The applications of glass and the structure of glass from molecular dynamics

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finanziato dalla Regione Sardegna.

Outline

1) Glass is a important material
2) Molecular dynamics of glass
3) Structure of oxide glasses

   including: silicate glasses

   phosphate glasses
4) Relationship of properties and structure

   including: dopants in glasses

   phase separation

   chemical durability
5) Summary

1) Glass is an important material

Materials are essential for our way of life

- we use materials to create tools

- materials science "triangle":
  - synthesis - structure - properties

- we need glass because it is transparent and strong
  - windows, containers, lighting, optics
  - what is the alternative to glass?

Glass is transparent and strong

- We cannot use:
  - metals - not transparent
  - ceramics / oxide minerals - not transparent
  - polymers - not strong
- Glass was discovered approx. 4000 years ago
  - probably a mixture of sand, ash and bone
  - melting of mixture on a fire
  - rapid cooling of melt, i.e. "melt-quenching"

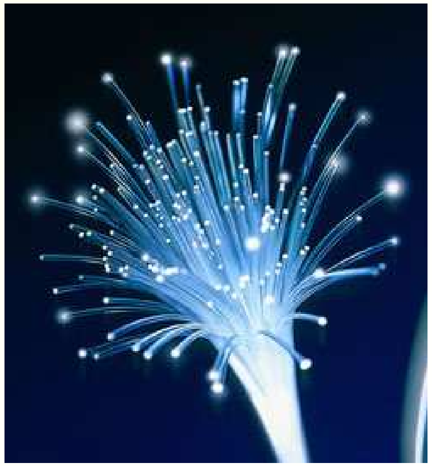
- Modern glass industry
  - much glass is based on $15Na_2O$-$10CaO$-$75SiO_2$

20^{th} century glass

- window glass
  - 10% Na_2O - 15% CaO - 75%SiO_2
  - electrical/chemical resistance: remove Na
  - heat resistance: add B
  - radiation resistance: add Ba
- container glass (add Al)
  - i.e. bottles
- lighting glass (add Mg)
  - i.e. light bulbs
- optical fibres
  - pure SiO_2
  - need < 1ppb OH^- groups

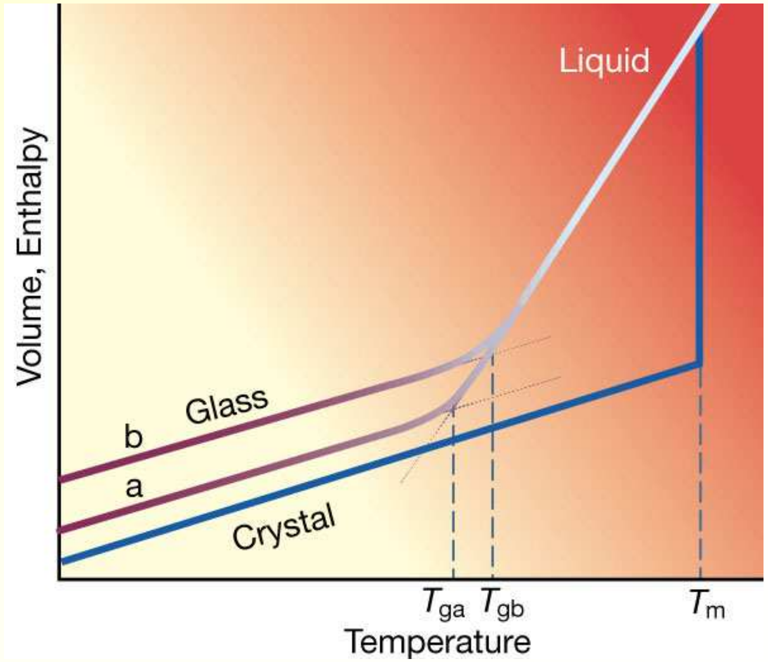
window glass
global production
~40 million tonnes/yr
($20bn)

optical fibre
global production
~70 million km/yr
($4bn)



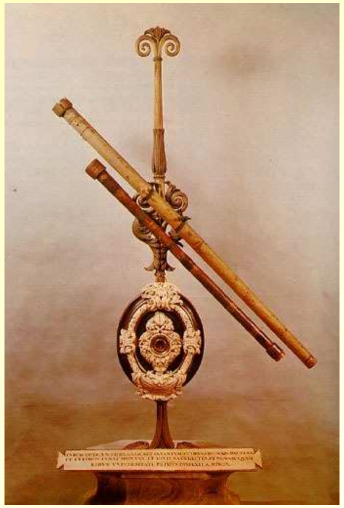
Glass is non-crystalline

- Crystalline ceramics are transparent
  - small crystals reflect light and look "white"
  - large crystals are hard to manufacture
- Melt-quenching stops crystalisation
  - only works for special compounds
  - glass typically has 90% density of crystal
  - glass has no crystals to reflect light
- Thermodynamics: solids are crystals
  - periodic structure has lowest energy
  - crystallisation occurs extremely rapidly



Glass has a variable shape

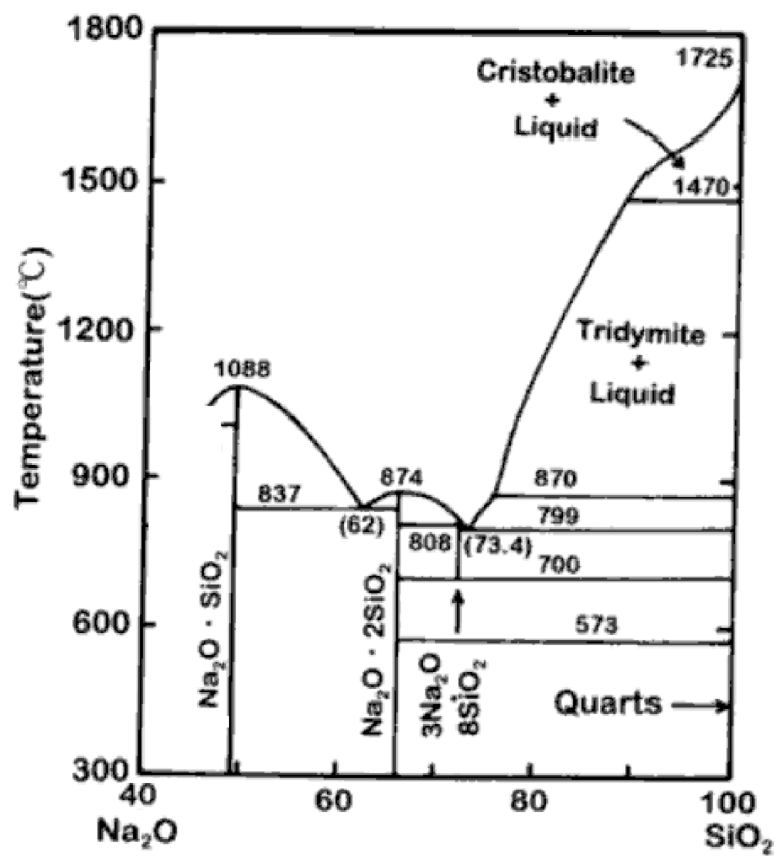
- Melt-quenching allows control of the shape
- very useful for making <u>containers</u>
- very useful for making <u>scientific instruments</u>
  - lenses for microscope and telescopes
  - glassware for chemistry
  - valves for electronics



Glass has variable composition

- Crystals have fixed compositions
  - except for dopants and alloys

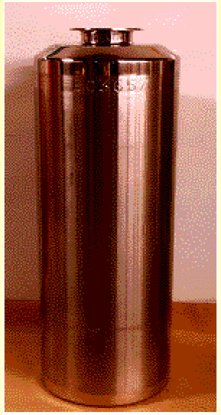
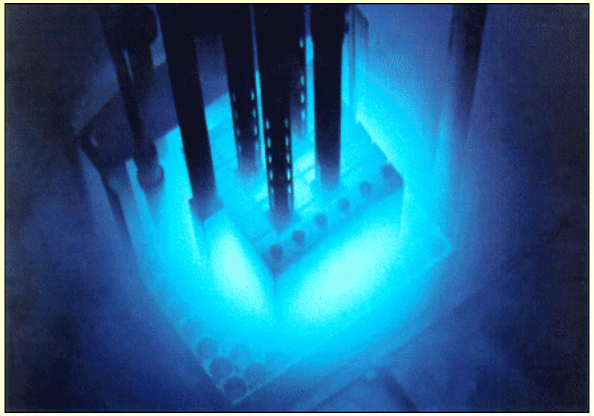
- Glass composition is defined by mixture
  - glasses form more easily near the eutectic



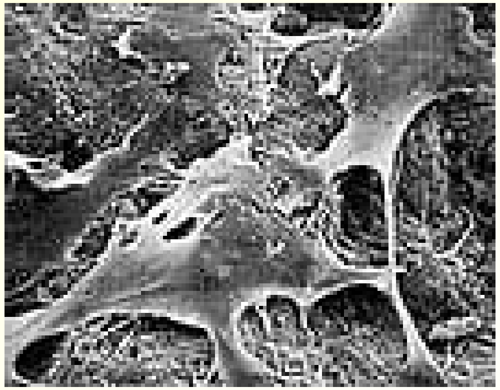
- needed to make glass cheaply
  - pure silica (quartz) is a stronger glass
  - adding soda reduces melting temperature

- need to make different applications
  - e.g. chromium is added to make green bottles

21^{st} century glass

- vitrification of nuclear waste
  - easy to add waste to glass mixture
  - need to find glass that is more durable

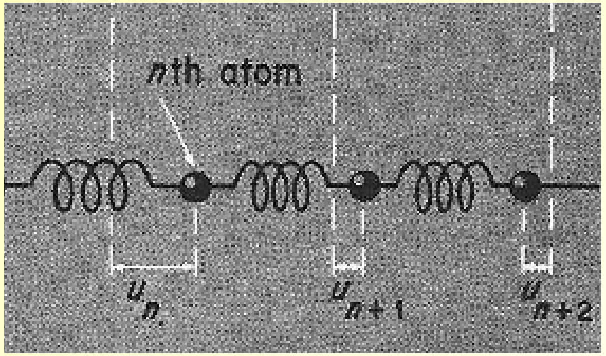


- bioglass for bone replacement therapy
  - glass is dissolved and replaced with bone
  - composition and pores stimulate cells

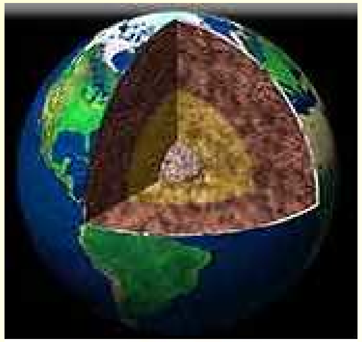
- solar energy
  - transparent protective layer for solar cells
  - need to find glass that weighs less

Wider interest in glass

- glasses are challenging for solid state theory
  - e.g. how to describe vibrations without lattice



- Earth's interior contains silicate melts
  - glass represents frozen liquid



- biomineralisation of amorphous oxides
  - living organisms precipitate amorphous phases
    e.g. amorphous calcium carbonate in shells

- non-oxide glasses include
  - metallic, covalent and molecular compounds

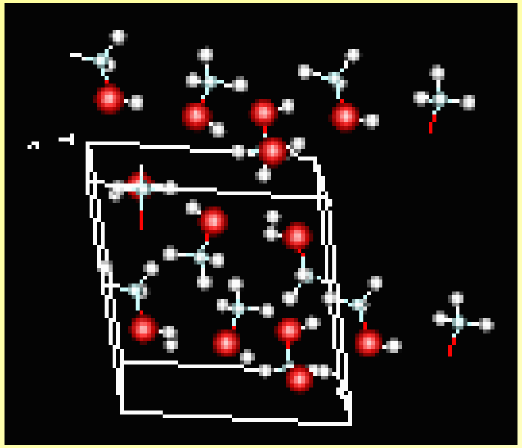
molecular

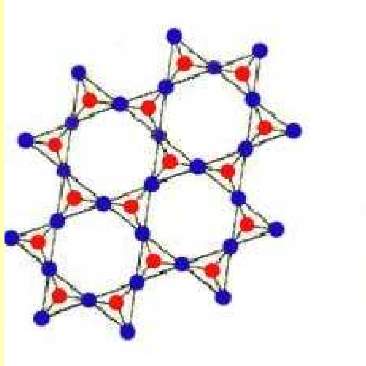
ionic

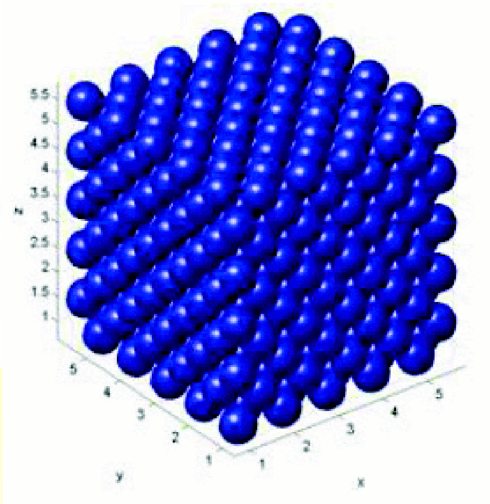
metallic

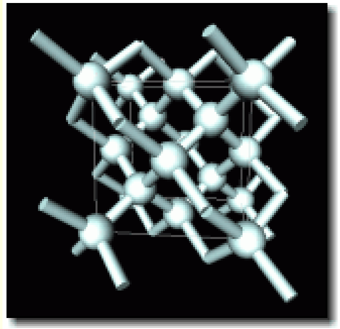
covalent

crystal









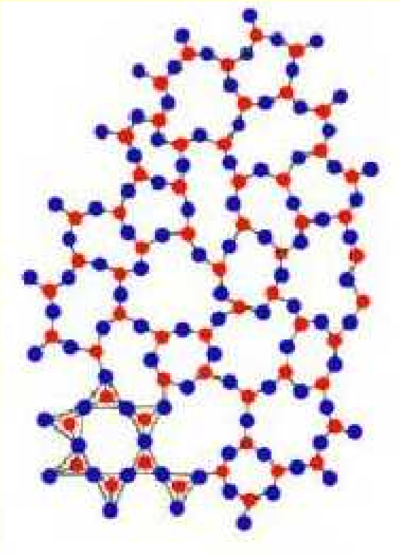
ethanol

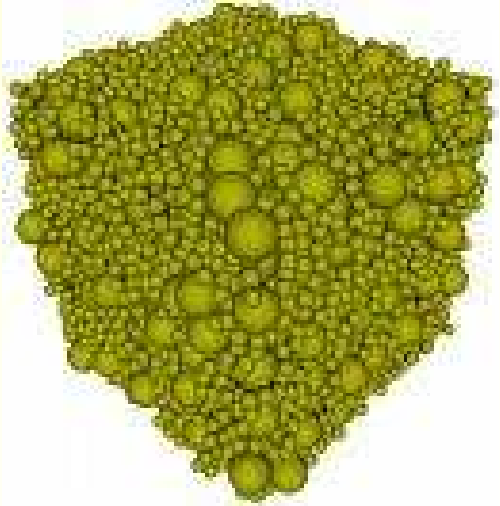
silica

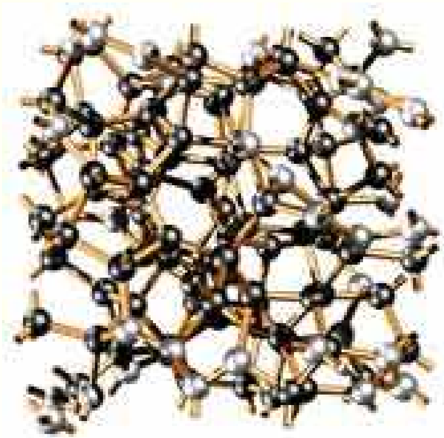
Cu-Zn alloy

carbon

glass







2) Molecular dynamics of glass

Structure is knowledge of atom positions

- crystal is described by repeated unit cell:

