



Atomistic Computer Simulations

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Outline

- Introduction
- Classical methods: the Born Model
- Static lattice methods
 - energy minimisation
- Molecular dynamics
- Monte Carlo methods

Atomistic Simulations

- Classical or quantum?
- Static or dynamic?
- Availability of computer resources

Atomistic Simulations

- Classical or quantum?
- Static or dynamic?
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Classical v. Quantum

● Classical

- Based on Born Model

- » Electrostatic (point charges) & short-range potentials
- » Representation of inter-atomic forces

- Can handle tens of thousands of atoms

● Quantum mechanical

- Solutions to Schrodinger wave equation

- » Electronic property calculations

- Limited to 10^2 atoms

- » Computationally expensive

Static v. dynamic

● Static

- Structure and physical properties
- Point defect modelling
- No explicit temperature handling
- Not well suited to non-crystalline materials

● Dynamic

- Based on solutions to laws of motion
- Includes temperature (nominally)
- Useful for non-crystalline materials

The Born Model

- Ions treated as point charges
 - Coulomb potential is long range
 - Magnitude as model parameter
- Short range potentials
 - Pauli repulsion
 - Dispersion forces
- Polarisability

Structure + Potential = Thermodynamics

- **Energy minimisation**
 - Perfect lattice properties
 - Point defect energies and structure
- **Glasses pose a problem because of non-crystalline structure**
 - Hence appeal to computational methods - molecular dynamics (or Monte Carlo)

The Born Model

- Lattice energy:

$$E_{lattice} = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{r_{ij}} + V(r_{ij}) + U(r_{ij}, r_{ik})$$

- Forces obtained from derivatives of $E_{lattice}$

- Equilibrium from zero net forces

– Second derivatives of $E_{lattice}$

- Elastic, dielectric constants are second derivative properties

Polarisability: The Shell Model

- Simple mechanical model
- Ion charge partitioned between core and (mass-less) shell
- Electronic polarisability,
 $\alpha = Y^2/k_{c,s} + R$
- Other models:
 - Breathing shell
 - Point polarisable ion
- Transferability issues

Short range potentials

- Effective potentials:

$$V(r_{ij}) = A_{ij} \exp(-r_{ij} / \rho_{ij}) - C_{ij} / r_{ij}^6$$

$$U(r_{ij}, r_{ik}) = \frac{1}{2} k_{ijk} (\theta - \theta_0)^2$$


- Usually parametrised
- Fit to known physical properties or to quantum mechanically calculated energy surface

Assumptions

- **Transferability of potentials**
 - Between polymorphs
 - Between compounds, e.g. oxygen...oxygen interaction
- **Oxygen ion polarisability**
- **Restriction to pair potentials, and/or three body terms**

Energy minimisation

- Structure refinement/prediction
- Calculation of physical properties
- Thermochemistry
- Zero Kelvin technique
 - Can include temperature behaviour through use of phonon calculations (e.g. Helmholtz energy)
- Supercell approach to defects




Structure Refinement/Prediction

● Refinement

- Equilibration of an ideal model

● Prediction

- *Ab initio* generation of crystal structure parameters
 - Exercise in global optimisation
- 

Potential Model for MgF₂

Crystal Properties

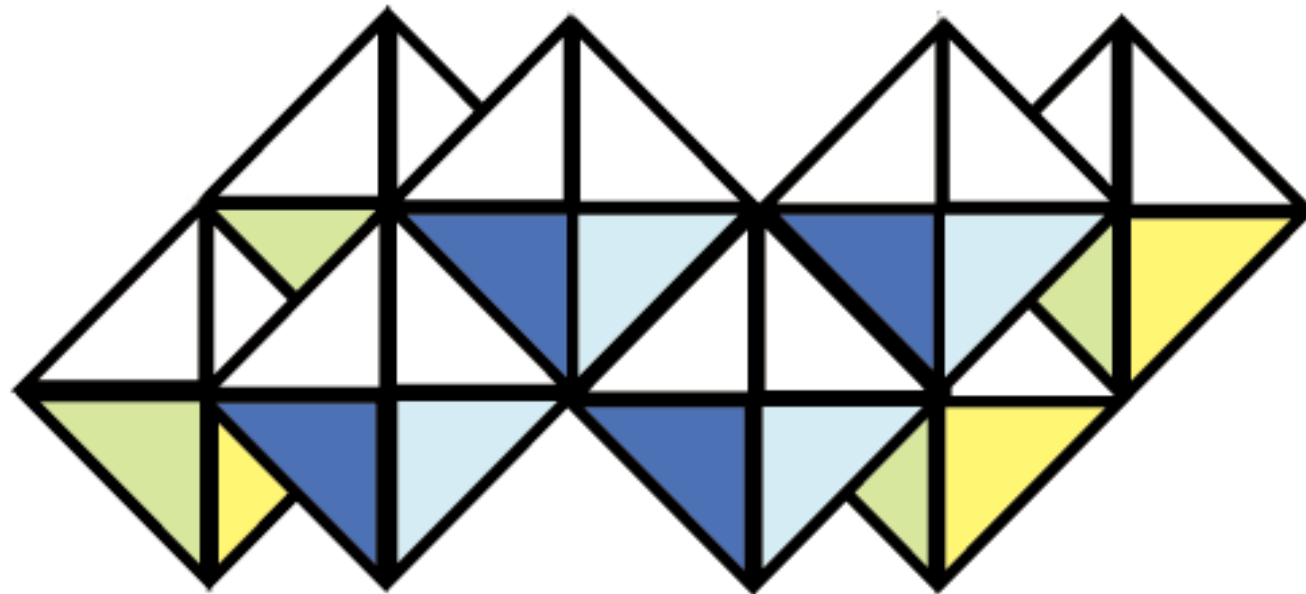
Experimental Calculated

C_{11}	13.99	13.59
C_{12}	8.93	9.59
C_{22}	6.37	6.19
C_{33}	20.42	23.19
C_{44}	5.70	5.25
C_{66}	9.54	9.63
$\epsilon_0 \perp$	5.5	5.6
$\epsilon_0 \parallel$	4.8	4.6
$\epsilon_\infty \perp$	1.9	1.9
$\epsilon_\infty \parallel$	1.9	1.9
E_{lattice}	-60.74	-59.08

