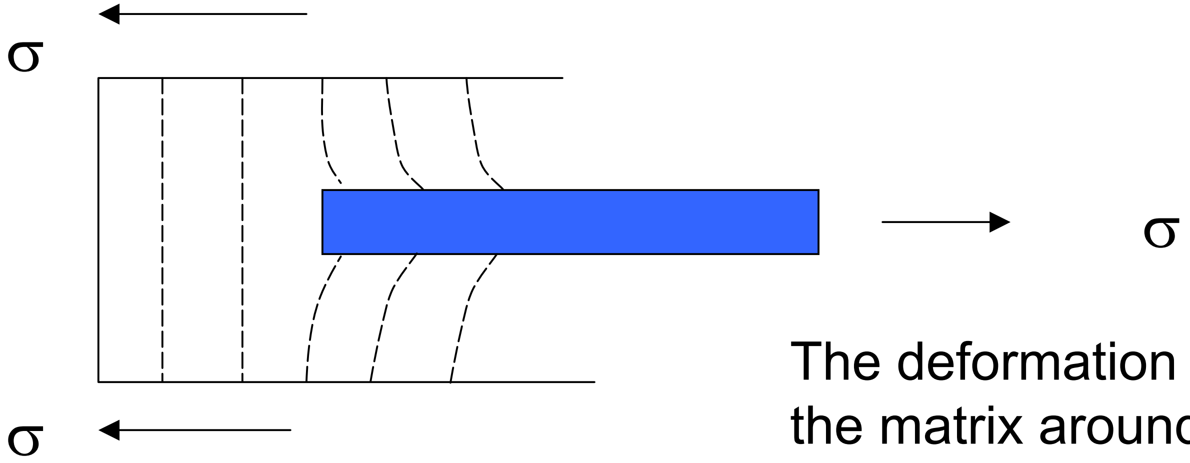
- Metals strengthened with uniform dispersion of fine hard particles (10-100 nm)
- Mechanism involves interaction between dislocation in matrix and particles
- Dispersion strengthening not as pronounced as precipitation strengthening but more stable at high temperature
- Examples
  - Thoria-dispersed Ni
  - Aluminium- aluminium oxide

Fibre Reinforced Composites

- Technologically the most important type of composite
- Examples
  - – GFRP
    - Boats
  - – CFRP
    - Planes, sports equipment
  - – Kevlar Fibre Reinforced Polymer
  - – Carbon fibres in C matrix
    - Disk brakes, nose cones

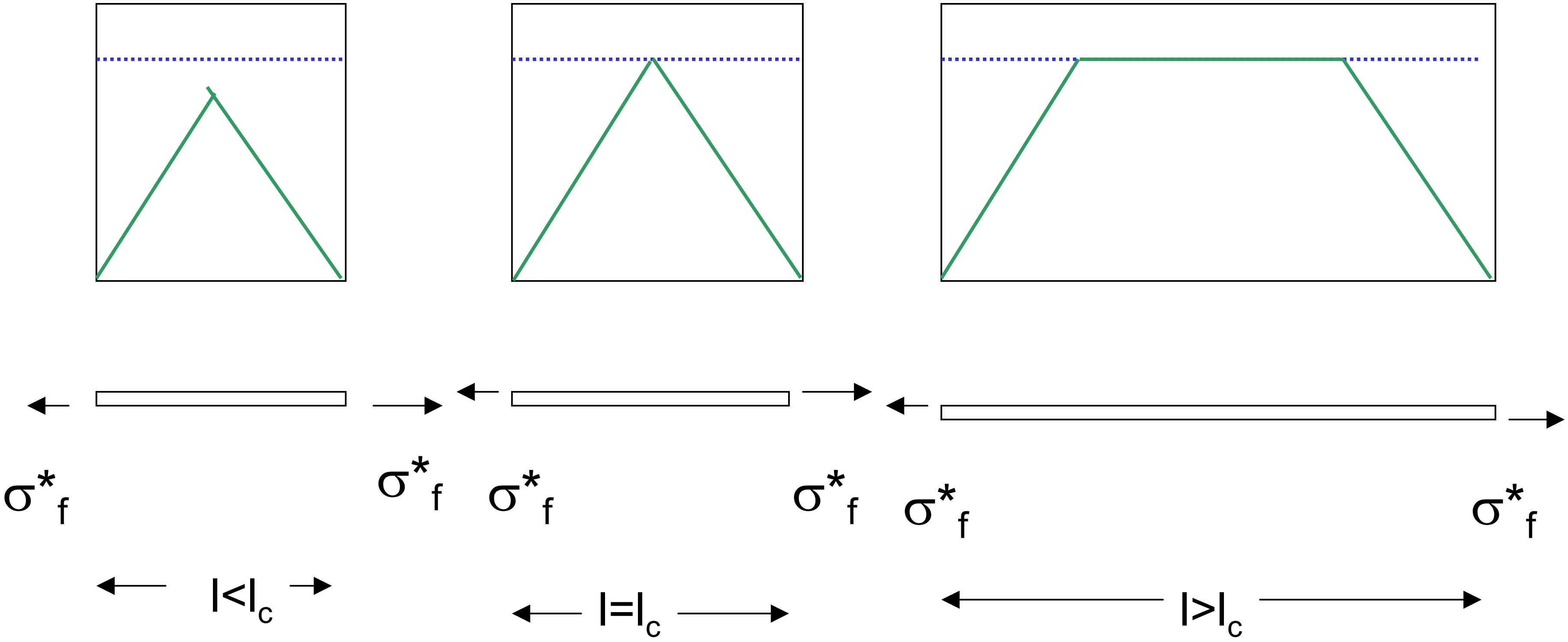
Properties

- Mechanical properties depend on the fibre properties and the degree to which the load is transmitted to the fibres by the matrix
- Critical length (l_c) required for strengthening
  - $l_c = \sigma^*_f d / 2\tau_c$: τ_c fibre matrix bond strength
  - d is fibre diameter; σ^*_f is fibre tensile strength

