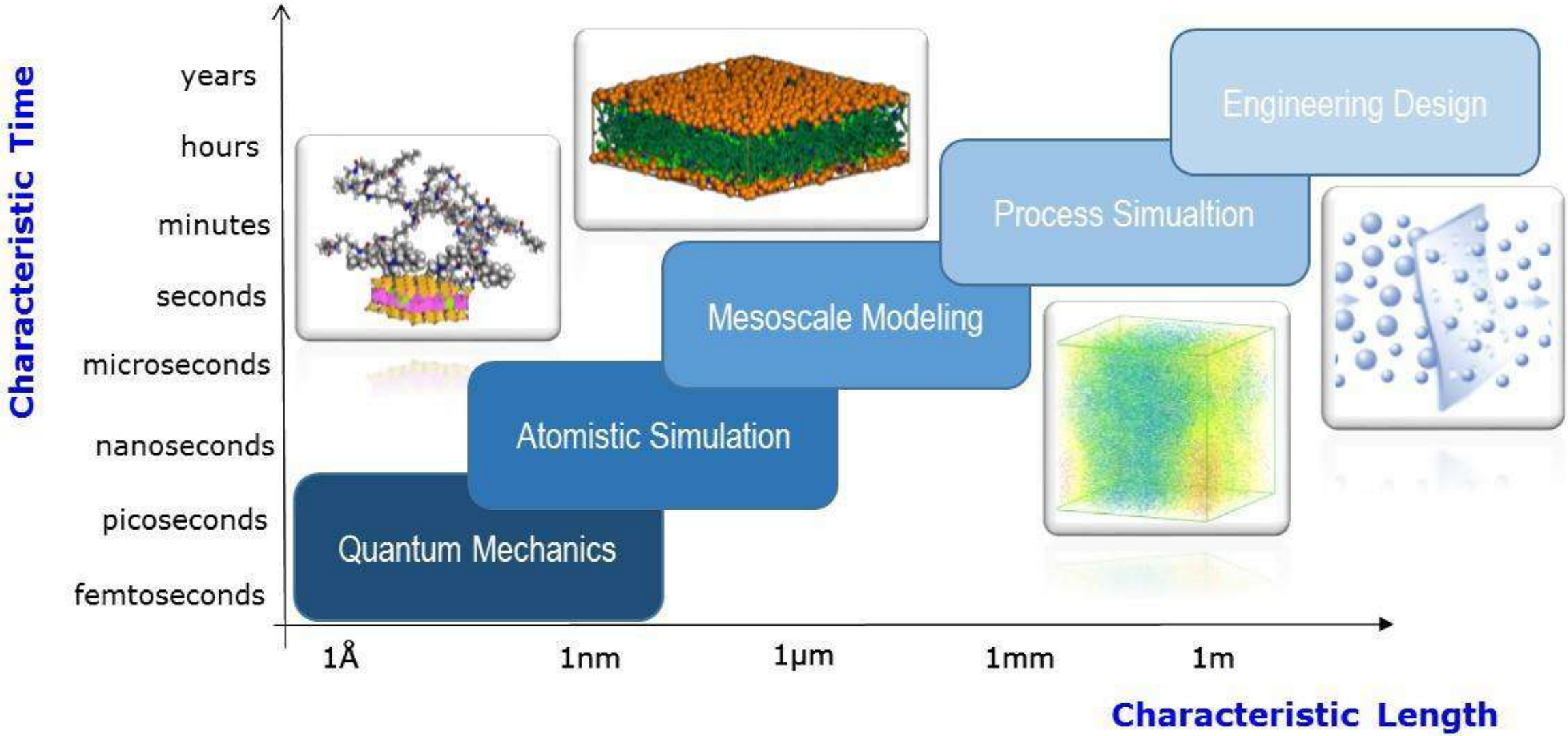
Modern Computational Methodologies for new glass development

Alfonso Pedone

Department of Chemical and Geological Sciences
University of Modena and Reggio Emilia

Outline of the Lecture

- **Computational Methods to Simulate Glasses**
  - Molecular Dynamics Simulations (Born-Oppenheimer, Carr-Parrinello, classical)
  - Density Functional Theory
  - Empirical Force-Fields
  - Machine Learning Potentials
- **Validation of Glass Structures**
- **Ab initio MD and DFT: when are mandatory**
- **Performance of Empirical and ML-potentials: Sodium Silicate Glasses and Mixed Alkali Effect in Aluminosilicate Glasses**
- **Mechanical Properties: tensile, compression and indentation tests**
- **The timescale problem: studying Crystallization through Metadynamics Simulations**
- **Conclusions**

