Apport des modélisations *ab initio* pour la compréhension des propriétés structurales et dynamiques de verres borosilicatés

Laurent Pedesseau[1,2], Simona Ispas[1] & Walter Kob[1]

[1]Laboratoire Charles Coulomb
Université Montpellier 2 – CNRS

[2]Foton - INSA Rennes

USTV – GDR Verres 2012, Montpellier

OUTLINE

- Glass composition and simulation details
- Dynamics: diffusion constants, activation energies
- Structure: liquid vs glass, pair correlation, coordinations, structure factor, etc...
- Vibrational properties. Infrared spectra
- Conclusions

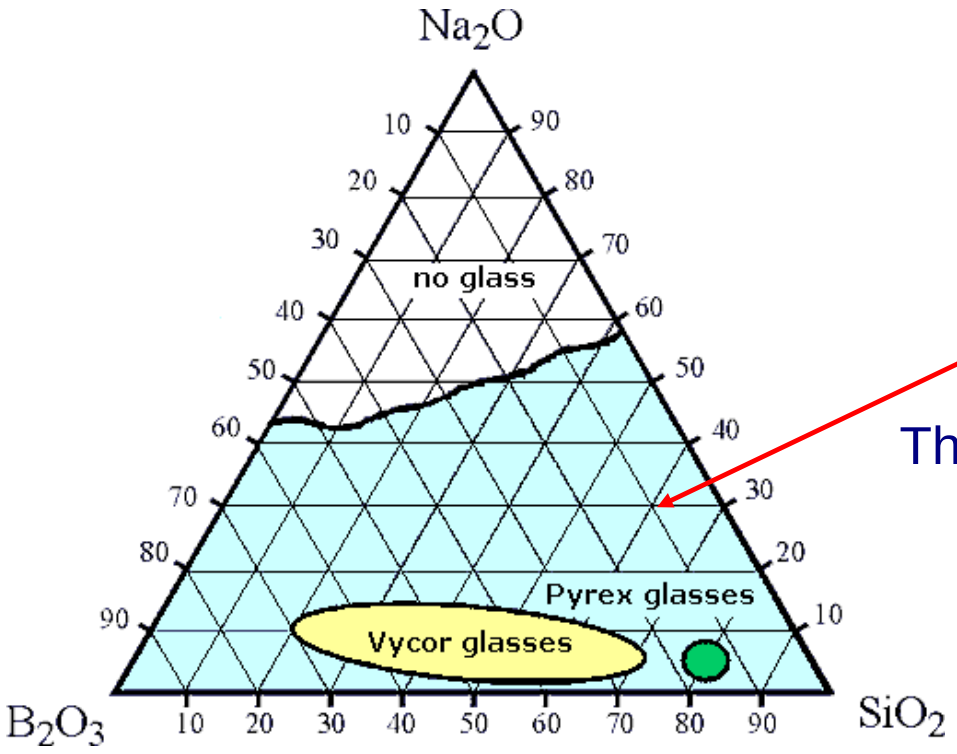
Borosilicate glasses present remarquable properties:
SiO_2-B_2O_3+(Al_2O_3+P_2O_5)+alkali and/or alkaline-earth oxides+....

- high resistance to thermal shock
- low thermal expansion properties and low electrical conductivity
- highly resistant to corrosion

→ real-life glasses, e.g. laboratory glassware, E-glass, heat resistant cookware
→ glass fibre insulation materials
→ optical glasses
→ used to immobilize nuclear waste

→ Design and engineering: search for optimal compositions being energy- and environmentally-friendly
→ How does boron modify the structure/integrate into the structure?

Sodium borosilicate glasses: Na_2O - B_2O_3- SiO_2 **(NBS)**



Our NBS composition (mol%)

30% Na_2O-10%B_2O_3-60%SiO_2

Theoretical composition of the glass wool

- Complex relationships between macroscopic properties and atomistic structure
- Use computer simulations to study the structure and dynamics

Models and simulation details (1)

First principles molecular dynamics simulations: we need reliable results

- **VASP:** DFT, GGA-PBEsol functional, PAW, E_{cut}=600 eV, Γ point, NVT Nosé-Hoover thermostat, time step 1fs
- **System sizes:**

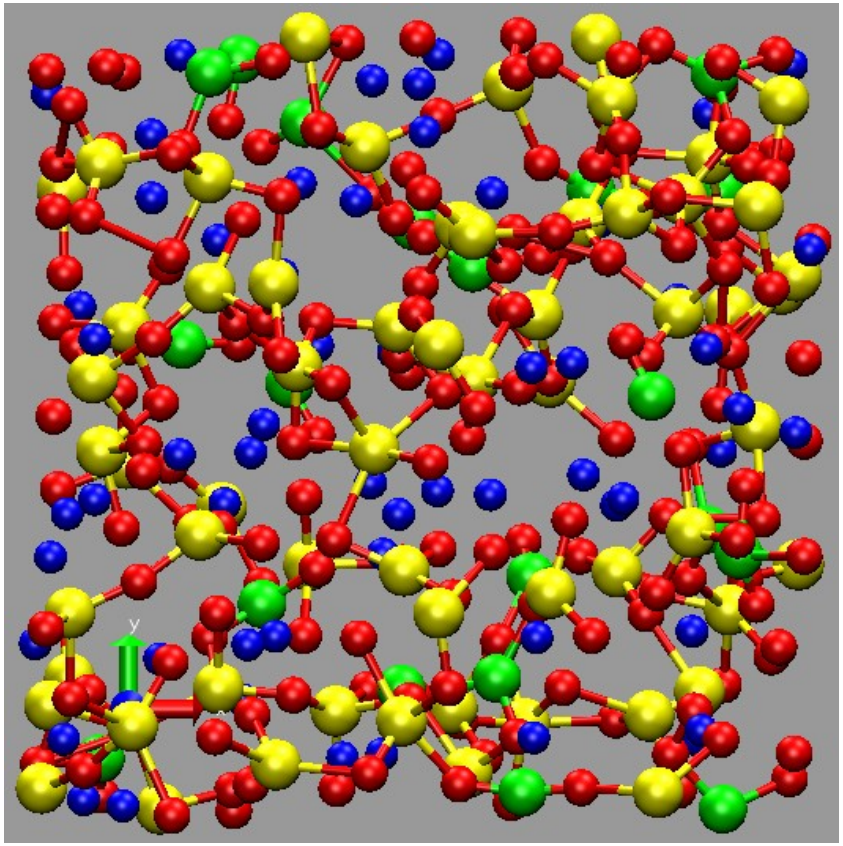
  320 atoms → 60 Si, 180 O, 60 Na, 20 B
- **Box sizes (PBC)**

  density = 2.51g/cm^3, box length = 15.93 Å
- Liquid: 2 independent samples and 5 temperatures

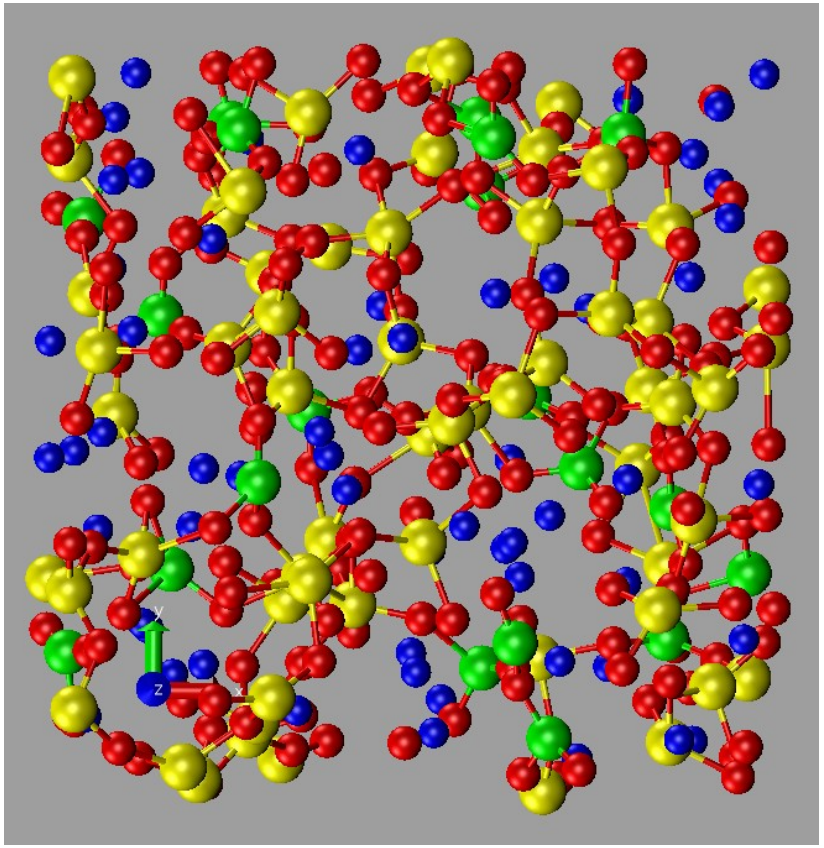
  → length of trajectories: 80-100 ps
- 6 to 8 independent glasses

Models and simulation (2)