Compound	La1 O9 P3 - Lanthanum catena-triphosphate [AB3X9] [oS52]				
Cell	11.303(4), 8.648(5), 7.397(3), 90., 90., 90. **C2221 (20)** V=723.04				
Atom (site) Oxid.			**x, y, z, B, Occupancy**		
La1	(4b)	3	0	0.12848(4)	0.25
P1	(4b)	5	0	0.7480(2)	0.25
P2	(8c)	5	0.3252(1)	0.9940(2)	0.2016(2)
O1	(4a)	-2	0.3738(6)	0	0

- glass is described by average over all atom positions:

Lanthanum metaphosphate glass

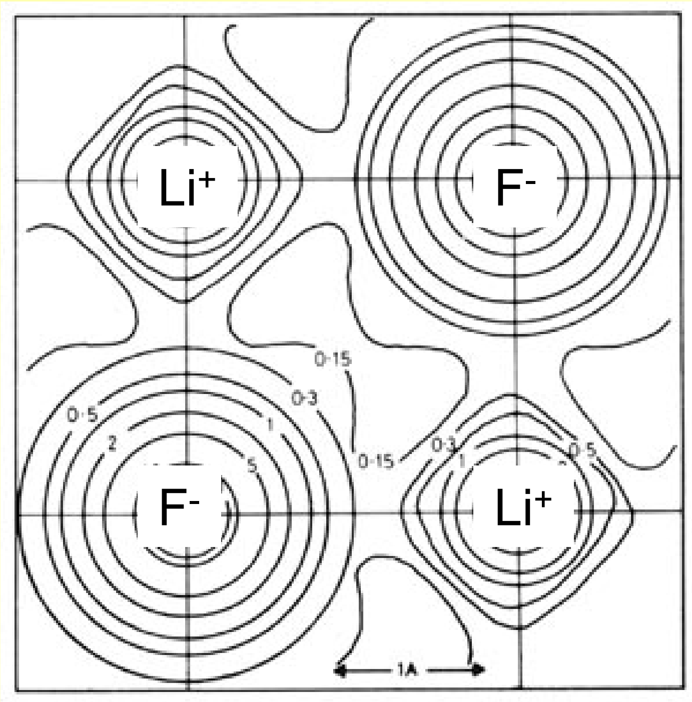
Atom pair	Coordination number	Distance (pm)
P–O	1.90 (10)	148.4 (5)
	2.05 (10)	160.4 (5)
La–O	7.1 (5)	245.8 (15)

Hoppe et al (1998) *JNCS* **232** 44

- predict atom positions using "modelling" methods:
  - by hand
  - Monte Carlo
  - reverse Monte Carlo (RMC)

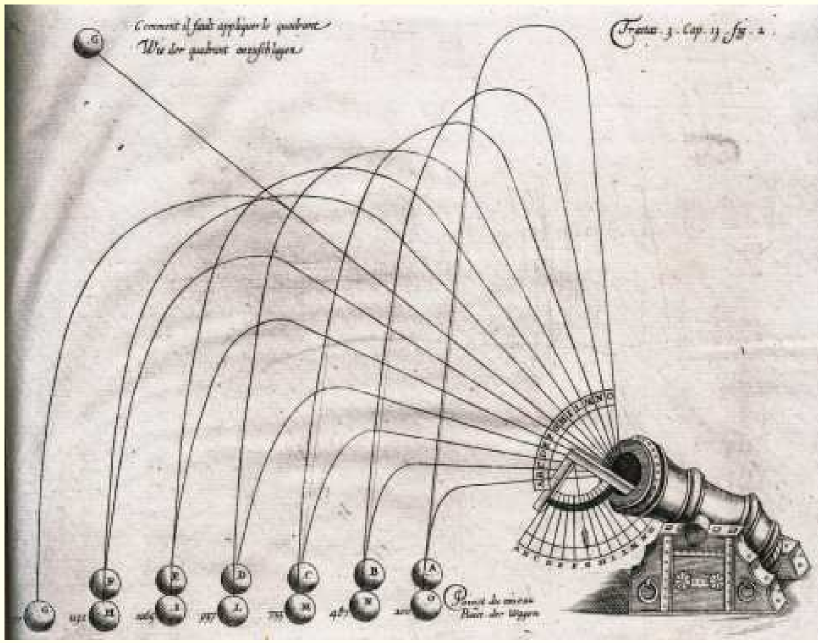
- molecular dynamics method:

Can think of atoms as solid spheres



e.g. electron density in LiF

Can predict motion of spheres using equations of physics



e.g. motion of cannonball under gravity

Molecular dynamics simulation

(1) simulate a liquid (melt):

(2) freeze the liquid (quench):

(i) atom positions derived from Newton's equations:

position $x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{1}{2}\frac{d^2x(t)}{dt^2}(\Delta t)^2$

velocity $v(t+\Delta t) = v(t) + \frac{d^2x(t)}{dt^2}\Delta t$

force $F_{tot}(t) = \sum_{i\neq j}^{N} F_{ij}(t) = m\frac{d^2x(t)}{dt^2}$

(ii) force derived from interatomic potential $U_{ij}(x)$:

$$F_{ij} = \frac{-d}{dx}U_{ij}(x)$$

(iii) temperature derived from velocity

$\frac{1}{2}k_BT = \frac{1}{2}mv^2$

Interatomic potentials

- long range force between ions:
  - unlike charges attract, like charges repel
- short range force between atoms:
  - electron clouds repel
  - e.g. "Buckingham" potential →

$$U_{ij}\left(x_{ij}\right) = A\exp\left(\frac{-x_{ij}}{x_0}\right) - \frac{C}{x_{ij}^{6}}$$

- Where to get potentials?

- from the literature →

11780 *J. Phys. Chem. B* **2006**, *110*, 1178

A New Self-Consistent Empirical Interatomic Potential Silica-Based Glasses

Alfonso Pedone,† Gianluca Malavasi,† M. Cristina M Ulderico Segre*,†

- How to check potentials?

- simulate a crystal →

oxide		*a* (Å)	*b* (Å)	*c* (Å)
SiO_2	expt	4.9160	4.9160	5.4054
α-quartz	calcd	4.9241	4.9241	5.4333
	% error	0.16	0.16	0.52

- typical software is GULP

https://www.ivec.org/gulp/

Molecular dynamics simulation of glass

coordinates ← new coordinates

timestep

coordinates → MD

potential → MD

temperature → MD

MD → new coordinates

temperature → new temperature

typically:

duration of simulation

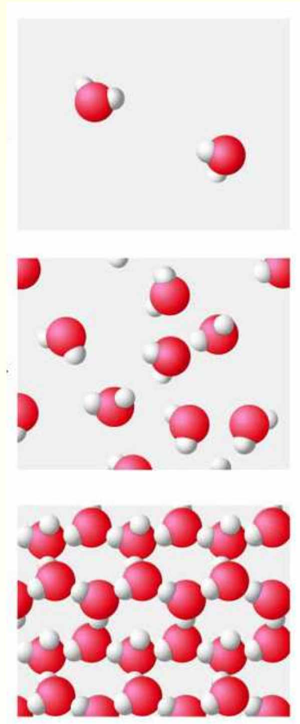
(1) randomise

(2) 3000 K

(3) 2000 K ← MELT

(4) "quench" ← QUENCH

(5) 300 K



- typical software is DLPOLY

http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/

Analysing atom positions

- chemical information

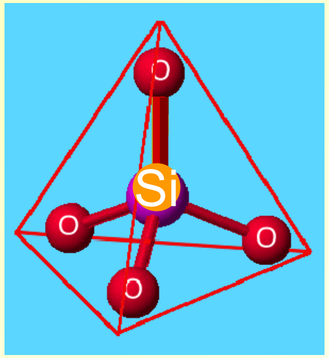
  e.g. SiO_2 glass:

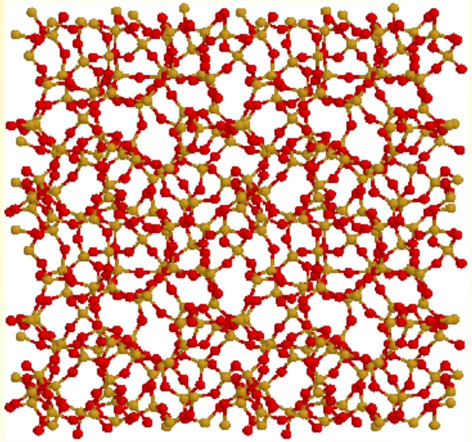
  bond length $R_{Si\text{-}O}$=1.60Å

  coordination number $N_{Si\text{-}O}$=4

  polyhedral shape = SiO_4 tetrahedra

  connectivity of tetrahedra = 4



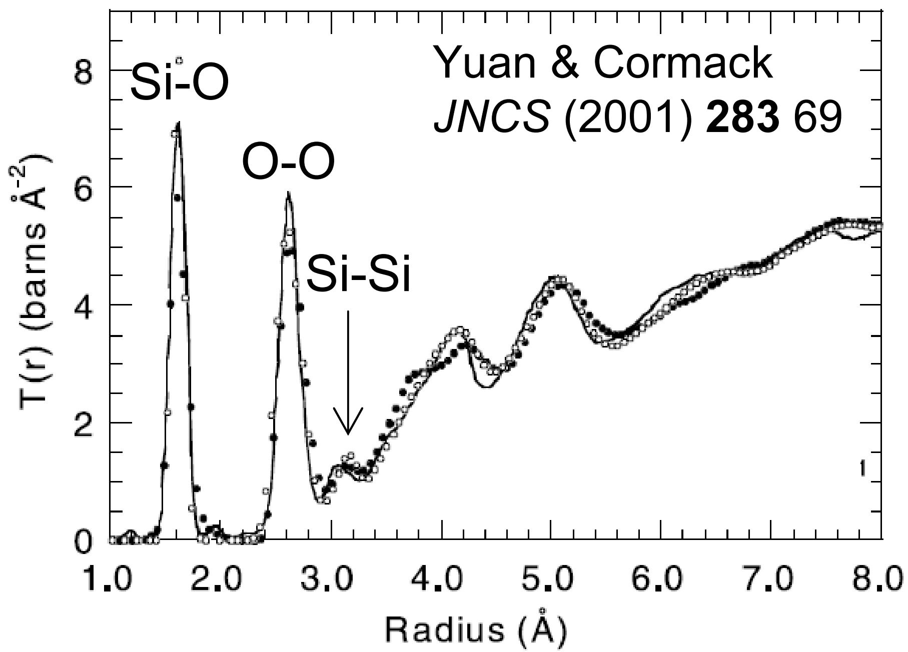


- interatomic distances r

  described by $T_{ij}(r)$

  where R_i is atom coordinates

$$T_{ij}(r) = \frac{1}{r}\frac{1}{N_i}\sum_i \sum_j \delta\left(\left(R_i - R_j\right) - r\right)$$



Comparing atom positions with experiment

X-ray absorption spectroscopy shows bond lengths

for excited atom

diffraction shows interatomic distances

- measures total interference function *i(Q)*

  where ρ_i is no. density

$$Qi(Q) = \sum_i \sum_j w_{ij}(Q) \int_{Q_{\min}}^{Q_{\max}} \left(T_{ij}(r) - 4\pi r \rho_j\right) \sin(Qr)\, dQ$$

- weighted by $w_{ij}(Q)$ due to scattering

  where c_i is concentration, and b_i / Z_i is scattering

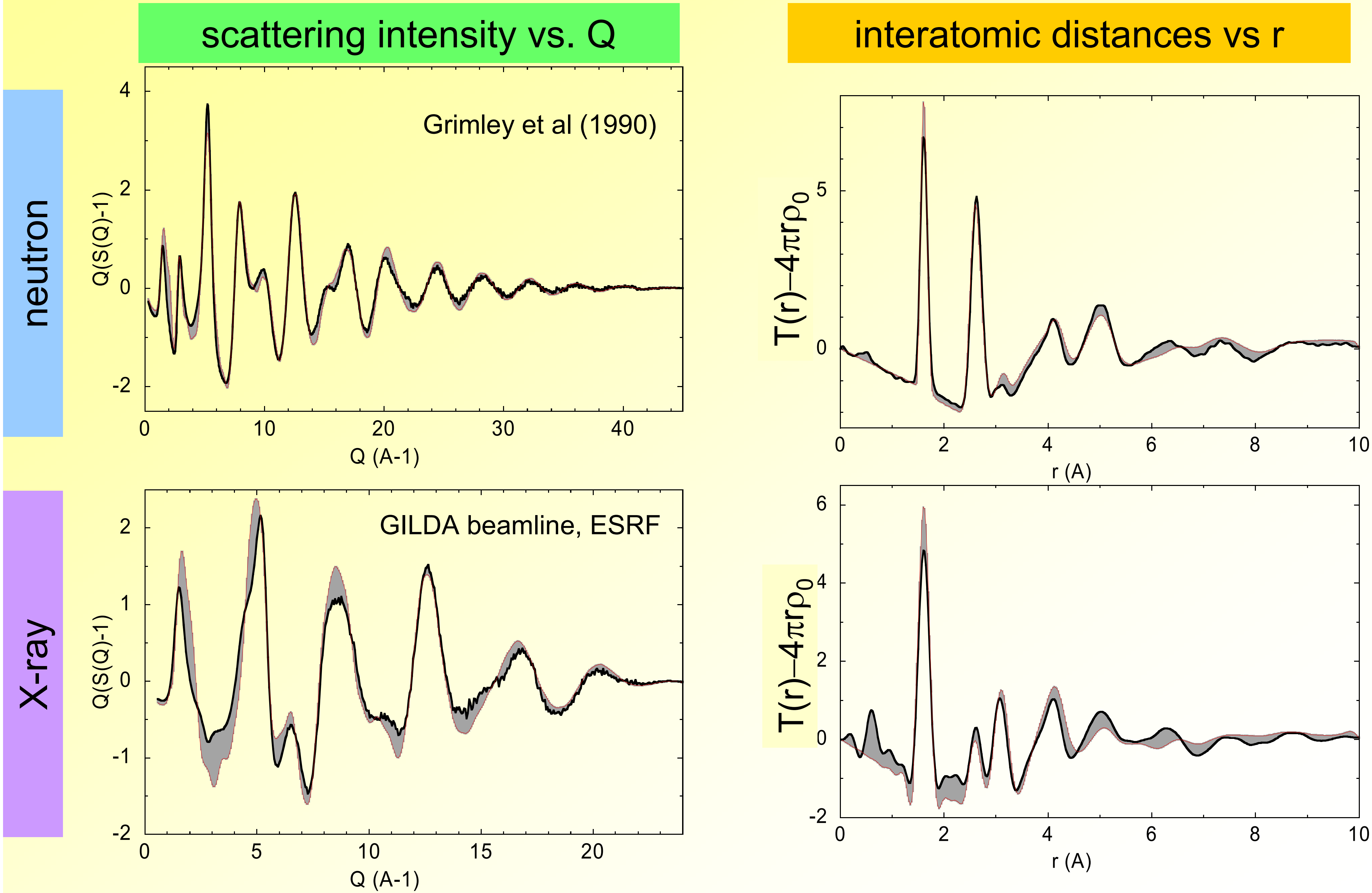
$$w_{ij}(Q) = \left(2 - \delta_{ij}\right) c_i b_i c_j b_j / \bar{b}^2$$