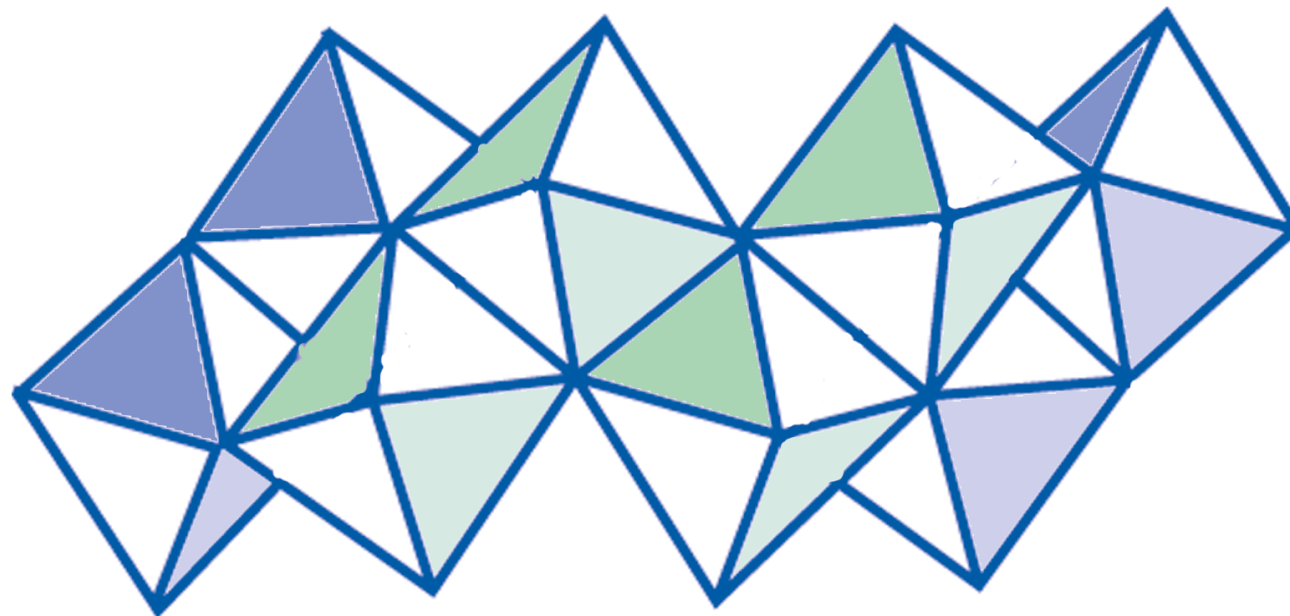
Potential

Parameters

$A_{\text{Mg-F}}$	682.59
$R_{\text{Mg-F}}$	0.29797
$C_{\text{Mg-F}}$	0.00
$A_{\text{F-F}}$	1127.7
$R_{\text{F-F}}$	0.2763
$C_{\text{F-F}}$	15.8
Y_{Mg}	2.0
K_{Mg}	
Y_{F}	-1.23357
k_{F}	17.496

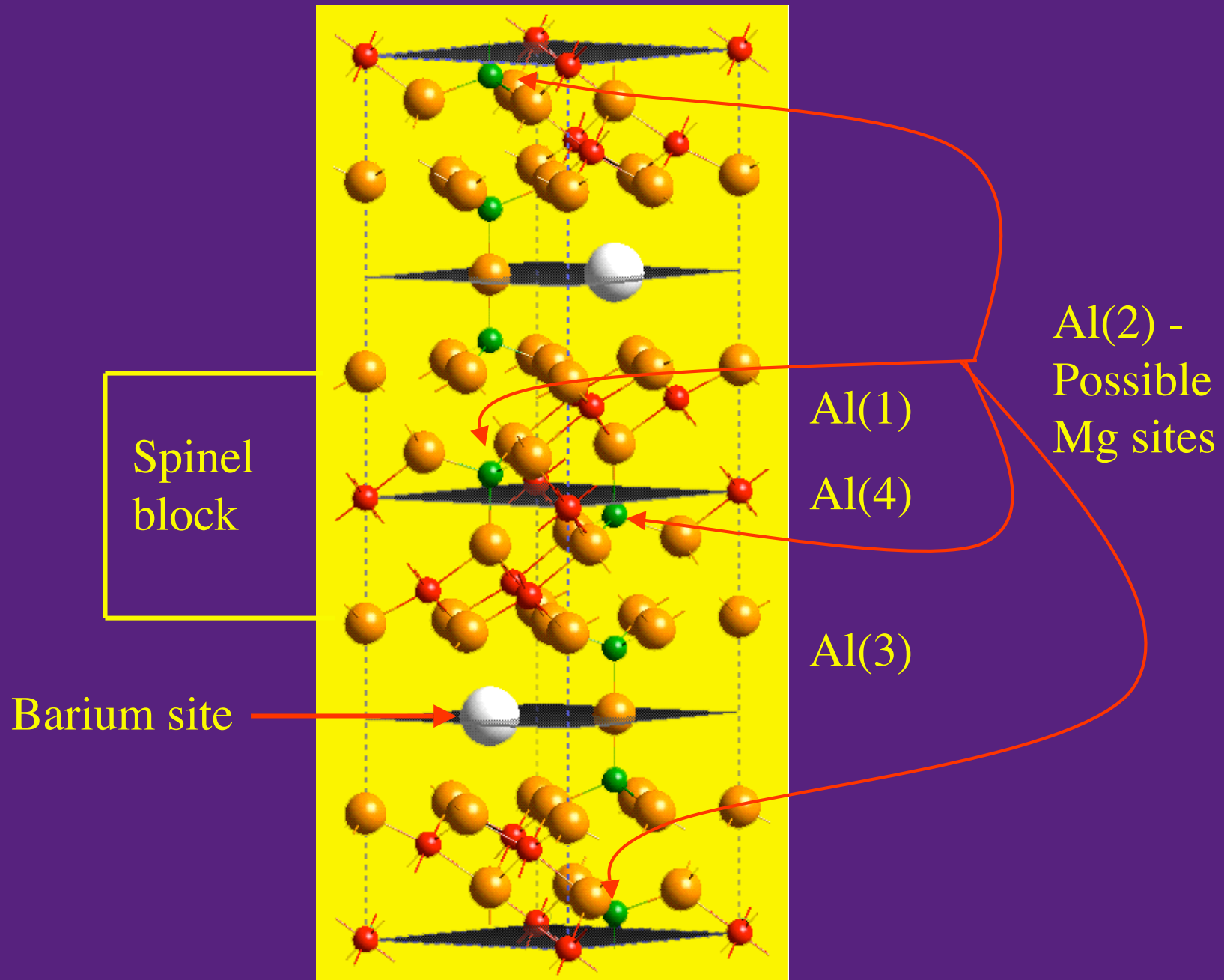


Ideal structure of $\text{VO}_2(\text{B})$



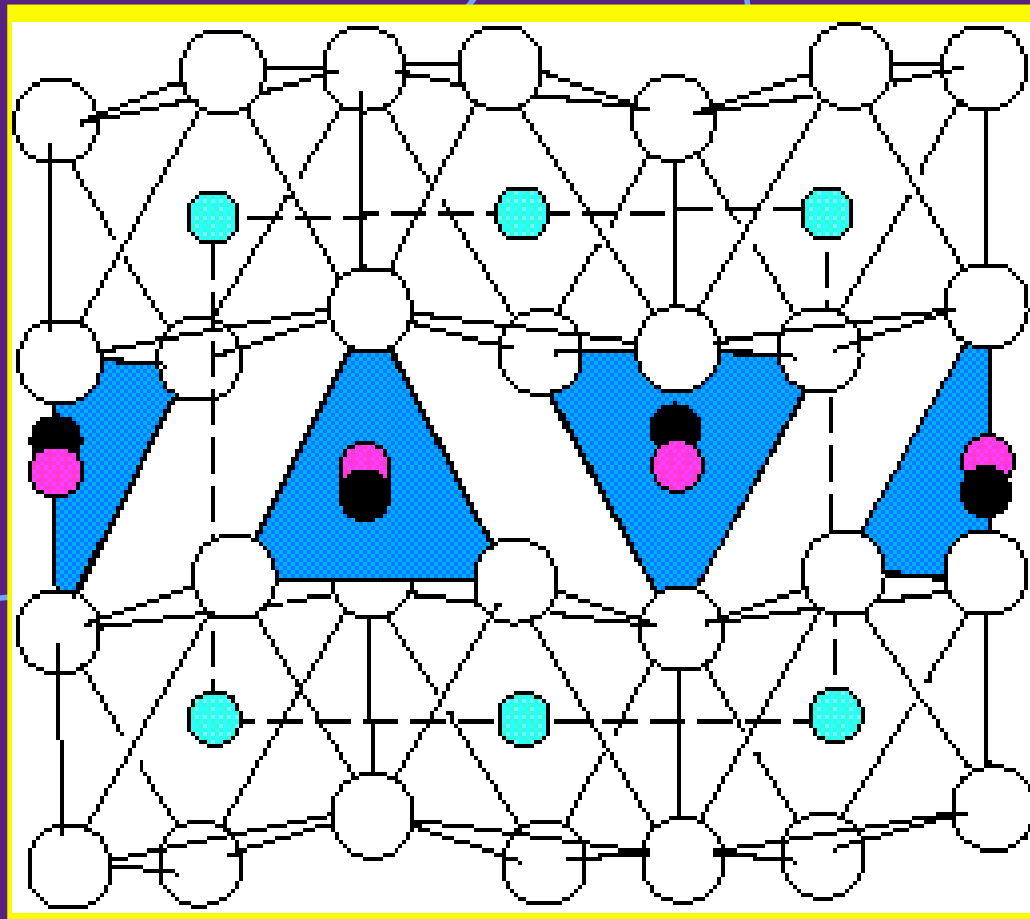
Energy minimised structure of $\text{VO}_2(\text{B})$