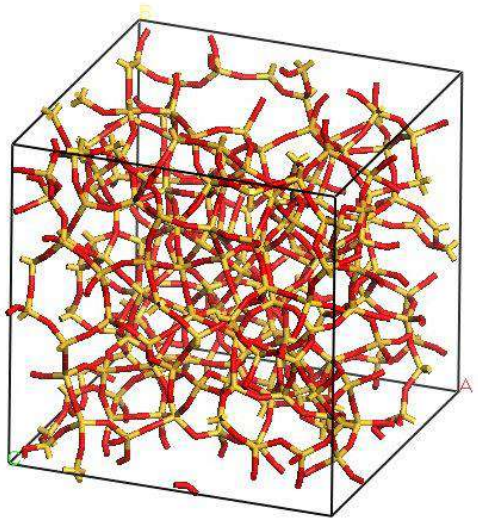

Characteristic Time
years
hours
minutes
seconds
microseconds
nanoseconds
picoseconds
femtoseconds
Quantum Mechanics
Atomistic Simulation
Mesoscale Modeling
Process Simualtion
Engineering Design
1Å
1nm
1μm
1mm
1m
Characteristic Length

Molecular Dynamics Simulations

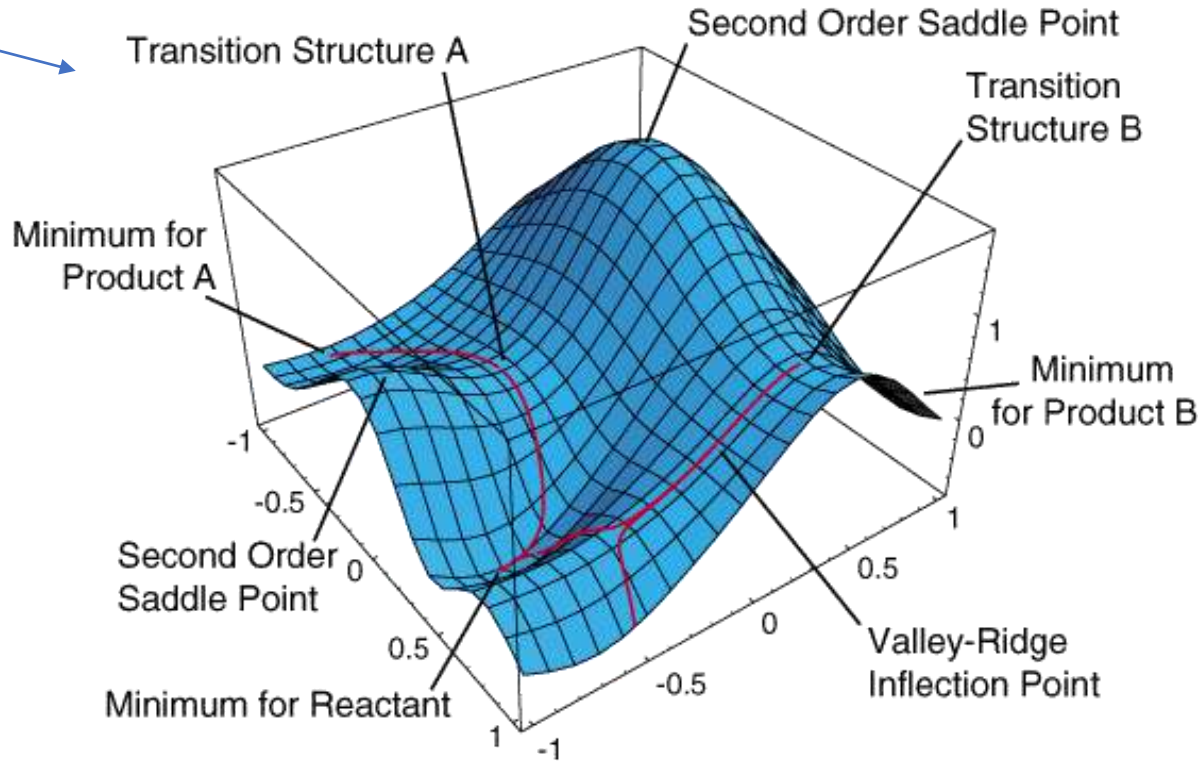
The classical equations of motion (netwon II law) are integrated numerically

$$\frac{\partial^2 \mathbf{r}_i}{\partial t^2} = \frac{\mathbf{F}_i}{m_i} = -\frac{\nabla_i U(\mathbf{r})}{m_i}$$