NMR data shows connectivity of tetrahedra

- measures chemical shift of ^{11}B, ^{27}Al, ^{29}Si, ^{31}P

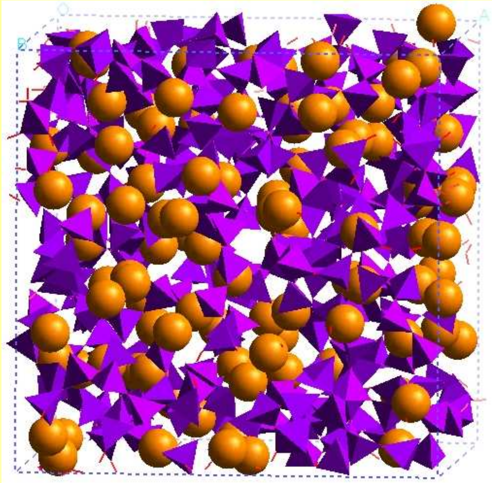
  depends on coordination number and connectivity

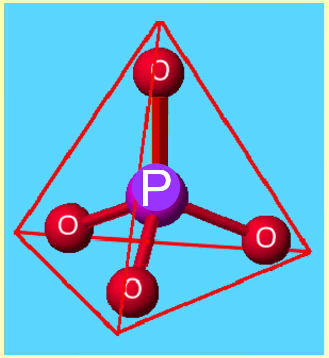
- comparing molecular dynmics of SiO_2 glass with diffraction



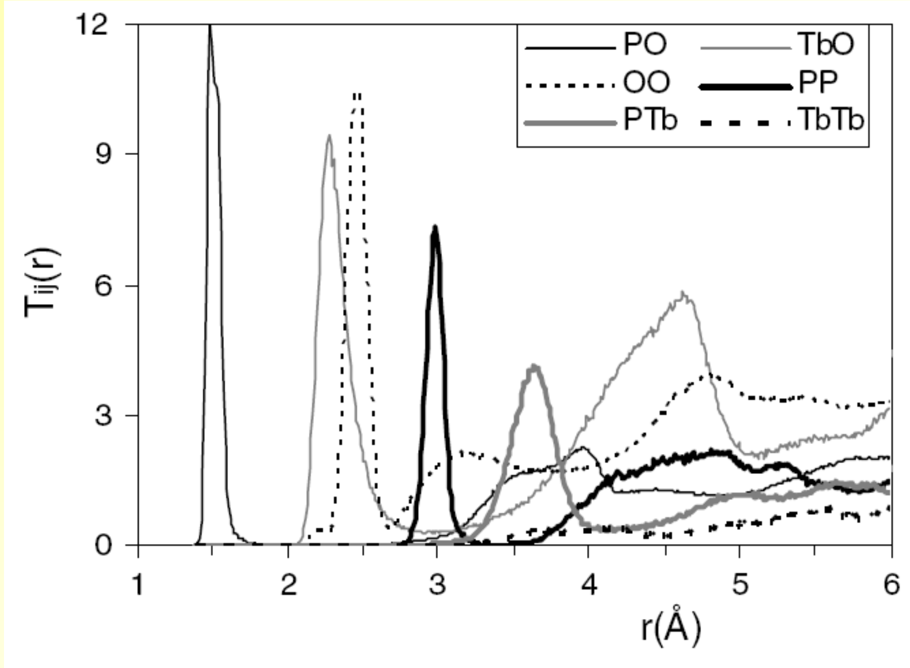
Example: analysis of Tb_2O_3-$3P_2O_5$ glass

molecular dynamics model





distribution of interatomic distances



coordination numbers:

$N_{P\text{-}O}$=4 (96%)

$N_{Tb\text{-}O}$=6 (68%)

connectivity of tetrahedra:

n=2 (50%)

comparison with experiment:

	Neutron diffr. [9]	EXAFS [13]	MD
R_{PO} (Å)	1.49(1)/1.60(1)	—	1.48/1.54
N_{PO}	1.7(4)/1.9(4)	—	2.10/1.95
R_{TbO} (Å)	2.27(2)	2.27(1)	2.28
N_{TbO}	5.6(6)	5.8(2)	5.7

Time for molecular dynamics simulation

(i) potentials:

slower if use complex potentials

we use "rigid" ions

(ii) timesteps:

slower if use short timesteps

we use 10^{-15} s

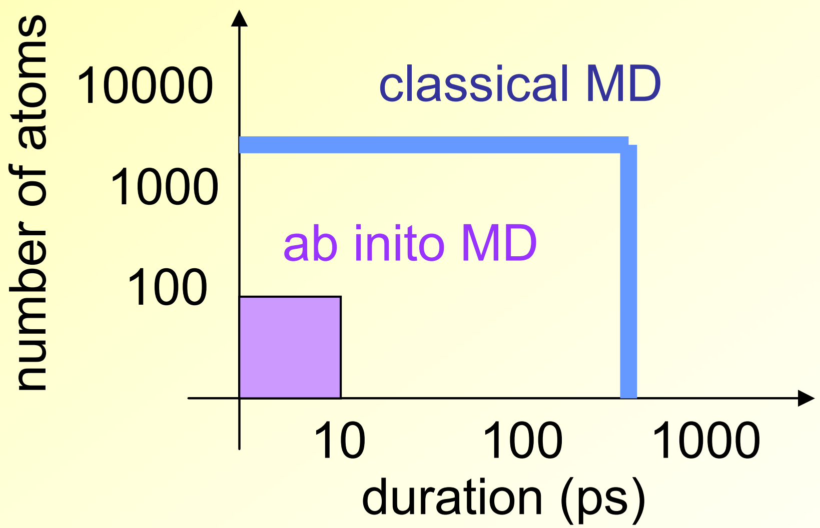
slower if use many timesteps

we use 40,000 steps

(iii) size of simulation:

slower if use many atoms

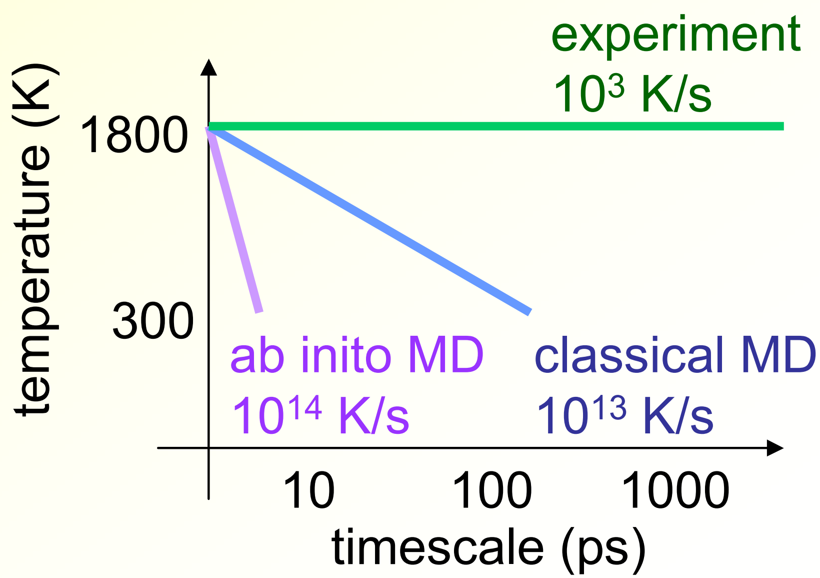
we use 1000 atoms



(iv) quench rate:

slower if use low quench rate

we use 10^{13} Ks^{-1}



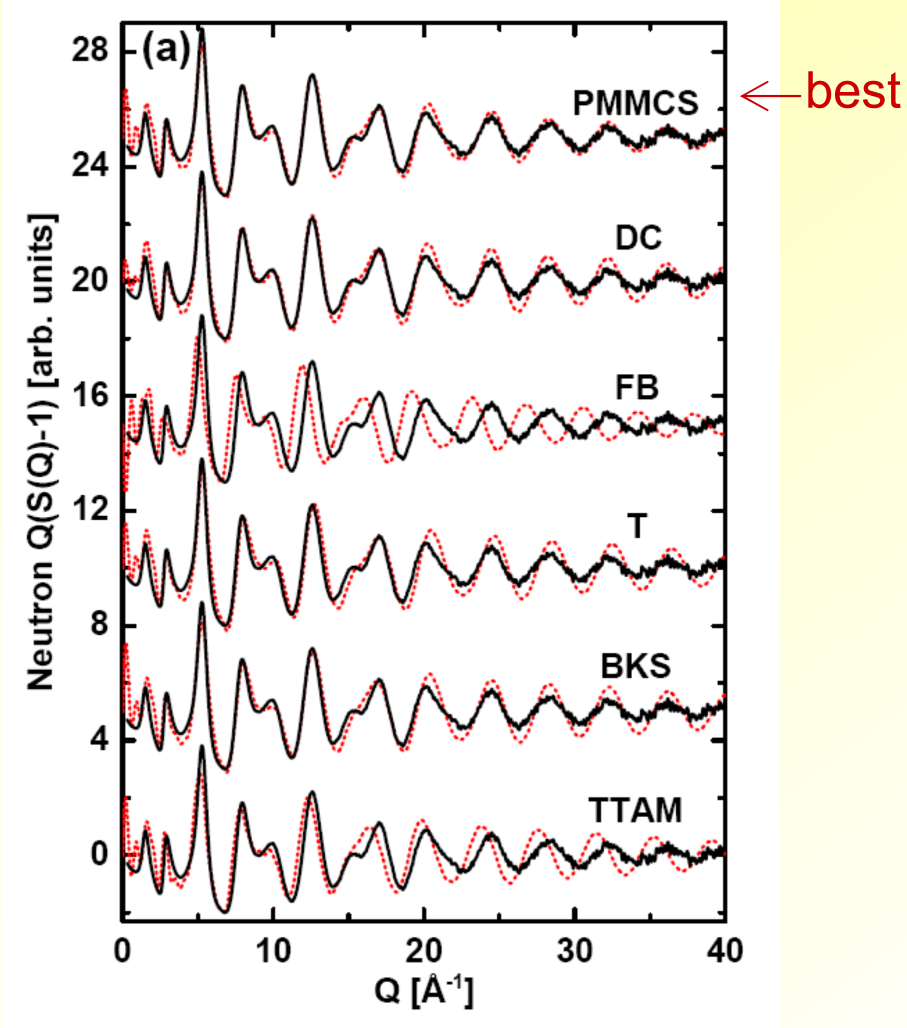
Improving molecular dynamics of glass

- molecular dynamics does not agree with experiment
  1. quench rate (too high)
  2. density
  3. diffraction (especially X-ray)
  4. NMR (connectivity of tetrahedra too variable)
  5. vibrational spectra (frequencies too low)

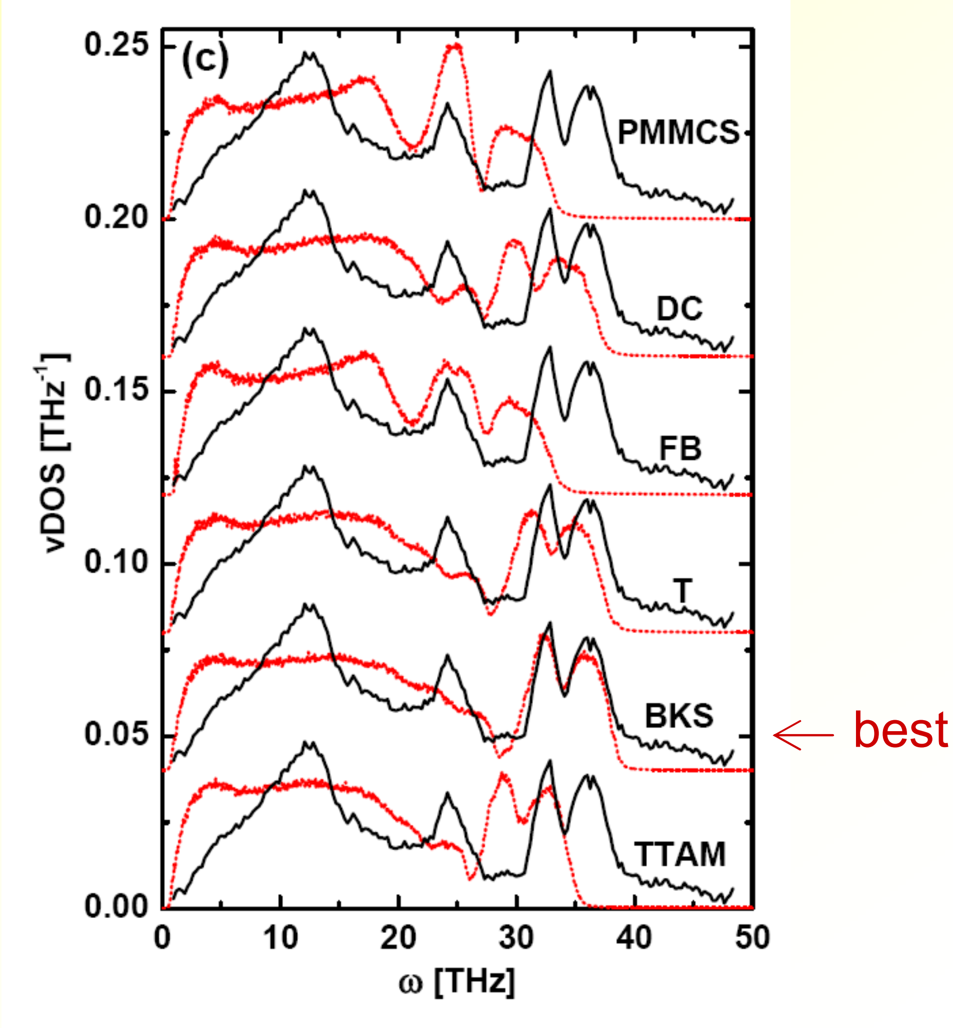
- "ab initio" molecular dynamics
  - uses quantum mechanics
  - treats electrons separately
  - very slow!