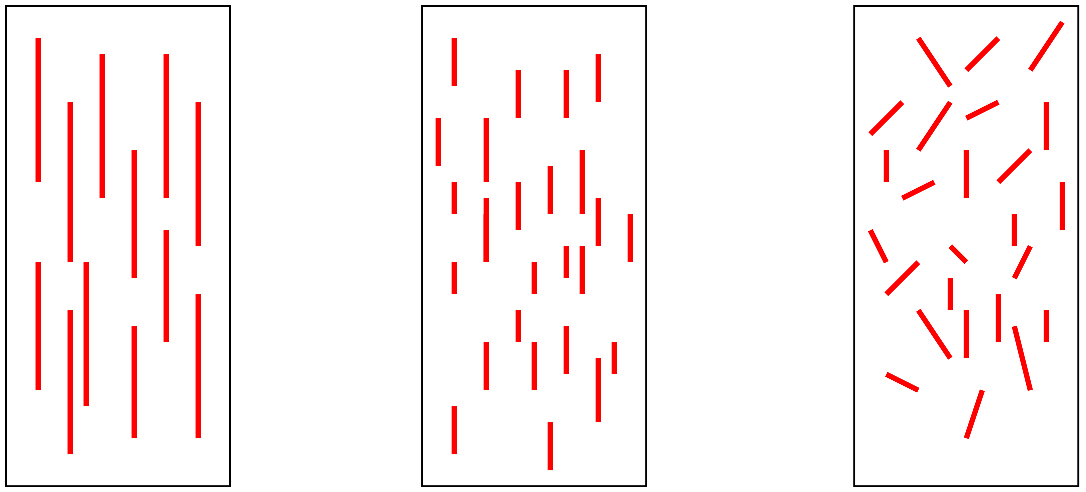


The deformation pattern in the matrix around a fibre subjected to a tensile stress

Stress Position Profiles



Types of fibre composites



Continuous and aligned

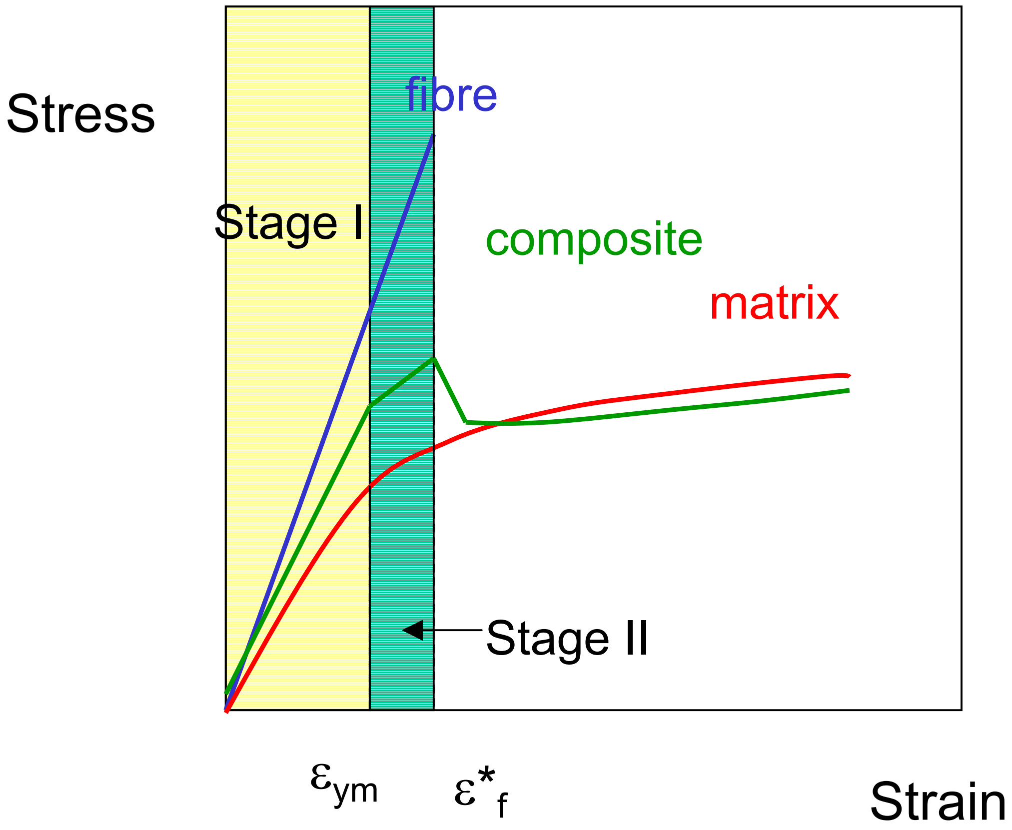
l > 15 lc

Discontinuous and aligned

Discontinuous and randomly oriented

Elastic Behaviour

Longitudinal Loading – Aligned Fibres

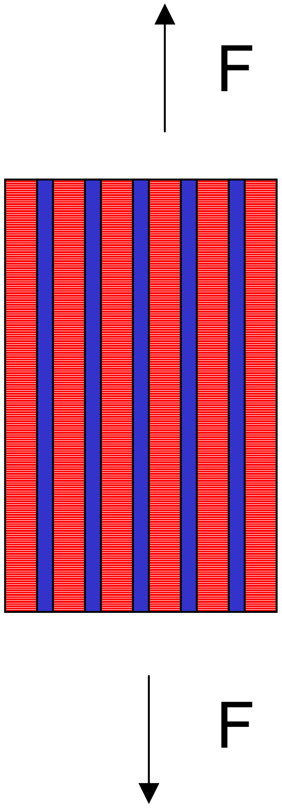


Stage I – fibre and matrix deform elastically

Stage II – fibre deforms elastically and matrix deforms plastically

At tensile strength of the fibre the fibres start to fail – however failure is gradual as matrix is still intact