Crystal structure of BAM: Eu phosphor



Comparison between calculated and experimental structures

Atom type	$X_{\text{obs.}}$	$X_{\text{calc.}}$	ΔX	$Z_{\text{obs.}}$	$Z_{\text{calc.}}$	ΔZ
Ba	0.6678	0.6667	0.0011	0.2500	0.24662	0.00338
Al(1)	0.8343	0.8338	0.0005	0.10544	0.10268	0.00276
Al(2)	0.3333	0.3333	0	0.02400	0.01848	0.00552
Al(3)	0.3333	0.3333	0	0.17416	0.17052	0.00364
Al(4)	0.0000	0.0000	0	0.00000	0.00000	0
O(1)	0.1534	0.1488	0.0046	0.05152	0.05130	0.00022
O(2)	0.5042	0.5040	0.0002	0.14799	0.14333	0.00466
O(3)	0.6667	0.6667	0	0.05901	0.05409	0.00492
O(4)	0.0000	0.0000	0	0.14437	0.139590	0.00478
O(5)	0.3333	0.3333	0	0.25000	0.24789	0.00211



The oxygen layers in olivine rumples from ideal close packing to a lower energy configuration

Molecular Dynamics

- **What is it?**

- Approach to the computer simulation of materials

- **What does it do?**

- Calculates dynamic properties by solving, iteratively, (classical) equations of motion

- **How does it work?**

- Computational approach to statistical mechanics

Statistical Mechanics

- Conversion of atomic scale information into macroscopic quantities
- Thermodynamic state defined by variables such as P, T, N .
- Other thermodynamic properties, such as ρ, μ, C_v etc., derived from equations of state
 - Their values are dictated by variables characterizing thermodynamic state
- atomic positions and momenta define instantaneous mechanical state (phase space)

Statistical Mechanical Ensembles

- Microcanonical: constant N, V, E
- Canonical: constant N, V, T
- Grand Canonical: constant μ, V, T

- Standard MD simulations model the microcanonical ensemble
 - Newton's laws conserve energy

Integrating the equations of motion

● Verlet algorithm

- Direct solution of $m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \Delta t^2 \mathbf{a}_i(t)$$

- Velocities eliminated by adding Taylor expansions

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t)$$

NVE *v.* NVT: Thermostats

- Equations of motion conserve energy
- For Temperature control, system is kept in contact with a heat bath
- Thermostats work by scaling the velocities so that the kinetic energy is appropriate to the target temperature

- **Nosé:** $\mathbf{v}_i = s \, d\mathbf{r}_i / dt$

- **Hoover:** $\mathbf{v}_i = d\mathbf{r}_i / dt = \mathbf{p}_i / m$

with $d\mathbf{p}_i / dt = -\nabla\Phi - \zeta\mathbf{p}_i$

- with kinetic energy controlled by

$$\frac{Q}{2} \frac{d\zeta}{dt} = \sum_i p_i^2 / 2m_i - g / 2k_B T$$

- **Berendsen:**

- scale velocities by $\chi = \left(1 + \frac{\Delta t}{\tau_T} \left(\frac{T}{\bar{T}} - 1 \right) \right)^{1/2}$

Calculation of Forces

- MD technique hinges on accurate forces
- Forces are obtained from an inter-atomic potential model
- Classical models based on Born model of solid
 - Point ions with short-range (Pauli) repulsive forces
 - Can include polarisability via the Shell Model
- Models need validation: check on parameters

Computational considerations

- **Size of simulation box**

- Periodic boundary conditions used to generate infinite solid
- Ewald summation of Coulombic interactions

