Non-crystalline materials

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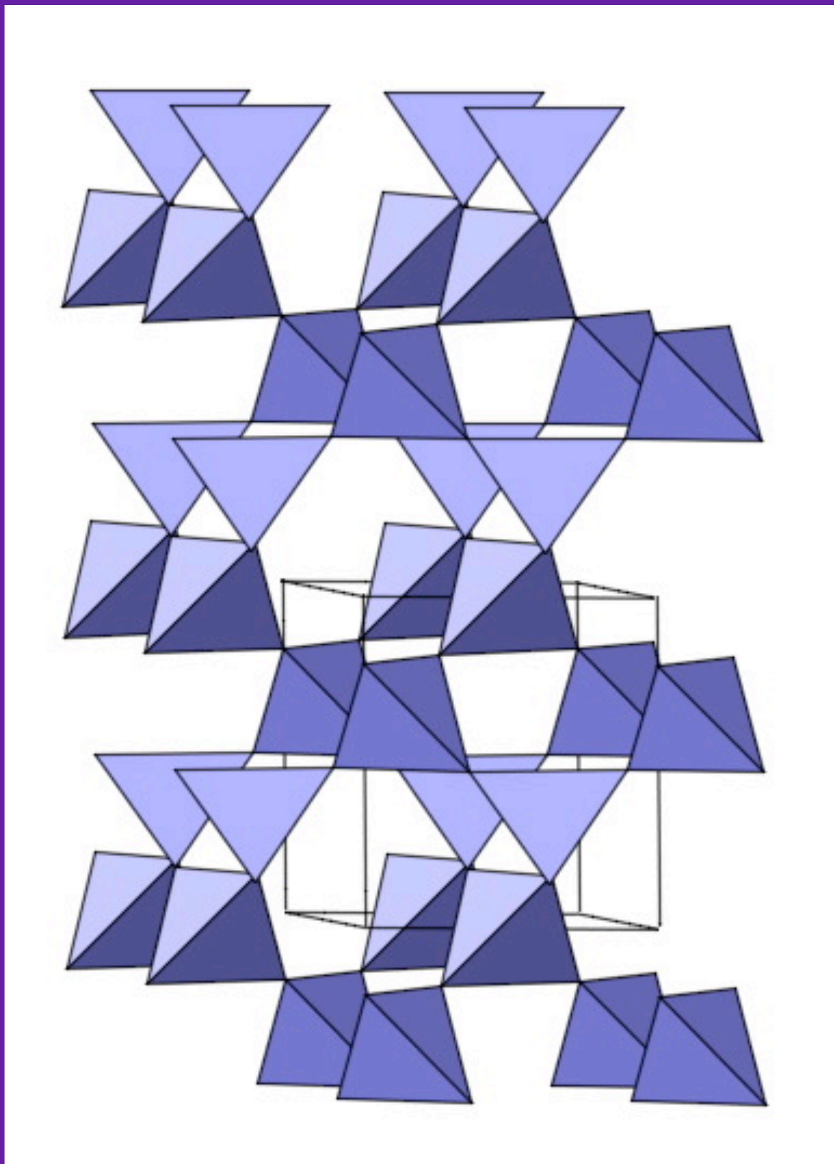
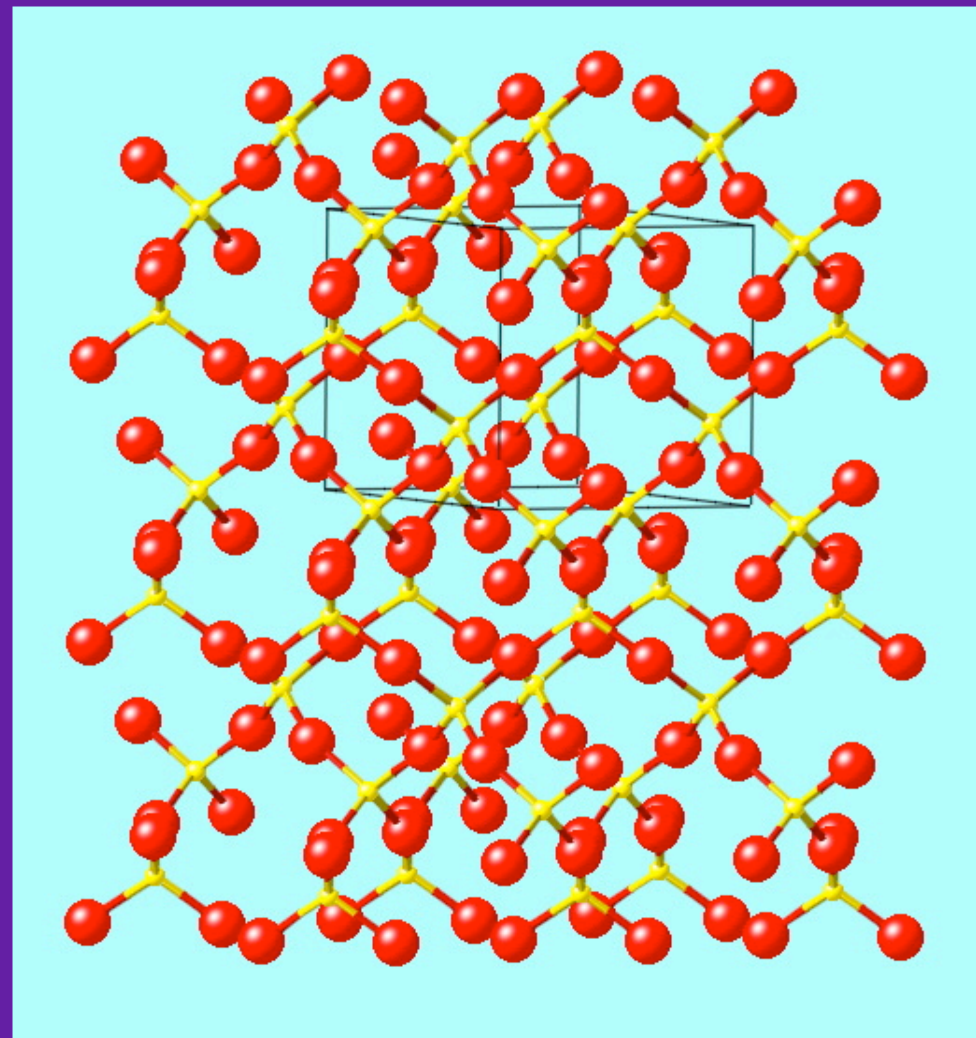
What Is A Glass?

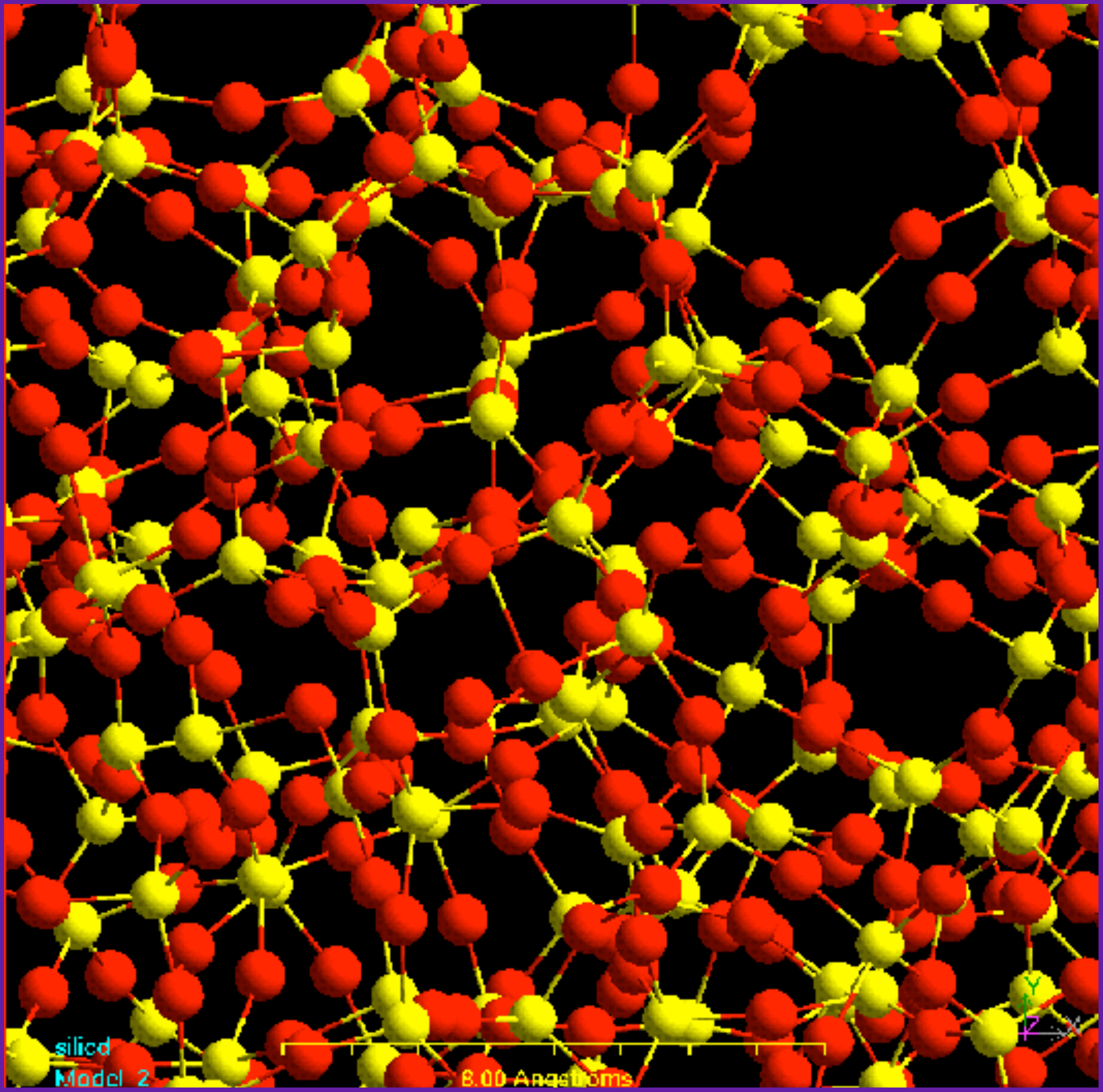
- Derived from *glaesum*, a Latin term for a lustrous and transparent material
- *An inorganic product of fusion which has been cooled to a rigid condition without crystallizing* (ASTM definition)
  - sol-gel ?
  - chemical vapour deposition?
- A solid with liquid like structure: noncrystalline; amorphous

what is a glass (continued)?

- structurally
  - non-crystalline: no long range order

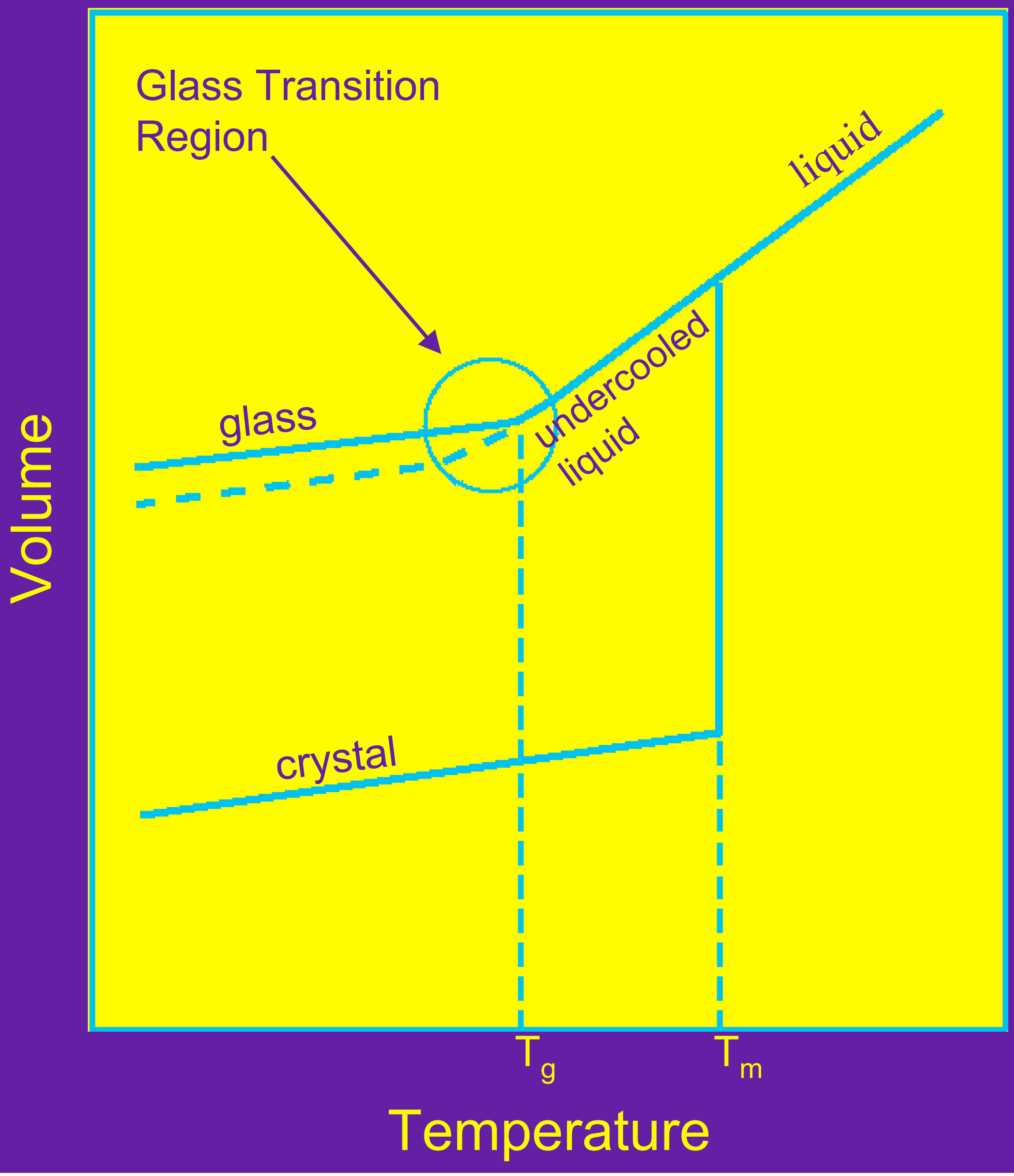
Representations of SiO_2, quartz, showing translational symmetry



Snapshot of model structure for vitreous silica

what is a glass?