Elastic Modulus – longitudinal loading



Total load $F_c = F_m + F_f$

or $\sigma_c A_c = \sigma_m A_m + \sigma_f A_f$

$\sigma_c = \sigma_m A_m / A_c + \sigma_f A_f / A_c$

For continuous fibres

$\sigma_c = \sigma_m V_m + \sigma_f V_f$

Both phases have the same strain

$\varepsilon_c = \varepsilon_f = \varepsilon_m$

$\sigma_c / \varepsilon_c = (\sigma_m / \varepsilon_c) V_m + (\sigma_f / \varepsilon_c) V_f$

$$E_c = E_m V_m + E_f V_f$$

Elastic Modulus – Transverse Loading

In this case the stress is the same in both phases

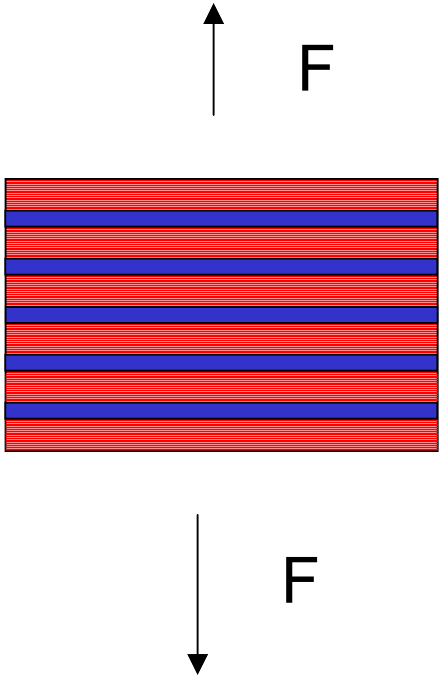
$$\sigma_c = \sigma_f = \sigma_m$$

And the strain is a sum of the strains in the 2 phases

$$\varepsilon_c = \varepsilon_m V_m + \varepsilon_f V_f$$

Or $\sigma_c/E_c = (\sigma_c/E_m)V_m + (\sigma_c/E_f)V_f$

So $E_c = (V_m/E_m + V_f/E_f)^{-1}$



$$E_c = E_m E_f/[(1-V_f)E_f + V_f E_m]$$

Tensile Strength

Longitudinal

Before we found $\sigma_c=\sigma_m(1-V_f)+\sigma_f V_f$

Composite will fail when stress in fibre reaches tensile strength therefore

$$\sigma_c{}^*=\sigma_m(1-V_f) + \sigma_f^* V_f$$

Transverse

Very low

~ 20-30 MPa

Strength – Typical values (MPa)

Material (Fibre-matrix)	Longitudinal tensile strength	Transverse tensile strength
Glass-polyester	700	20
Carbon-epoxy	1000	35
Kevlar-epoxy	1200	20

Toughness

- Measure of energy adsorbed per unit crack area (G_c)
- For crack propagated straight through matrix and fibre
  - $G_c = V_f G_c^f + (1-V_f) G_c^m$
- If fibres pull out of matrix instead of breaking
  - $G_c = (V_f/2d)\ \tau_c\ l^2 = V_f\ \sigma_f^2\ d\ /8\tau_c$ for fibres equal to critical length
  - $l_c = \sigma^*_f\ d/\ 2\tau_c$

Discontinuous Composites

$$E_c = E_m V_m + K E_f V_f$$

K = 1	aligned continuous
K = 3/8	Random (2D) discontinuous
K = 1/5	Random (3D) discontinuous

Random Composites are less stiff than aligned composites but much cheaper to manufacture

Fibres

- Whiskers
  - Very thin single crystals
  - Few flaws
  - Exceptionally strong
  - Very expensive
  - Eg graphite, SiC, SiN, Al_2O_3
- Fibres
  - Polycrystalline or amorphous
  - Thicker than whiskers
  - Polymers (kevlar) or ceramic (glass, C, B)
- Wires
  - Relatively large diameter
  - High strength steel, Molybdenum, Tungsten
  - Reinforcing tyres, filament wound rocket casings

The Matrix Phase

- Matrix
  - Binds fibres together
  - Medium through which stress is transmitted to fibres
- Polymers
  - The most common type of matrix is epoxy
  - Also polyester (cheaper) and HMWPE
- Metals
  - Ductile metals (Al, Mg, Ti)
  - Higher operating temperature than polymers
  - Greater resistance to degradation by organic fluids

Glass Fibre Reinforced Polymer

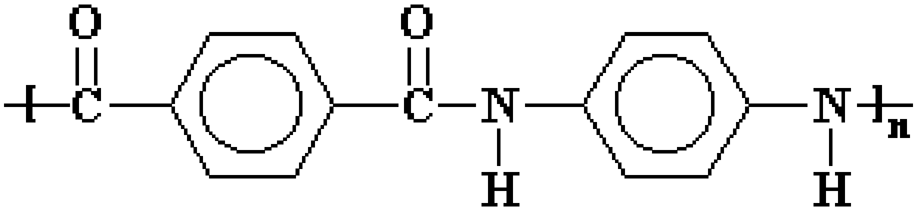
- Most commonly used composite
- Fibres 3-20μm in diameter
- Glass popular for fibre reinforcing because
  - Easily drawn into high strength fibres from molten state
  - Relatively strong
  - Chemically inert
  - Readily available
- GFRP is not very stiff or rigid
- Uses
  - Car and boat bodies
  - Pipes
  - Storage containers

Carbon Fibre Reinforced Polymer

- Most common advanced composite
- Carbon fibres are popular because
  - Highest specific modulus and specific strength of all reinforcing fibres
  - Retain stiffness and strength at high temperatures
  - Not affected by water, solvents or acids
  - Cost effective manufacturing process
- Fibres are mixture of graphite and a-carbon
- Uses
  - Sports equipment
  - Pressure vessels
  - Aircraft components
- Anisotropic properties – woven or laminated

Aramid Fibre Reinforced Polymers

- Kevlar and Nomex
- Outstanding strength to weight ratio
- Molecules aligned along fibre axis
- Bullet-proof vests, tyres, ropes, sporting goods



In Kevlar the aromatic groups are all linked into the backbone chain through the 1 and 4 positions. This is called *para-* linkage.