- Production:
  - equilibrate sample at 4500K
  - cool down stepwise to lower temperatures and equilibrate
  - cool down to 300 K and anneal (2-15 ps)



T=4500 K

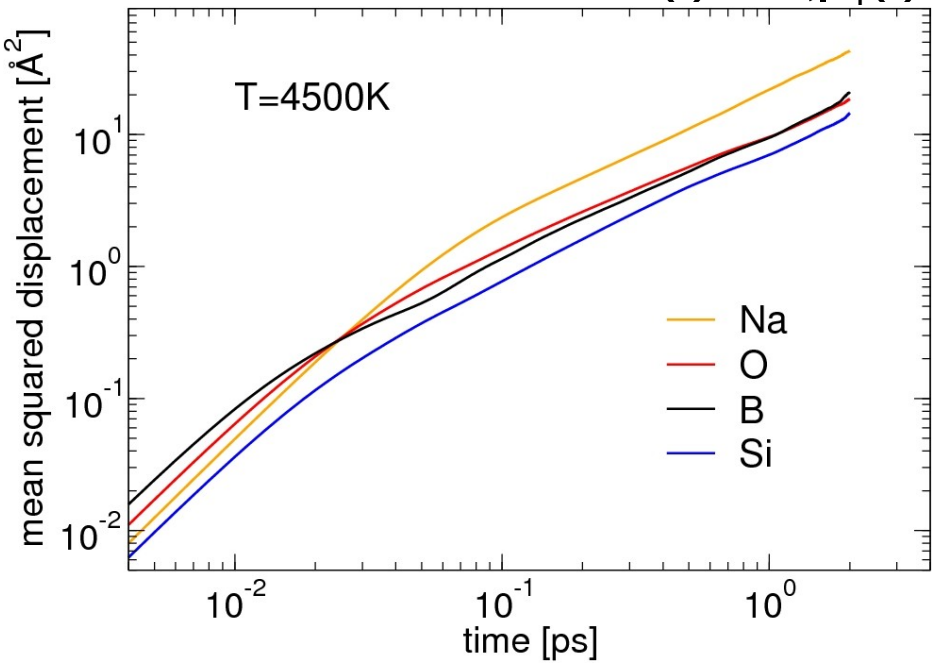


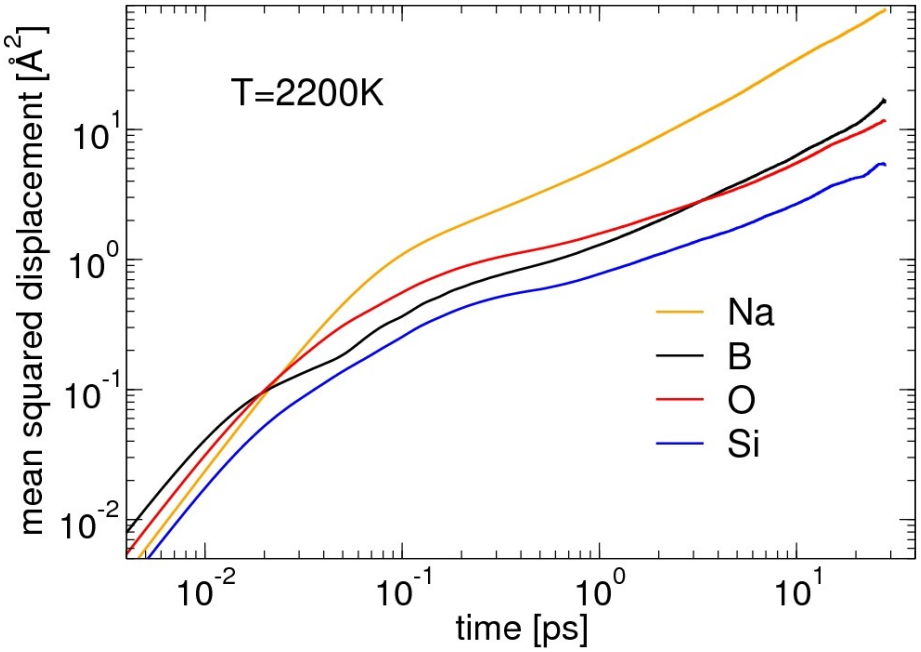
T=300K (glass)

Relaxation dynamics of the NBS liquid (1)

- Use mean squared displacement **(MSD)** to characterize the dynamics

$$MSD(t) = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$$





⇒ we can equilibrate the sample down to 2200K

⇒ MSD depends strongly on species considered

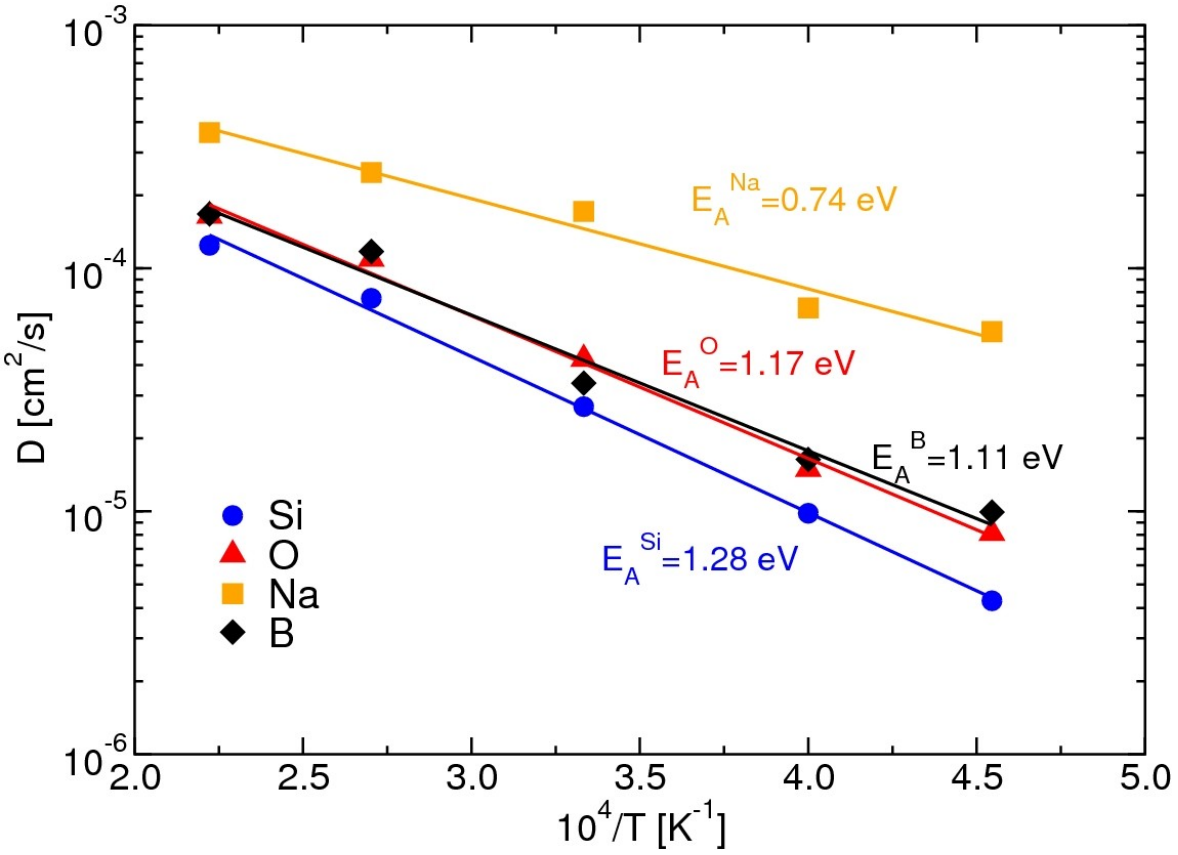
⇒ Boron dynamics seems to be complex

Liquid temperatures: 4500 K, 3700 K, 3000 K, 2500 K, and 2200 K

Relaxation Dynamics of the NBS liquid (2)

- Use Einstein relation to obtain the diffusion constants D_α

$$D_\alpha = \lim_{t\to\infty} \mathrm{MSD}(t) \,/\, 6t$$



- Diffusion constants show Arrhenius dependence with activation energy that depends on species
- Decoupling of Na motion at low T
- Arrhenius law suggested equally by extrapolating exp. data