- **Length of simulation**

- CPU time per time-step
- Number of time-steps

- **Accumulation of data**

- Post-run analysis

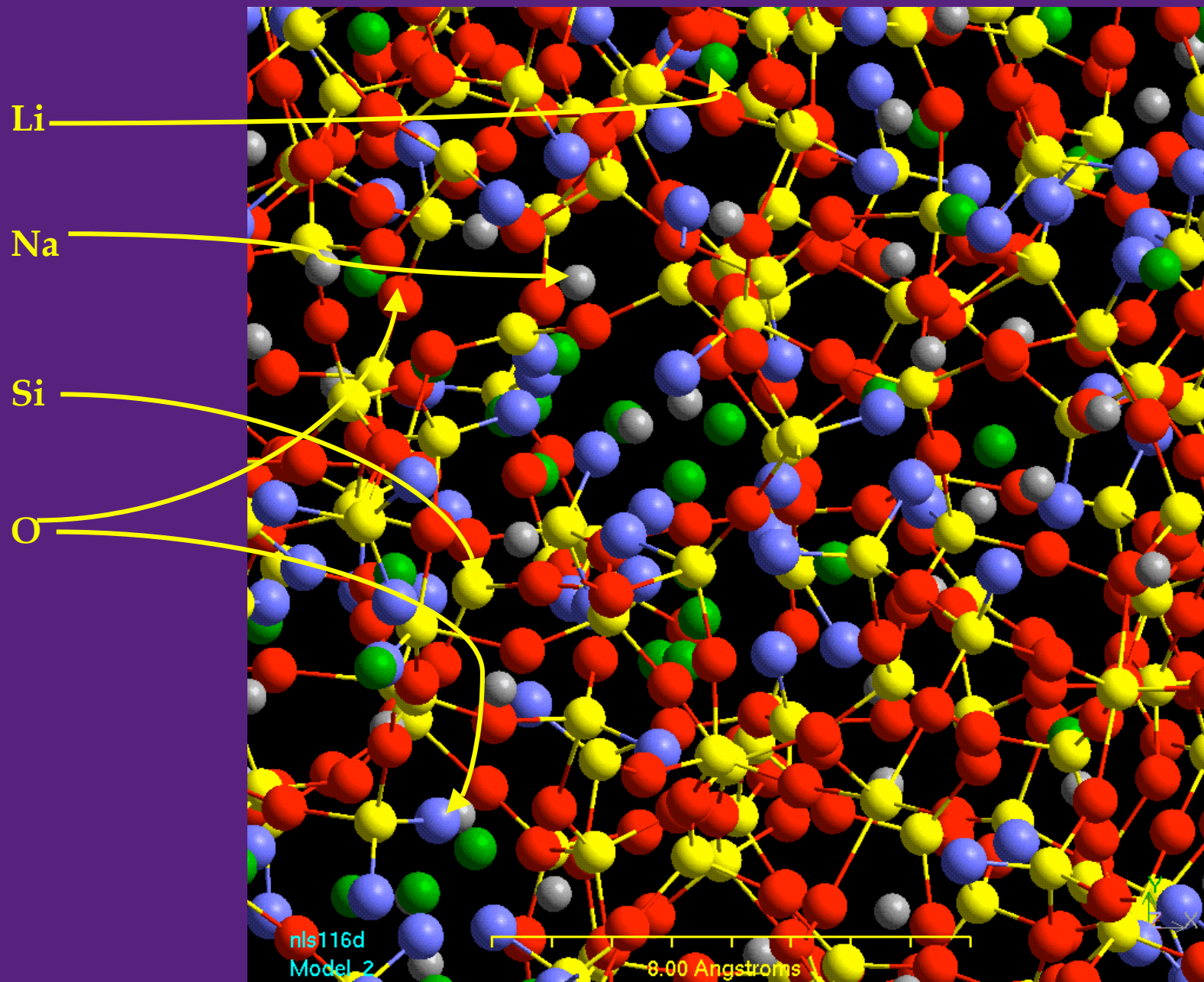
Post-run analysis

● Structure

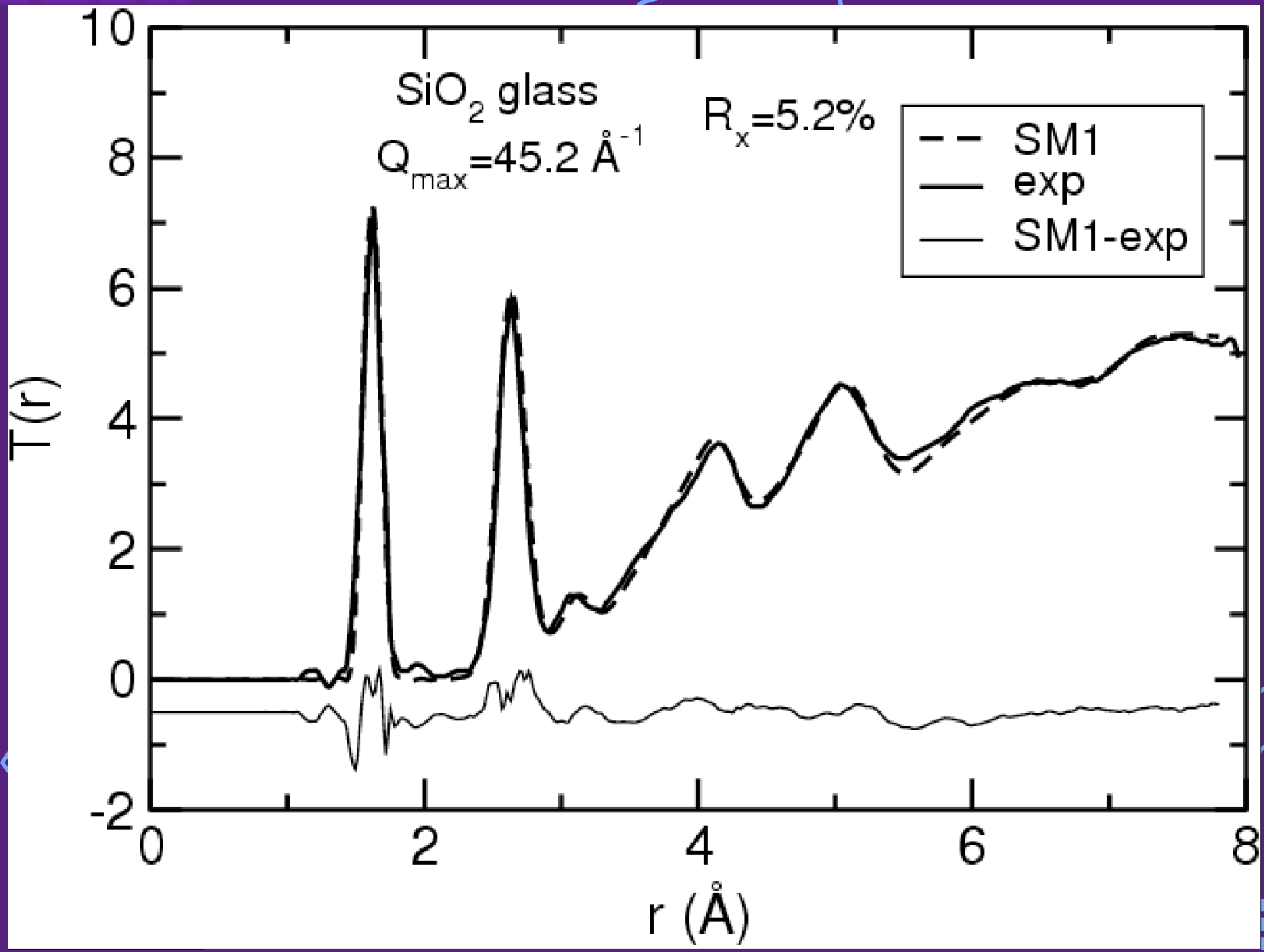
- Radial distribution functions
- Co-ordination numbers
- Spatial distribution of different atomic species