Properties – epoxy matrix composites

Material (Fibre)	Longitudinal tensile strength/modulus		Transverse tensile strength/modulus	
	(MPa)	(GPa)	(MPa)	(GPa)
Glass	1020	45	40	12
Carbon	1240	145	41	10
Kevlar	1380	76	30	5.5

Other Composites

- Metal matrix
  - Reinforcement improves strength, abrasion resistance, creep resistance, thermal conductivity
  - Al, Mg, Ti, Cu matrices with C, SiC, B, Al_2O_3

- Ceramic Matrix
  - Eg PSZ
  - ZrO_2 used to toughen Al_2O_3

Properties - comparison

Material	Good	Poor
Metals	Stiff, Ductile, Tough High Tm, Thermal shock	Yield strength, Corrosion Hardness, fatigue strength
Ceramics	Stiff, yield strength, high Tm	toughness, t-shock formability
Polymers	Ductile, Formable, Corrosion low density	Stiffness, Yield, low Tg, creep
Composites	Stiff, Strong, Tough, Corrosion fatigue, low density	Formability, Creep cost

Colloids

Homogenous mixture of 2 materials that are not in solution

Dispersed phase in a dispersing medium

Particles of dispersed phase

$10^{-9} – 10^{-6}$ m

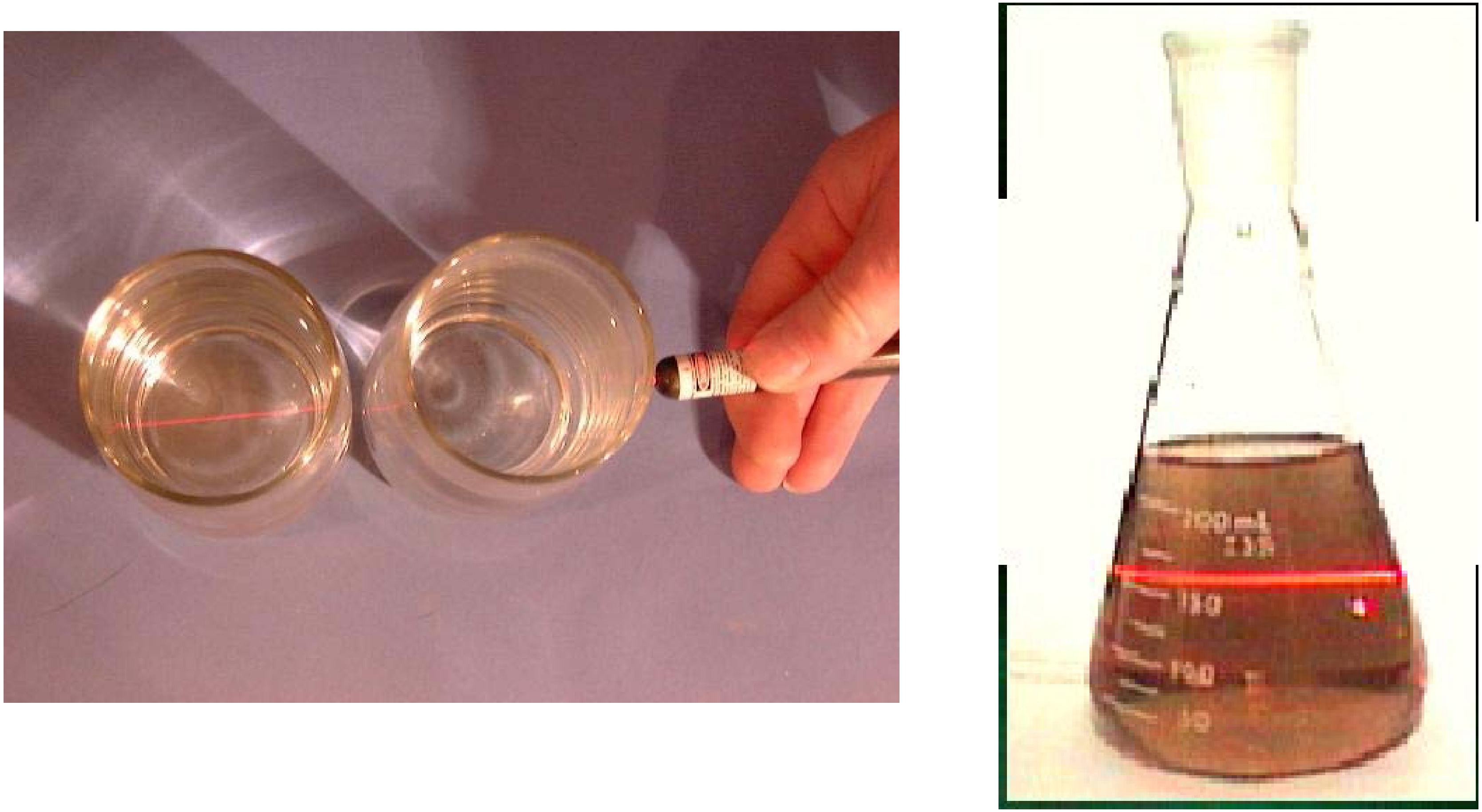
Types of Colloids

Dispersing medium	Dispersed phase	Name	Example
gas	liquid	Aerosol	fog
gas	solid	Solid aerosol	smoke
liquid	gas	foam	Whipped cream
liquid	liquid	emulsion	Milk, mayonnaise
liquid	solid	sol	Paint, ink, mud
solid	gas	Solid foam	Marsh mallow
solid	liquid	gels	Butter, jelly
solid	solid	Solid sol	Pearl, opal