Trajectory: positions, velocities and accellerations of atoms in time

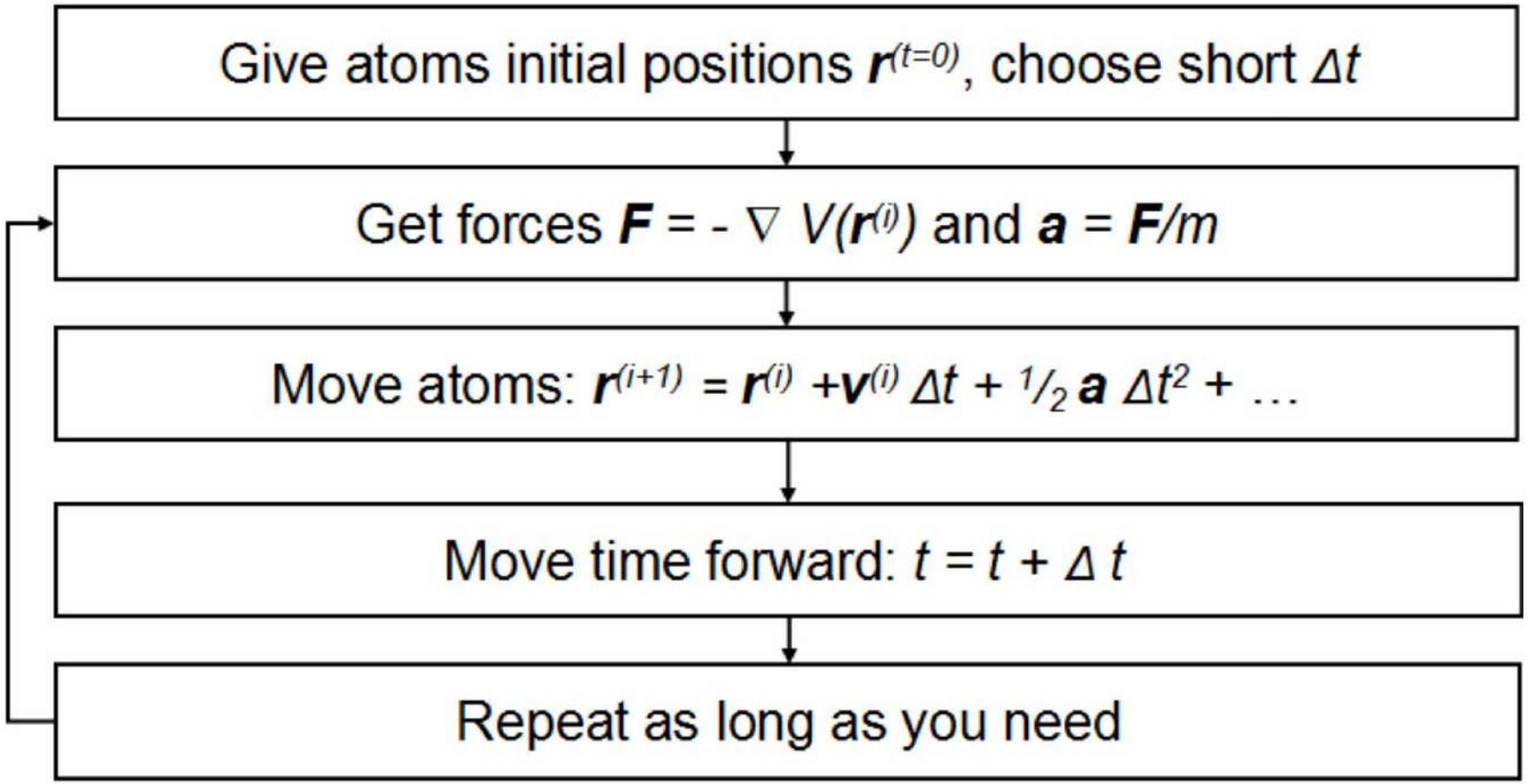


Potential Energy Surface



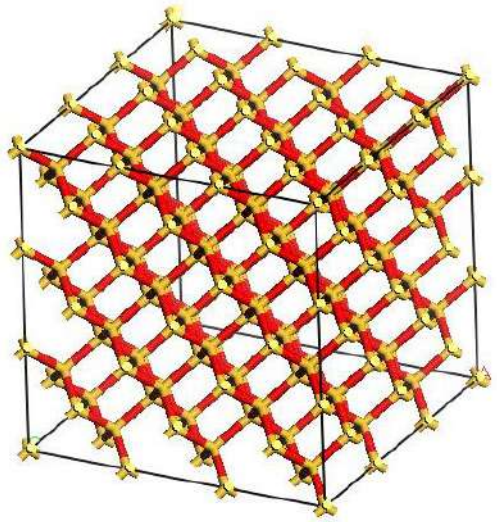
(Image taken from http://www.chem.wayne.edu/~hbs/chm6440/PES.gif)