Grandjean et al. PRB75 2007

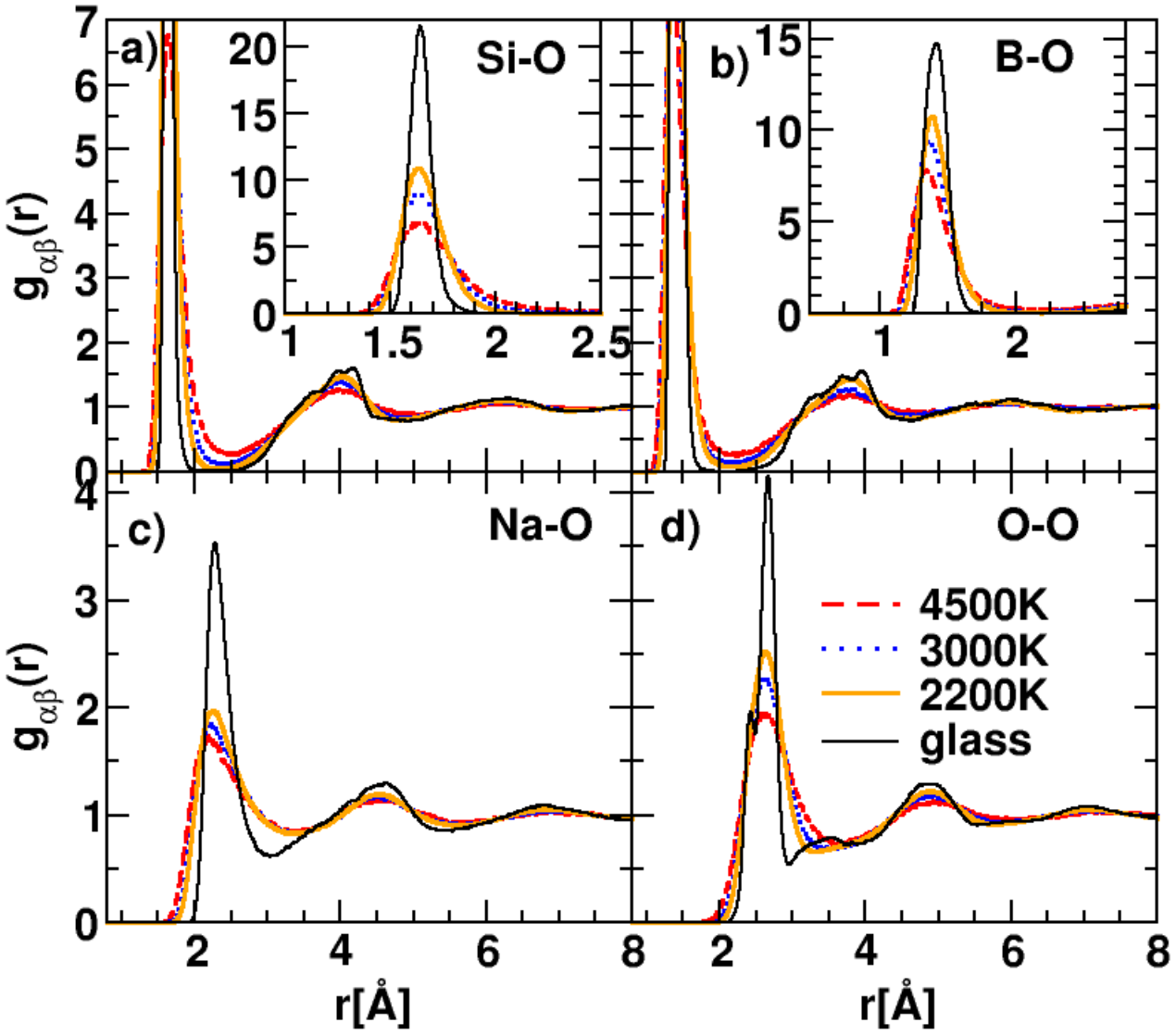
- Oxygen activation energy in agreement with exp data

Cochain, PhD thesis

Liquid temperatures: 4500 K, 3700 K, 3000 K, 2500 K, and 2200 K

NBS liquid and glass: Structure (1)

- Pair correlations of **oxygen** atoms



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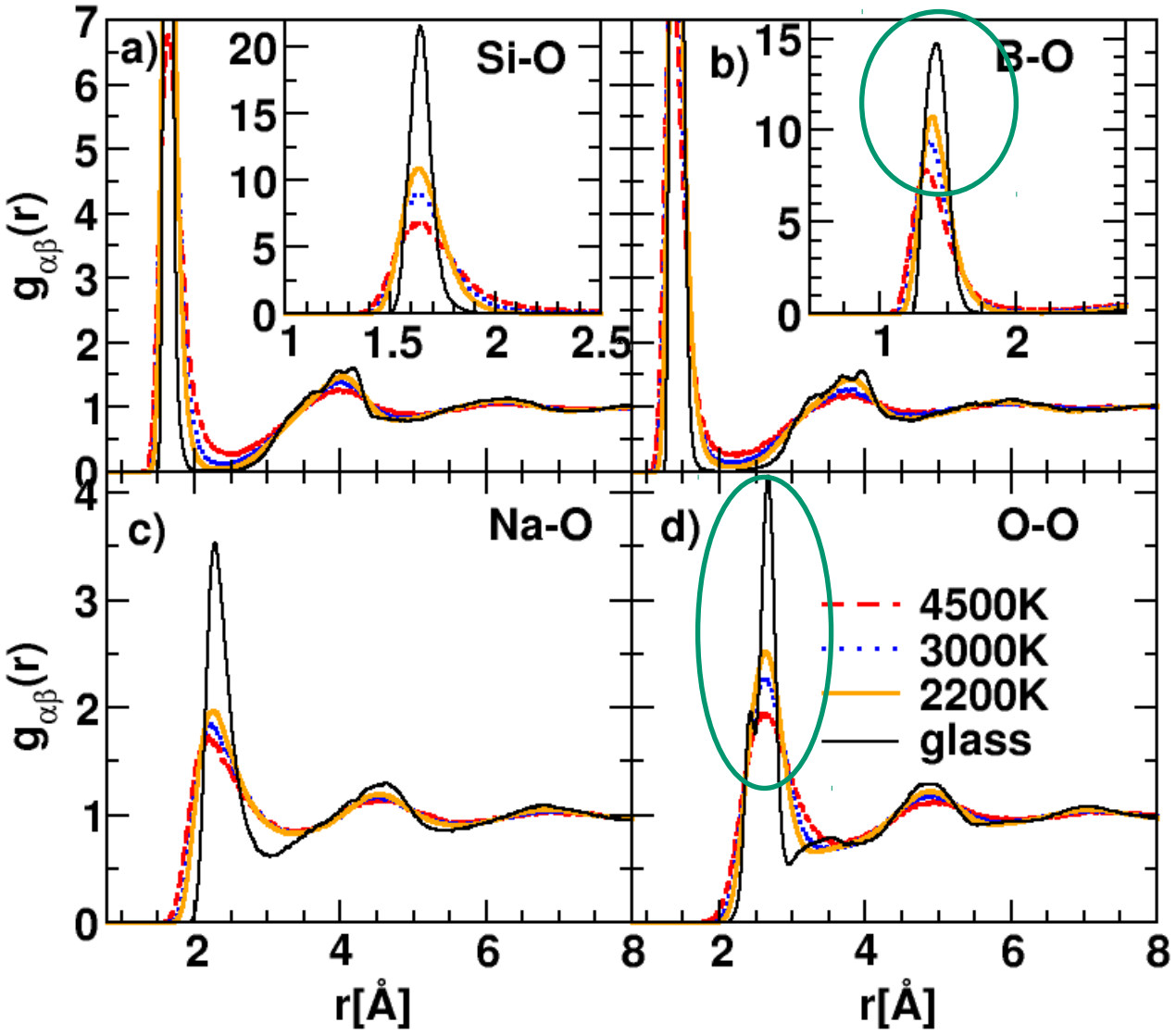
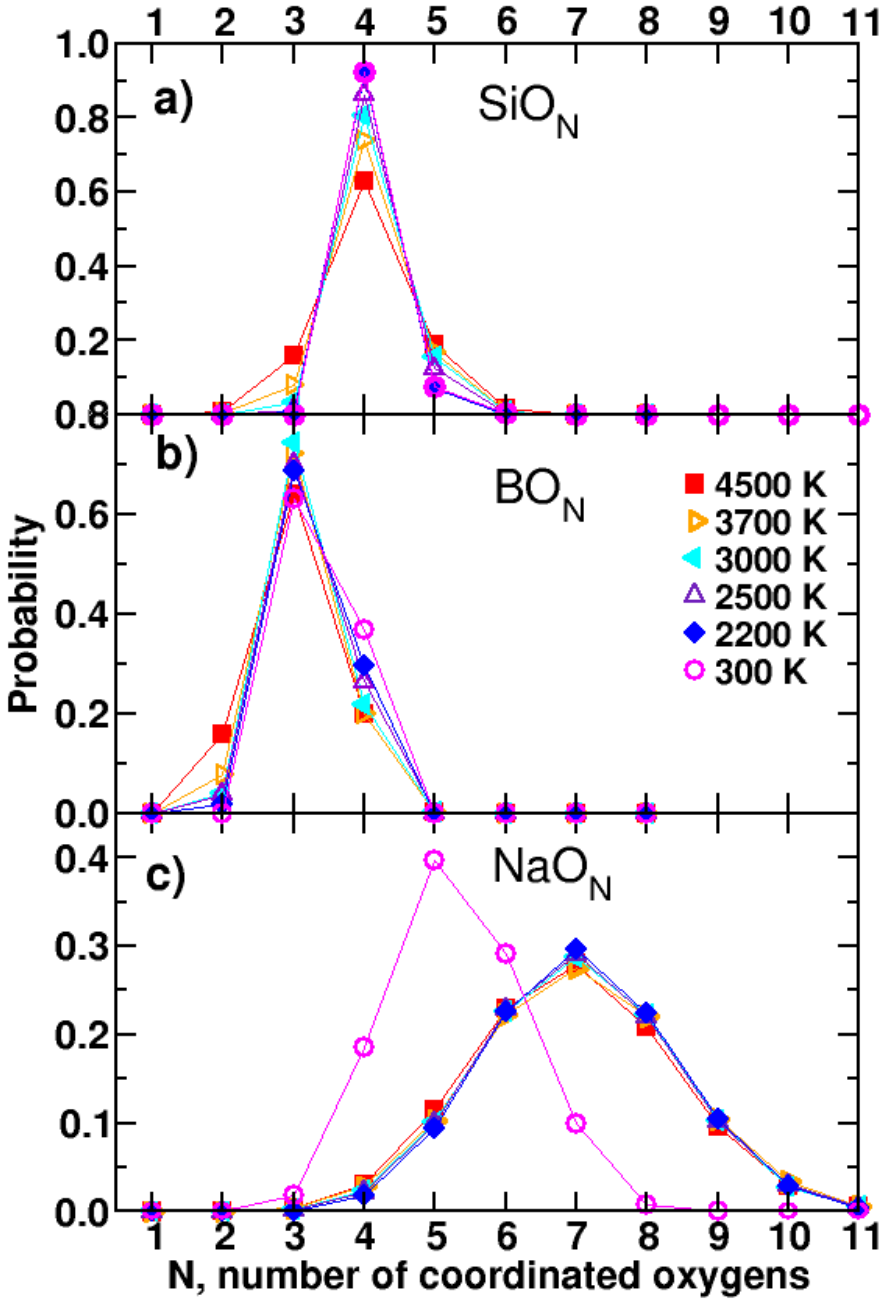
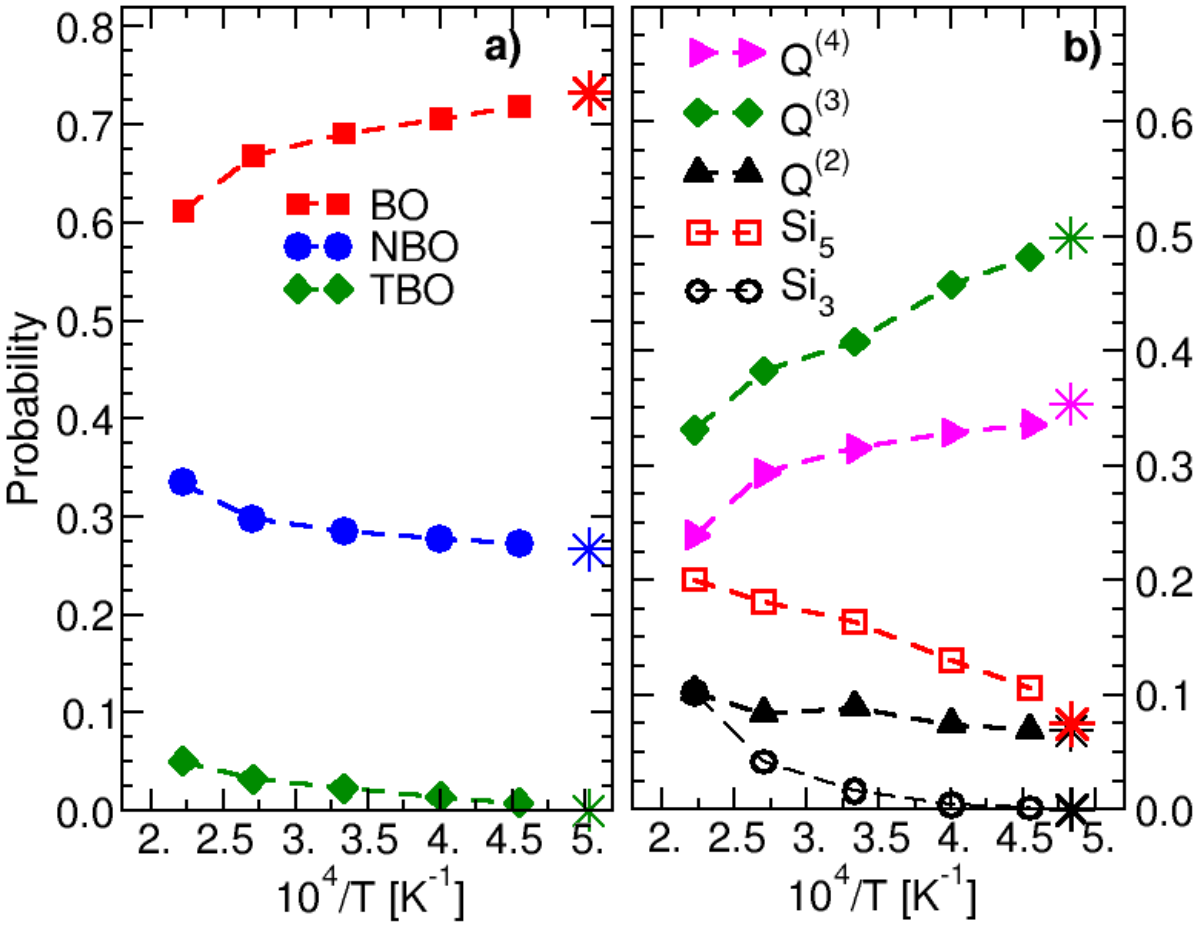