Properties

- Large surface to volume ratio
  - High absorption
- Colloid particles become charged by selective ion absorption
  - Move under influence of electric field (Electrophoresis)
- Certain gels appear solid until force applied then they flow easily
  - Thixotropy
- Light and lasers trace a path through colloids
  - The Tyndall effect

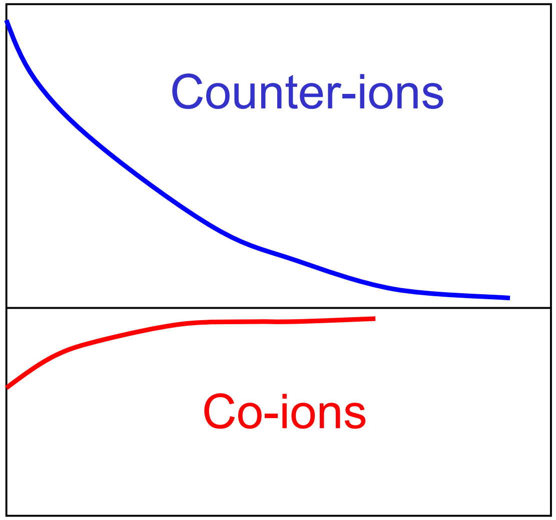
The Tyndall Effect



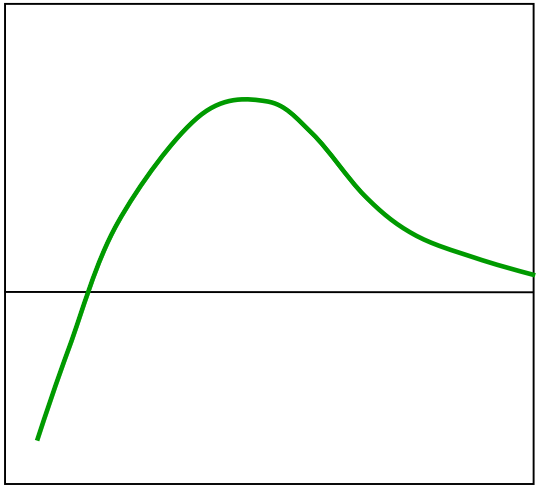
Stability

- Lyophobic (solvent repelling) colloids
  - Tend to coagulate due to van der Waals forces
  - Need to balance these with repulsive Coulomb interactions
  - Most surfaces acquire charge in solution
    - Ion adsorption
    - Ion dissolution
    - Ionisation
  - Charge of opposite sign is attracted to region near the surface
  - Electrical double layer (repulsive) is formed

Stability



Distribution of ions close to colloidal particle



Interaction energy as a function of distance between particles

If energy barrier is greater than kT the colloid is stable – otherwise coagulation will occur

Gels

- Gels are formed when the attraction between the dispersion particles become so strong that they form a rigid network
- Interactions can be electrostatic, Hydrogen bonds, van der Waals or chemical bonding
- Adding an electrolyte can cause gelation by reducing the repulsive force
- Process of converting a solid-liquid colloid (sol) to a gel is called the sol-gel process

Preparation

- Dispersion methods – break down material to colloidal dimensions
  - Comminution
    - Grind particles to colloidal size
    - Surface energy penalty reduced by grinding in a liquid
    - Dispersing agent added to aid dispersion
    - Eg glucose added to sulpher sol
  - Emulsification
    - Breakdown one liquid in the presence of another
    - Shake
    - Force through small hole under pressure
    - Lowering interfacial tension promotes emulsification

Preparation

- Condensation methods – prepare molecular complexes of increasing size until colloidal size attained
  - Chemical reaction with insoluble products
    - Supply of chemicals must run out while particles colloidal size
    - Seeding restricts nucleation to a short time period and gives monodisperse colloid (even particle size)
  - Dispersion polymerisation
    - Polymerisation in continuous phase
    - When critical size reached polymers become insoluble and form colloidal particles

Colloids - Summary

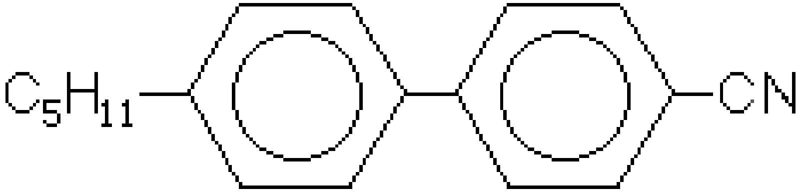
- Fine dispersion of one phase (dispersed phase) in a second phase (dispersing medium)
- Often meta-stable – stability depends on properties of dispersing medium (pH of solution)
- Dispersion scatters light (Tyndall effect)
- Under some conditions the dispersion forms a rigid network (gels)

Liquid Crystals

Liquid crystals possess some properties of both liquids and crystals

Liquid properties – molecules are mobile

Crystal properties- molecules are ordered



5CB p-n pentyl-p′-cyanobiphenyl (PCB)