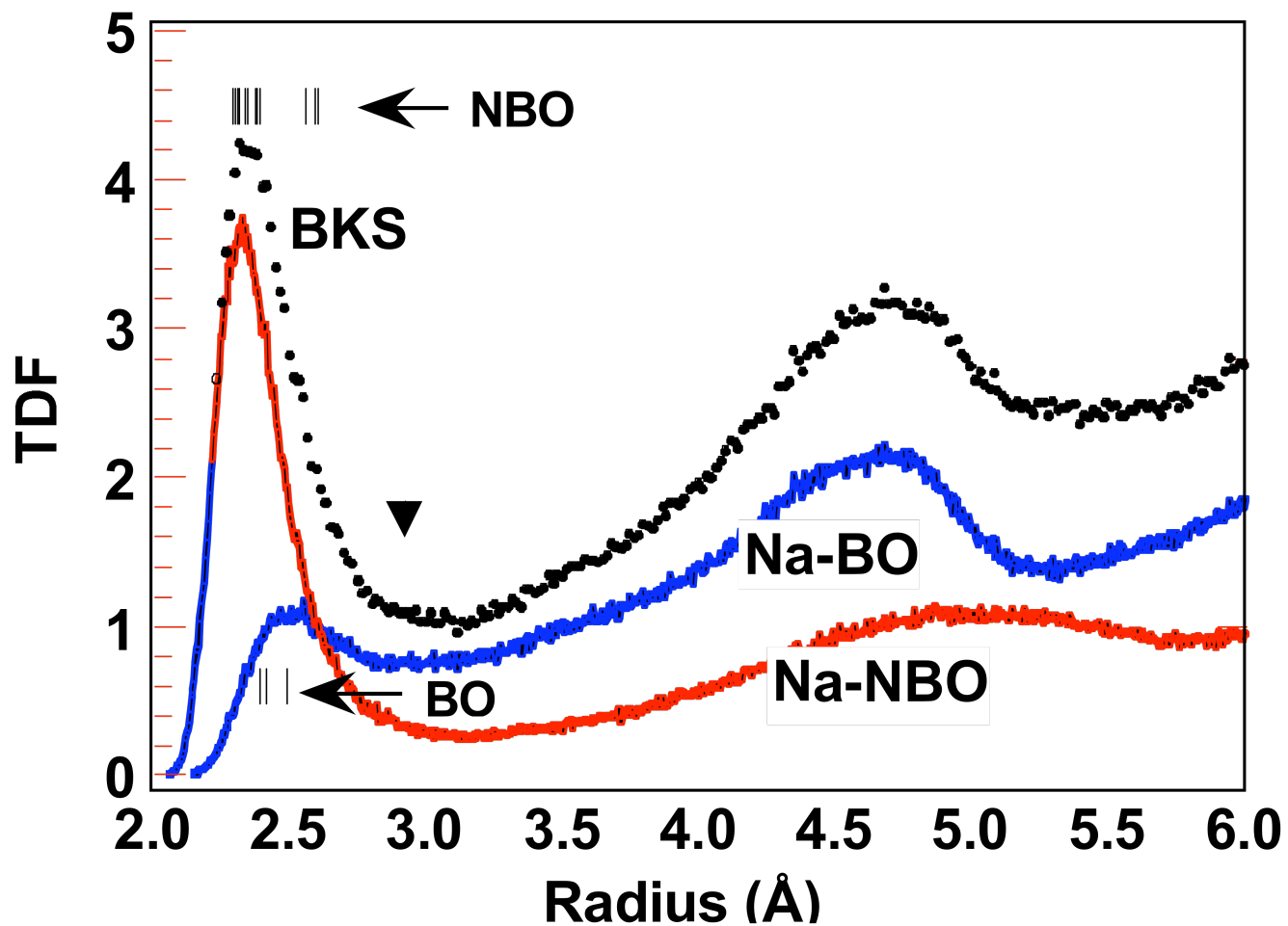
● Transport

- Diffusion co-efficients
- Migration mechanisms



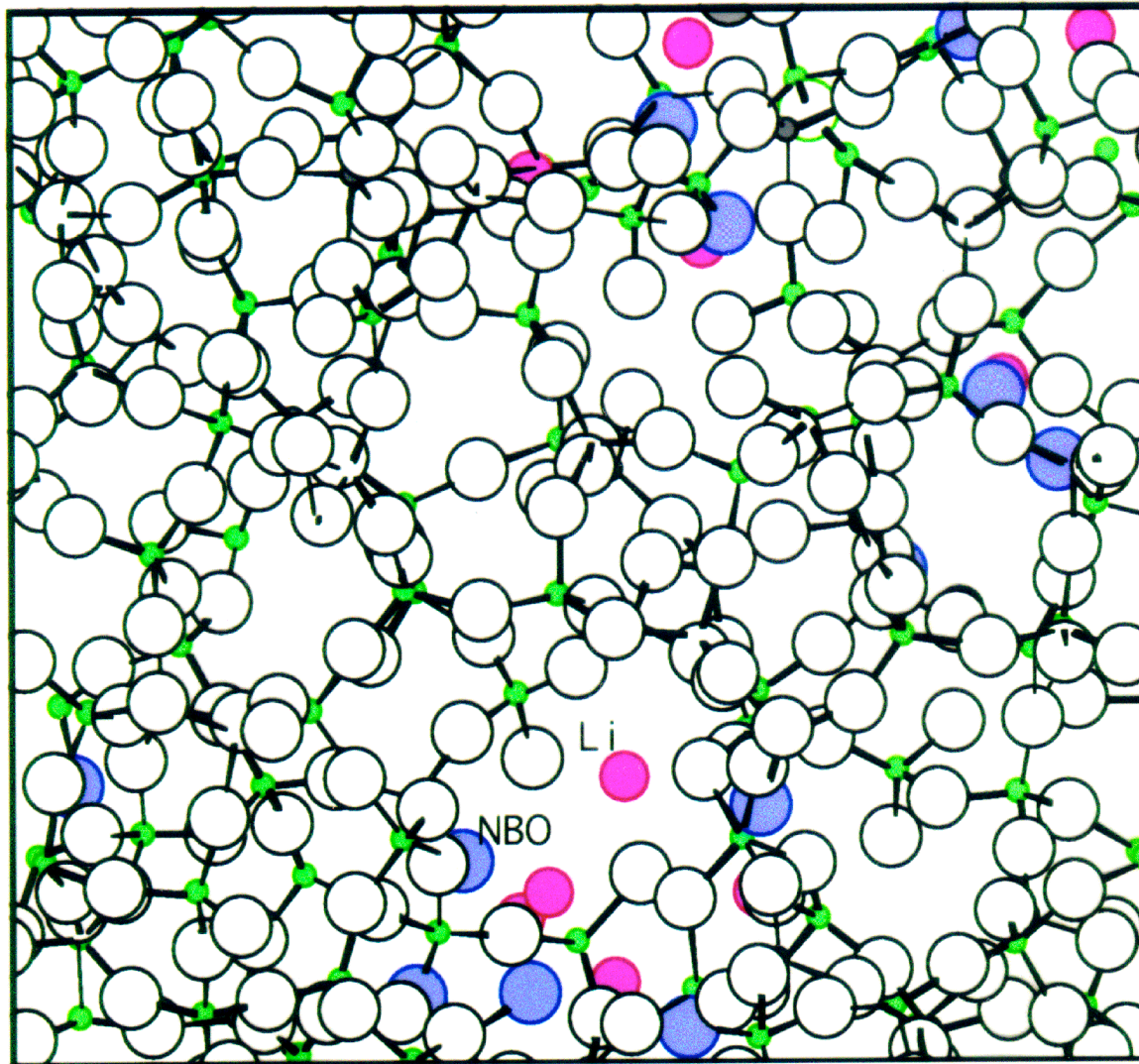
Snap-shot structure of a lithium sodium silicate glass