Interatomic potentials for SiO_2 glass

- good match to structure
  - compare to neutron diffraction



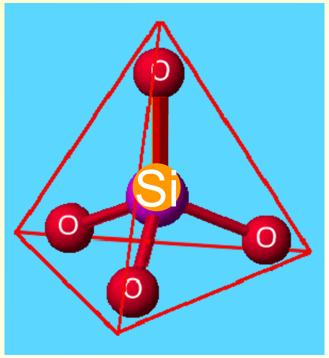
- poor match to vibrational spectra
  - compare to inelastic neutron scattering

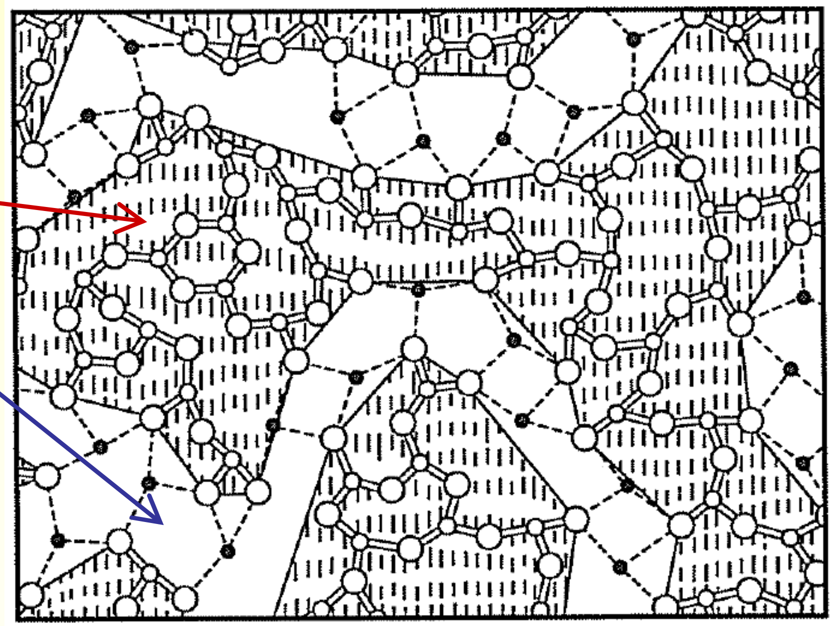


3) Structure of oxide glasses

Modified random network model

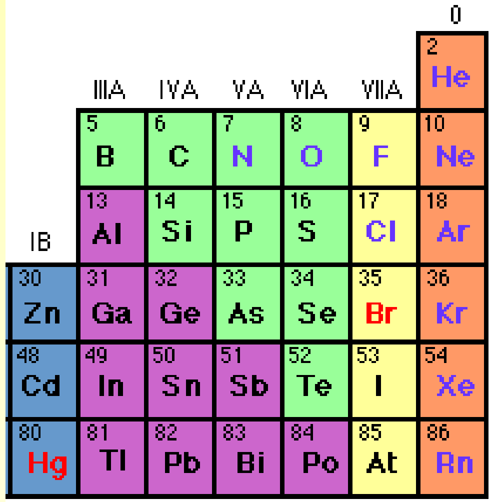
- Si, B, P, Ge are network formers
  - provide the strong part of the glass
- alkali, alkali earths are network modifiers
  - make glass useful for applications
  - they break up the network
  - form "channels"
- some cations have intermediate behaviour
  - e.g. Al can be network former





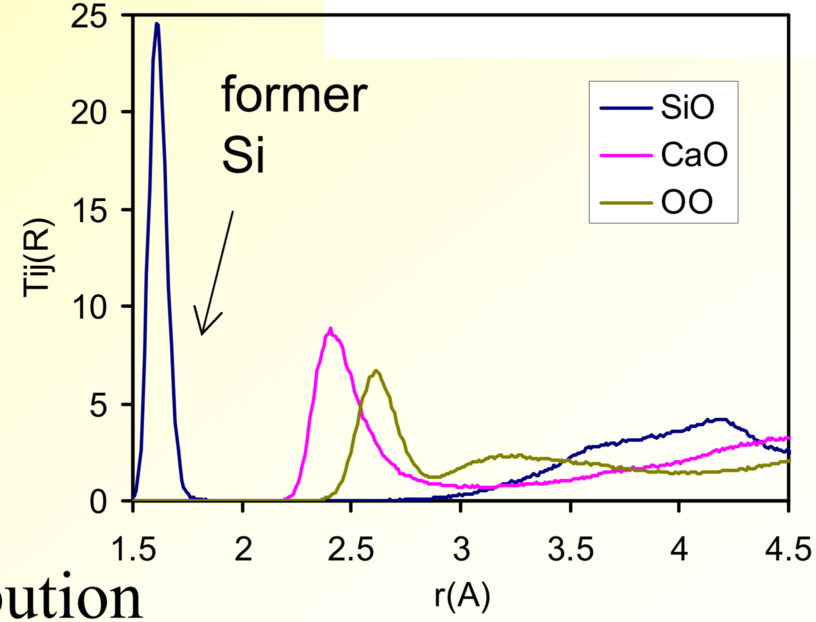
after Greaves (1985)

Network formers



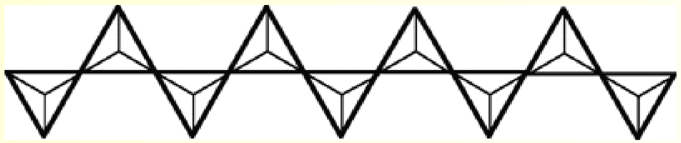
- network formers are p-block elements
  - in particular: Si, B, P, Ge
  - strong bonds to oxygen
  - tend to favour tetrahedral coordination

- coordination is sharply defined
  - well defined bond lengths and polyhedra

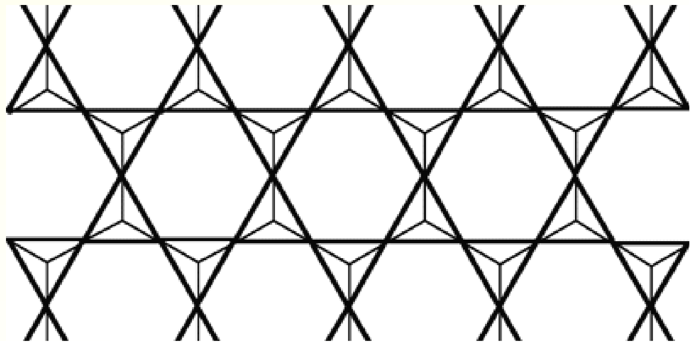


- connectivity is described by Q^n distribution
  - where Q is tetrahedra and n is connections

Q^2

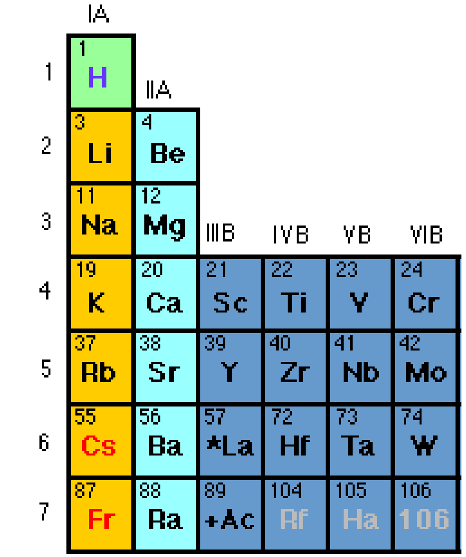


Q^3

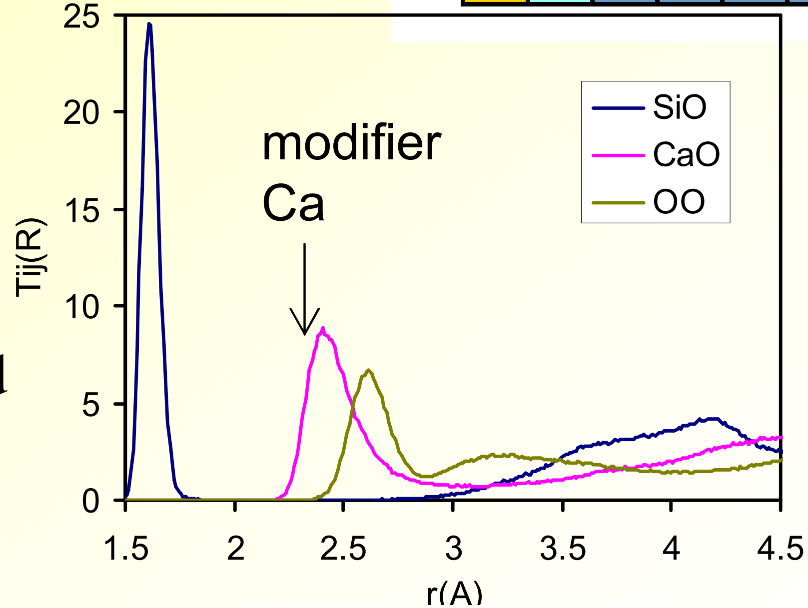


Network modifiers

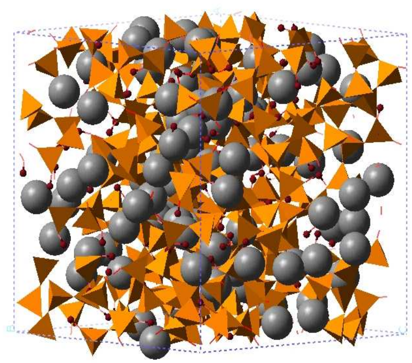
- network modifiers are s-group elements
  - e.g. Na, Ca (but not Be, Mg)
  - weak, non-directional bonds to oxygen
  - flexible coordination geometries



- coordination is variable
  - broad distribution of bond lengths
  - coordination number not precisely defined

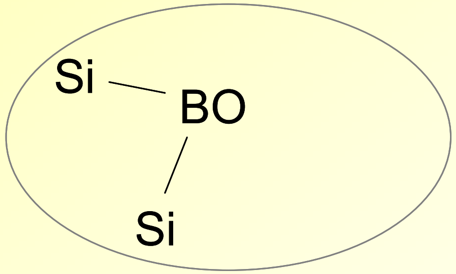


- modifiers tend to group together
  - at small content are "mixed" into glass network
  - at large content form "channels"

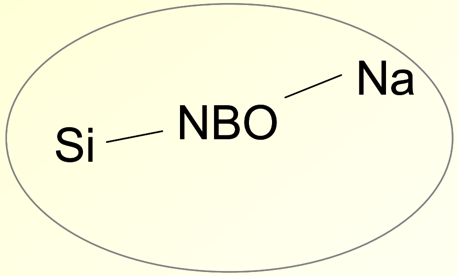


Role of oxygen

- "bridging" oxygen
  - used to form links in network



- "non-bridging" oxygen
  - adding network modifier means breaking links
  - e.g. Si–O–Si + $Na_2O \rightarrow$ Si–O·Na + Si–O·Na



- oxygen bonding to modifiers

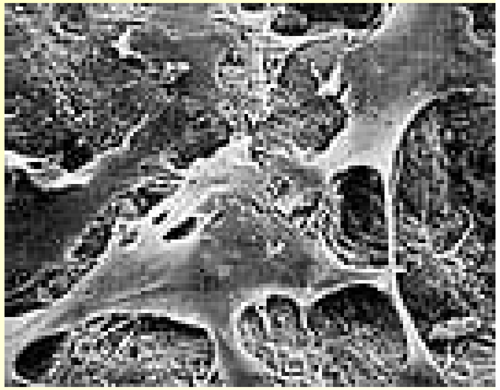
  (i) non-bridging oxygens are shared between modifiers

  e.g. Si–O·Na·O–Si is not possible, but Si–O·$\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}$·O–Si is possible

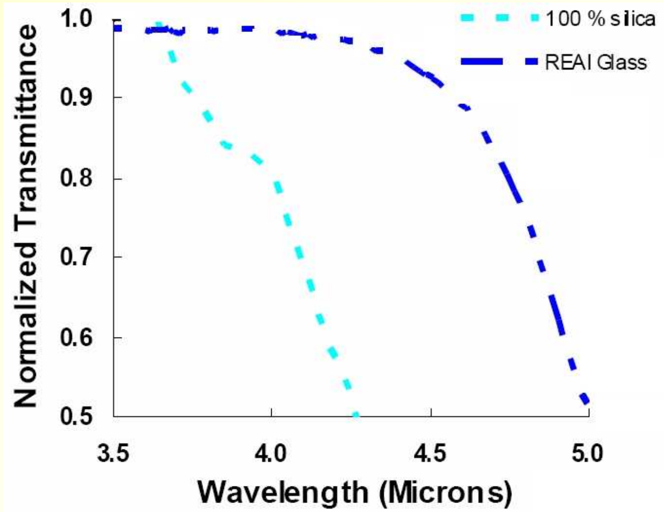
  (ii) bridging oxygen is also bonded to modifiers

  e.g. Si–O–Si
  Na

Examples of oxide glass structures



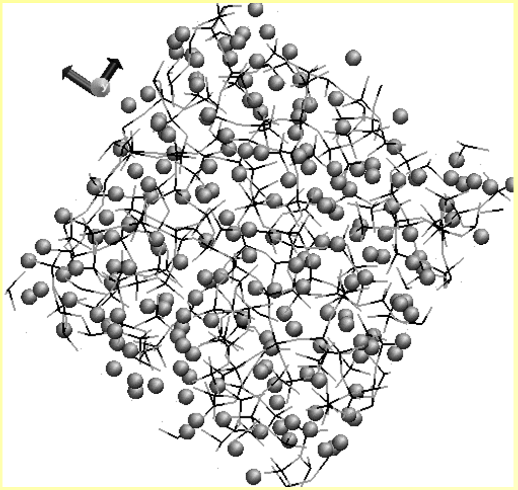
- $CaO\text{-}SiO_2$ glass
  - component of soda-lime (window) glass
  - stimulates cells to deposit bone

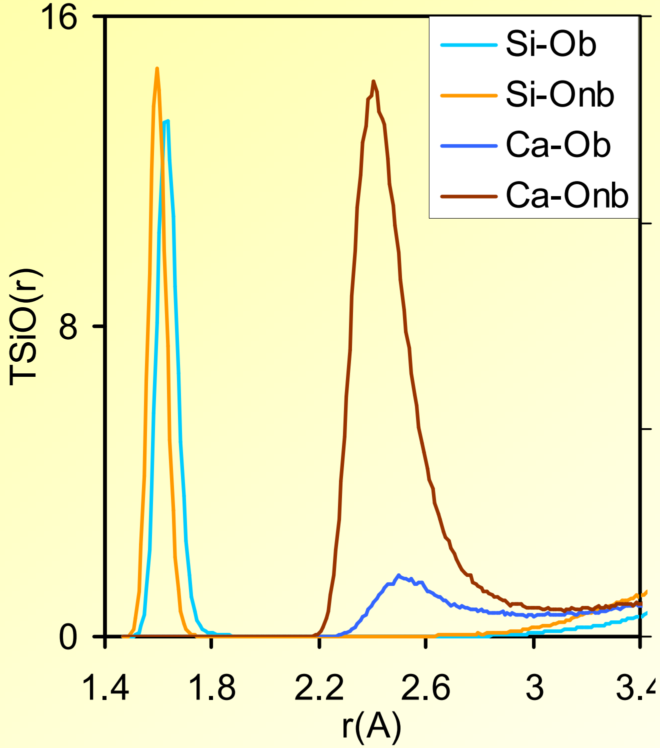


- $5CaO\text{-}3Al_2O_3$ glass
  - Al is a conditional glass former
  - prepared by rapid quenching or gas levitation
  - have greater transparency than silicates

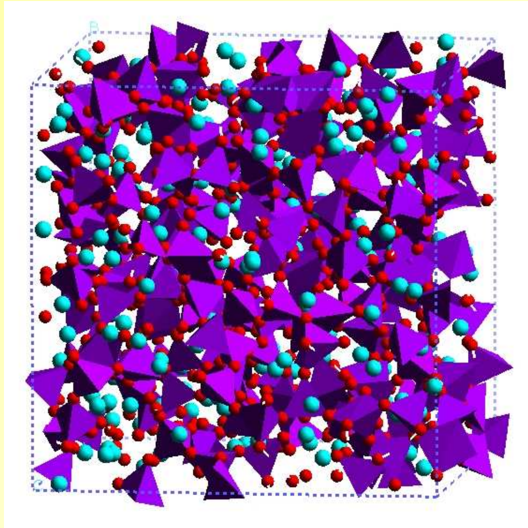
- $Tb_2O_3\text{-}3P_2O_5$ glass
  - RE-doped glasses used in optical applications
  - unusual thermal, acoustic, magnetic properties