- structurally
  - non-crystalline: no long range order
- thermodynamically
  - a material supercooled through its melting point (exemplified through a volume-temperature plot)
  - metastable with respect to crystalline phases
- Glasses are isotropic in their physical properties


Glass Transition
Region
liquid
glass
undercooled
liquid
crystal
Volume
T g
T m
Temperature

glass thermodynamics

- T_g, glass transition/transformation temperature
  - defines the onset of the solid state
  - is a function of cooling rate (thermal history)
  - is actually a range of temperatures
  - is the temperature below which most structural relaxation (effectively) ceases

Glass chemistry

- The historical development of glass chemistry is centered around vitreous silica
- "Additives" include Al, Na, Li, K, Ca
  - Changes to properties and structure
- Other oxide glass compositions centered around B_2O_3 and P_2O_5 and combinations with SiO_2
- Non-oxide glasses include fluorides, chalcogenides, and metallic glasses

Typical silica based glass compositions

	Vitreous silica	Plate	Window	Bottle	Pyrex	Glass halogen lamp	E glass
SiO_2	100.0	72.7	72.0	74.0	81.0	60.0	52.9
Al_2O_3		0.5	0.6	1.0	2.0	14.3	14.5
B_2O_3							9.2
CaO		13.0	10.0	5.4		6.5	17.4
MgO			2.5	3.7			4.4
Na_2O		13.2	14.2	15.3	4.5	0.01	
K_2O				0.6		Tr	1.0

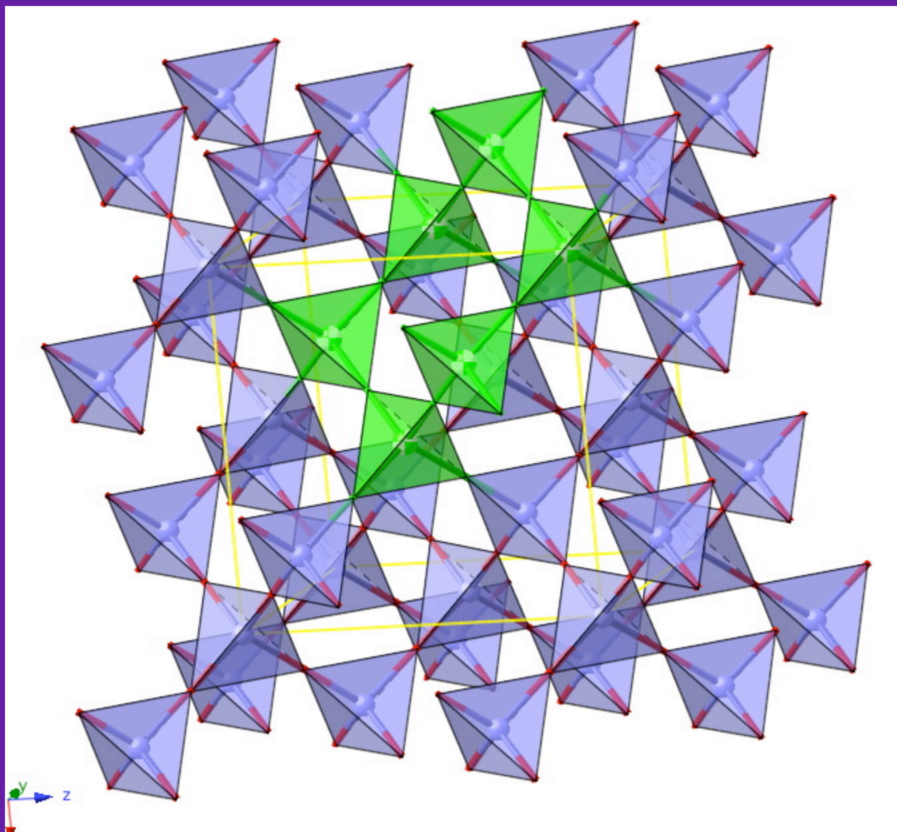
basic concepts

- starting point is a (3-D) random network
- network nodes are coordination polyhedra
  - tetrahedron: e.g.SiO_4; BO_4
  - triangle: BO_3
- network is constructed by linking polyhedra together; oxygens at the vertices are shared between polyhedra
  - These are Bridging Oxygens

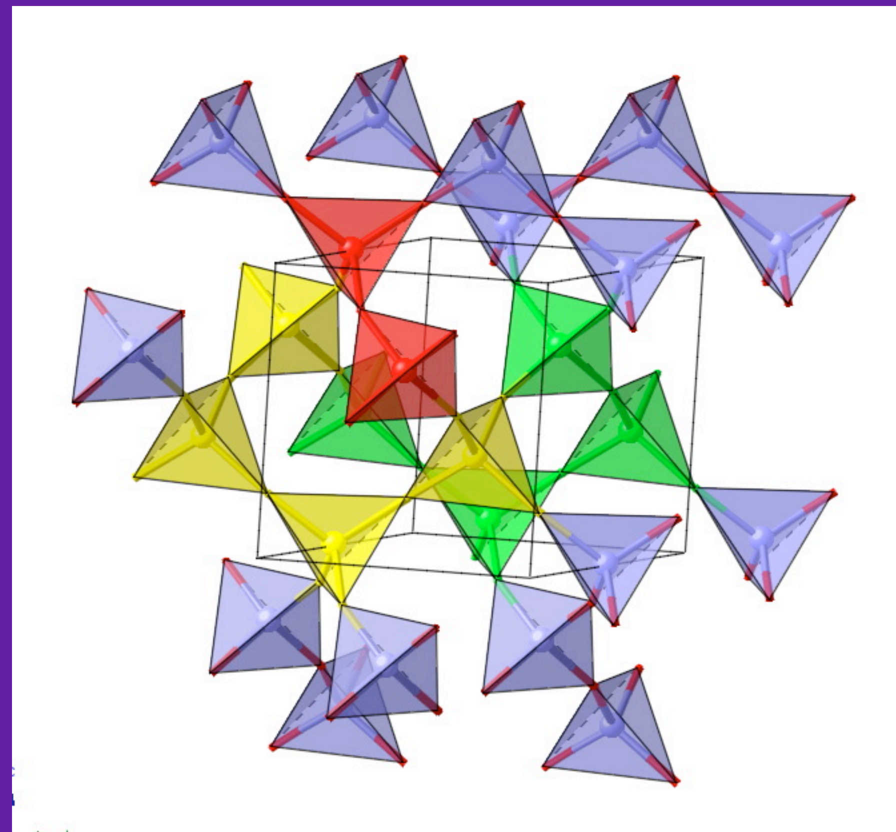
Zachariasen's Rules

- each oxygen should be linked to not more than two cations
- coordination number of oxygens around the central cation should be small, 4 or less
- oxygen polyhedra should share corners, not edges or faces
- at least three corners of the polyhedron should be shared, i.e. linked, to form a 3-D network
- Network is disordered
  - Distribution of ring sizes