Coordinations of network and modifier cations



- **SiO_N coordination**: tetrahedral coordination dominant with decreasing temperature (*as expected*) and a large concentration of Si_5~8% in the glass due to the high quench rate
- **BO_N coordination** shows a complex behavior with decreasing temperature
- **NaO_N coordination** in the glass shifts to lower values w.r.t the liquid

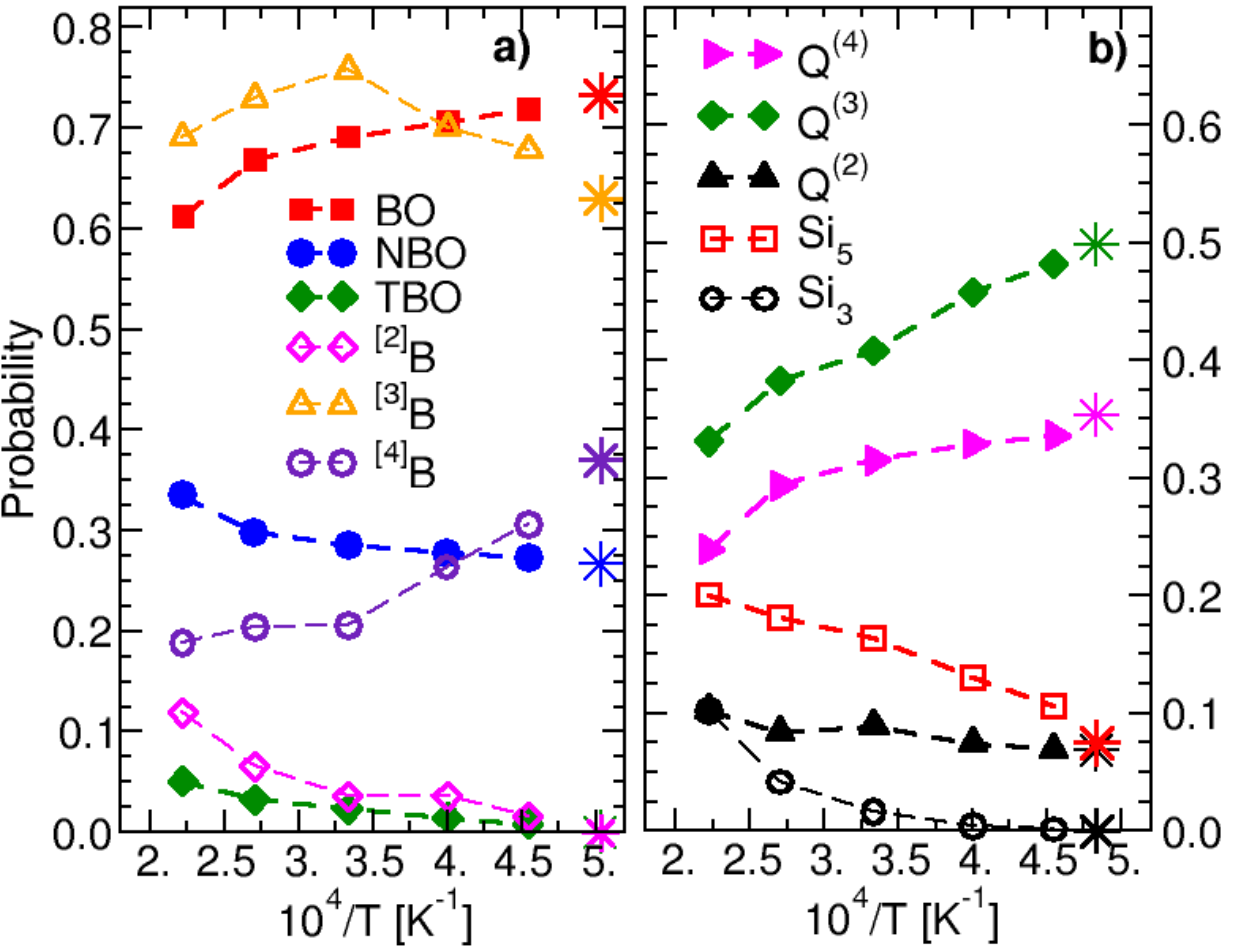
Temperature dependence of network connectivity