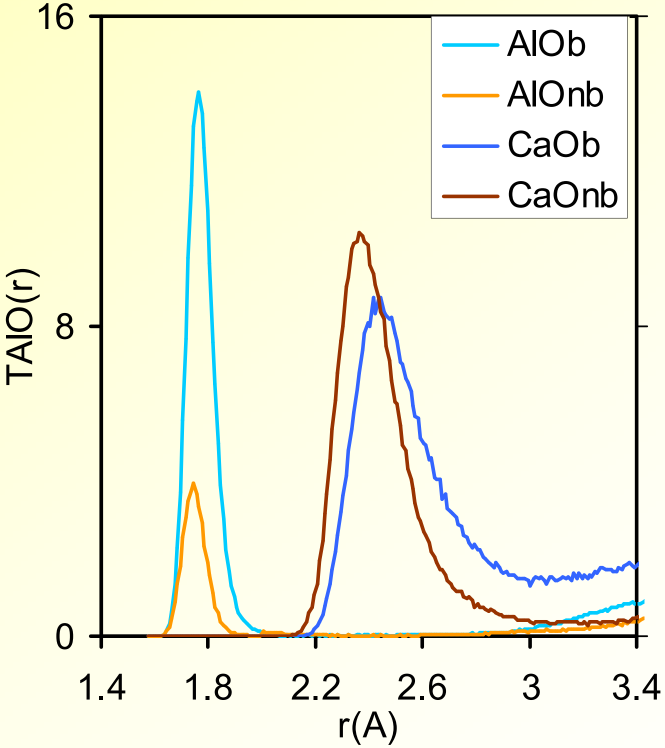
$CaO-SiO_2$ glass



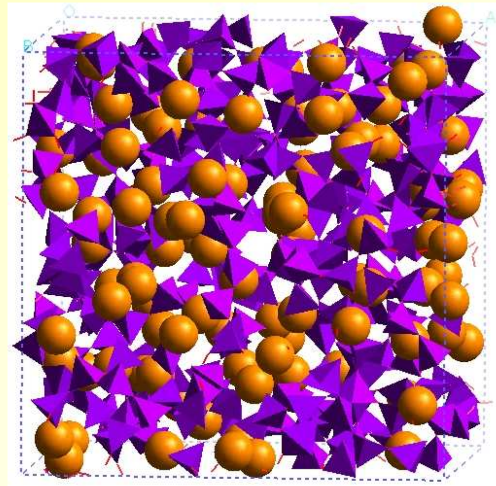


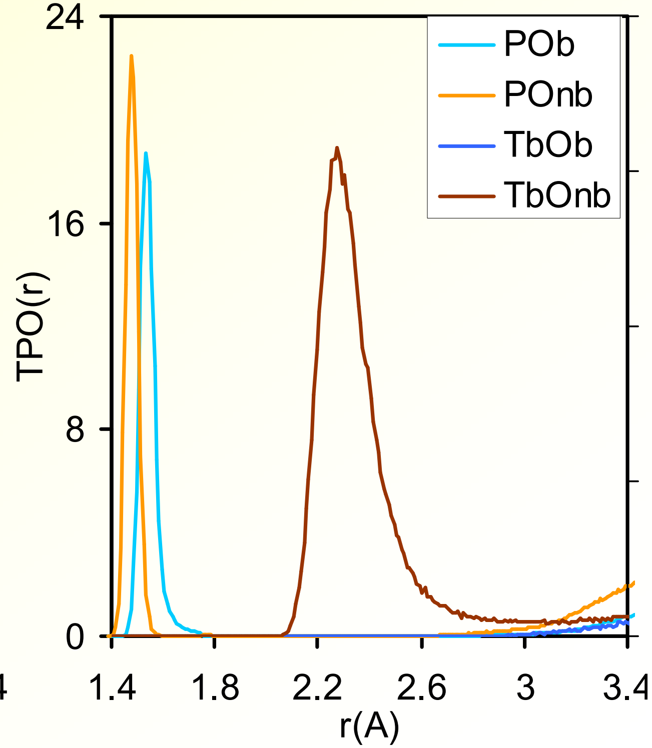
$5CaO-3Al_2O_3$ glass





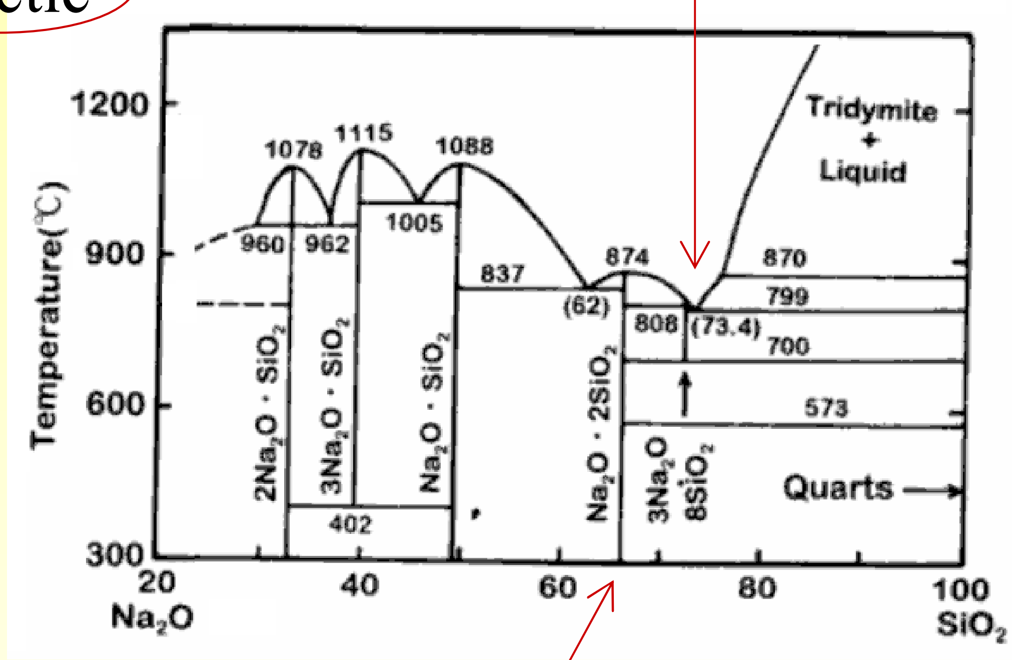
$Tb_2O_3-3P_2O_5$ glass





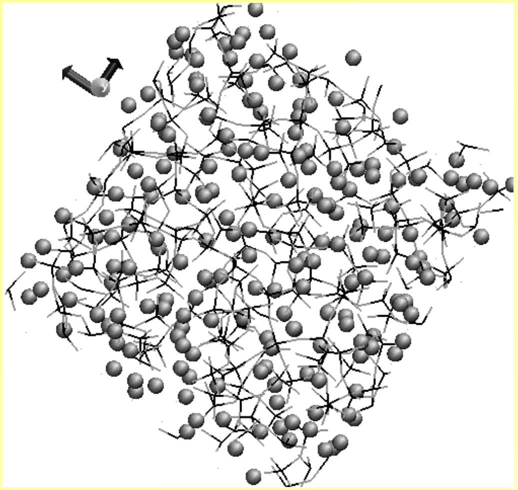
Comparing glasses with crystals

- glasses are formed near the eutectic
  - lower melting temperature
  - easier melt-quenching
  - short range order is like crystal

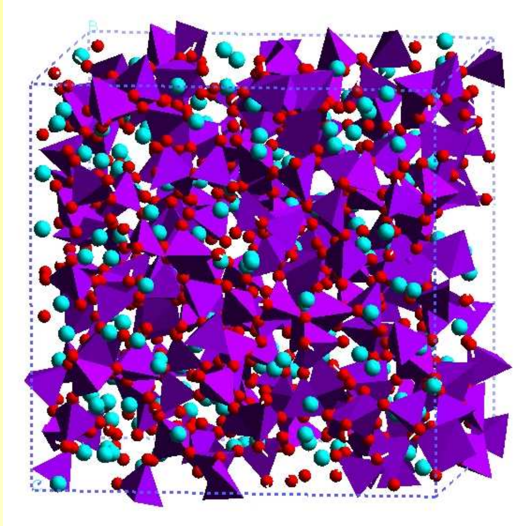


- crystals with same composition might exist
  - e.g. Na_2O-$2SiO_2$ glass and sodium disilicate $Na_2Si_2O_5$ crystal
  - other crystals will have higher melting temperature
  - crystals have strong ordering over larger distances

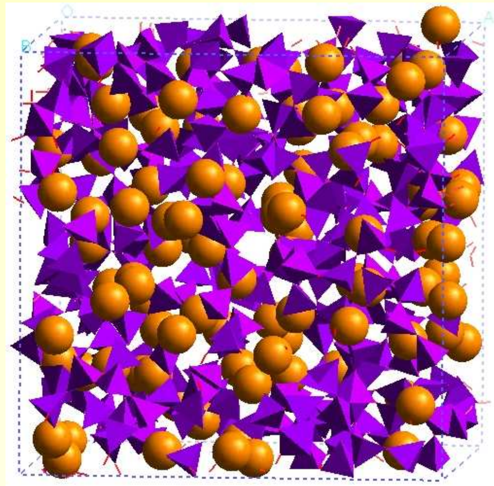
CaO-SiO_2 glass



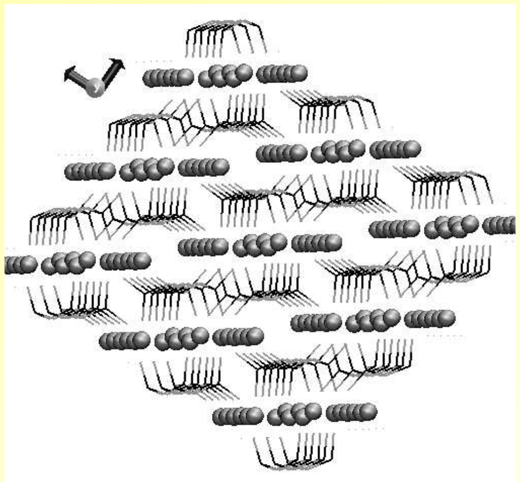
5CaO-$3Al_2O_3$ glass



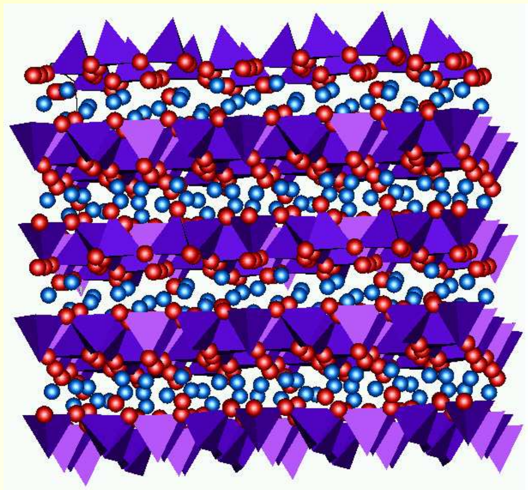
Tb_2O_3-$3P_2O_5$ glass



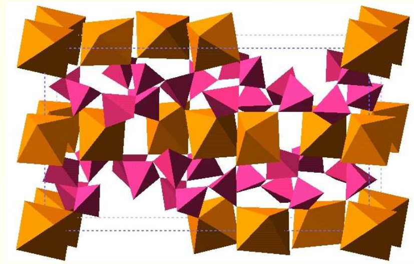
$CaSiO_3$ crystal



5CaO-$3Al_2O_3$ crystal

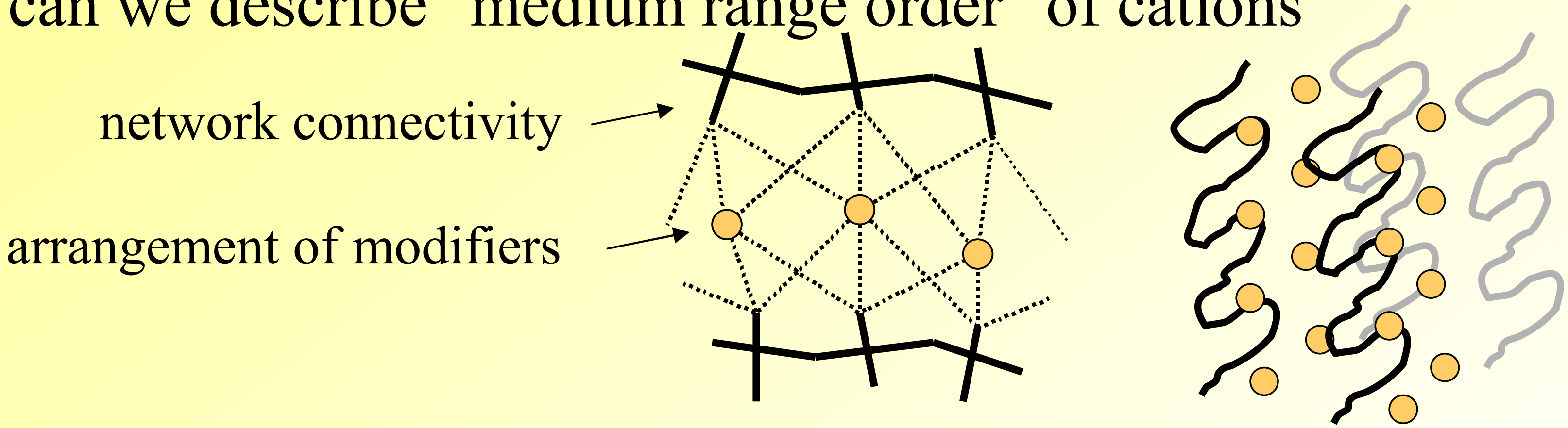


TbP_3O_9 crystal



Arrangements of modifiers over larger distances

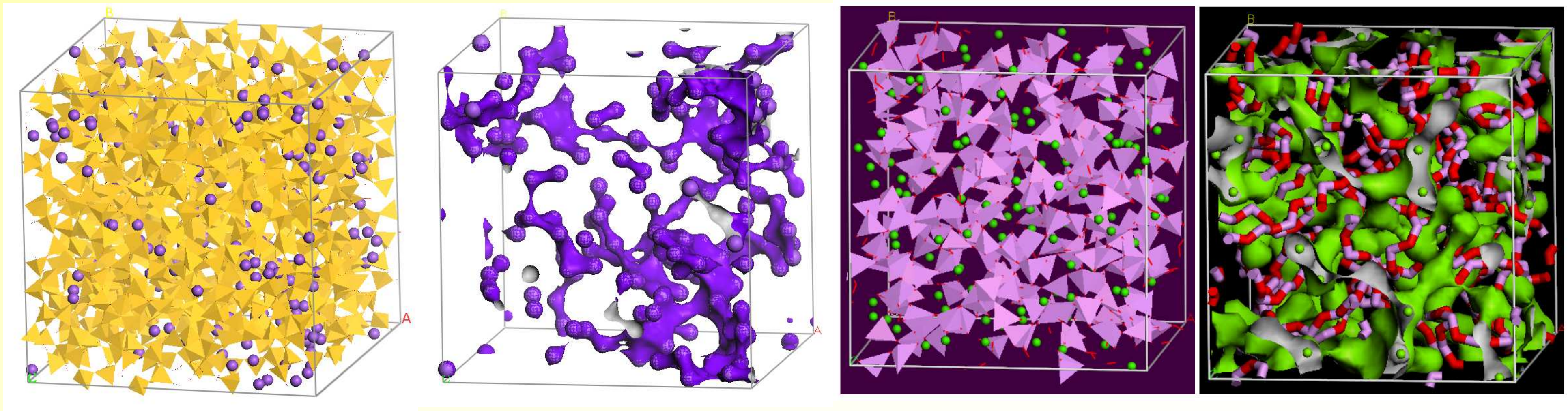
- how can we describe "medium range order" of cations



- our recent work has looked at "channels"