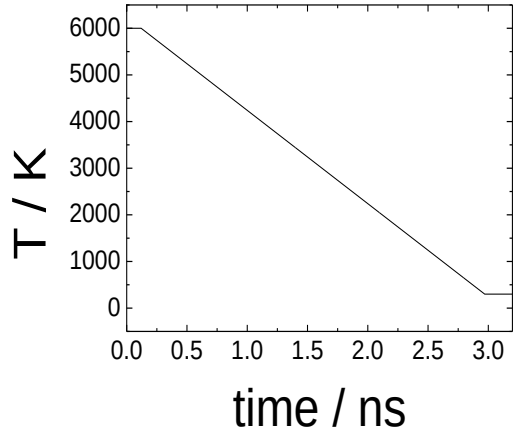
Scheme of a basic classical MD algorithm

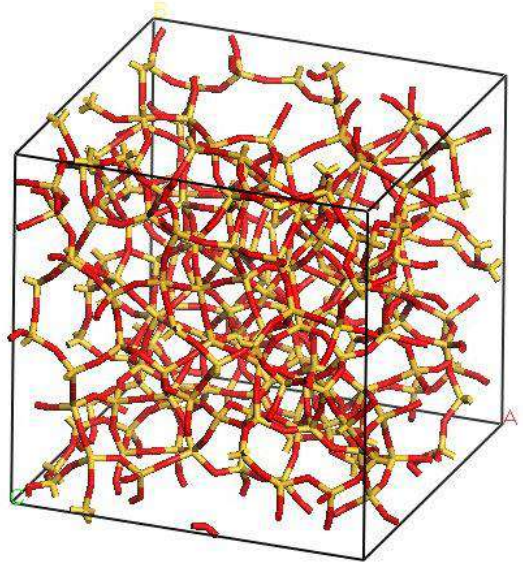


Exploiting MD simulations to generate Glass Structures

• Simulated glass structures are prepared computationally in the same way as real glasses.
• Models of crystalline (or random) systems are melted; the melts are then quenched , freezing the structure into a disordered glassy phase.







- Quenching rates much higher than the experimental ones (0.5-5 10^{12} K/s vs 1-100 K/s)
- The fictive temperature of the simulated glass is higher than the target temperature
- More disordered structure than the real ones

Molecular Dynamics Simulations

$$m\frac{d^2\mathbf{R}}{dt^2} = -\nabla U(\mathbf{R})$$

Classical MD

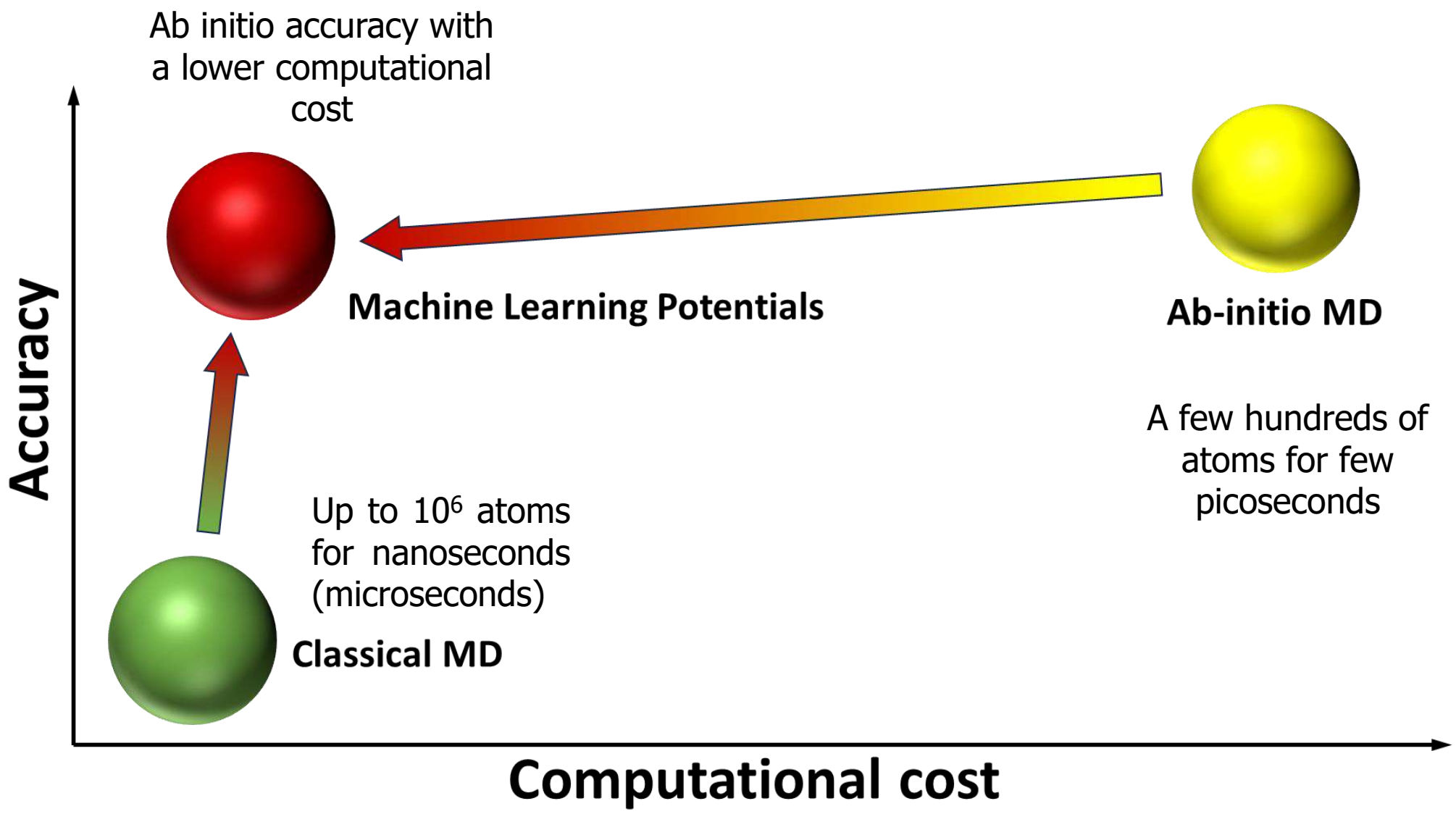
The PES is described by empirical parametric functions of nuclear (internal coordinates) (Force-Fields)