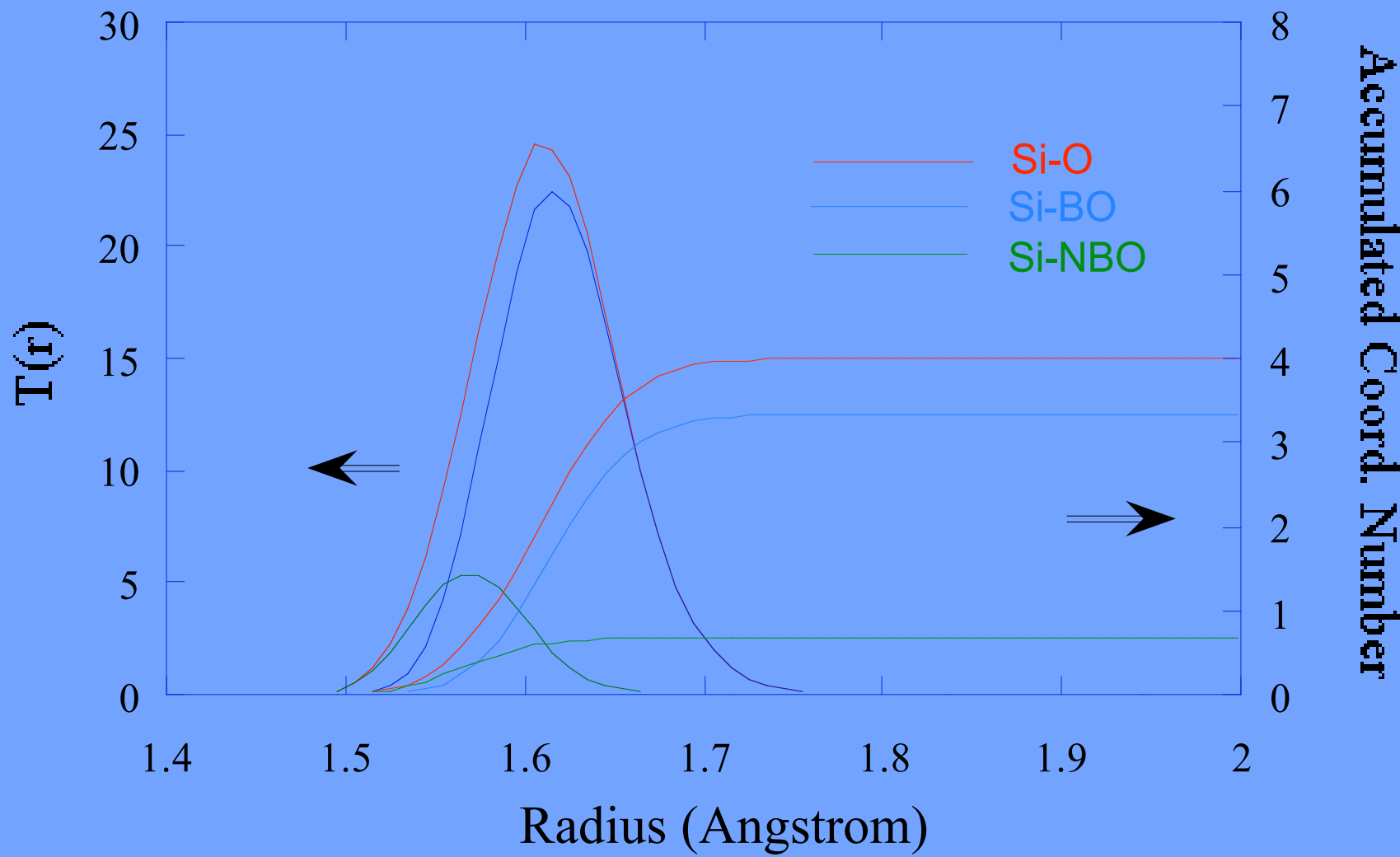
Na-O pdf for 30Na₂O•70SiO₂ glass deconvoluted into bridging and non-bridging oxygen components. Note the shorter Na-NBO distances. The lines represent crystalline Na-O distances.

Segregation of Li and NBO in a silicate glass containing 5mol% lithia.

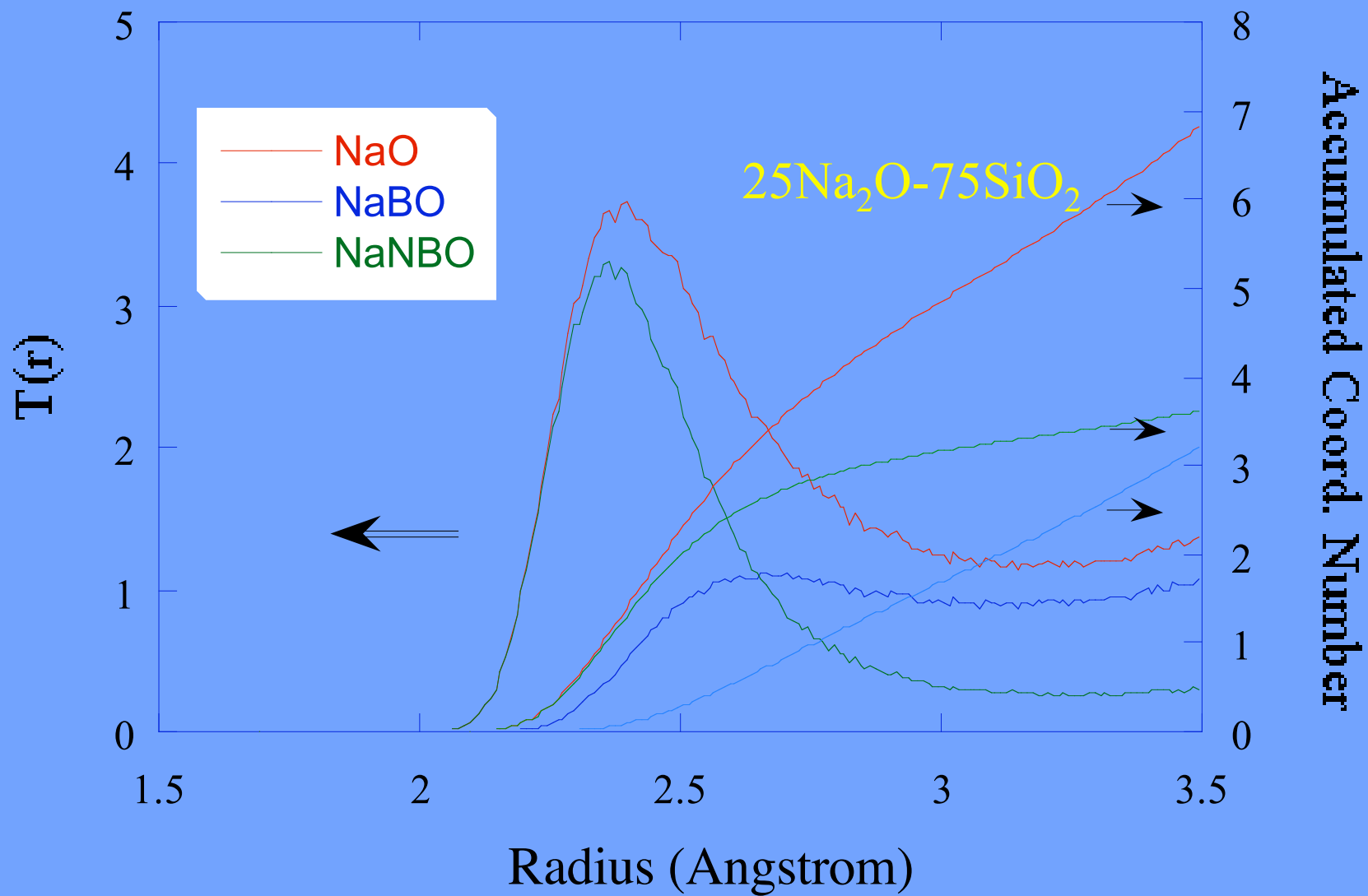


Local Cation Environments

- Network formers: tetrahedra
- Network modifiers
 - Nature of polyhedron depends on cation size
- How are modifier polyhedra linked together?
 - Share corners and edges, sometimes faces
 - Underlying feature of the Modified Random Network Model
- Connectivity of modifier polyhedra play key role in diffusion processes