Tetrahedral rings in crystalline network structures



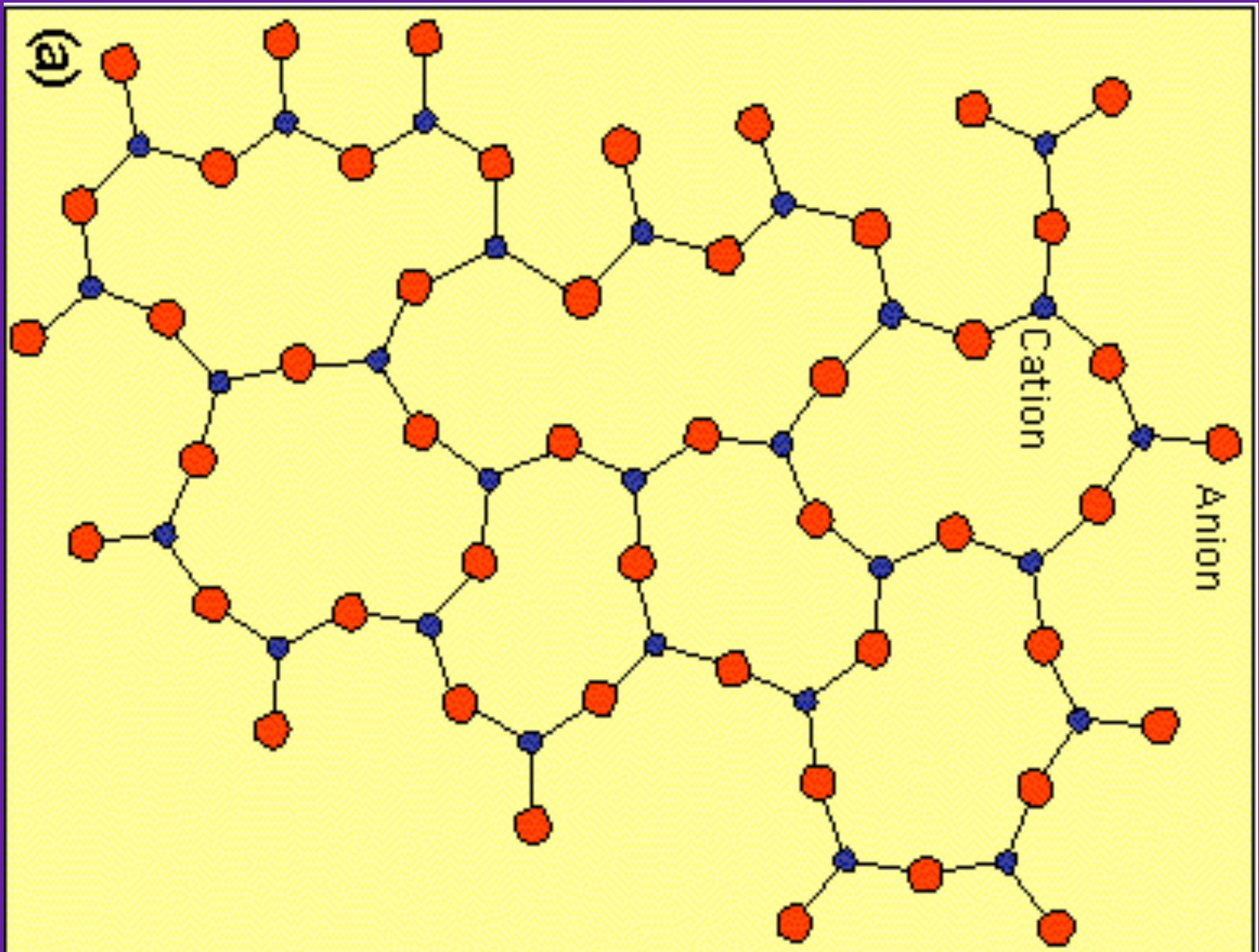
6-ring in cristobalite



6- and 8-rings in quartz

Crystalline networks have discrete ring sizes

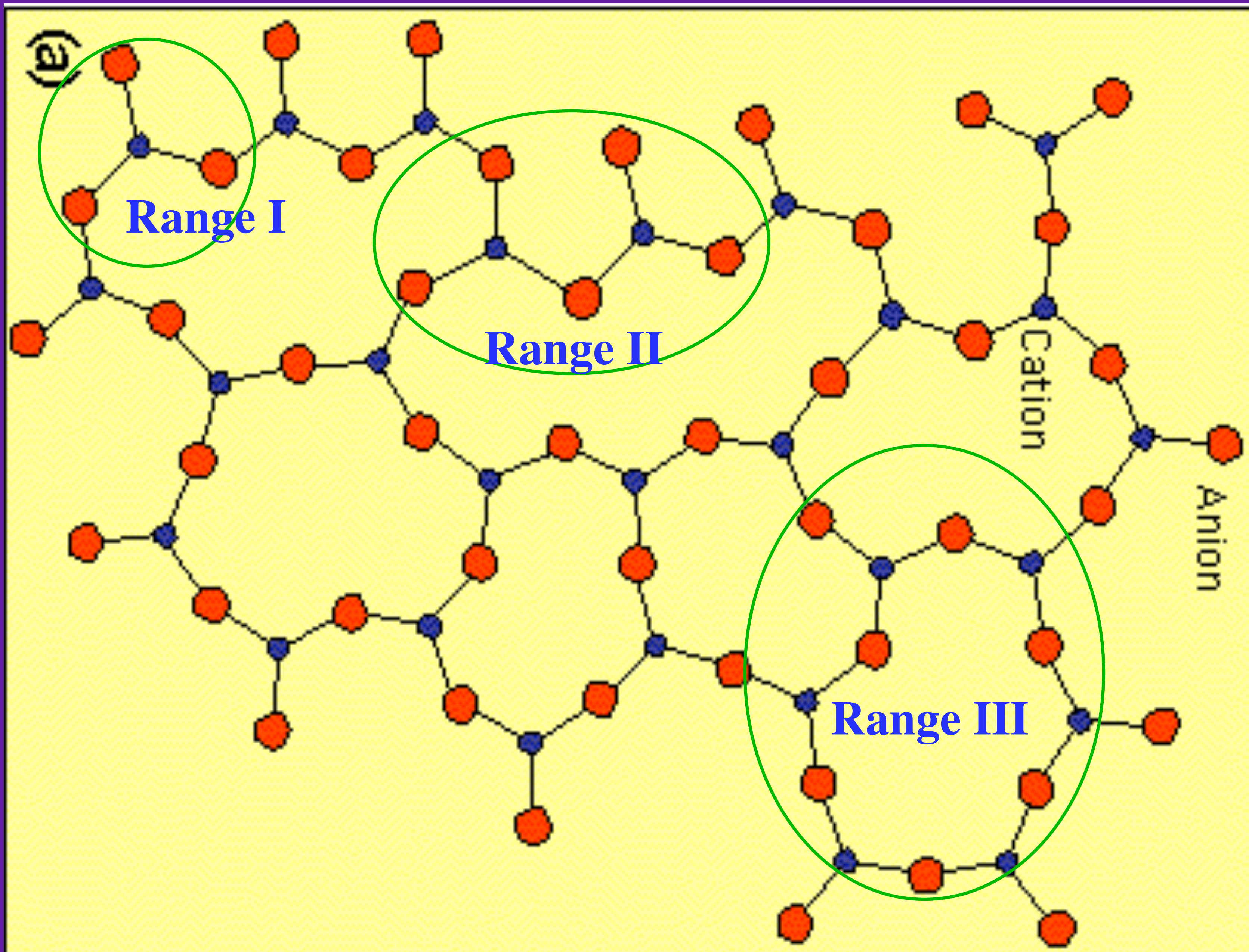
Zachariasen's random network structure



Glass structure length scales

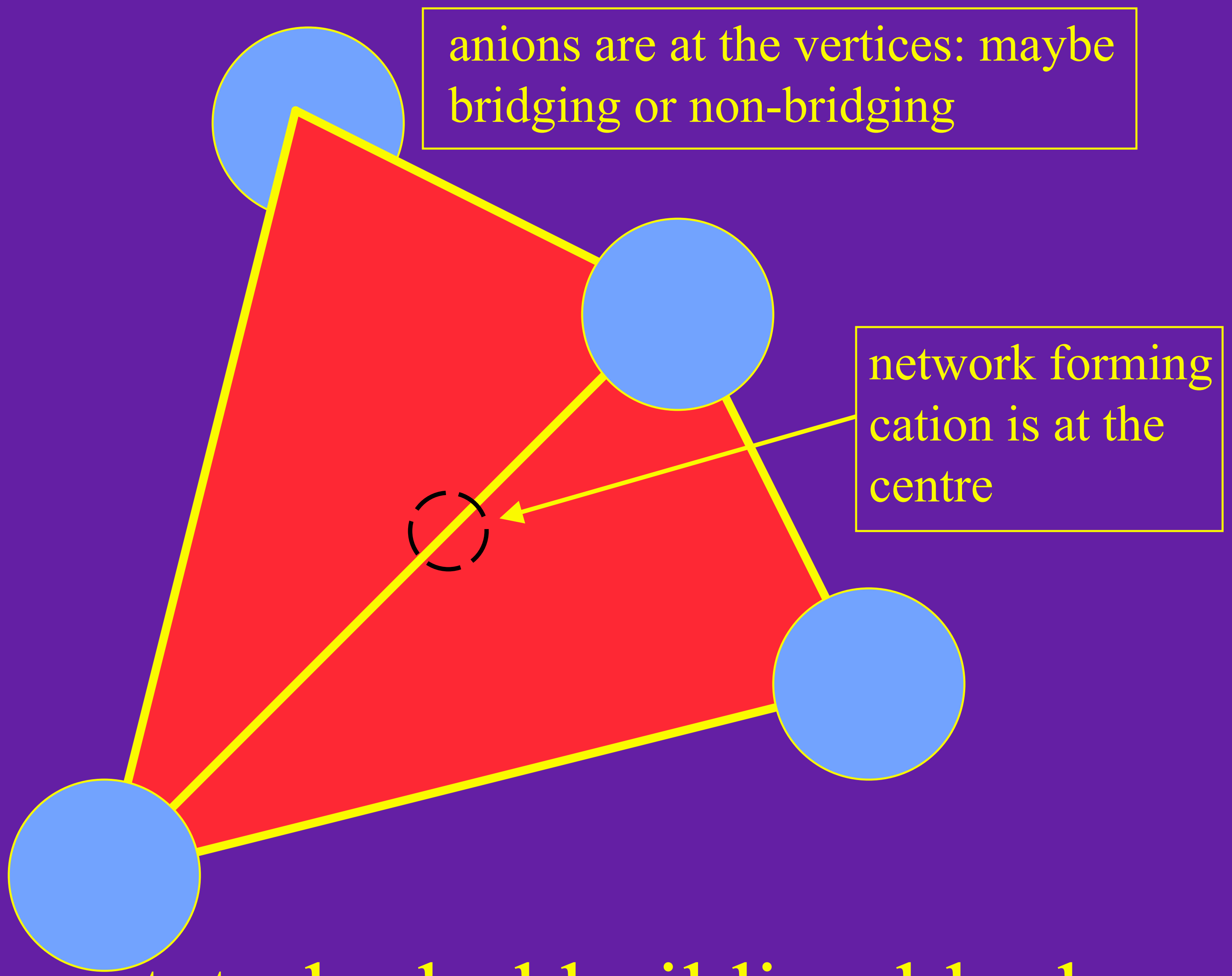
- Consider three ranges of structure
- Range I concerns structure/geometry of coordination tetrahedron
- Range II is related to relative orientation of two connected tetrahedra
- Range III describes the medium range - ring sizes, etc.

Zachariasen's random network structure

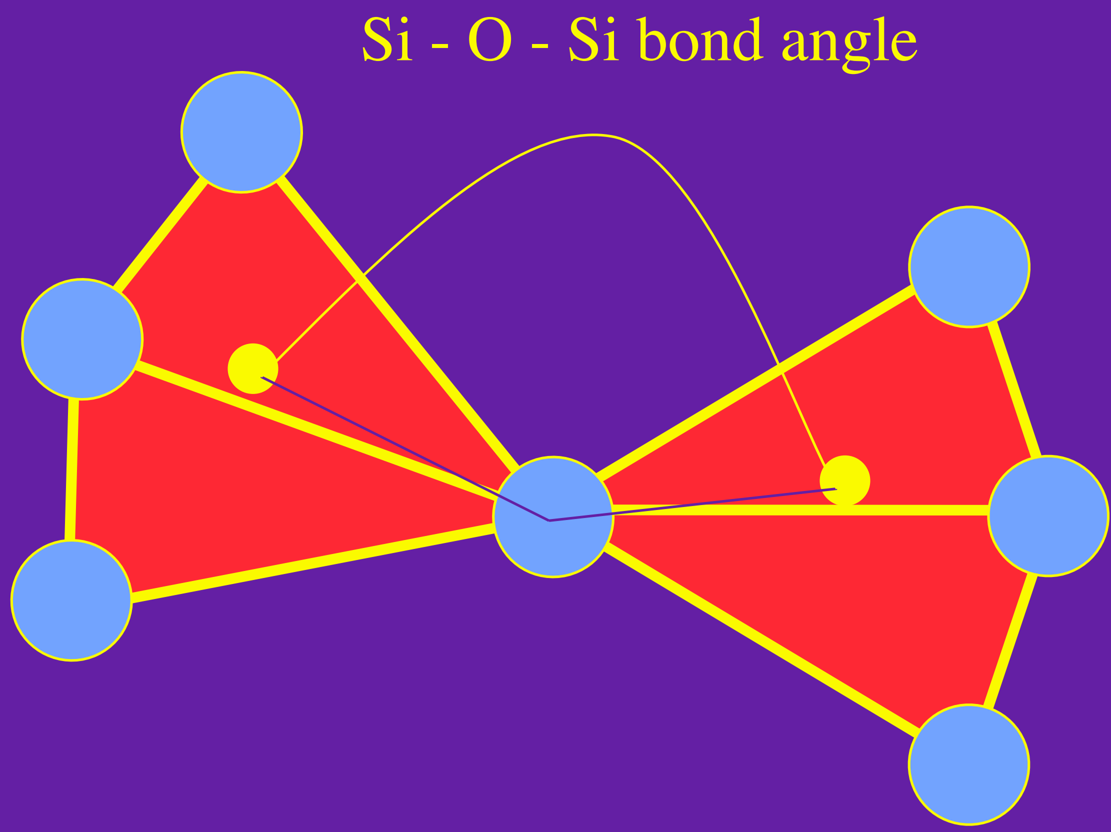


silica

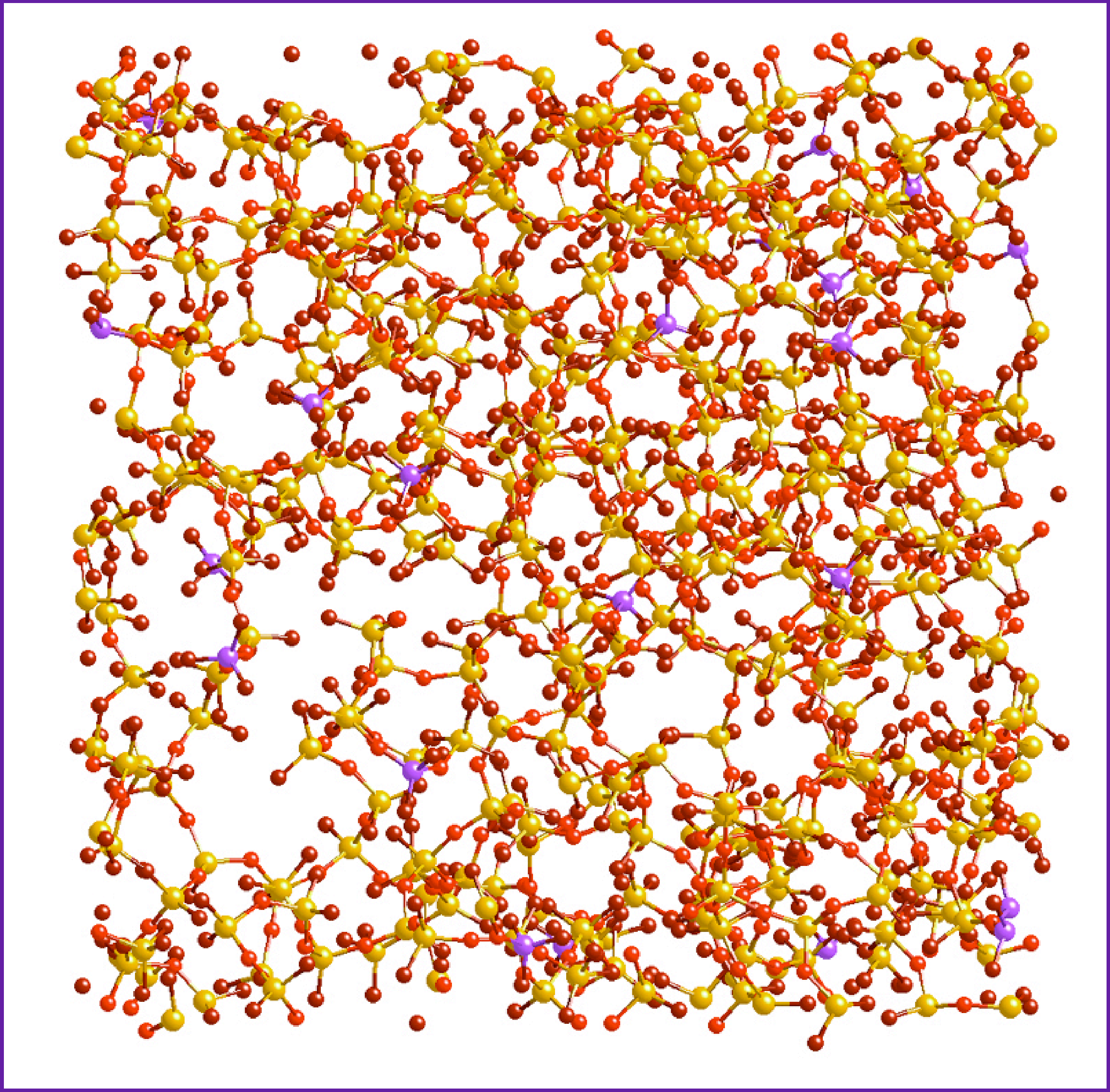
- the building block is a tetrahedron
- randomness is due to variable Si - O - Si bond angles (and torsion angles)
- all the vertices are shared between tetrahedra
  - all oxygens are bridging oxygens
  - all network nodes are Q_4



a tetrahedral building block



Si - O - Si bond angle distribution is discrete in crystals, but not in glasses

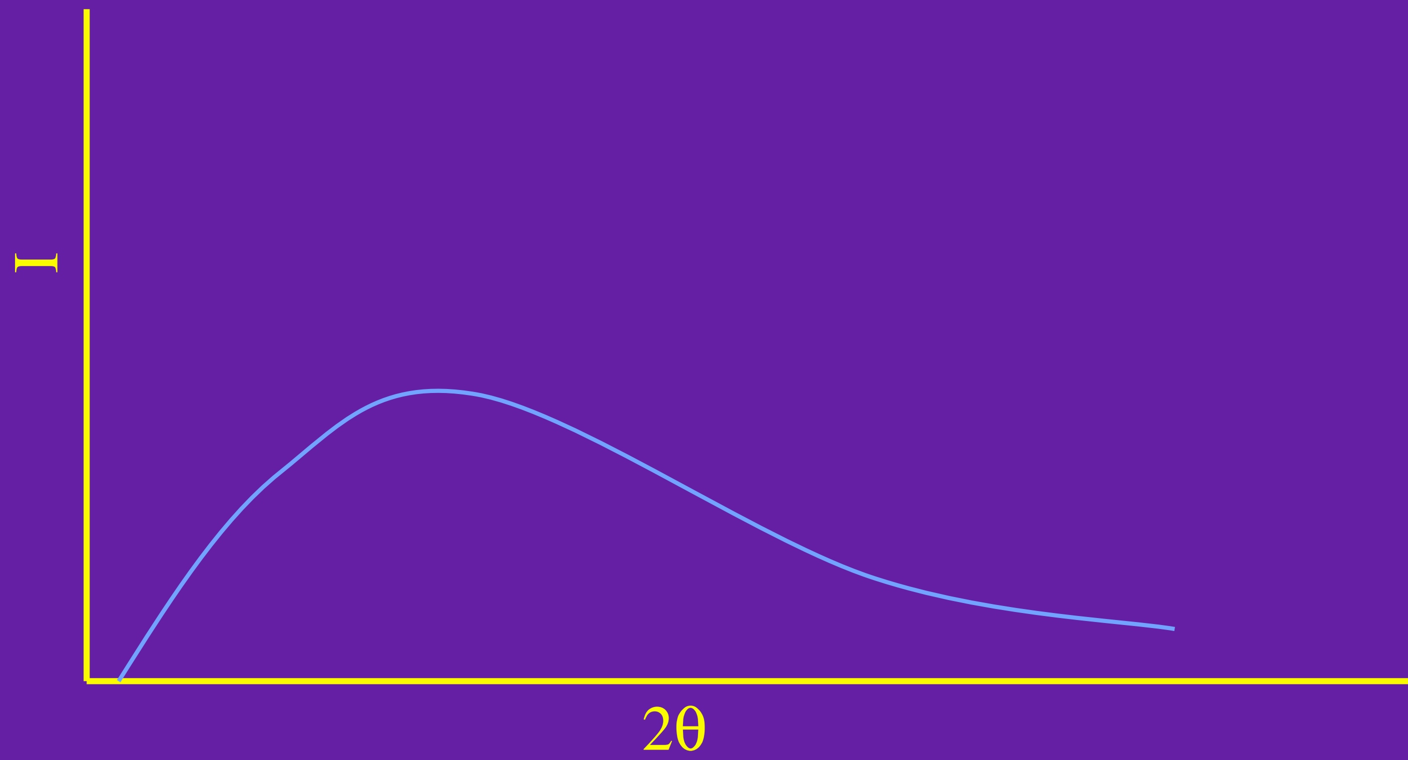


Tetrahedral network structure of 45S5 bio-active glass

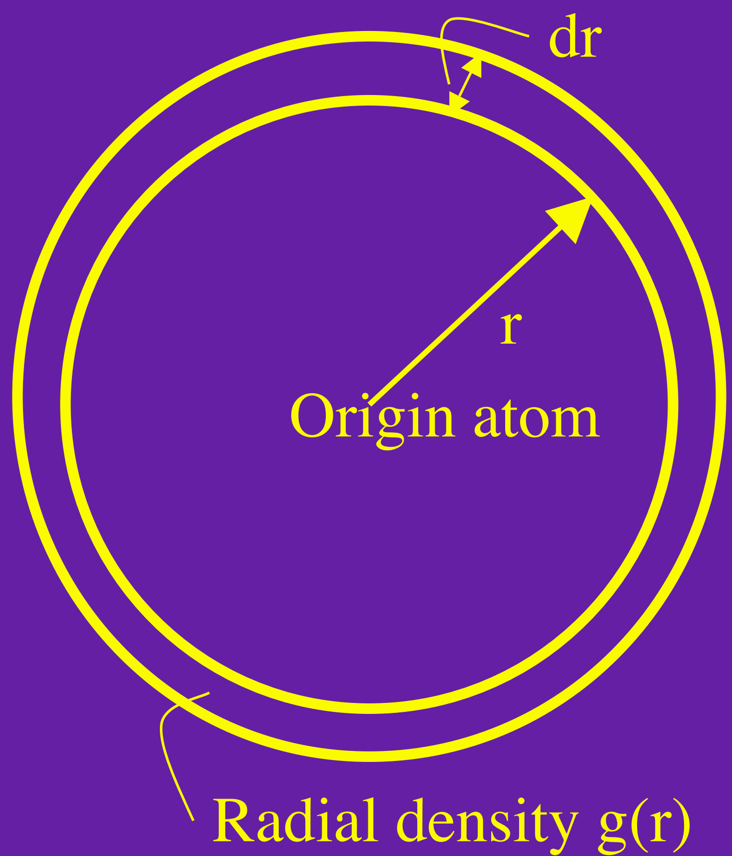
How is the structure measured?