Na_2O-$9SiO_2$ glass

CaO-P_2O_5 glass

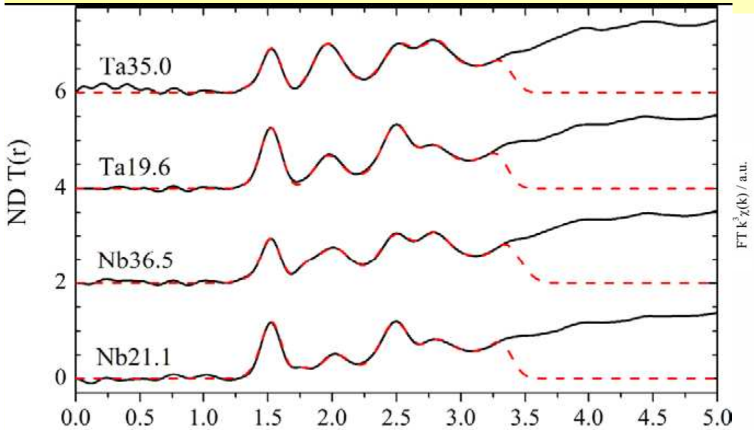


Complex glass structures

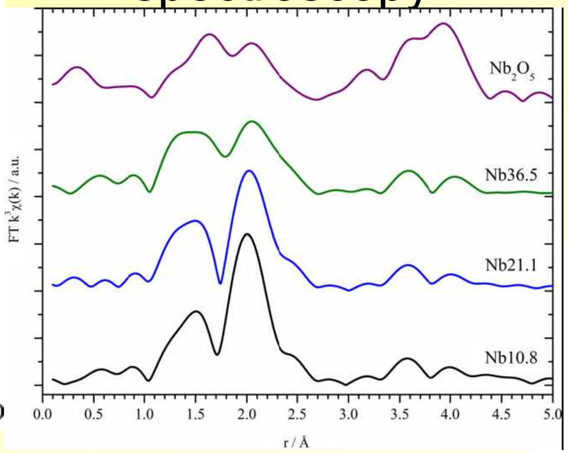
K.M. Wetherall, P. Doughty, G. Mountjoy, M. Bettinelli, A. Speghini, M.F. Casula, F. Cesare-Marincola, E. Locci & R.J. Newport *JPCM* (2009) **21** 375106

- $10Nb_2O_5$-$5Na_2B_4O_7$-$85NaPO_3$ glass

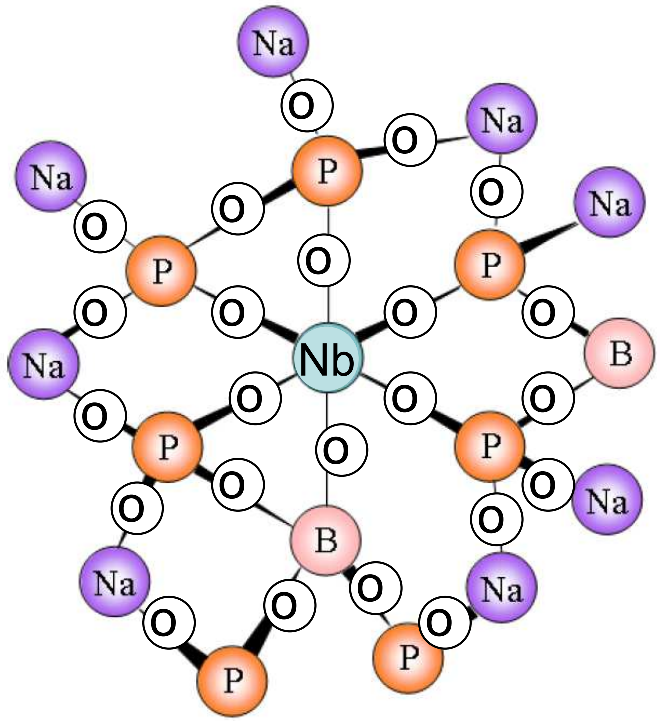
neutron & X-ray diffraction



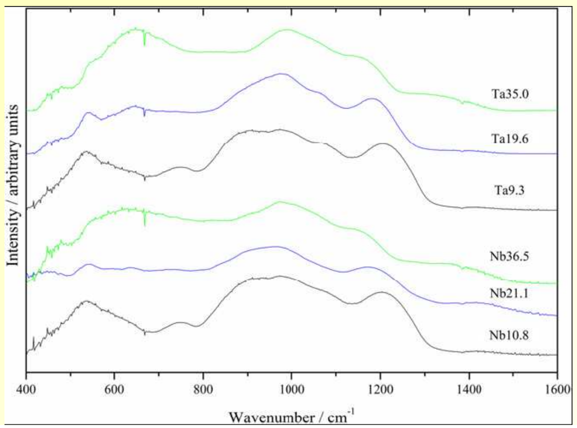
X-ray absorption spectroscopy



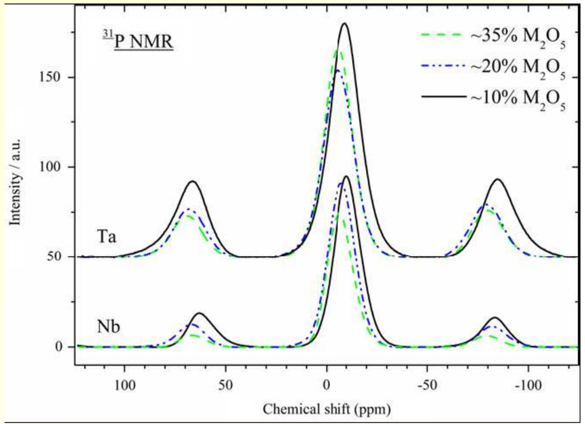
molecular dynamics



infrared & Raman spectroscopy



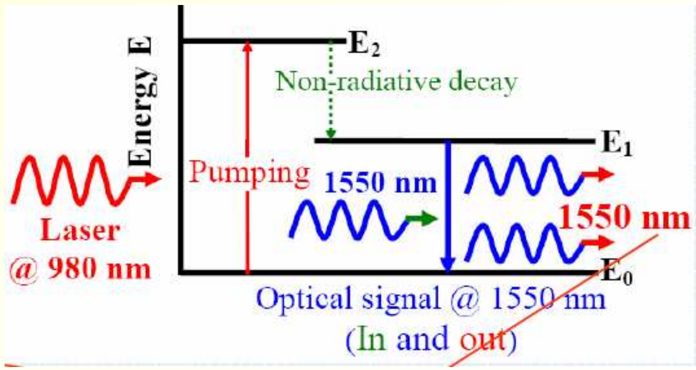
^{31}P & ^{11}B NMR



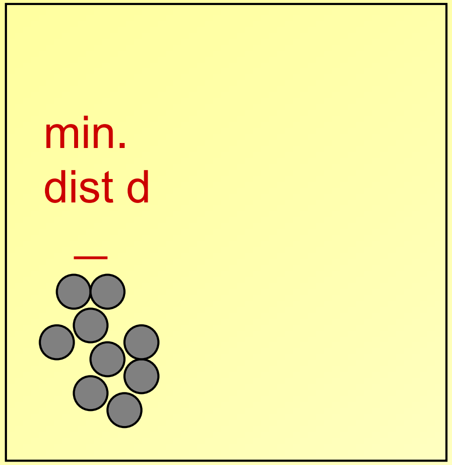
4) Relationship of properties and structure

Dopants in glasses

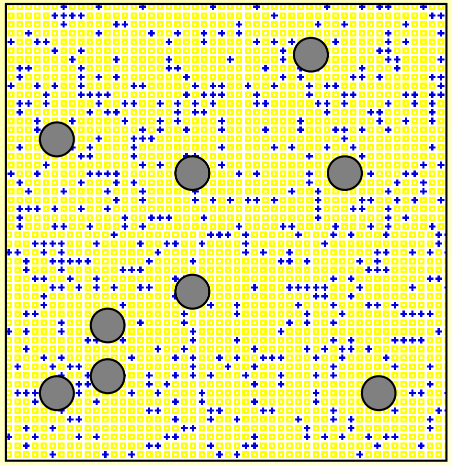
- Small amounts of modifiers (dopants)
- Dopant is beneficial
  - give new property to glass
  - e.g. lanthanide ions are luminescent
- Amount of dopant is limited
  - more dopant enhances properties, but...
  - dopants may interact with each other
  - lot of dopant causes phase separation



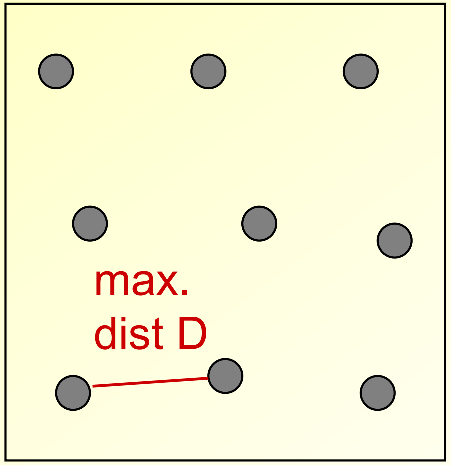
How are dopants distributed?



phase separation ☹



solution 😐

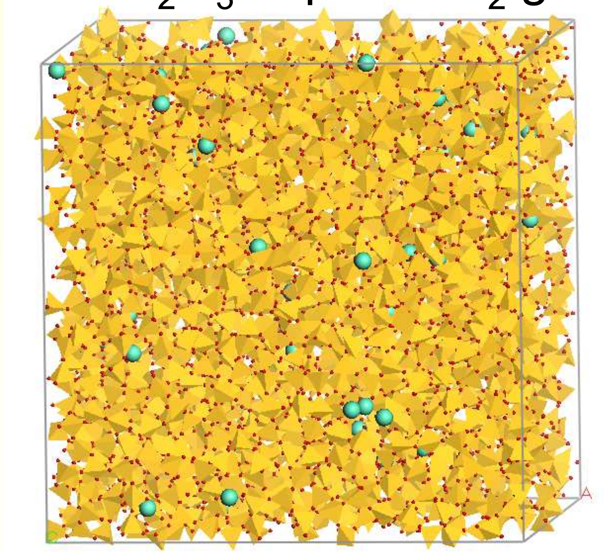


dispersed ☺

- dopants close together
  - increased dopant-dopant interactions
  - causes phase separation

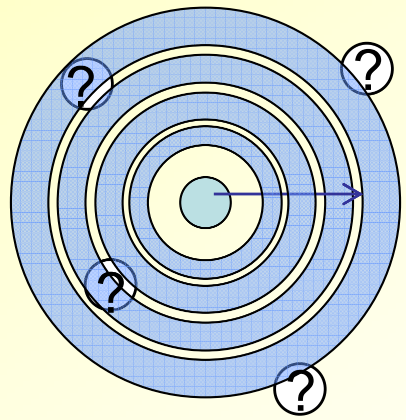
- dopants far apart
  - dopants well mixed
  - reduced dopant interactions

1 mol% Eu_2O_3 doped SiO_2 glass



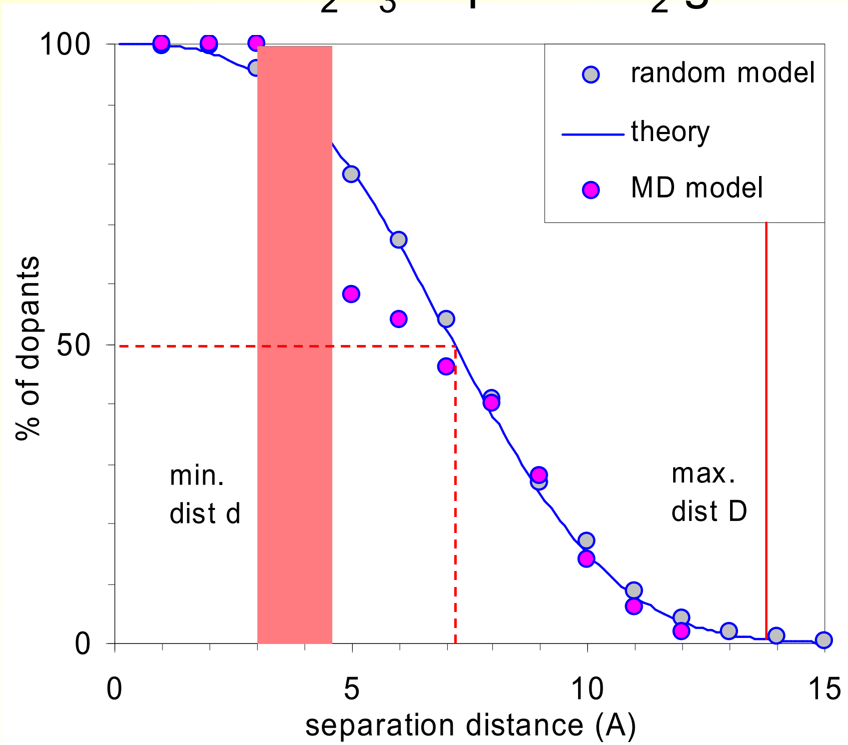
Separation of dopants in a random mixture

- shortest distance between dopants
  - probability that next dopant at distance r
  - follows a Poisson distribution



- no shortest distance < 3Å
  - dopants are separated by oxygens
- all shortest distances < 14Å
  - otherwise dopants would not fit in "box"
- 50% of shortest distances < 7Å
  - limits performance in optical applications

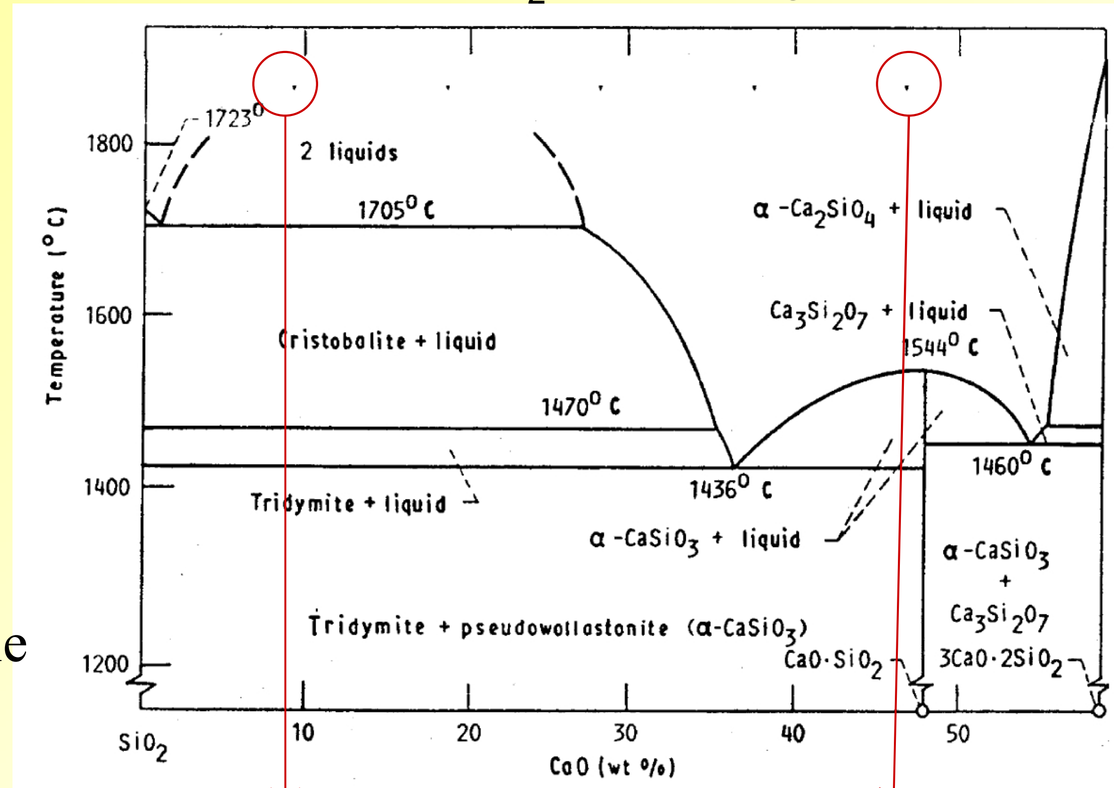
1 mol% Eu_2O_3 doped SiO_2 glass



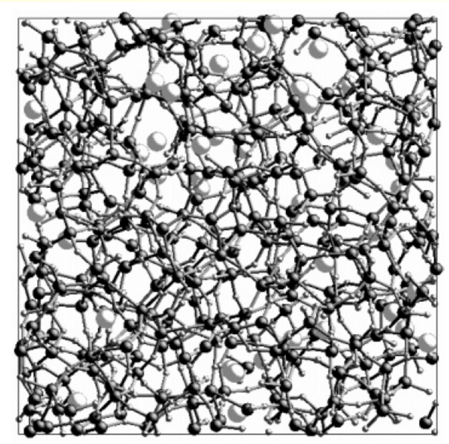
Phase separation in silicate glasses

- Medium amount of modifiers
- Phase separation in liquid
  - two liquid region, i.e. immiscible
  - common in silicates
- Glass has frozen phase separation
  - useful in (e.g.) borosilicate glasses
  - problem in (e.g.) ZrO_2-SiO_2 glasses