ML-accellerated MD

PES is described by ML algorithms

Ab initio MD
Born-Oppheneimer MD
Carr-Parrinello MD

PES computed at the Density Functional Theory level


Ab initio accuracy with a lower computational cost
Machine Learning Potentials
Ab-initio MD
A few hundreds of atoms for few picoseconds
Up to 10^6 atoms for nanoseconds (microseconds)
Classical MD
Accuracy
Computational cost

Density Functional Theory (DFT): basics

Hohenberg-Kohn and Kohn-Sham (1964) established the rules of the DFT (Density Functional Theory) to compute the ground state energy as a **functional** of the electron density

Based on 2 Theorems:

- **Theorem 1**. The external potential or the ground state energy E of a molecular system is a unique functional of electron density.

$$E = E[\rho(r)]$$

- **Theorem 2**. The electron density that minimizes the energy of the overall functional is the true ground state electron density

- $E[\rho(r)] \geq E_0[\rho_0(r)]$

KOHN-SHAM FORMULATION

$$\rho(\mathbf{x}) = \sum_{i=1}^{N^{occ}} f_i |\psi_i(\mathbf{x})|^2$$

single-particle wavefunctions $\psi_i(x)$ are used to express the electron density

f_i are the occupation numbers (1 – spin unrestricted ; 2 – spin restricted)

$$\int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})d^3x = \delta_{ij}$$

the wavefunctions are subjected to the orthonormality constraint

KS DFT total energy is written as

$$E^{KS}[\{\psi_i\}] = E_k[\{\psi_i\}] + E_H[\rho] + E_{xc}[\rho] + E_{eI}[\rho] + E_{II}$$

Electron-nuclei interactions

Electron-electron interactions

Nuclei-nuclei interactions

$$E_k[\{\psi_i\}] = \sum_{i=1}^{N^{occ}} f_i \int \psi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{x})\, d^3x$$

Schrödinger-like kinetic energy expressed in terms of the single particle wavefunctions

$$E_H[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d^3x\, d^3y$$

Hartree energy, i.e. the Coulomb electrostatic interaction between two charge distributions