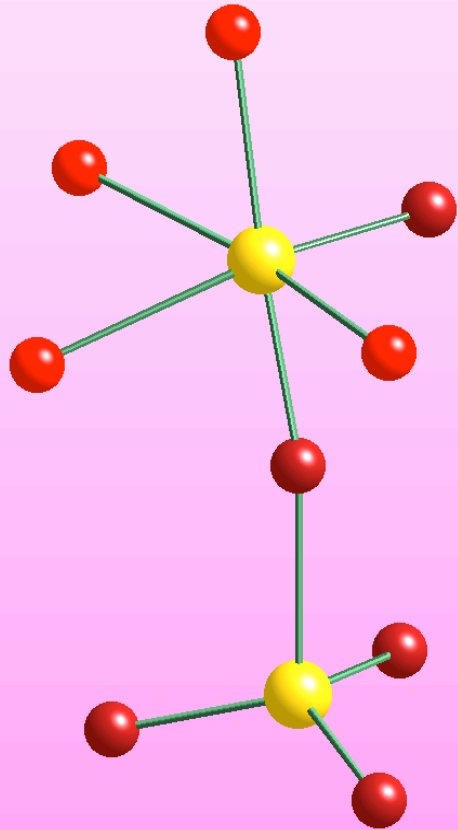


$25\text{Na}_2\text{O} \cdot 75\text{SiO}_2$: Si - O pair distribution function

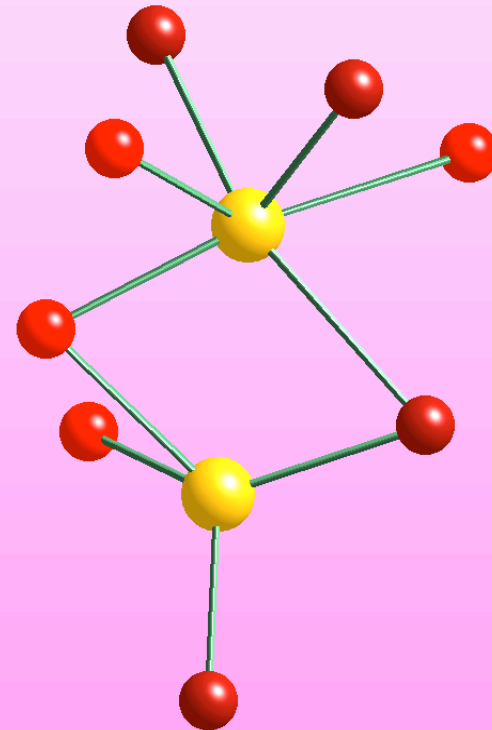


Na - O pair distribution function

Connectivity of Na-O polyhedra from a $25\text{Na}_2\text{O} \cdot 75\text{SiO}_2$ glass