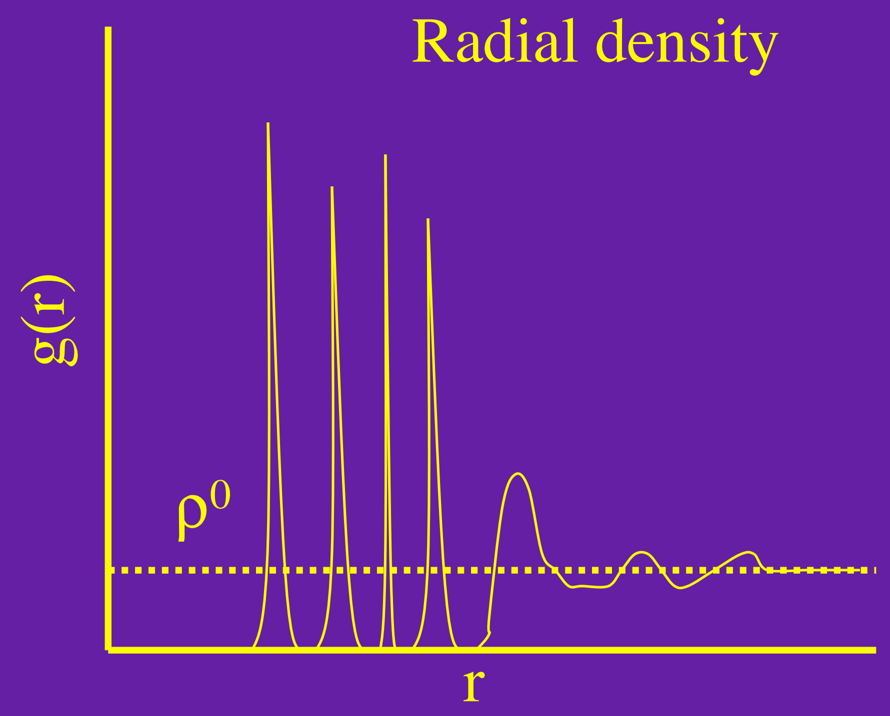
- Scattering from non-crystalline materials produces 1-D information
- Distribution functions convey 1-D structural information
  - Probability of finding an atom at a distance from a given atom
- Extract structure factor, S(Q), and T(r) from scattering of X-rays and neutrons
- For multi-component solids, total T(r) is sum of pair distribution functions

“Amorphous hump” seen in powder diffraction from non-crystalline material

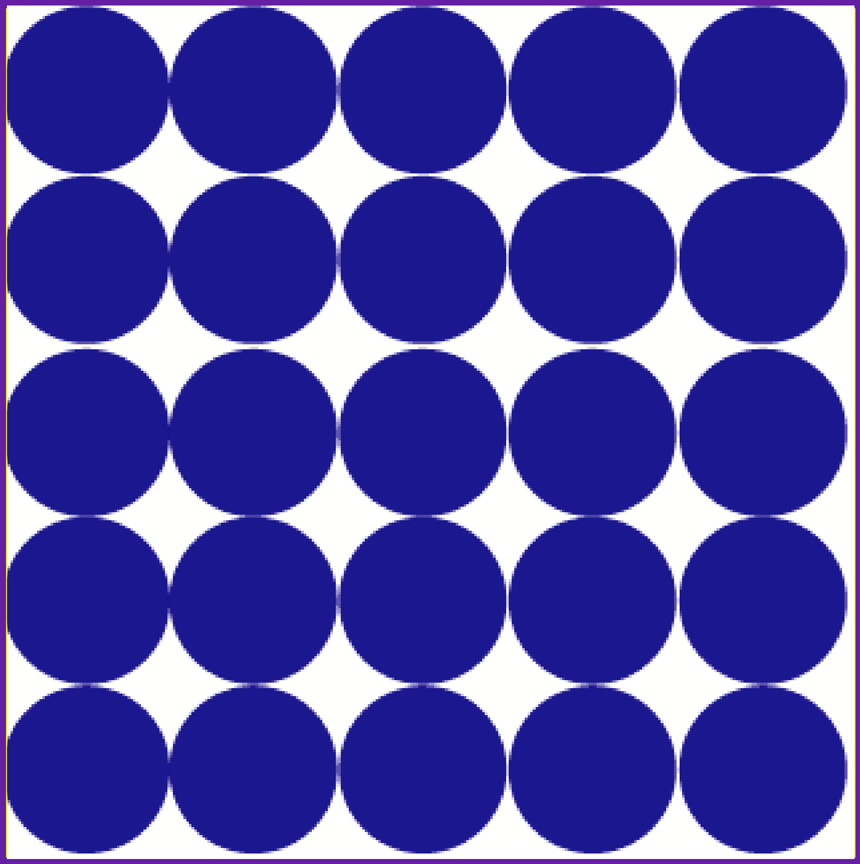


radial distribution functions

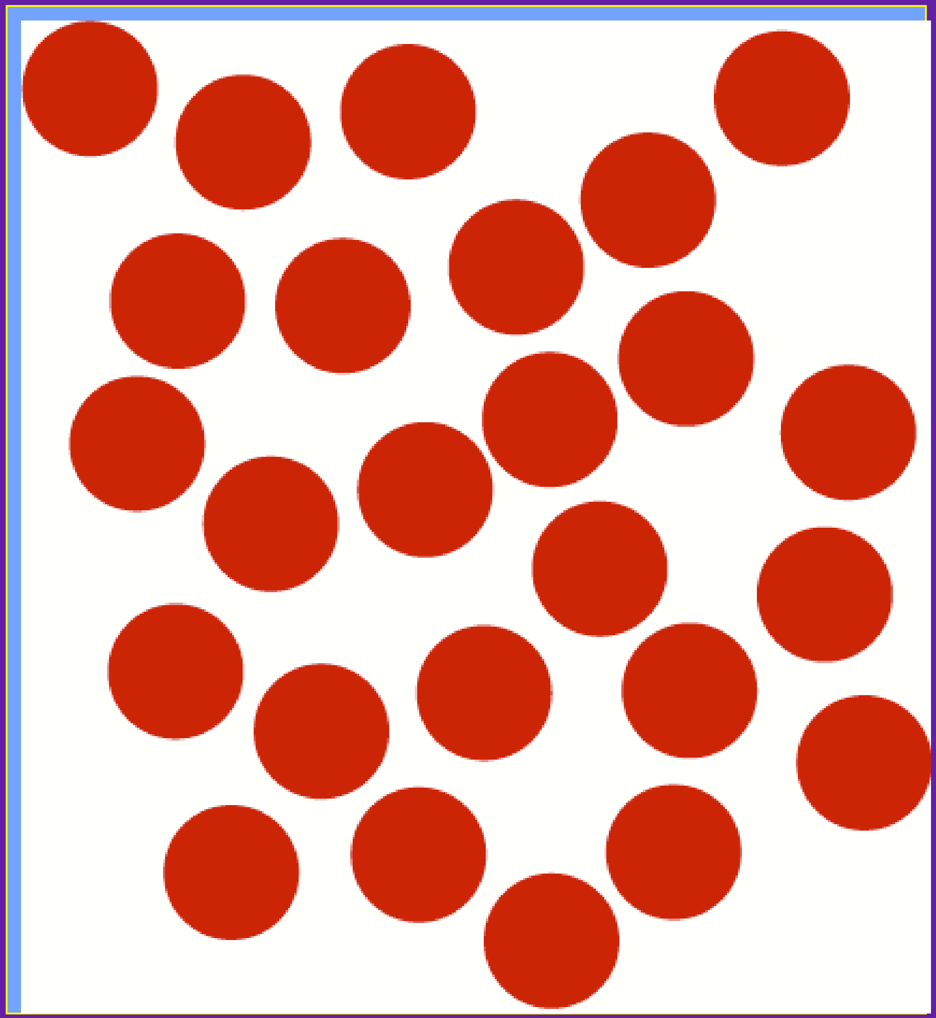




Rdfs measure the density of atoms (either all or specific types) as a function of distance from an atom

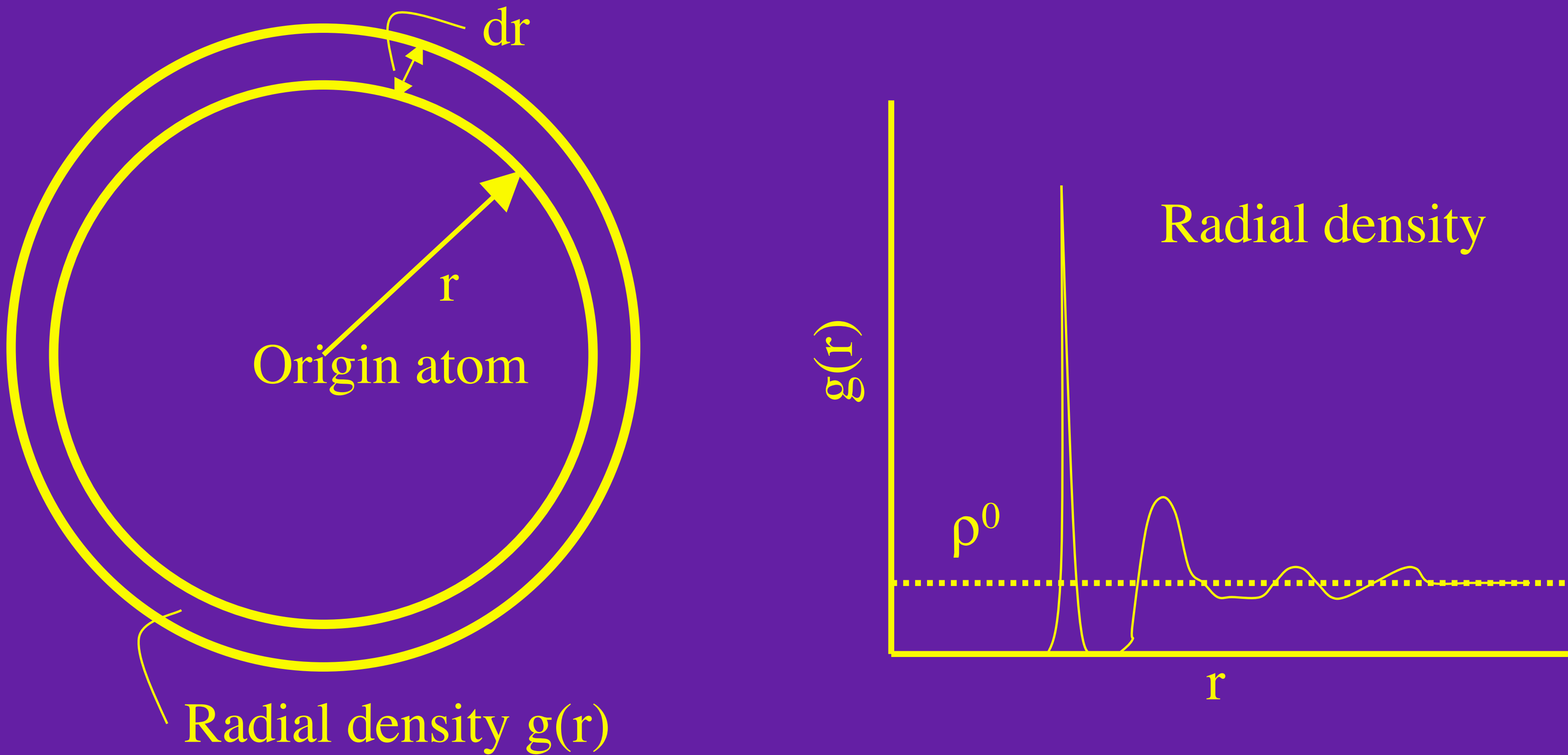


Crystals: interatomic separation distribution is discrete



Non-crystalline systems: distribution of interatomic separations is continuous, except for nearest neighbours