Properties of LC Molecules

Liquid crystal molecules have

a rod-like structure

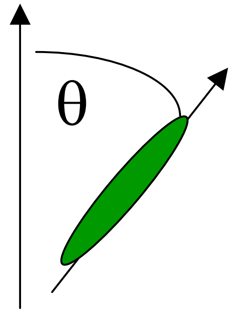
rigid long axis

a dipole moment or polarizable constituents

a strong tendency for the molecules to align

The alignment is measured by an order parameter

$$S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle$$

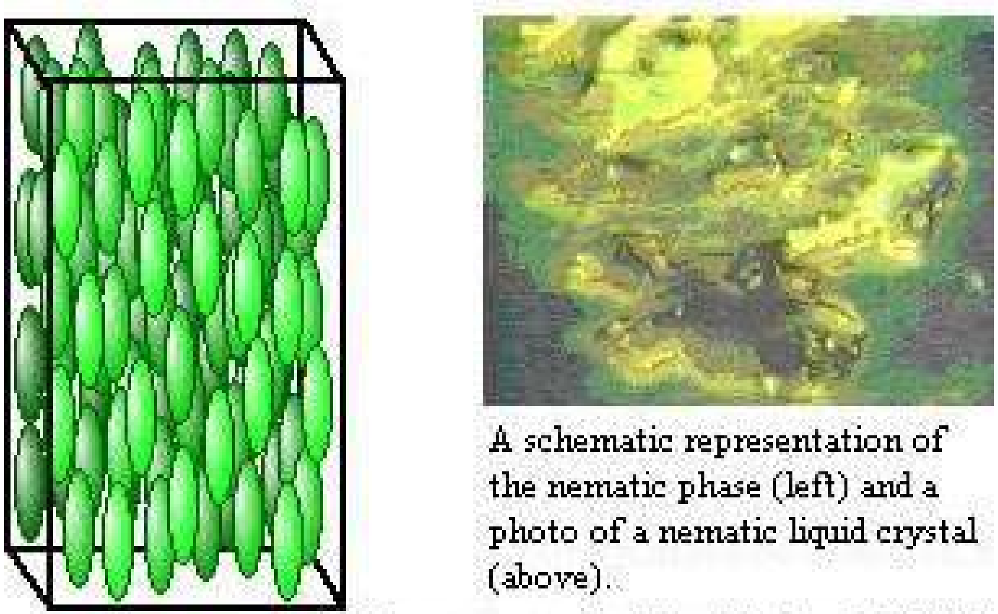


Types of Order

- Positional order
  - The extent to which group of molecules show translational symmetry
  - Crystals
- Orientational order
  - The extent to which the molecules are aligned
  - Liquid crystals

Liquid Crystal Phases - Nematic

Molecules aligned (strong orientational order) but no translational order



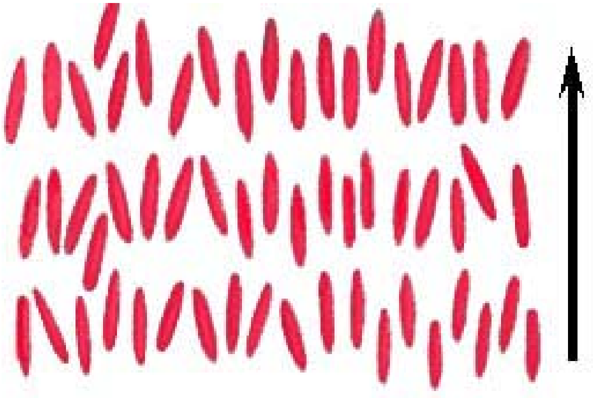
A schematic representation of the nematic phase (left) and a photo of a nematic liquid crystal (above).

Photo courtesy Dr. Mary Neubert LCI-KSU

http://plc.cwru.edu/tutorial/enhanced/files/hindex.html

Liquid Crystal Phases - Smectic

Strong orientational order - some translational order – molecules order in planes or layers

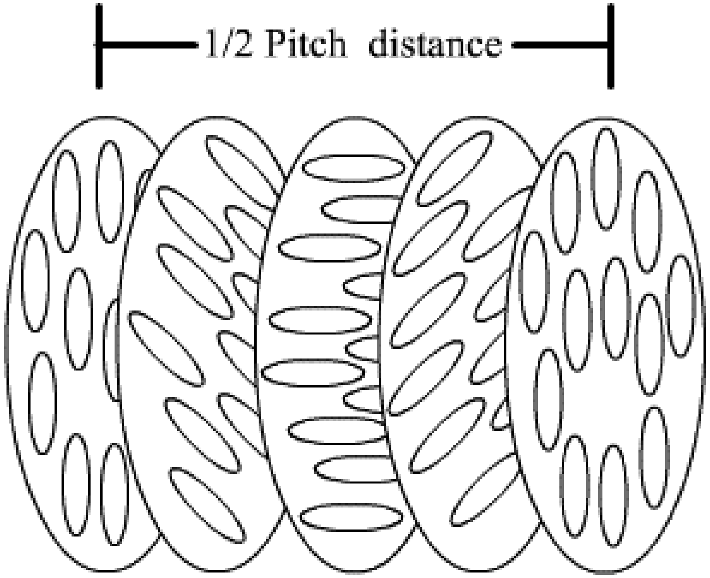


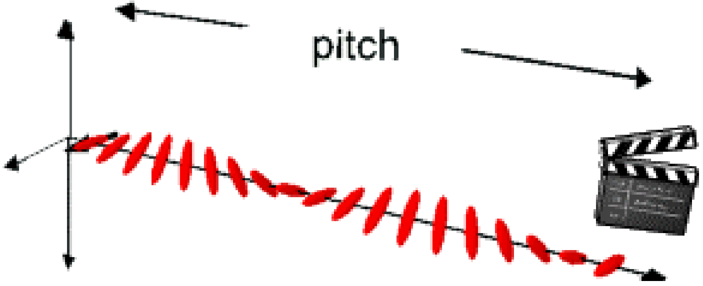
Smectic A

Smectic C

Liquid Crystal Phases - Cholesteric

Intermolecular forces favour alignment of neighbouring molecules at a slight angle