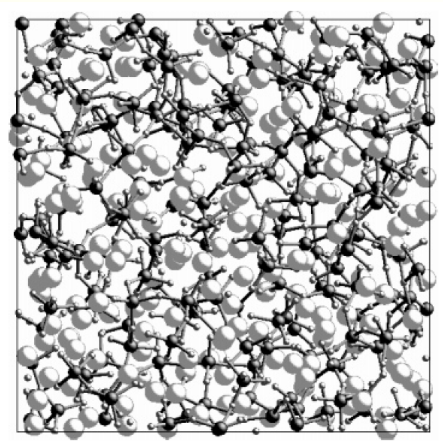
CaO-SiO_2 phase diagram



10 mol% CaO
two liquids

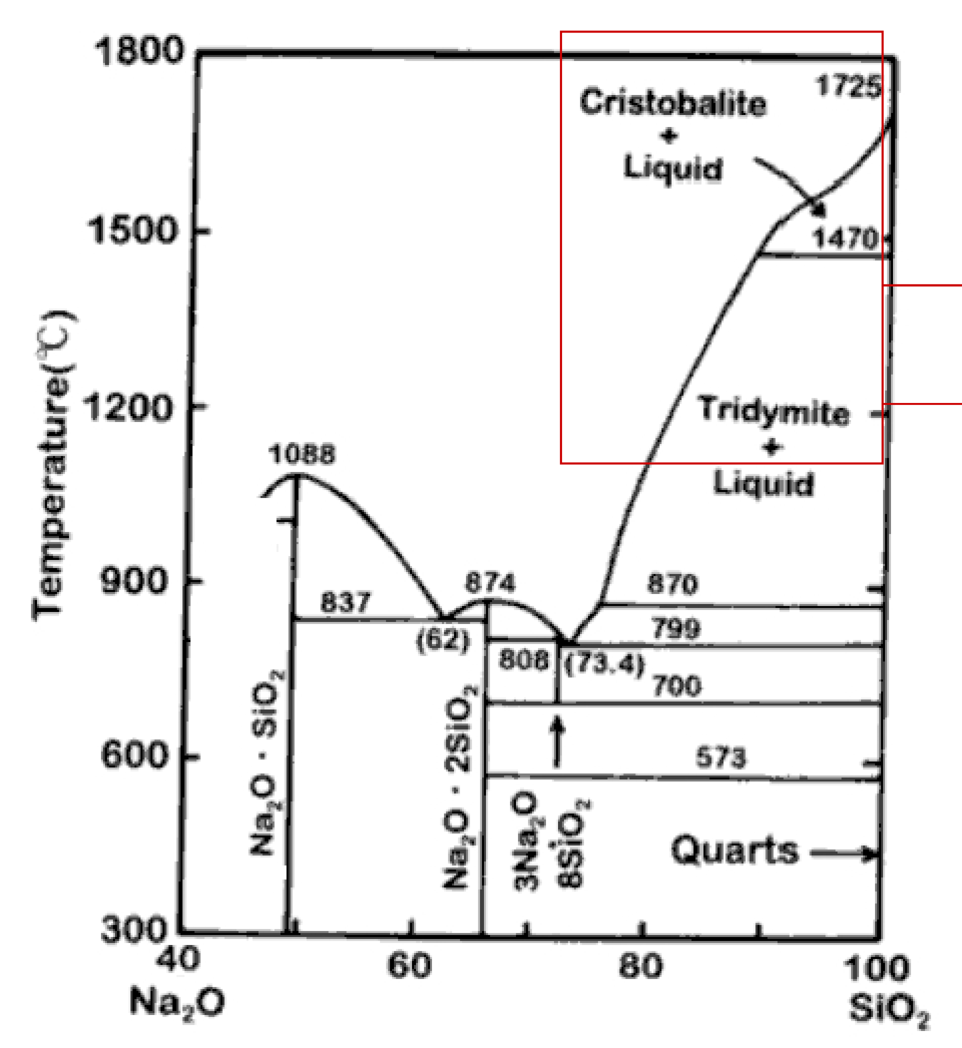


50 mol% CaO
one liquid

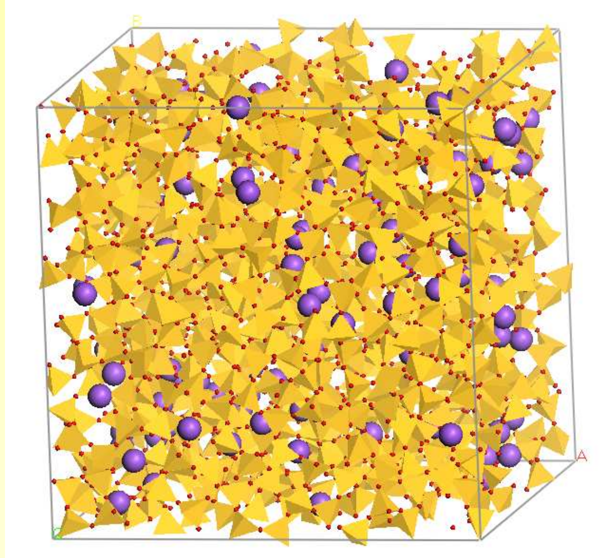


No phase separation in Na_2O-SiO_2 glasses

Na_2O-SiO_2 phase diagram

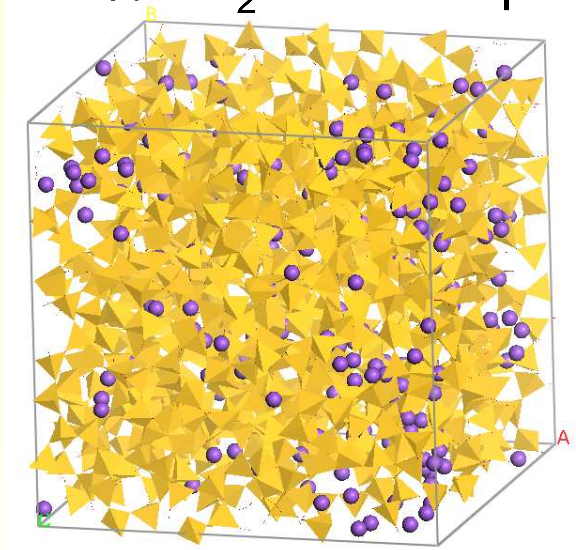


5Na_2O-95SiO_2 glass



5 mol% Na_2O: one liquid

10 mol% Na_2O: one liquid



10(Na_2O)·90SiO_2 glass

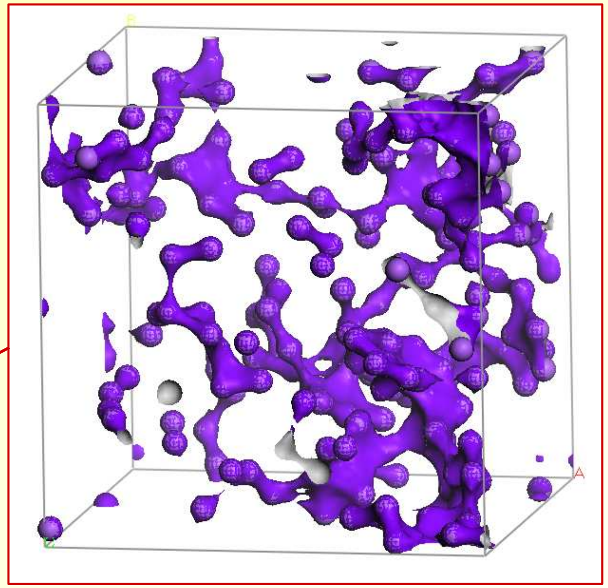
Percolation of "channels" in Na_2O-SiO_2 glasses

- "channels" are formed because

  Si–O·Na·O–Si is not possible

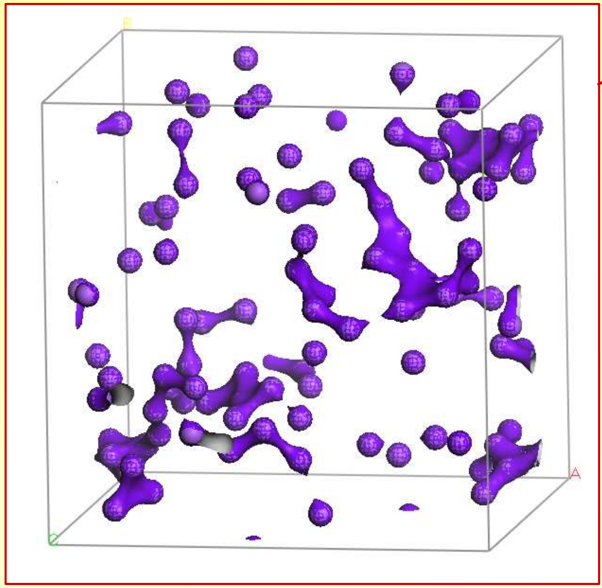
  but $\text{Si–O}\cdot{}^{\text{Na}}_{\text{Na}}\cdot\text{O–Si}$ is possible

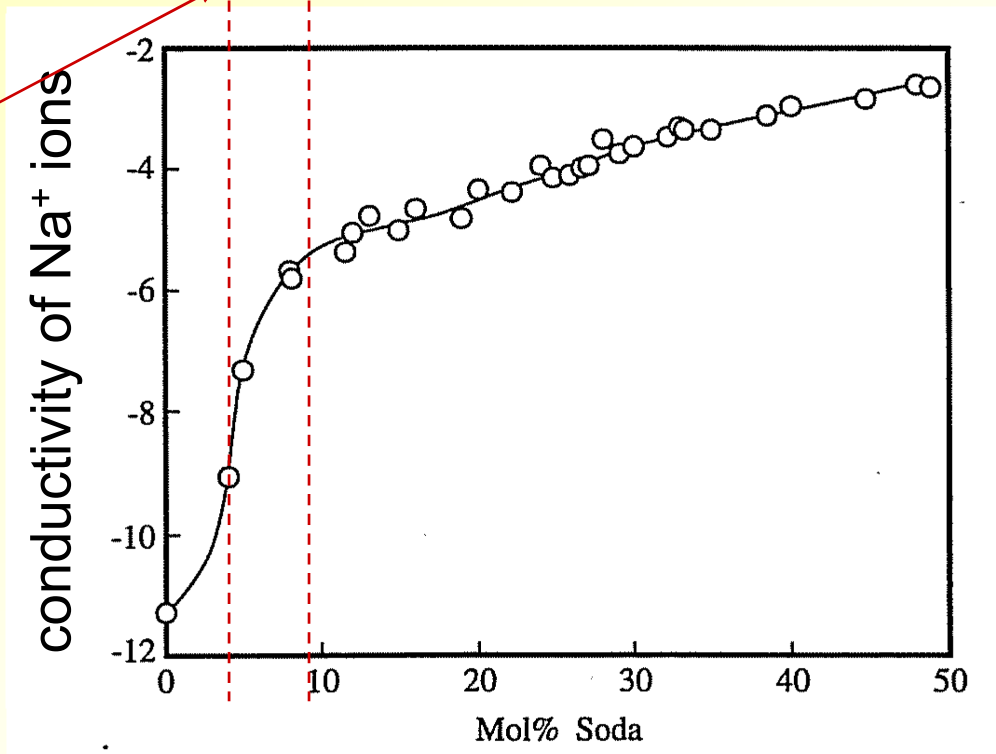
$10(Na_2O)\cdot 90SiO_2$ glass



onset of percolation

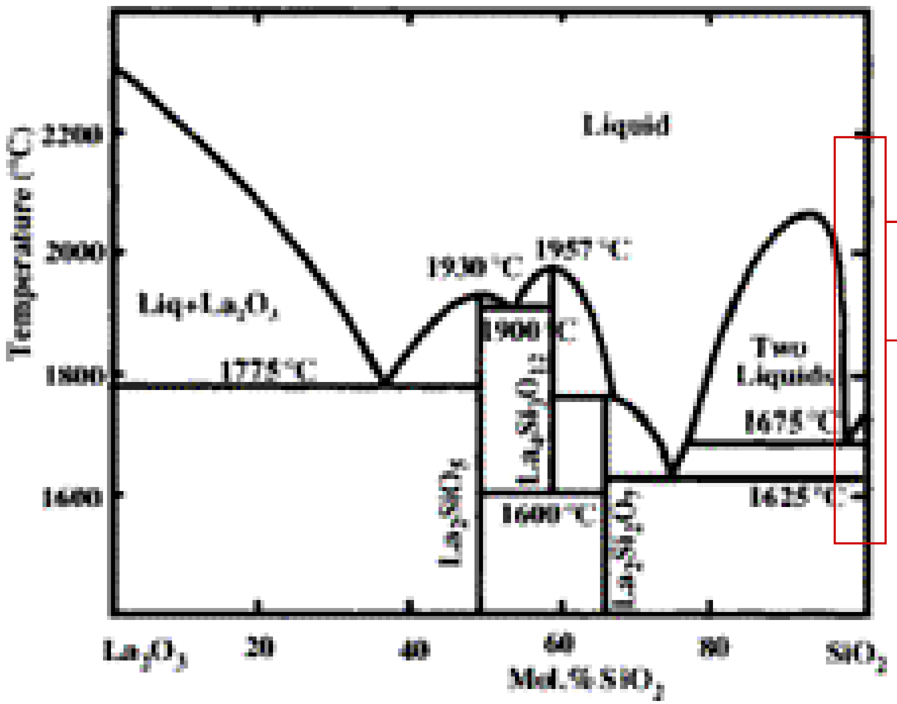
$5Na_2O$-$95SiO_2$ glass



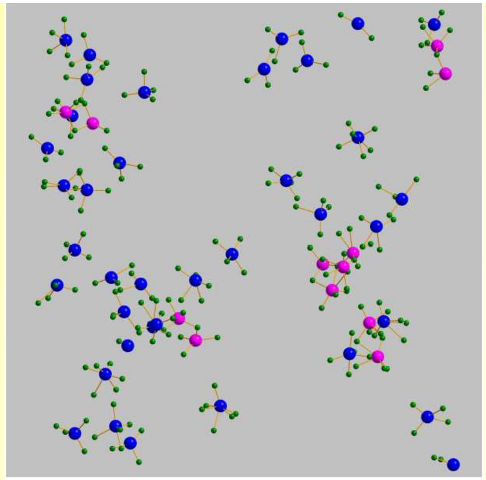


Phase separation in Eu_2O_3-SiO_2 glasses

Eu_2O_3-SiO_2 phase diagram



Eu_2O_3-99SiO_2 glass

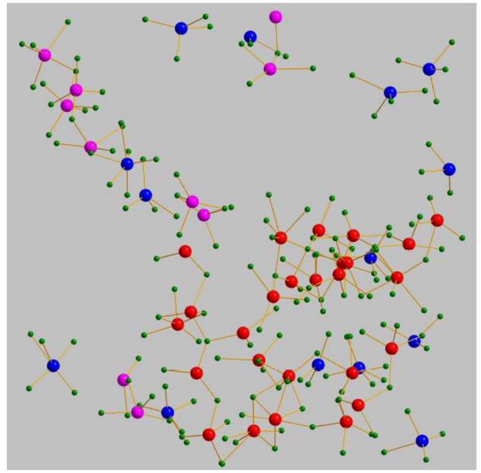


(a) 1 mol % Eu_2O_3.