- Increasing connectivity with decreasing temperature as #BO↗

- Silica sub-network: quite depolymerized as ~60% of Si are in Q_3 or Q_2 speciations

Temperature dependence of network connectivity

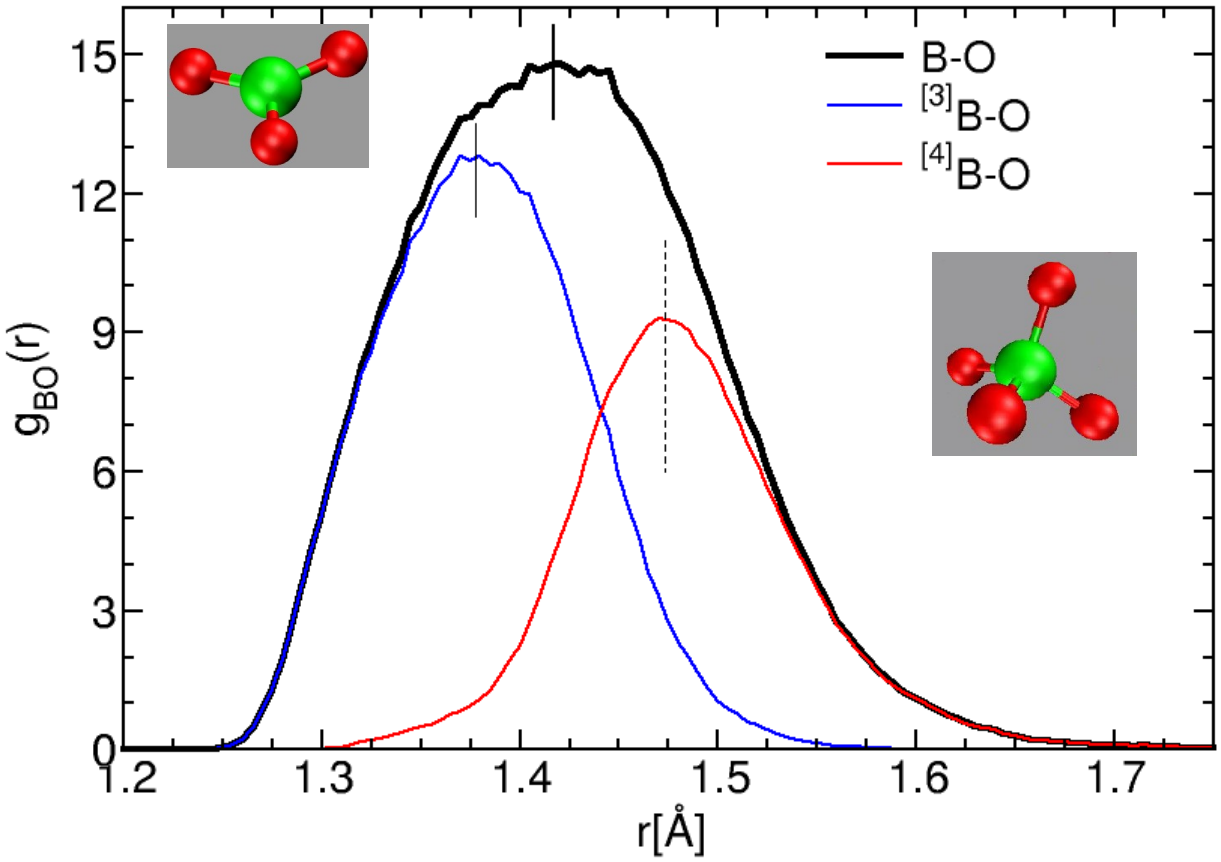


- Increasing connectivity with decreasing temperature as #BO↗
- Silica sub-network: quite depolymerized as ~60% of Si are in Q_3 or Q_2 speciations

- Borate sub-network: the conversion of $^{[3]}B$ into $^{[4]}B$ with decreasing temperature can't be explained only by the speciation reaction **$^{[3]}B$ +NBO<=> $^{[4]}B$**

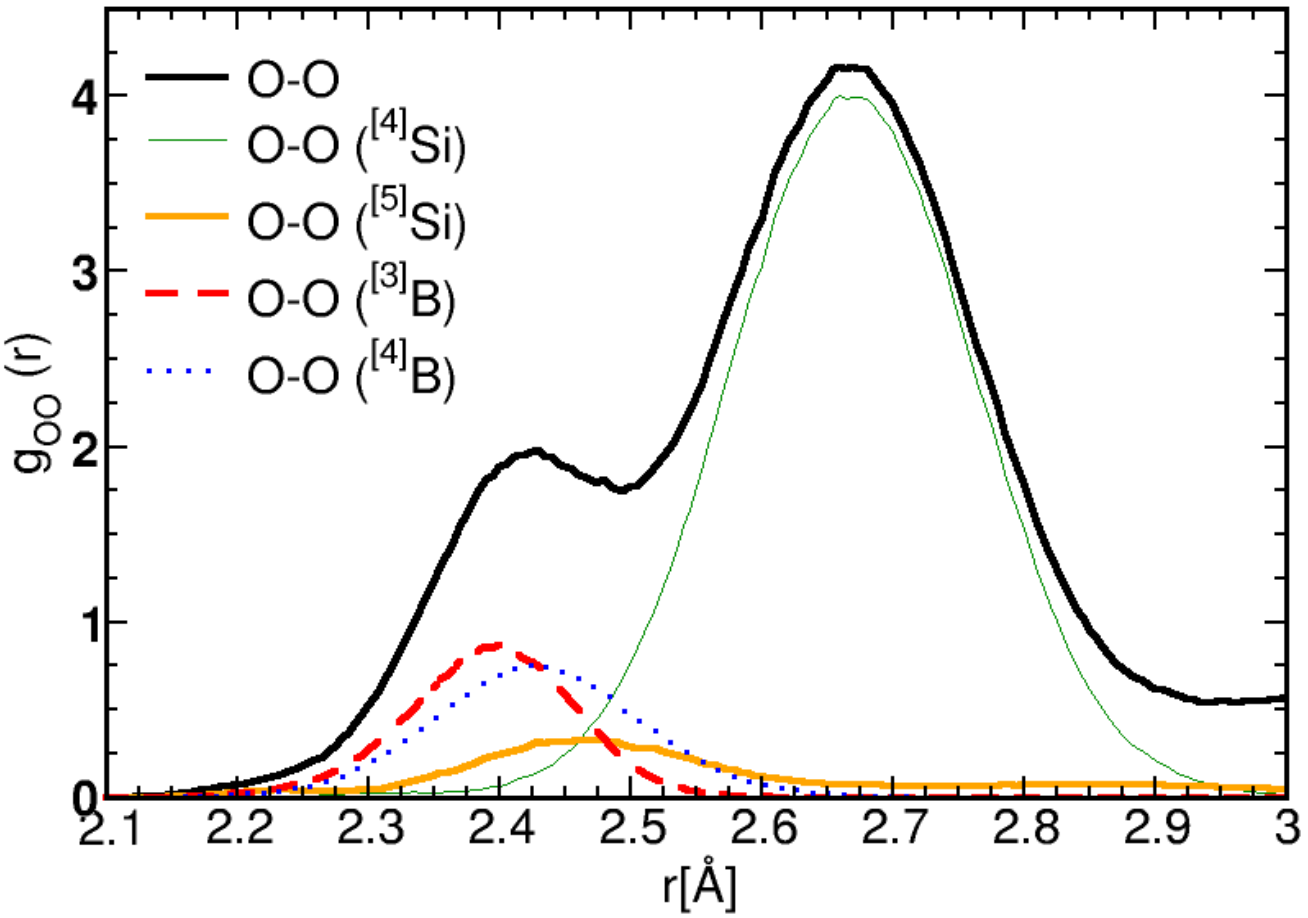
NBS glass: **boron-oxygen** correlation

- define B-O coordination number via $g_{BO}(r) \Rightarrow {}^{[4]}B$ and ${}^{[3]}B$



- $^{[4]}$B-O distances are larger than B$^{[3]}$-O
- in the glass we have 37% $^{[4]}$B and 63% $^{[3]}$B
- exp. data predicts ~70% $^{[4]}$B !?!
- **but** exp. data also predicts: $^{[4]}$B ↓ with ↑cooling rate