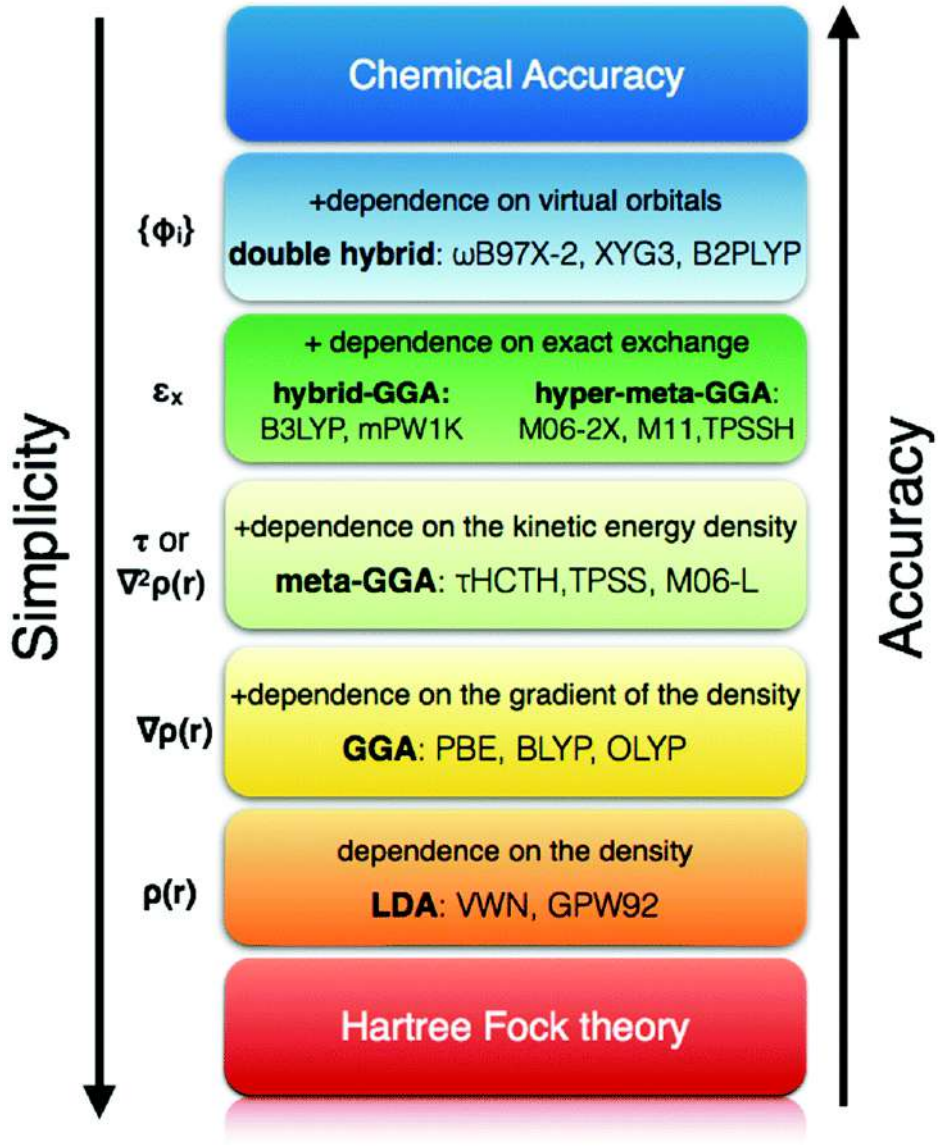
$$E_{eI}[\rho] = -\int \sum_{I=1}^{M} \frac{Z_I \rho(\mathbf{x})}{|\mathbf{x} - \mathbf{R}_I|} d^3x$$

electrostatic interaction between electrons and nuclei

$$E_{xc}[\rho] \quad = ? \quad \text{Exact Functional Unknown}$$

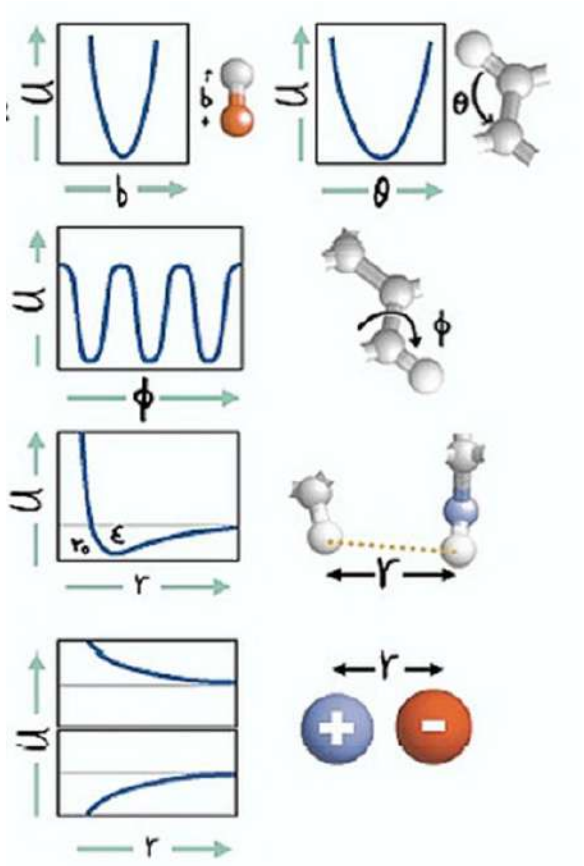
exchange interaction and the electron correlations due to many body effects