- isolated Eu
- pairs Eu
- clusters Eu

1 mol% Eu_2O_3: one liquid

5 mol% Eu_2O_3: two liquids

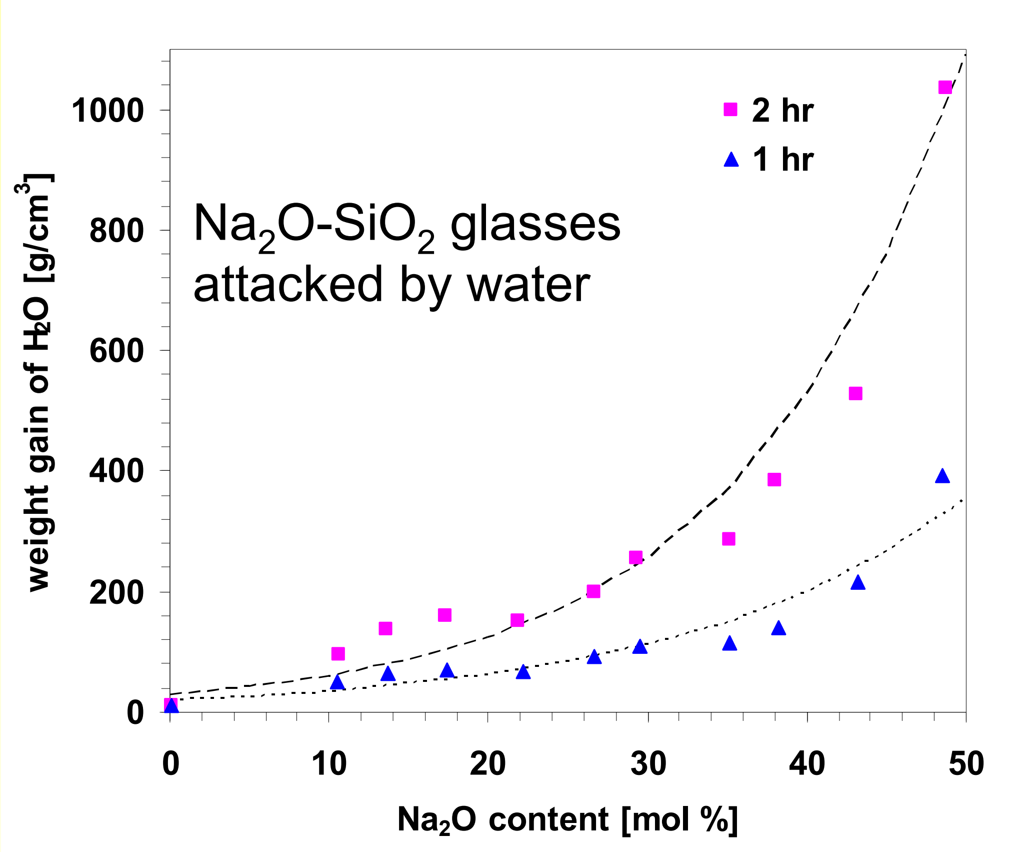


5Eu_2O_3-95SiO_2 glass

melt is immiscible

Chemical durability of glasses

- Large amounts of modifiers
- "Durability" is important
  - glass should be resistant to scratches, fracture, and chemicals
- chemical durability decreases when Na is added
  - other additives are ok, e.g. Ca

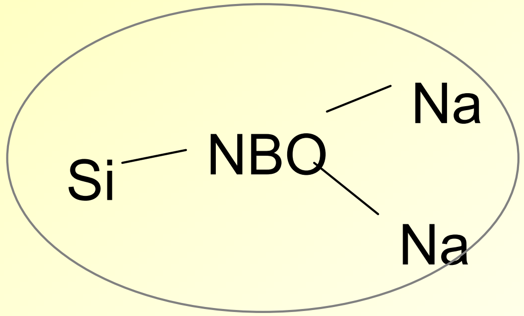


$$Si{-}O{-}Si + OH^- \rightarrow Si{-}OH + Si{-}O^-$$

"the breaking of a siloxane bond Si-O-Si... proceeds through the nucleophilic attack on the Si atom" Budd et al [1962]

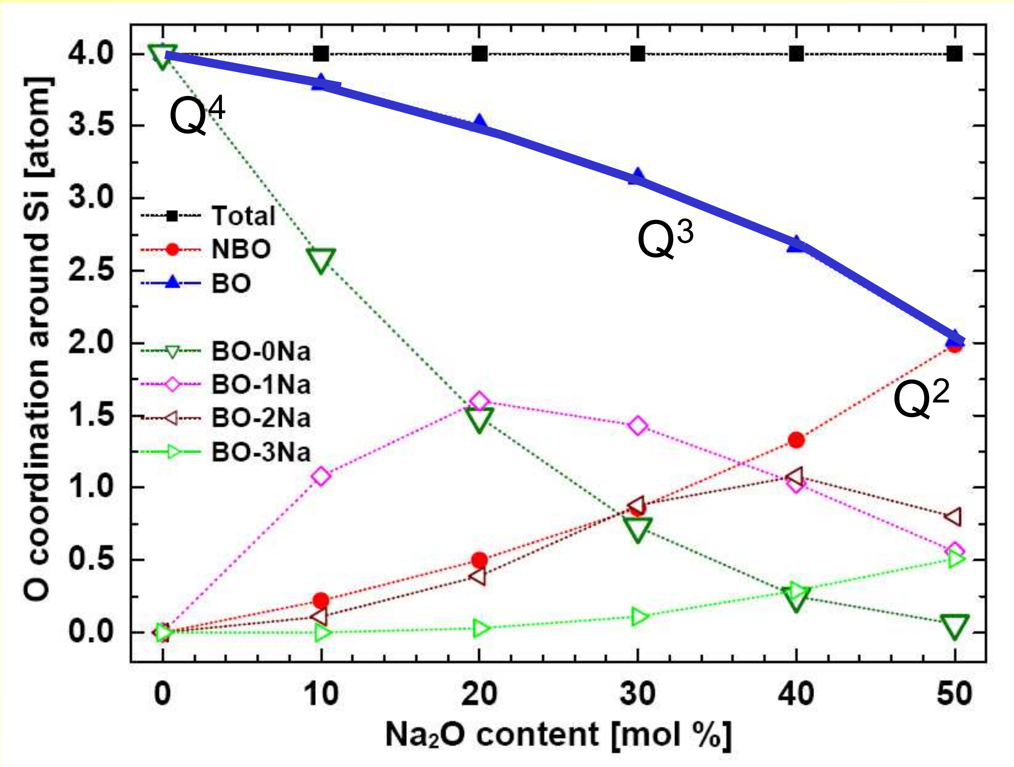
Sodium breaks links in silica network

- "non-bridging" oxygen are introduced
  - e.g. Si–O–Si + $Na_2O \rightarrow$ Si–O·Na + Si–O·Na

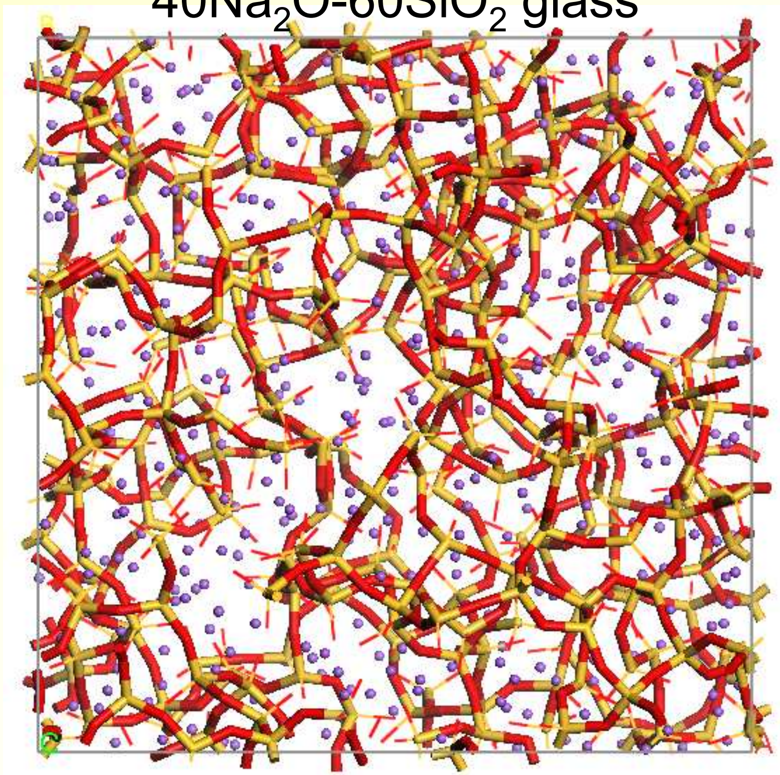


- connectivity of tetrahedra is decreased

connections per Si



$40Na_2O$-$60SiO_2$ glass

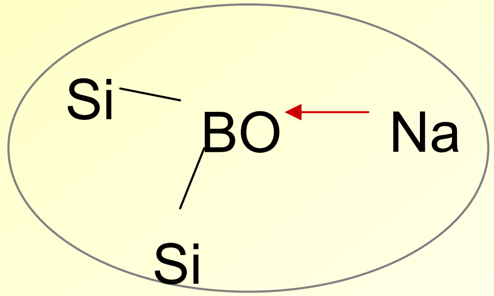


connections are shown

Sodium weakens links in silica network

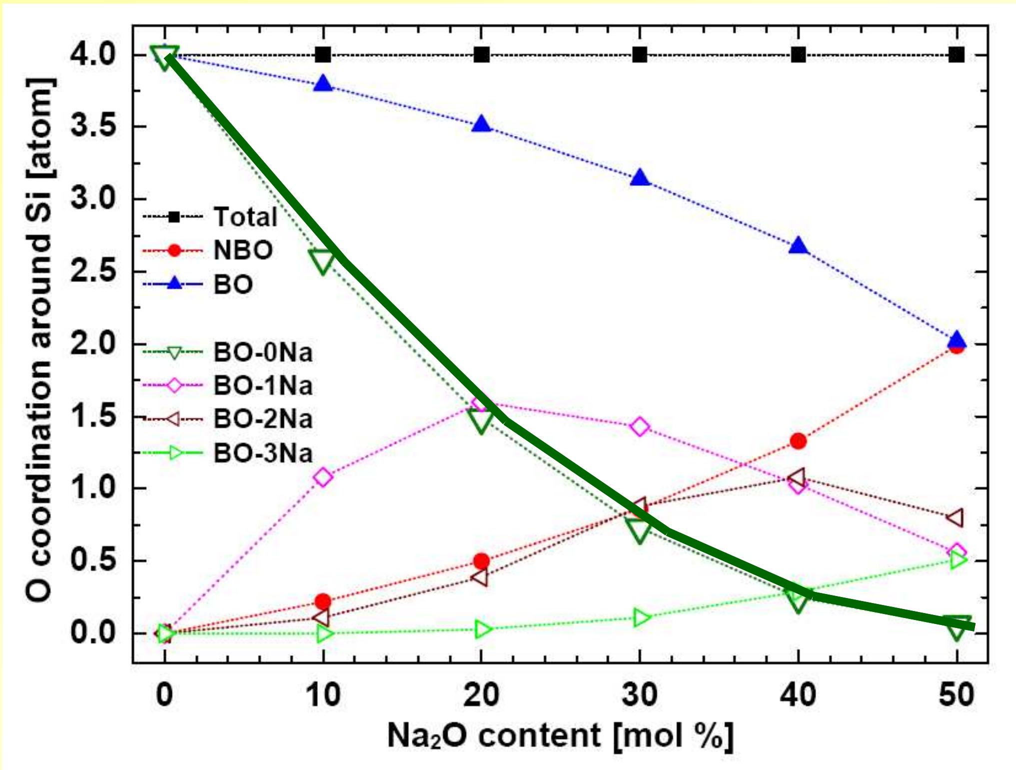
- bridging oxygen is also bonded to Na

  e.g. Si–O–Si
  Na

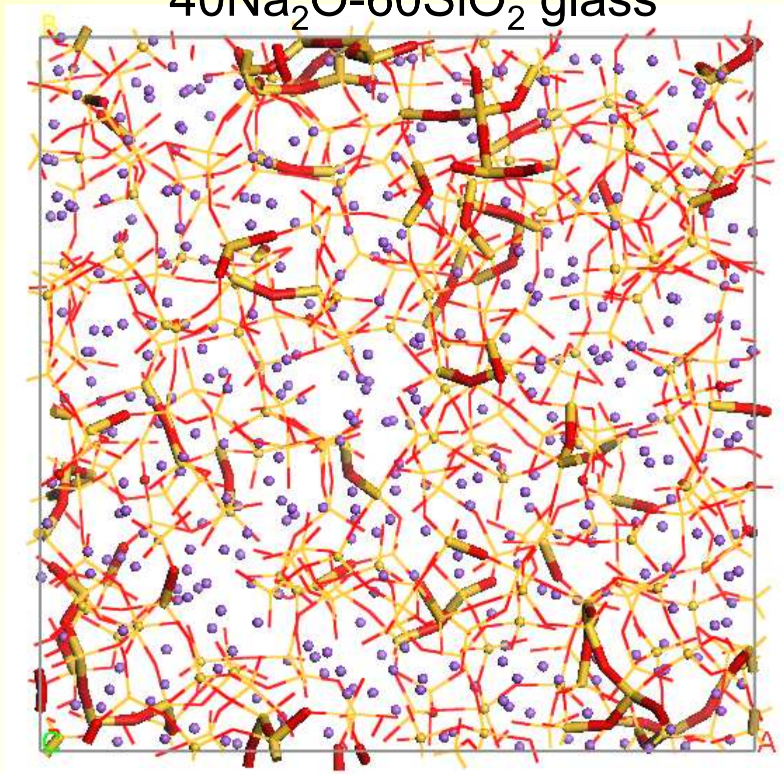


- links between tetrahedra are weakened

strong links per Si



40Na_2O-60SiO_2 glass



strong links are shown

5) Summary

- Applications of glasses
  - transparent and strong with variable shape and composition
- Molecular dynamics
  - provides detailed information on glass structure
- Oxide glass structure
  - network formers and modifiers
  - bridging and non-bridging oxygen
- Properties changed by adding modifiers
  - solubility or phase separation of modifiers
  - number and strength of network connections

Acknowledgements

- Co-workers in molecular dynamics
  - Ed Clark
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  - EPSRC
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