NBS glass: **oxygen-oxygen** correlation



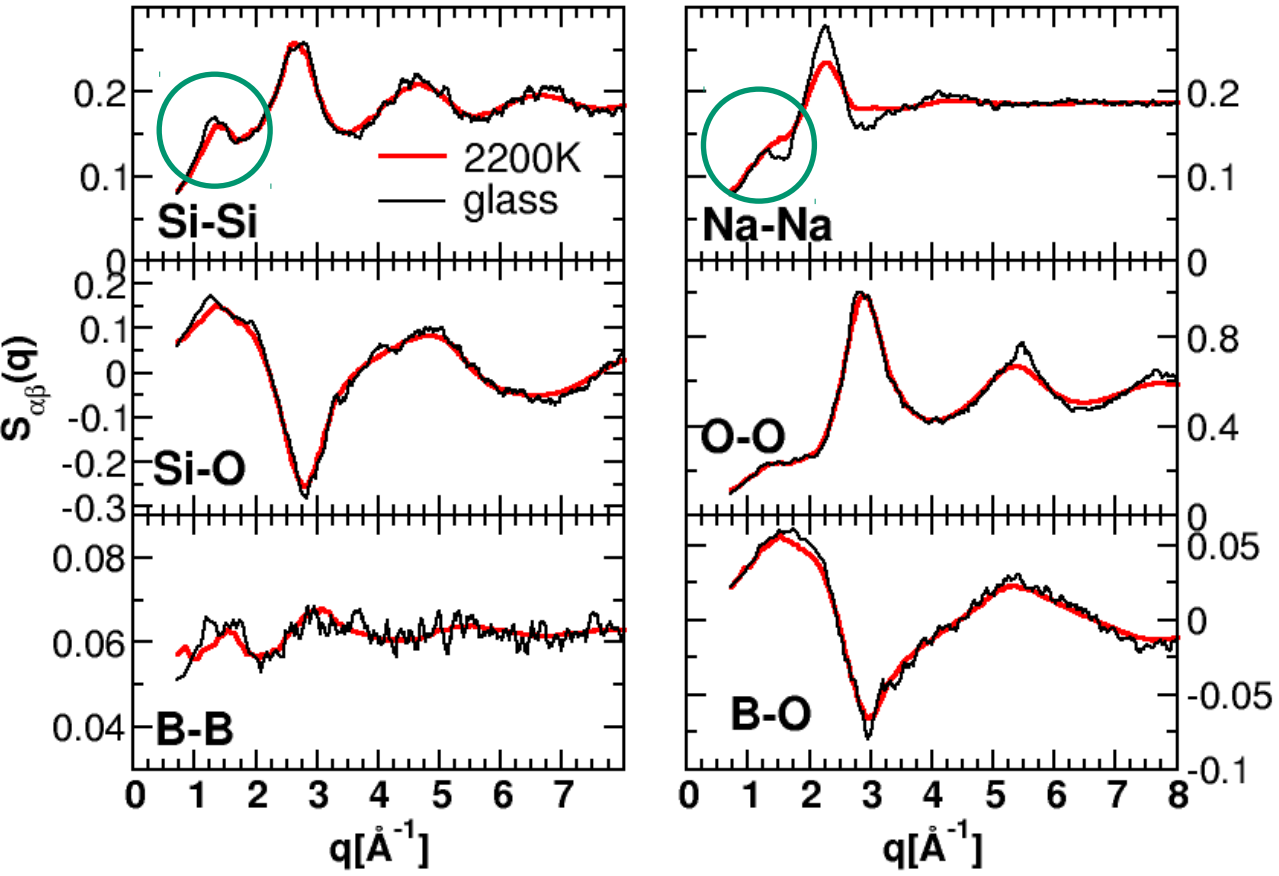
- Presence of **B** leads to splitting of **O-O** peak

Structure: Static structure factor (1)

- compute the partial static structure factors

$$S_{\alpha\beta}(\boldsymbol{q}) = \frac{f_{\alpha\beta}}{N} \sum_{j=1}^{N_\alpha} \sum_{l=1}^{N_\beta} \langle \exp[-i\boldsymbol{q} \cdot (\vec{r}_j - \vec{r}_l)] \rangle$$

$f_{\alpha\alpha}=1$; $f_{\alpha\beta}=1/2$ for $\alpha \neq \beta$

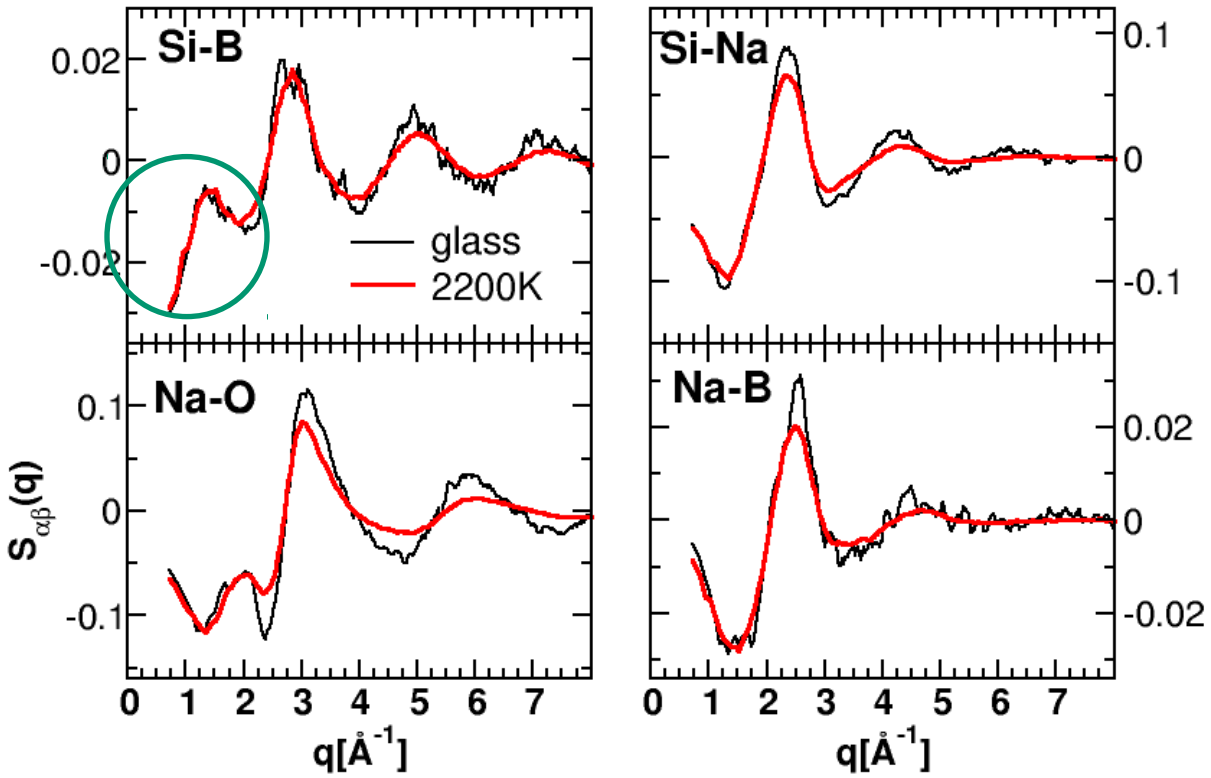


- prepeak at around 1.2 Å^{-1} $\Rightarrow$ evidence that channel-like structure seen in Na_2O-$xSiO_2$ is also present in NBS?

Structure: Static Structure factor (2)

$$S_{\alpha\beta}(\boldsymbol{q}) = \frac{f_{\alpha\beta}}{N} \sum_{j=1}^{N_\alpha} \sum_{l=1}^{N_\beta} \langle \exp[-i\boldsymbol{q} \cdot (\vec{r}_j - \vec{r}_l)] \rangle$$

$f_{\alpha\alpha}=1$; $f_{\alpha\beta}=1/2$ for $\alpha \neq \beta$



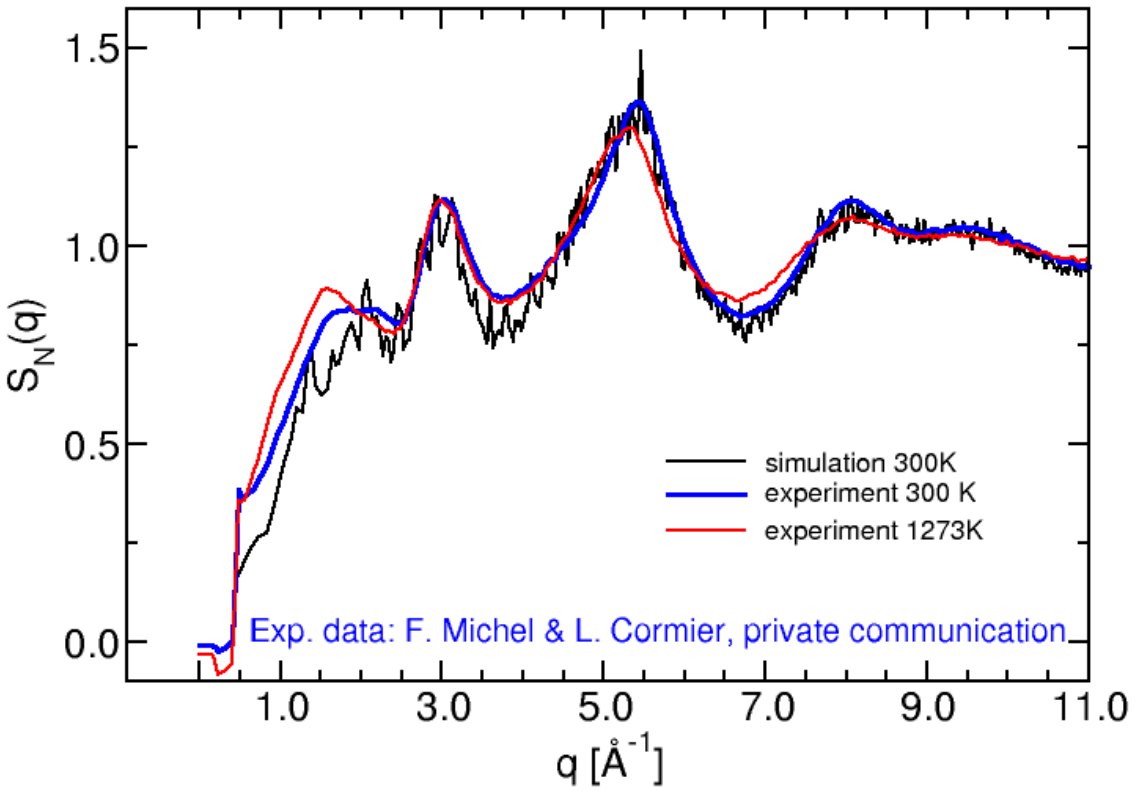
- the Si-B correlation does not go to zero in the accessible ***q***-range