radial distribution functions



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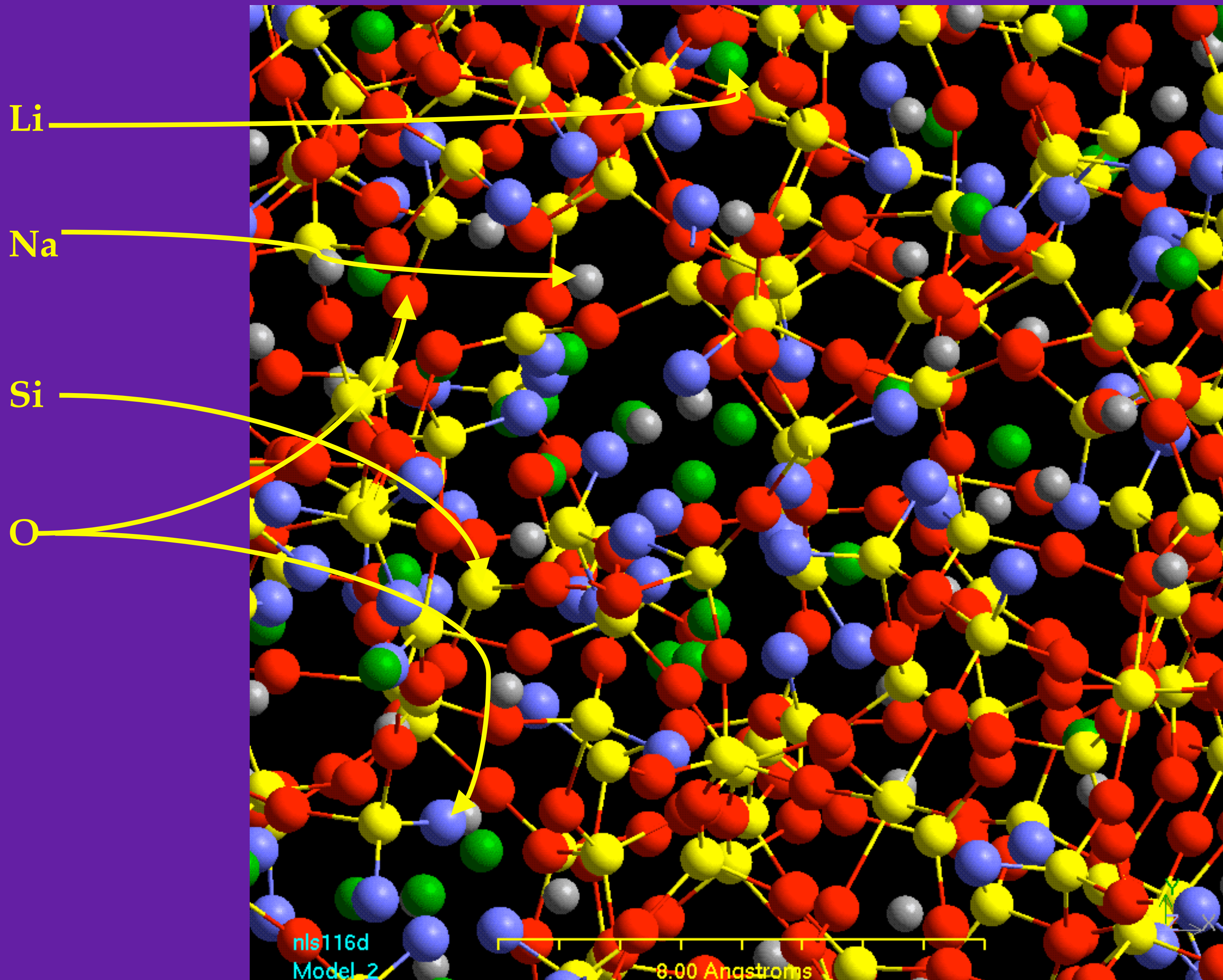
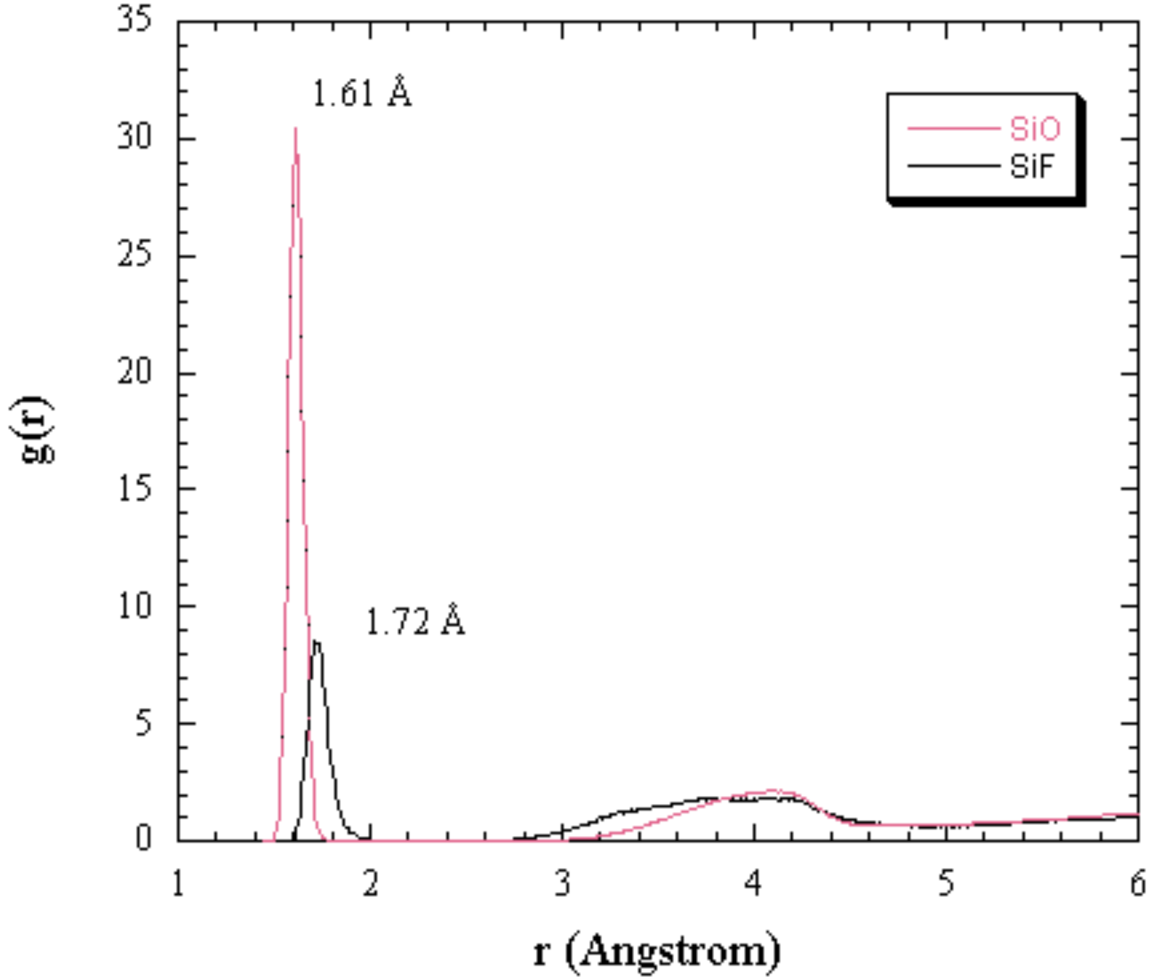


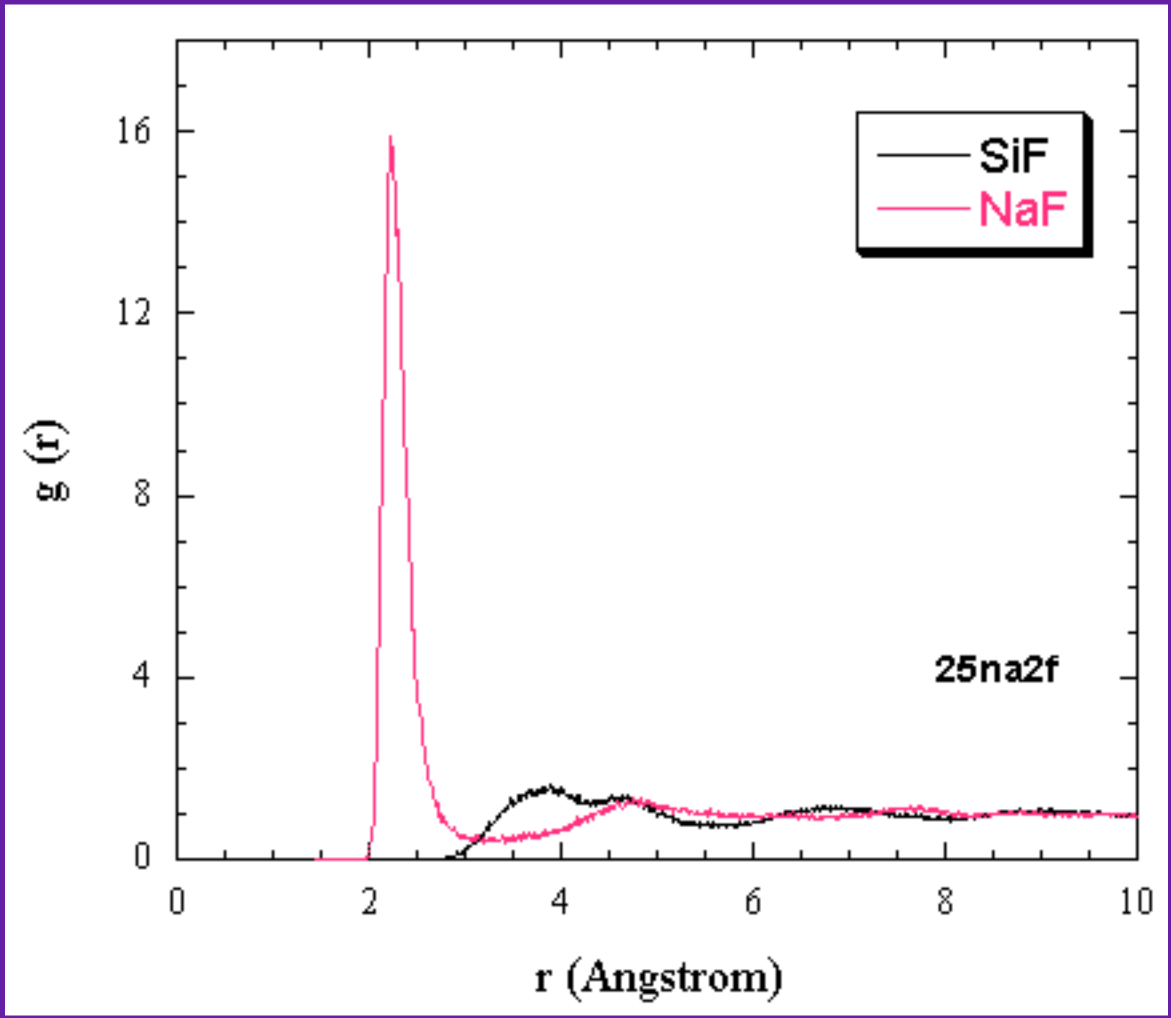
Snap-shot structure of a lithium sodium silicate glass

Multi-component glasses

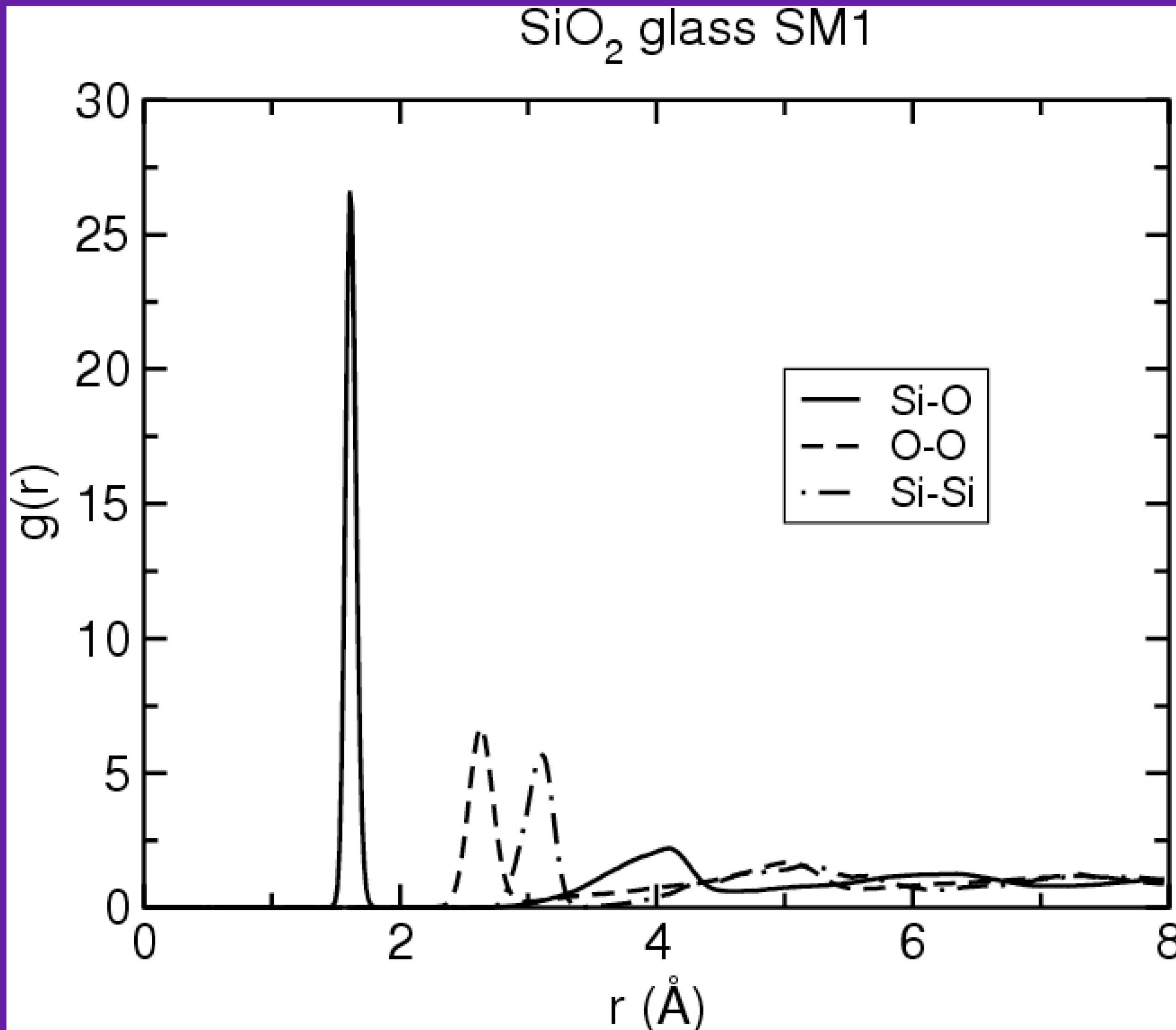
- There is a radial distribution function for each pair of atom types
- In the Li-Na-silicate glass there are
  - Li - O, Na - O, Si -O and O - O pdfs
  - Li - Li, Na - Na & Li - Na pdfs
  - Li - Si, Na - Si, and Si - Si pdfs
- What is obtained from measurements will be the sum of all of these …