Jacob's ladder of XC functionals

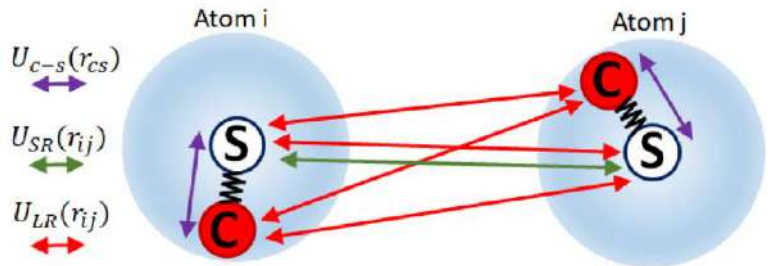


Force-Fields for Silica-based Glasses: our experience

Rigid Ionic Model

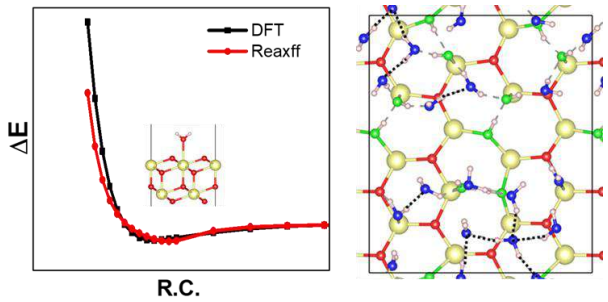


Core Shell Model

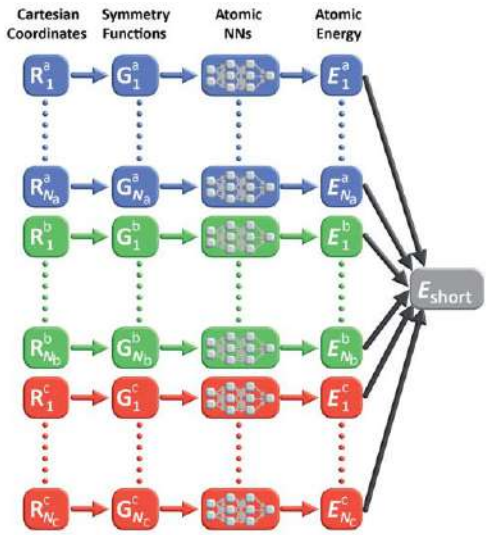


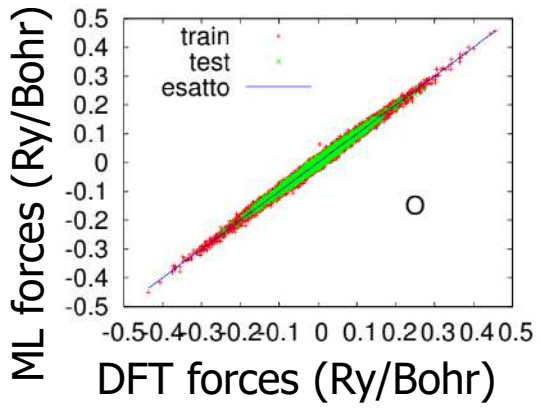
ReaxFF

$$E_{tot} = E_{bond} + E_{val} + E_{tors} + E_{over} + E_{under} + E_{lp} + E_{vdwals} + E_{coulomb}$$



ML-FFs





11780 *J. Phys. Chem. B* **2006**, *110*, 11780−11795

A New Self-Consistent Empirical Interatomic Potential Model for Oxides, Silicates, and Silica-Based Glasses

Alfonso Pedone,† Gianluca Malavasi,† M. Cristina Menziani,† Alastair N. Cormack,‡ and Ulderico Segre*,†

PHYSICAL REVIEW MATERIALS **5**, 045602 (2021)

Improved empirical force field for multicomponent oxide glasses and crystals

Marco Bertani, Maria Cristina Menziani, and Alfonso Pedone*
Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41125 Modena, Italy

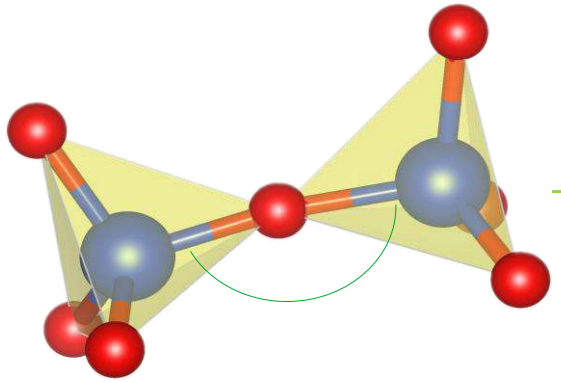
PMMCS

$$U_{ij} = \frac{z_i z_j e^2}{r_{ij}} + D_{ij}\left(\left\{1 - exp\left[-a_{ij}\left(r_{ij} - r_{ij}^0\right)\right]\right\}^2 - 1\right) + \frac{B_{ij}}{r_{ij}^{12}}$$

Coulomb

Morse function: Short term (VdW) interactions

Repulsive (high T and P)