  → evidence for nano-phase separation in $3Na_2O$-B_2O_3 -$6SiO_2$?

… hypothesis mentioned in a NMR work (Wang&Stebbins 1999)

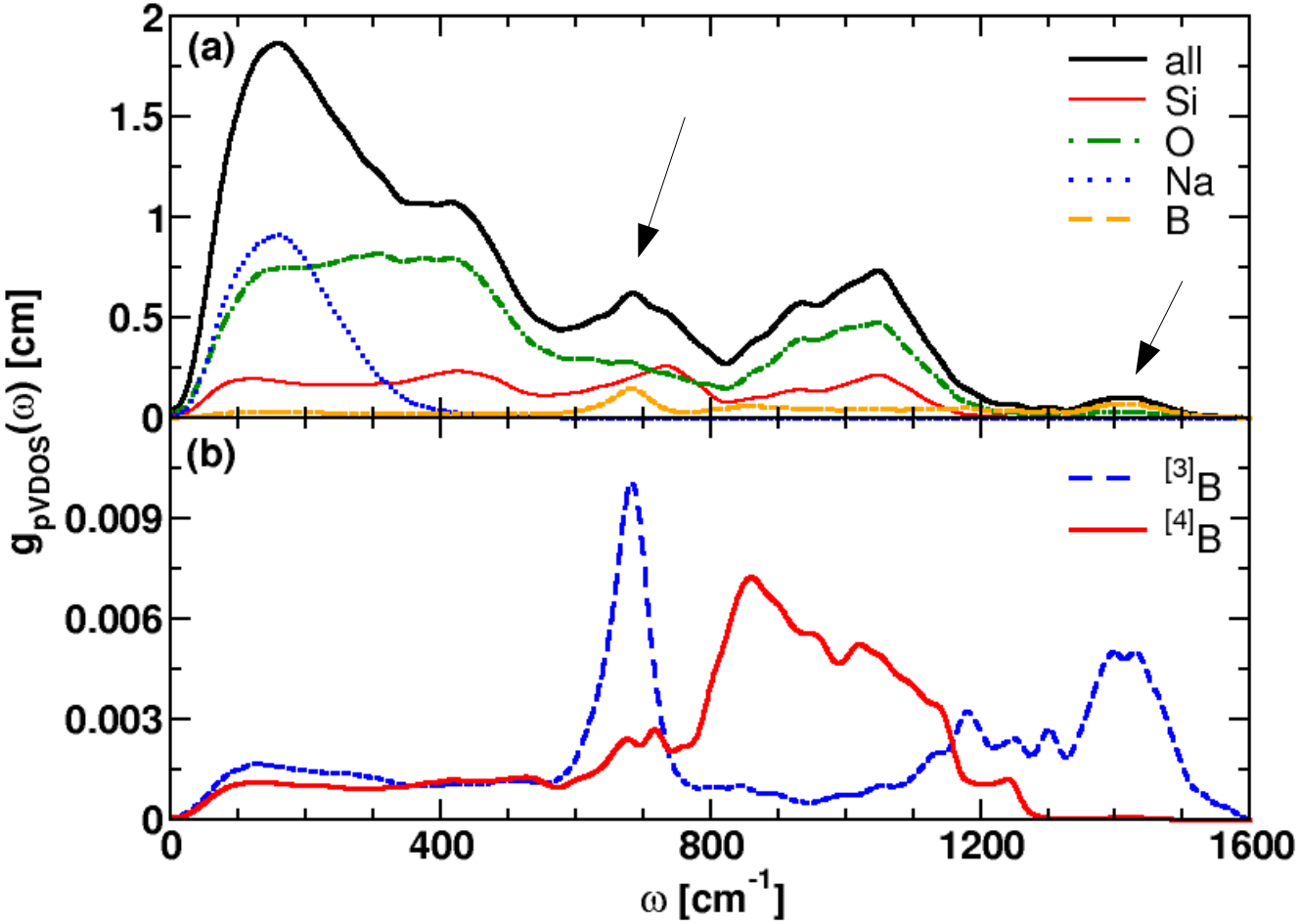
Structure: Neutron structure factor (2)

$$S^{\mathrm{neu}}(\boldsymbol{q}) = \frac{N}{\sum_{\alpha} N_\alpha b_\alpha^2} \sum_{\alpha\beta} b_\alpha b_\beta S_{\alpha\beta}(\boldsymbol{q})$$



- good agreement between experiment and simulations
- peak seen in experiments around 1.5 Å^{-1} might be two peaks

NBS glass: Vibrational density of states (VDOS)

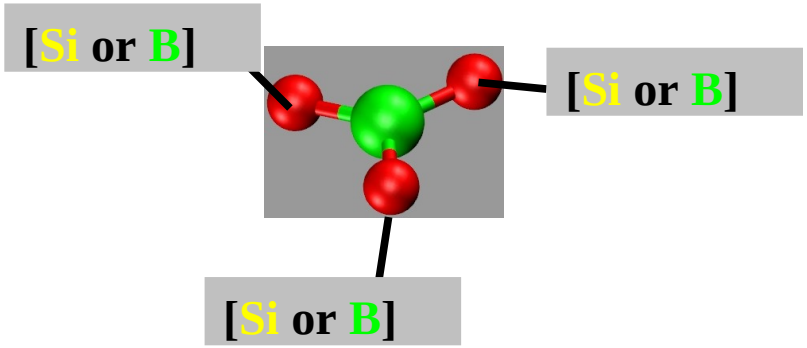


- 3- fold and 4-fold coordinated boron atoms give rise to specific features in the density of states
- peak at 650 cm^{-1} is mainly due to $^{[3]}$B
- modes at high frequencies (> 1200 cm^{-1}) are also due to $^{[3]}$B

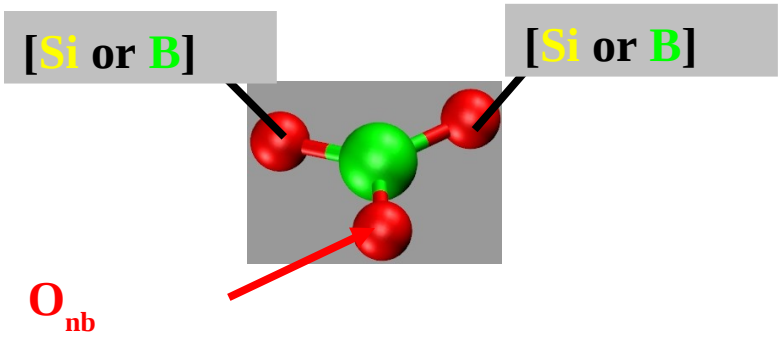
Partial VDOS of $^{[3]}$B units

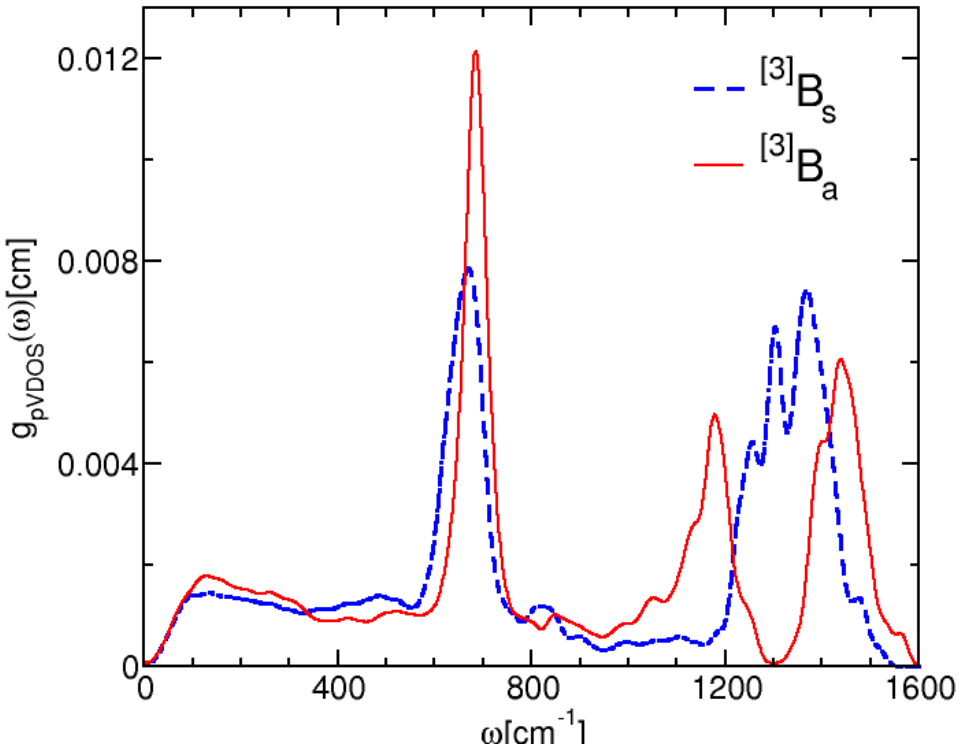
- 3- fold coordinated boron atoms give rise to specific features in the density of states