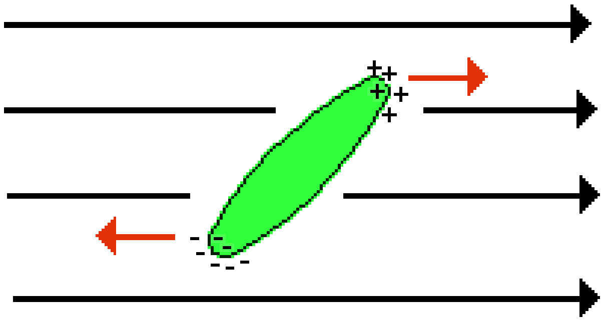




Cholesteric LCs can reflect light with wavelength equal to the pitch. Angle increases and pitch decreases with increasing temperature – thermometers

Electric Fields

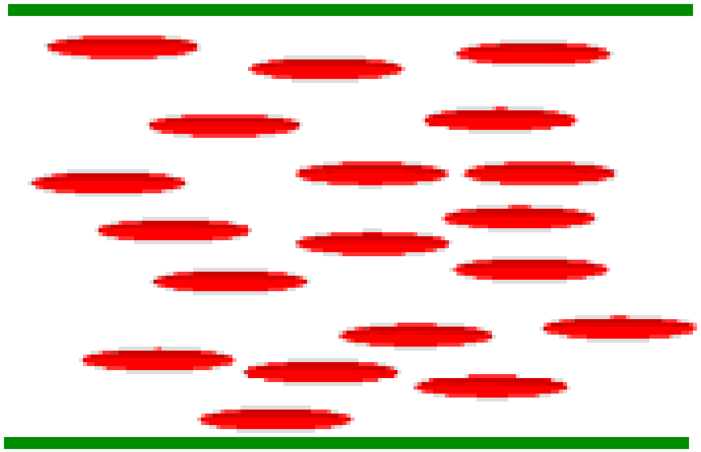
The response of LCs to electric fields is a major characteristic utilised in device applications



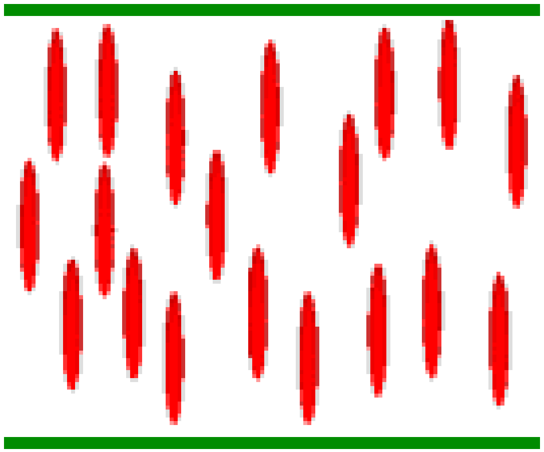
Dipole moment (permanent or induced) tends to align with the field

Textures

Texture is the orientation of the molecules near a surface



Planar Texture



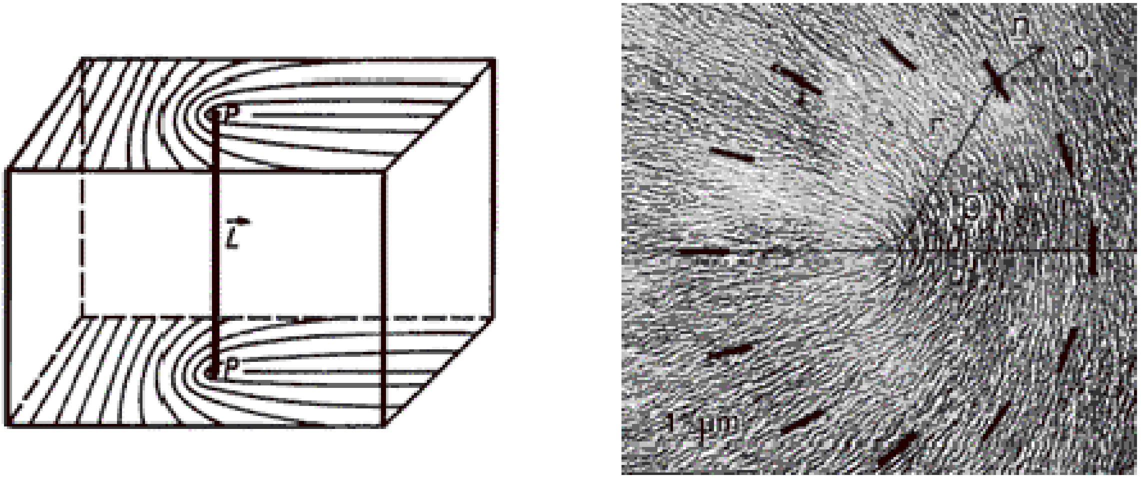
Homeotropic Texture

Defects

Orientational order has a rich variety of defects

Disclinations are line defects (cf dislocations)