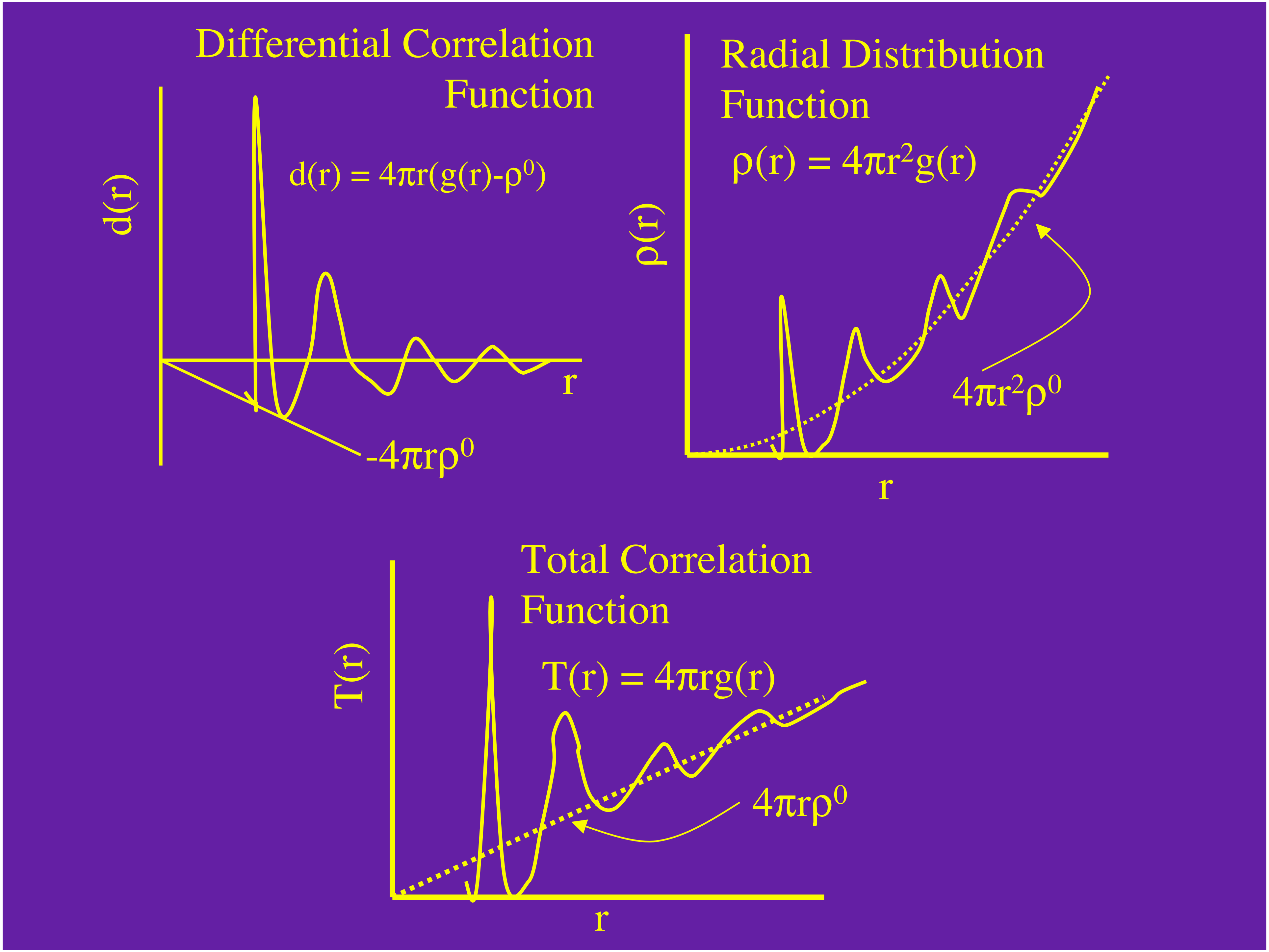
Si - O and Si - F pair distribution functions in silica glass



F pair distribution functions in F doped 25mol% sodium silicate glass



SiO_2 glass SM1
g(r)
r (Å)
Si-O
O-O
Si-Si
0
5
10
15
20
25
30
0
2
4
6
8



Differential Correlation Function
d(r) = 4πr(g(r)-ρ0)
d(r)
r
-4πrρ0
Radial Distribution Function
ρ(r) = 4πr2g(r)
ρ(r)
4πr2ρ0
r
Total Correlation Function
T(r) = 4πrg(r)
T(r)
4πrρ0
r

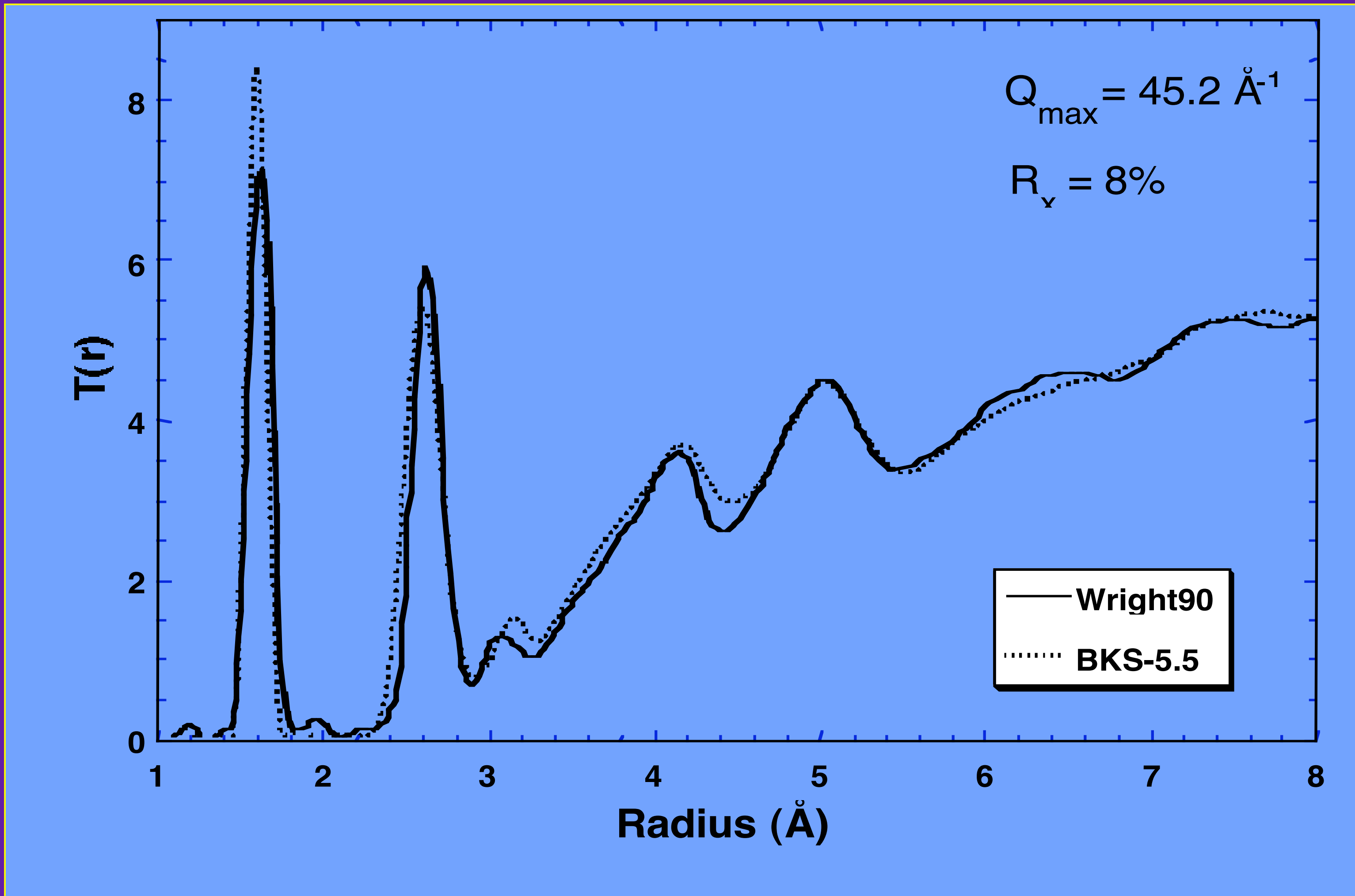
How T(r) is obtained from a scattering experiment

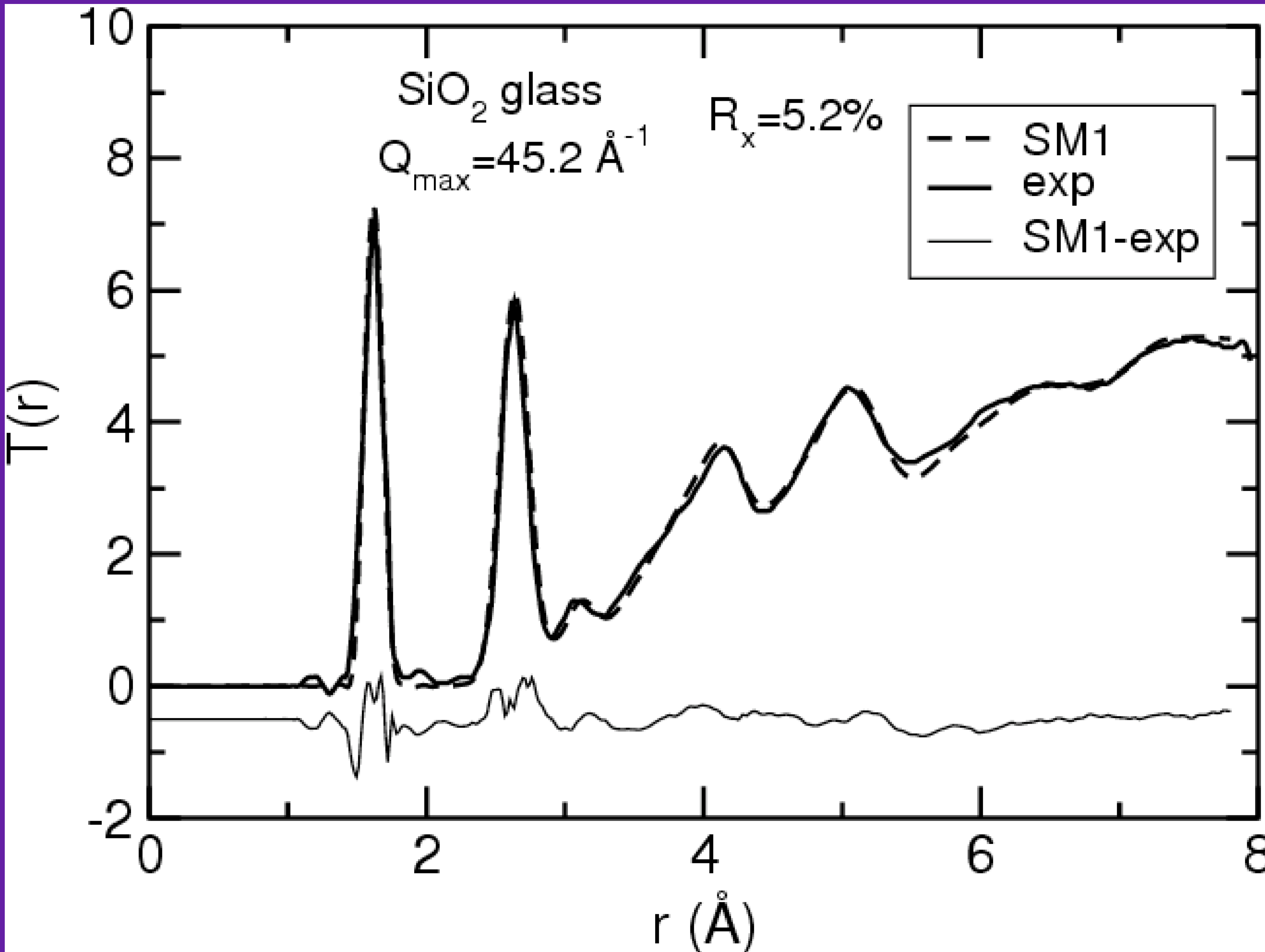
I(Q) = I^s(Q) + i(Q)

self distinct

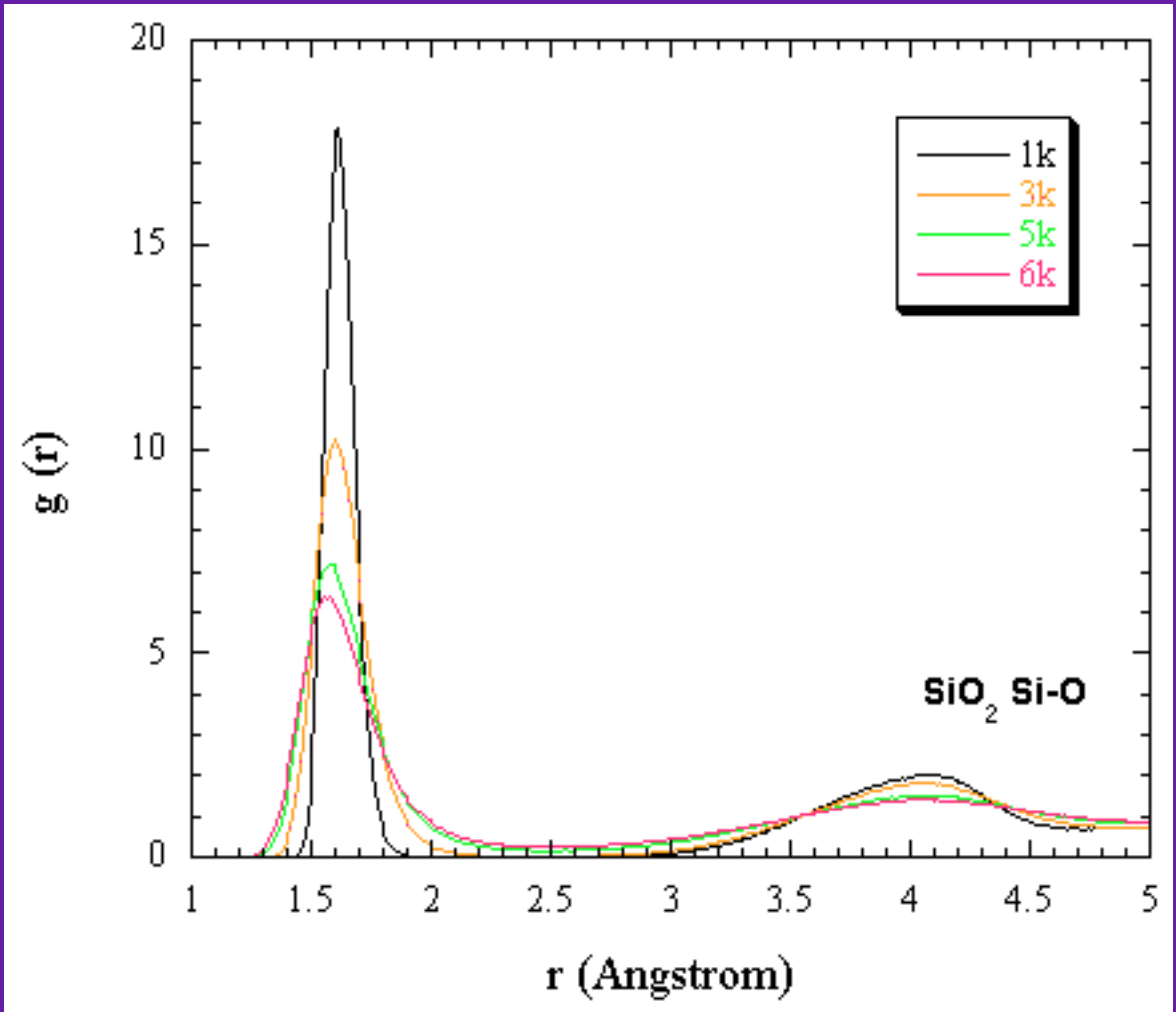
$$T(r) = 4\pi\rho^0 r + \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} \left[S(Q)-1\right] M(Q) \sin(Qr) Q dQ$$