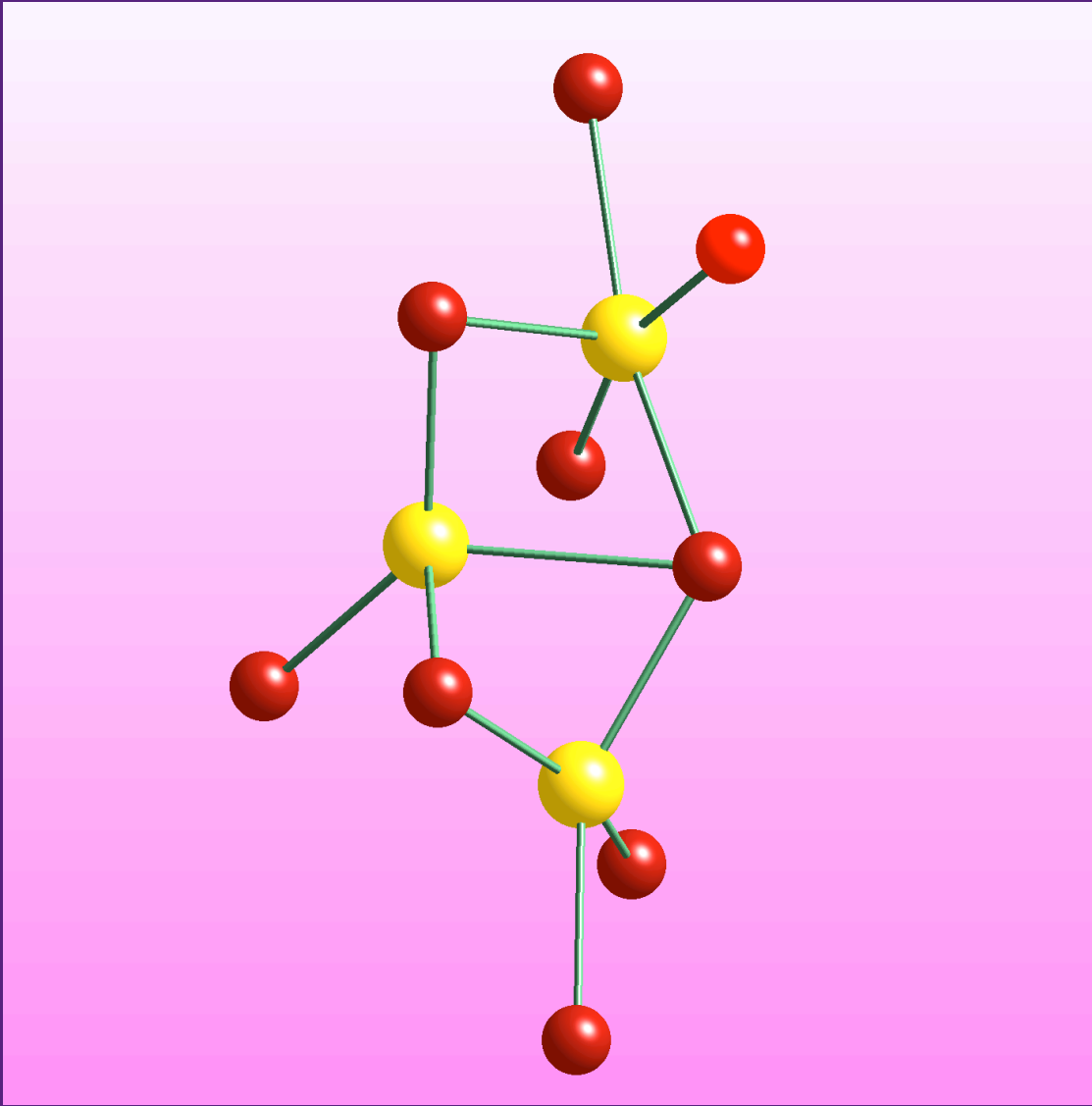


Corner Sharing



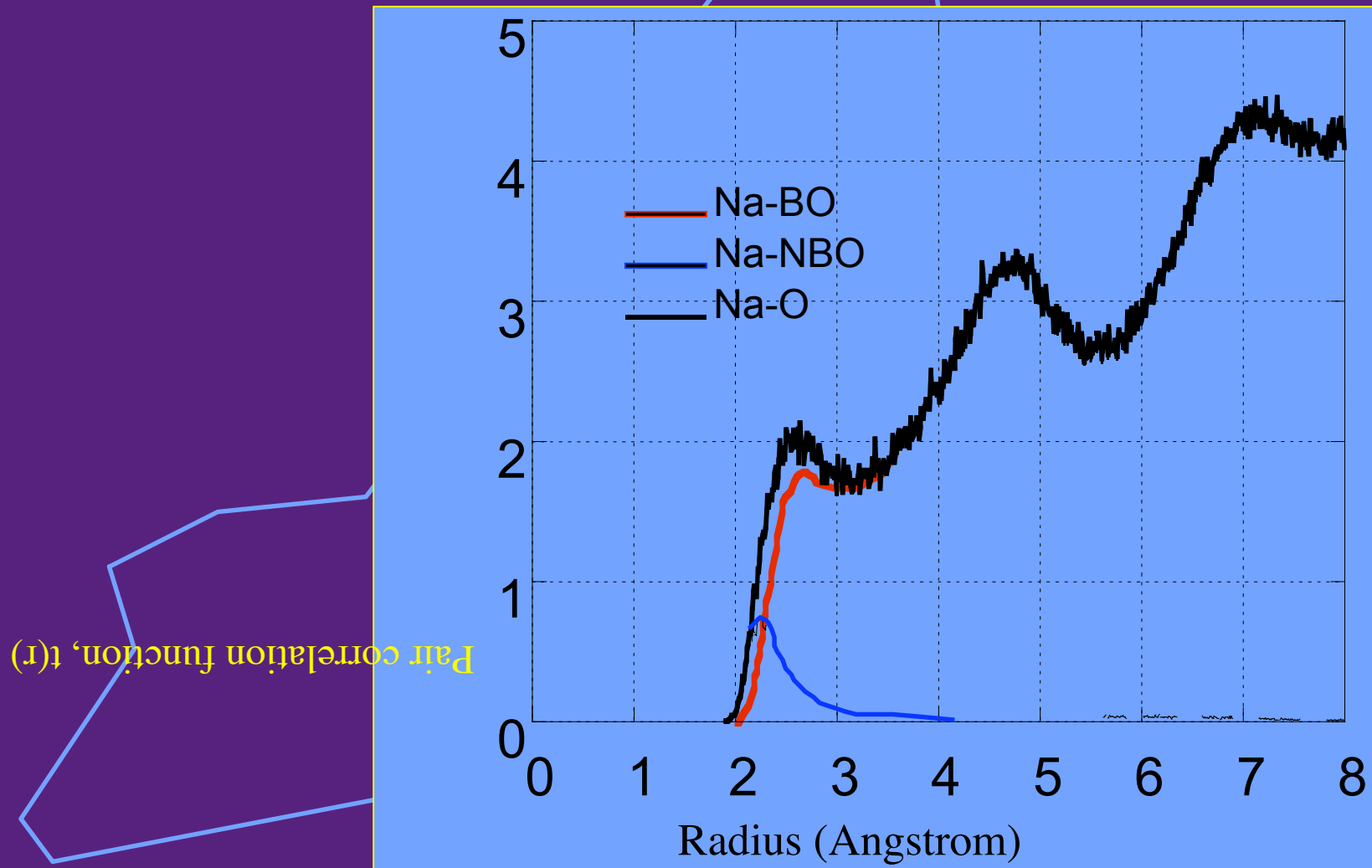
Edge Sharing

Connectivity of Na-O polyhedra from a $25\text{Na}_2\text{O} \cdot 75\text{SiO}_2$ glass

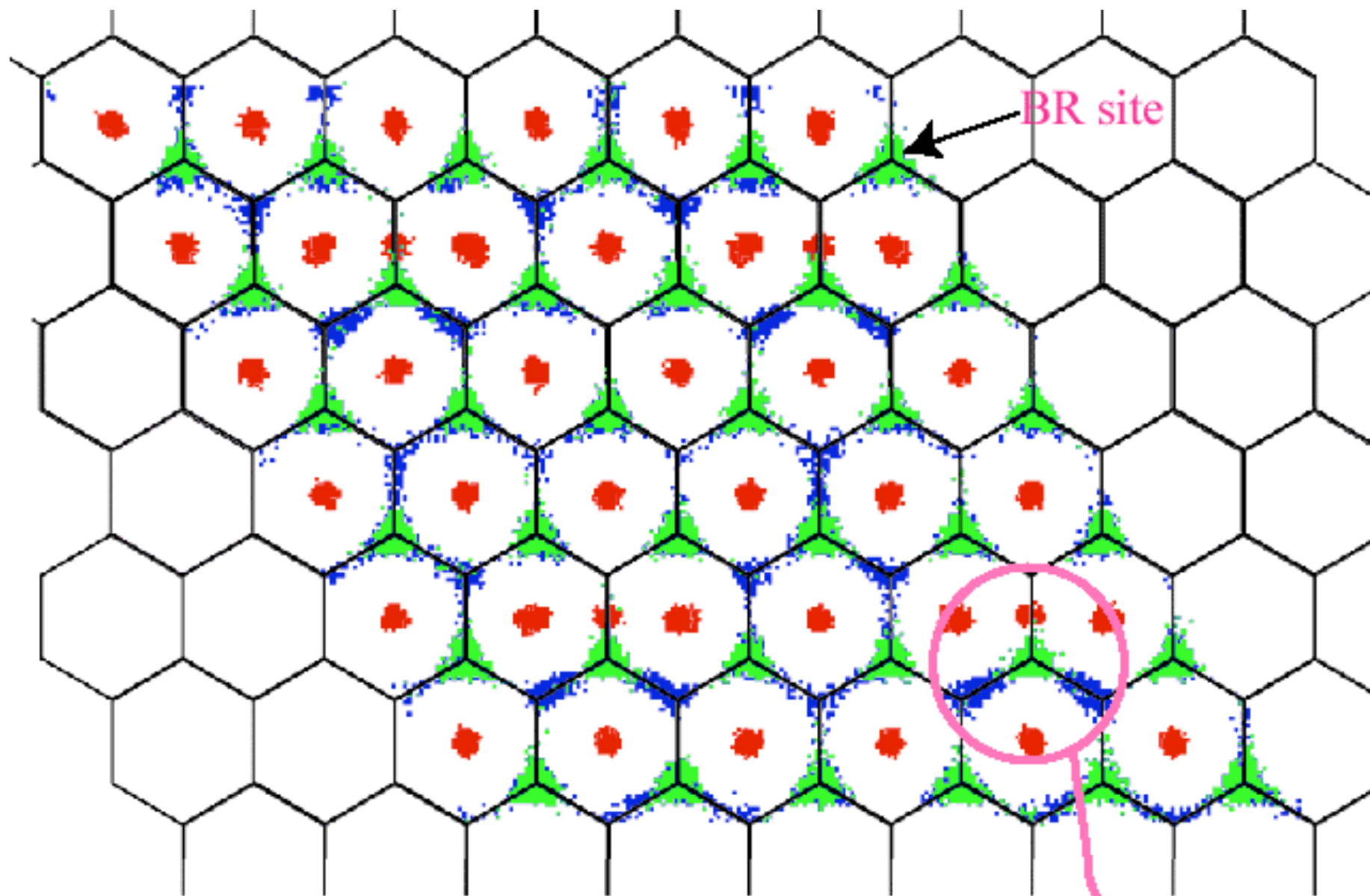


In this group, one polyhedron shares edges with two other polyhedra.

Na - O pdf in 1mol% sodium silicate



Majority of co-ordinating oxygen ions are BO



Superposition of trajectories from stoichiometric (Na: green) and non-stoichiometric (Na: blue) Na β -aluminas. The red atoms are oxygens. The Na associated with the O6 do not take part in diffusion.

Monte Carlo methods

- **Statistical mechanical approach**
- **An atom is moved: the move is accepted, if**
 - new configuration has lower energy, or
 - increase in energy is less than a randomly generated ΔE .
- **Reverse Monte Carlo**
 - Moves are intended to improve fit to experimental data

Defect Calculations

● Point defects

- Vacancies, interstitials, substitutional ions
- Dopants or impurities; trace elements

● Structure and energetics

- Formation energy
- Migration activation energy
- Association energy

Defect calculations

- Defects remove translational symmetry
- Use embedded regions or supercell methods
 - Atomistic region enclosed by dielectric continuum
- Mott-Littleton approximation
 - Polarisation due to defect (relaxation)
- Computer codes: HADES, CASCADE, GULP

Summary

- Atomistic simulations provide an important complement to experimental structural studies
- Quantum mechanical methods becoming more widely used
 - Restricted to small systems
- Classical methods can be used for “ab initio” determination of complex structures, including non-crystalline materials

Schematic of glass formation: melting a polycrystalline mixture