Symmetric units: $^{[3]}B_s$

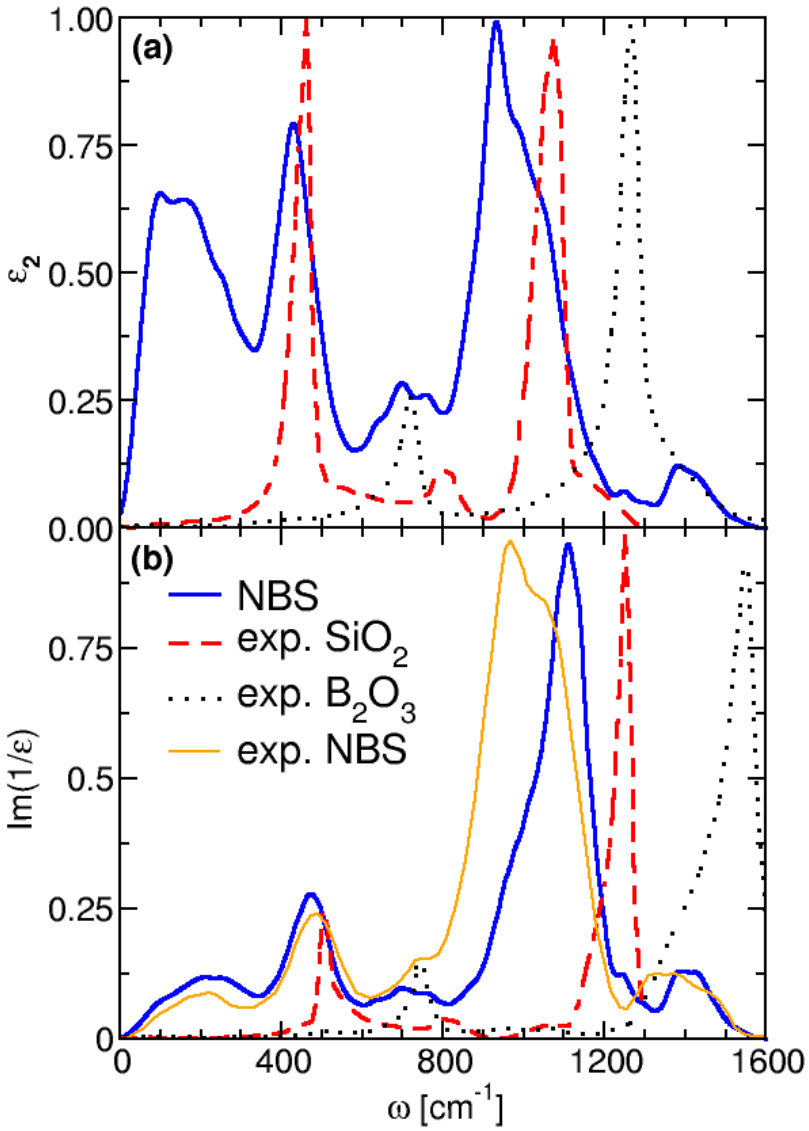


Asymmetric units: $^{[3]}B_a$





NBS glass : IR spectrum, theory vs. experiment



- w.r.t. pure SiO_2 and B_2O_3: low-frequency band, due to Na atoms

- good agreement to exp. data for band around 500 cm^{-1}

Exp. data Kamitsos et al. JNCS 171 (1994), on similar composition

Summary: simulations of borosilicates

- role of B is highly complex
- evidence for nano-phase separation between Si and B
- vibrational signature of $^{[3]}$B and $^{[4]}$B are very different
- Na structure and dynamics are equally complex
- need to get more insight into the nature of the vibrational modes and IR active modes

Acknowledgments

Agence Nationale de la Recherche GIP ANR

HPC facilities

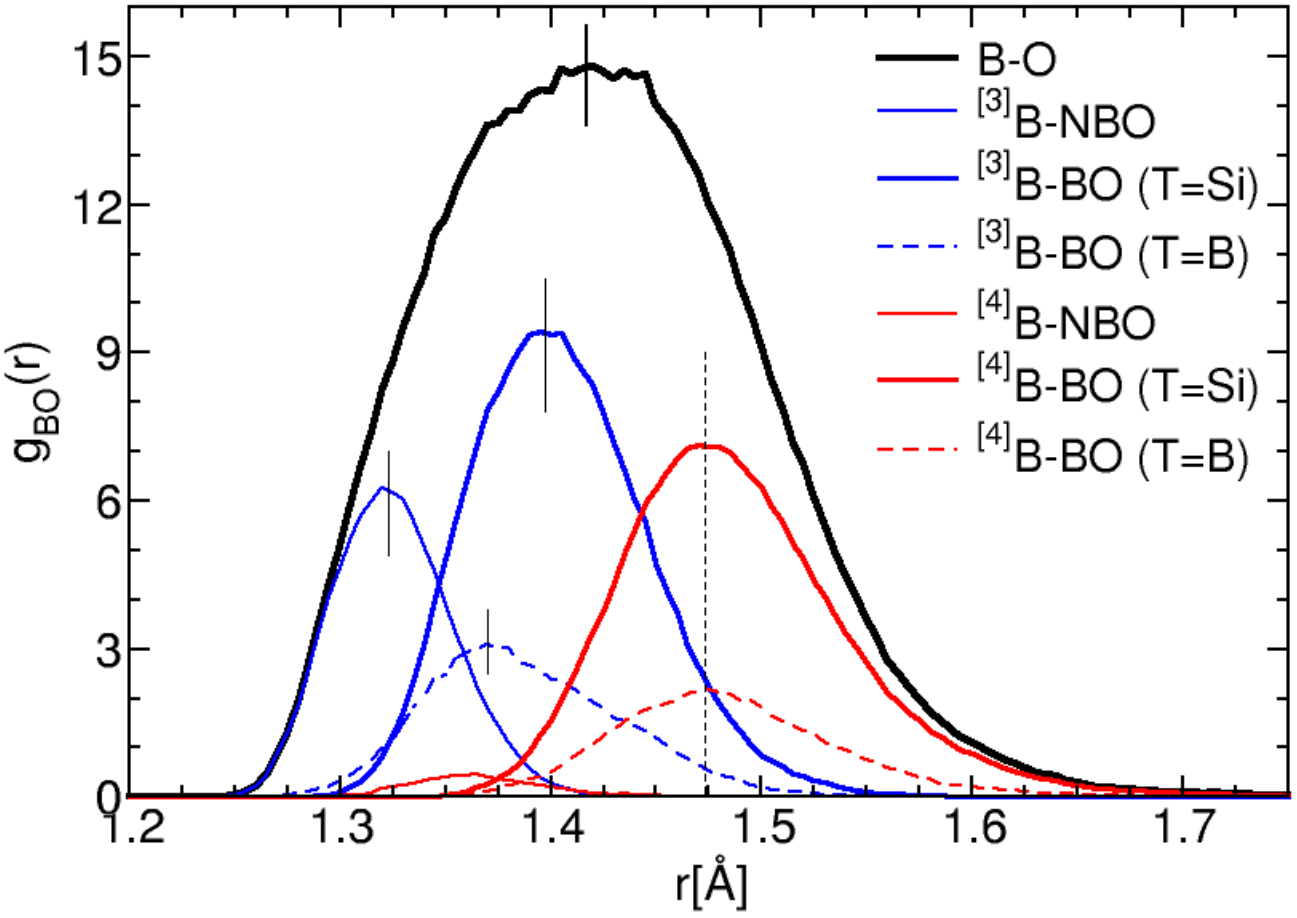
IDRIS

CINES

HPC@LR Centre de compétences Calcul haute performance LANGUEDOC-ROUSSILLON

NBS glass: **boron-oxygen** correlation

- **dependence on O speciation, as well as on the nature of the 2nd network-former cation**



- [4]B-O distances are larger than [3]B-O
- Almost no NBO on [4]B units
- [3]B-units with and without NBO → define **asymmetric** [3]B-units and **symmetric** [3]B-units, respectively