T(r) comparison with experiment

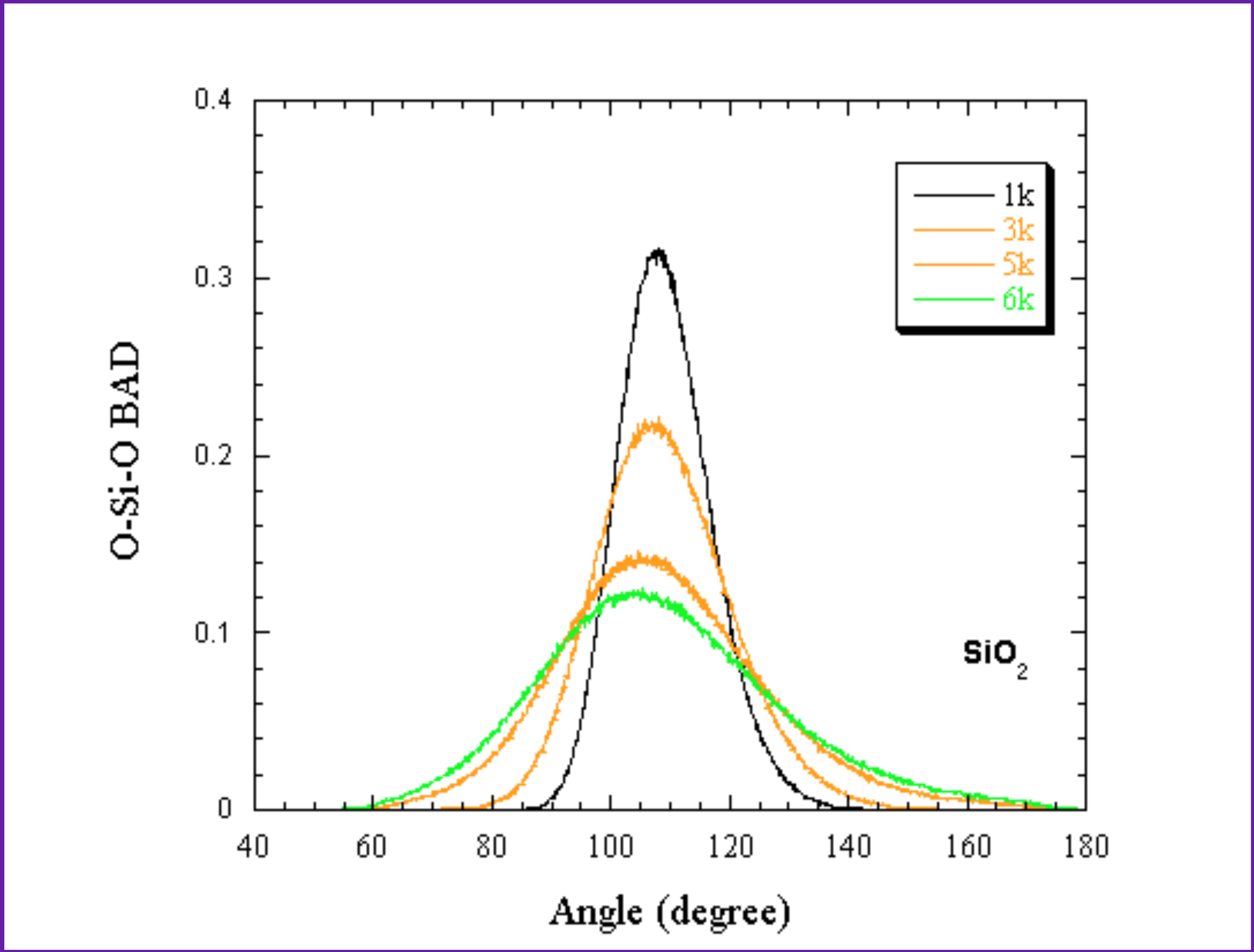




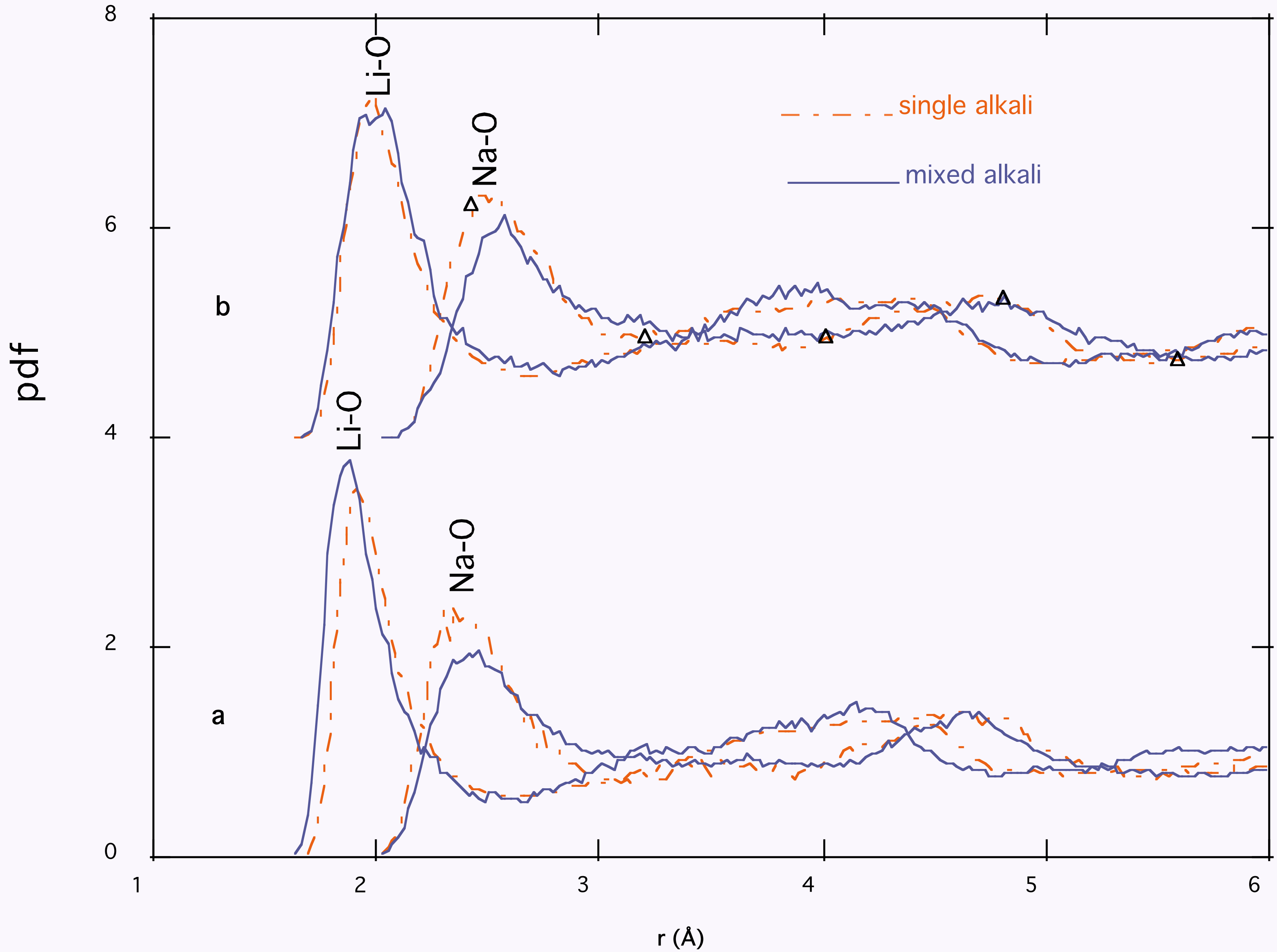
SiO2 glass
Qmax=45.2 Å-1
Rx=5.2%
SM1
exp
SM1-exp
T(r)
r (Å)
10
8
6
4
2
0
-2
0
2
4
6
8



Si - O pair radial distribution function as a function of temperature

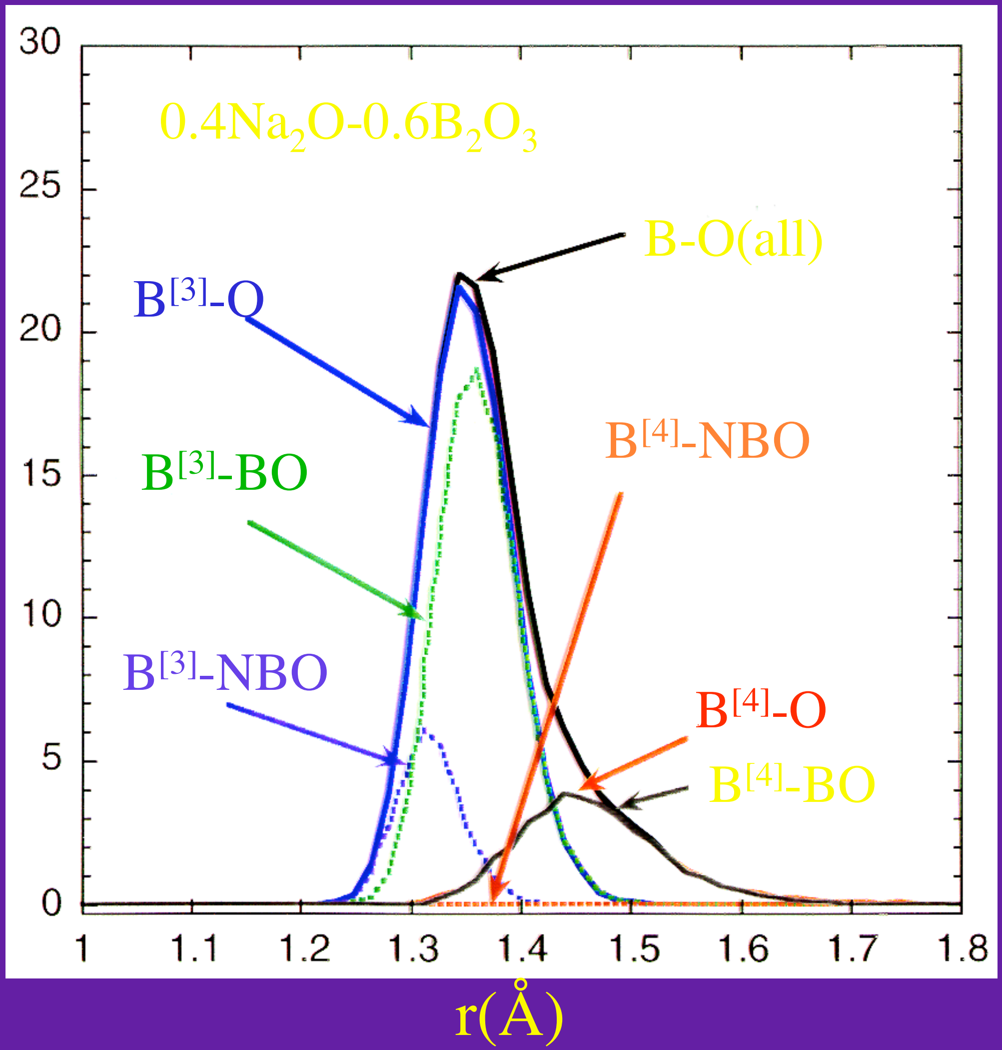


Intra-tetrahedral bond angle in silica melts as function of temperature



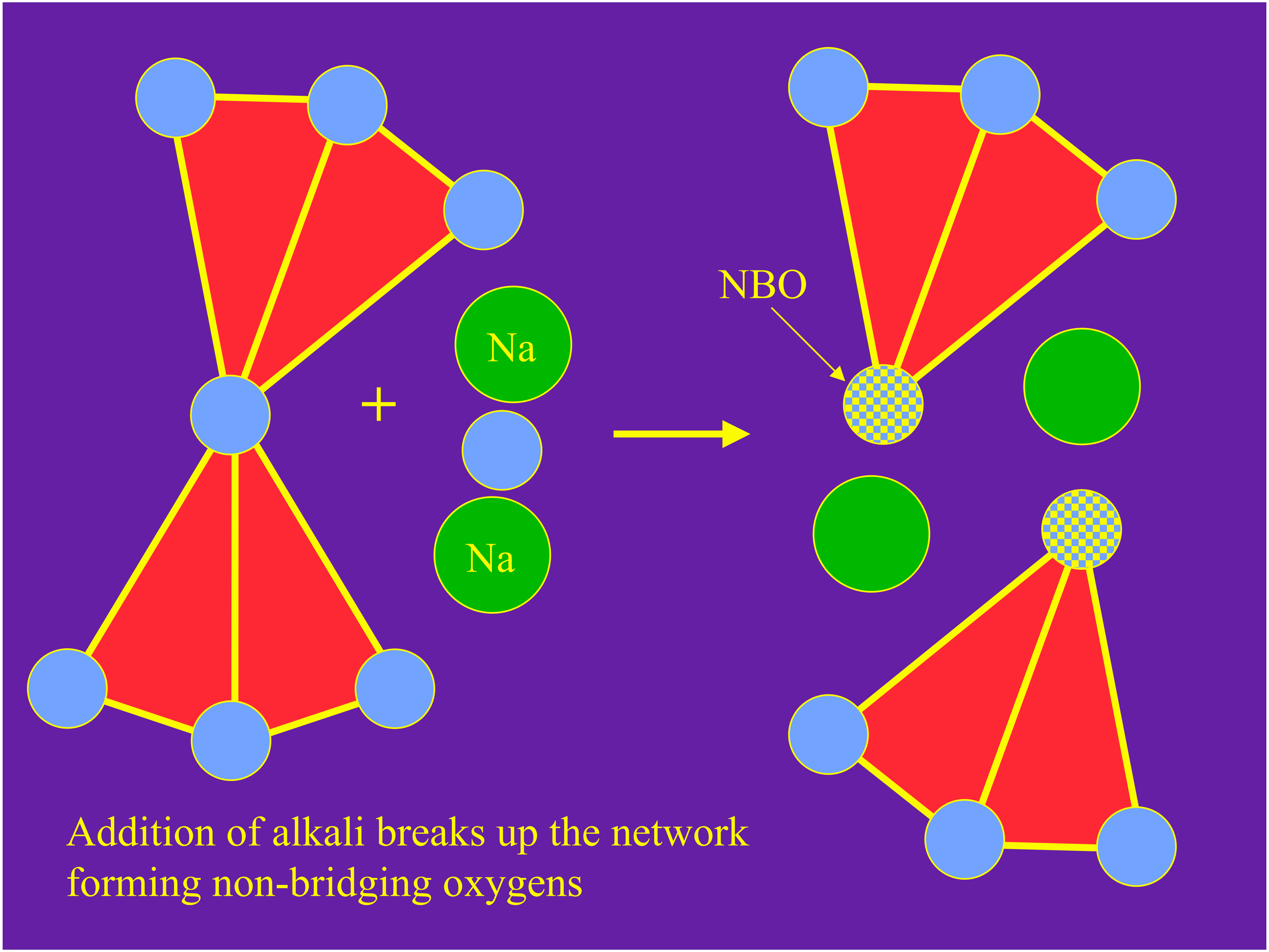
Li-O and Na-O pdfs in single and mixed alkali (a) silicate and (b) aluminosilicate glasses