The director rotates by nπ around a path enclosing the disclination

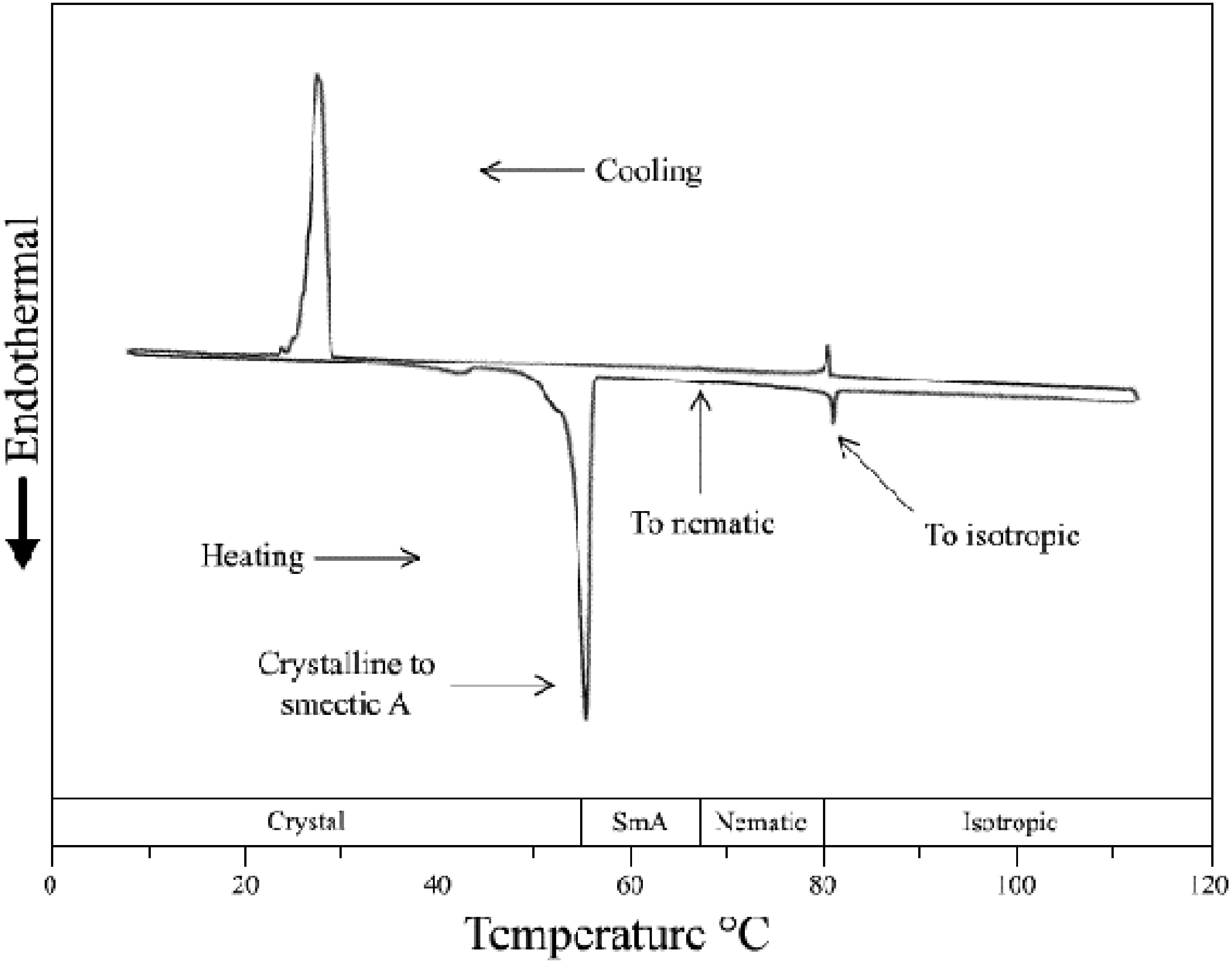


Director topology around a line disclination in a liquid crystal (left), and an electron micrograph of the same type of disclination. Crystalline lamellae are seen edge on and appear dark. The director field lines lie normal to the lamellae as illustrated by the vector n for a highlighted lamellae.

Optical properties of liquid crystals

- Scatter visible light
  - Affected by surfaces, electric fields, magnetic fields
- Birefringence
  - Anisotropic nature leads to 2 distinct refractive indices for parallel and perpendicularly polarised light
  - Results in change in polarization state
  - Strongly temperature dependent
- Rotation of polarization
  - Cholesteric LC's
  - Temperature dependent

Phase transitions



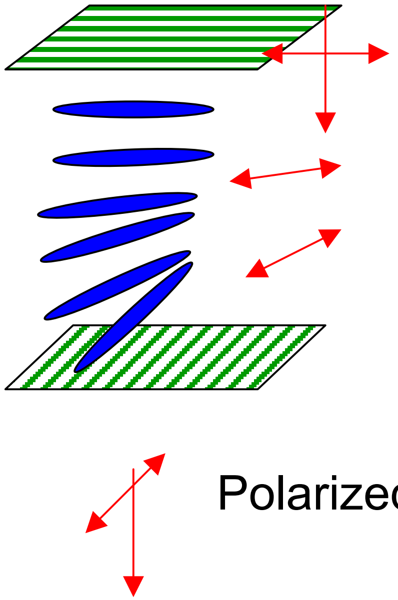
movie

Applications

- Displays
- Temperature sensors
- Optical switches
- Optical imaging
- Optical storage

Liquid Crystal Displays

- Multi-billion dollar industry
- Twisted nematics between cross polarisers
- Polarization of is rotated with the molecule twist
- Light transmitted through 2nd plate
- On application of field nematic untwists
- Light cannot pass through lower plate

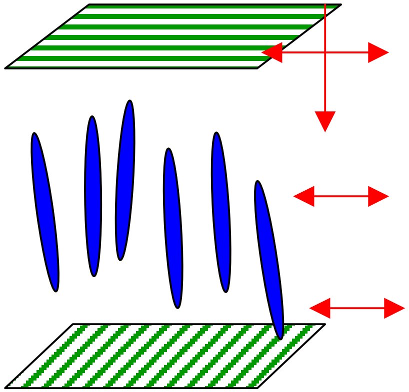


Polarised light

Direction of
polarisation rotates

Polarized light

Applied field



Light is not transmitted

Liquid Crystals - Summary

- Rod-shaped molecules with dipole moment
- Molecules align due to anisotropic orientational order
- Nematic, Smectic or Cholesteric ordering
- Very interesting electro-optical properties – widely used in displays