Deconvolution of First Peak of B-O PDF



addition of modifiers to silica

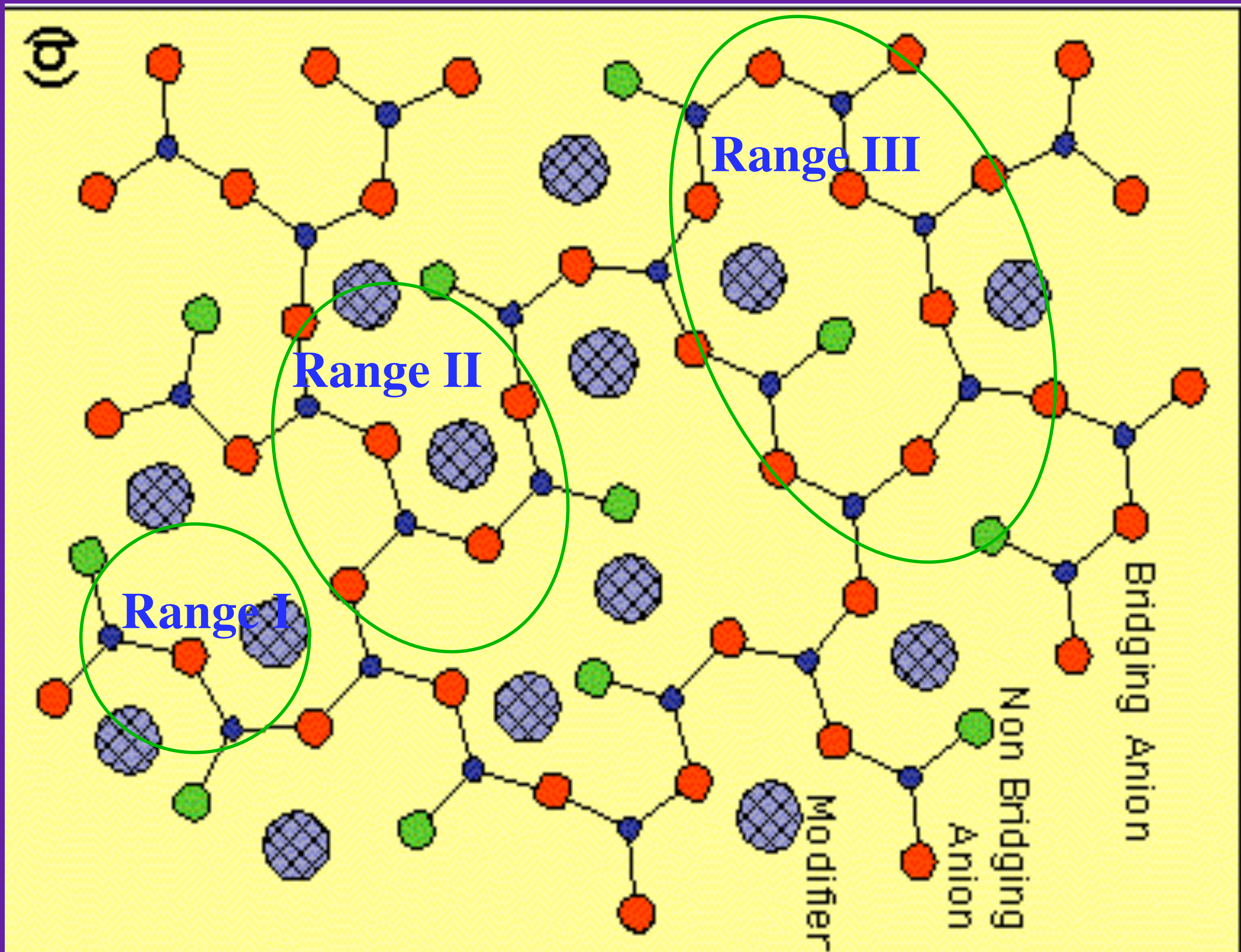
- Non-bridging oxygens are created
  - Association between NBO and modifier
    - Local charge neutrality
- “polymerised” 3-D network is disrupted
  - Larger rings are created
- What is distribution of modifiers in structure?
- Additional pair distribution function contribute to T(r)


NBO
Na
+
Na
Addition of alkali breaks up the network
forming non-bridging oxygens

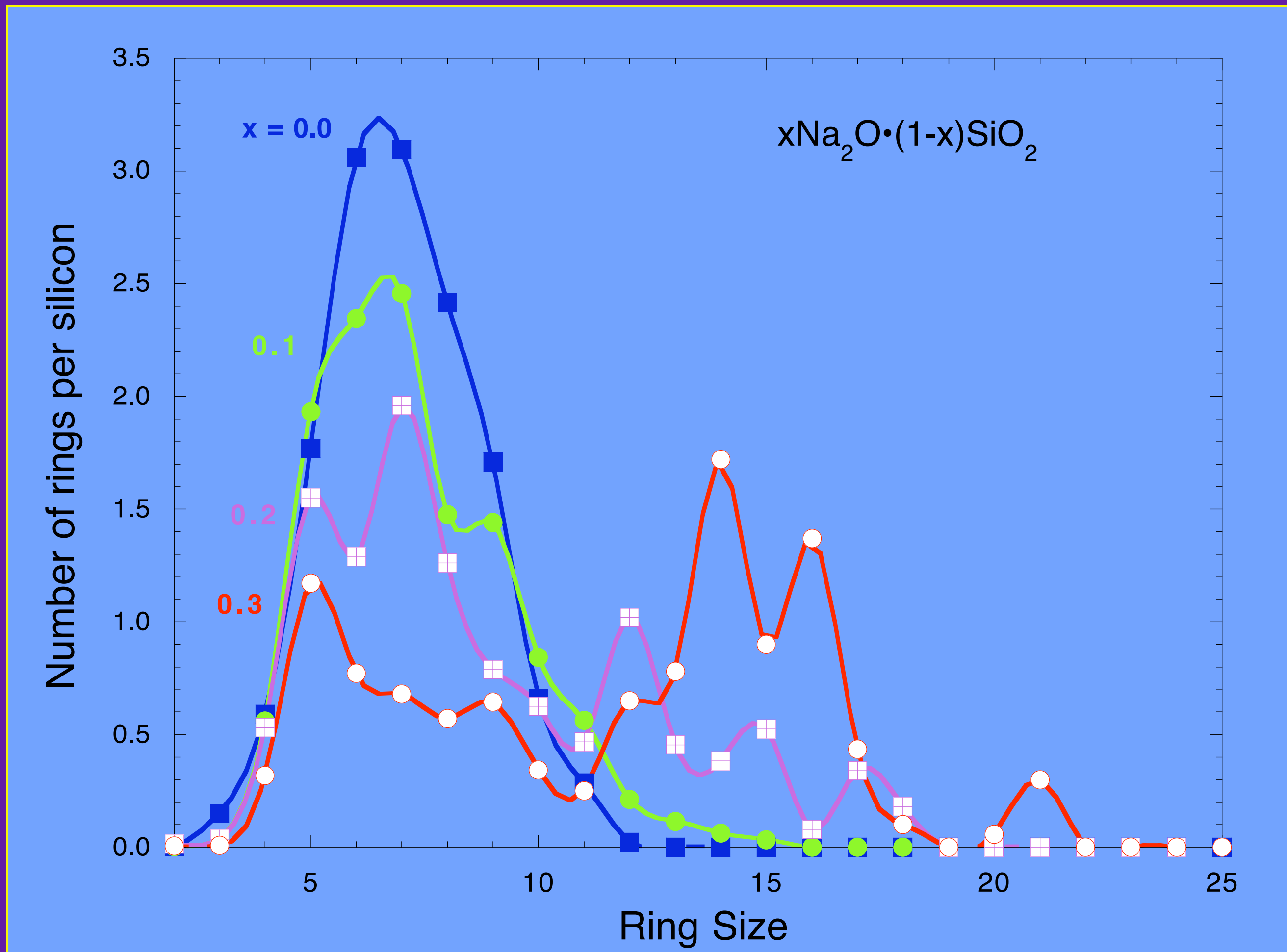
ring size distribution

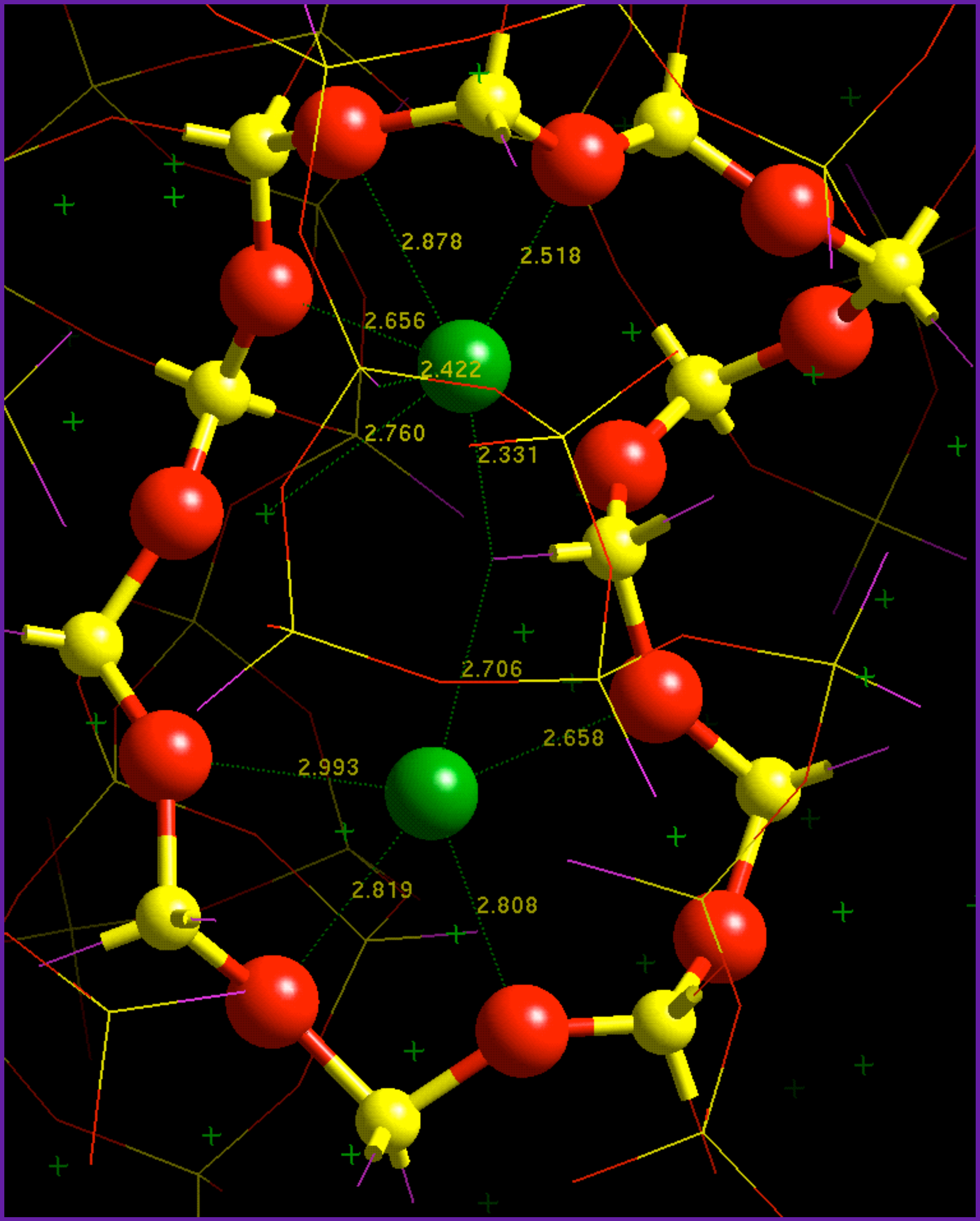
- a ring is a closed path round tetrahedral sites in the network
- crystals have discrete ring sizes,whereas the disordered nature of the glass structure leads to a distribution of ring sizes
- addition of alkali causes larger rings to form
- can be used to characterise the network structure

Effect of addition of modifiers to Zachariasen's model



Tetrahedral ring size distribution in sodium silicate glasses





- Large size rings are most likely associated with Na-rich regions
- Na is coordinated with around five oxygen
- Na in α-$Na_2Si_2O_5$ is in 5-fold coordination

• Si ● BO ● NBO
● Na

A 12-ring in Na_2O•$2SiO_2$ glass

Summary

- Non-crystalline materials do not diffract
  - Lack of translational periodicity
- Scattering experiments provide 1-D information
  - Isotropic nature of glass structure
  - Need to obtain structure factor, S(Q)
- Usually use real space function, T(r), for comparison with simulations
- Note that T(r) resolution limited by Q_{max}
  - Broadens peaks
- Simulations are almost essential in interpreting experimental data, especially from multi-component systems