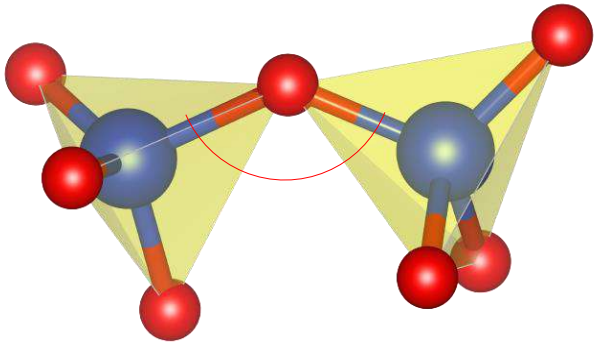
Repulsive interaction

$$U(r_{ij}) = A_{ij} \cdot e^{-\frac{r_{ij}}{\rho_{ij}}}$$

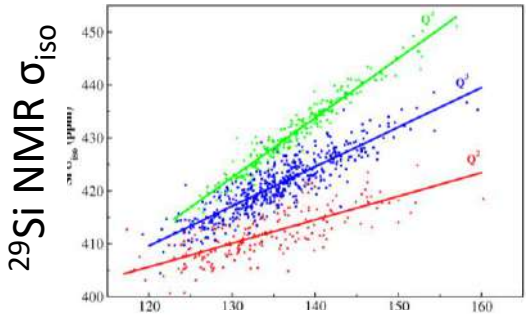
Three-body screened harmonic

$$U(\theta_{ijk}) = \frac{K_{ijk}}{2}\left(\theta_{ijk} - \theta_0\right)^2 \cdot e^{-\left(\frac{r_{ij}}{\rho_{ij}} - \frac{r_{jk}}{\rho_{jk}}\right)}$$

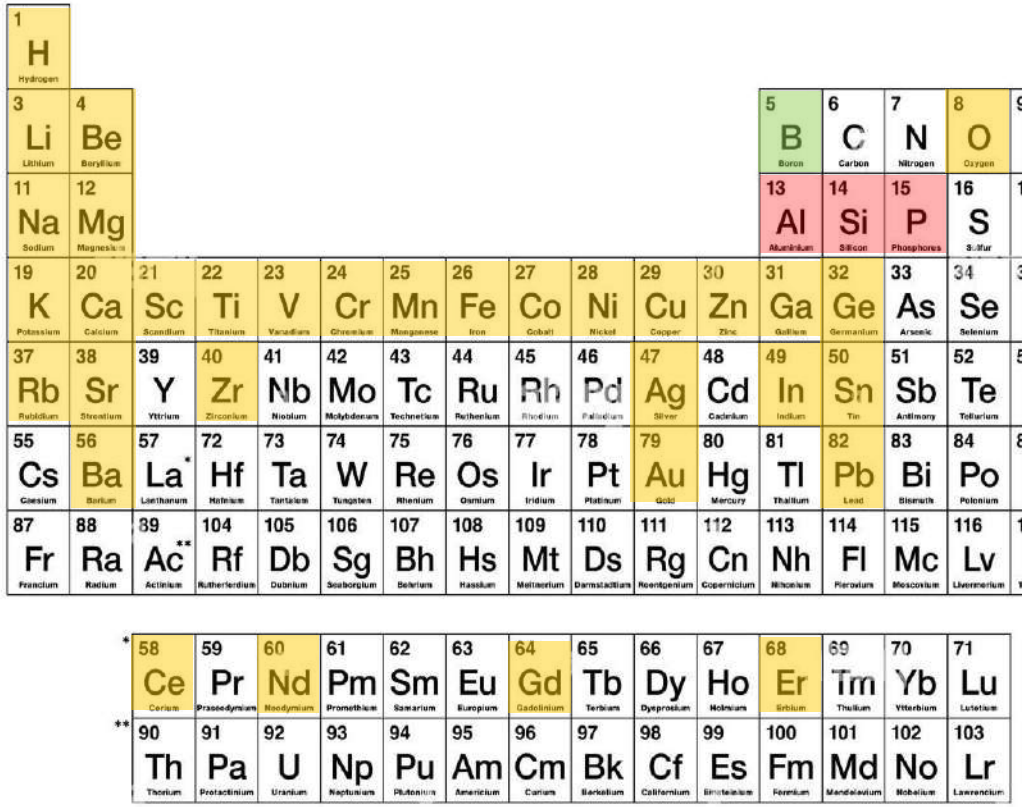
BMP



M. Bertani
UNIMORE



Elements Covered by our FFs



PMMCS

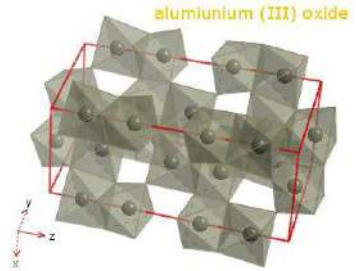
BMP only

BMP & PMMCS

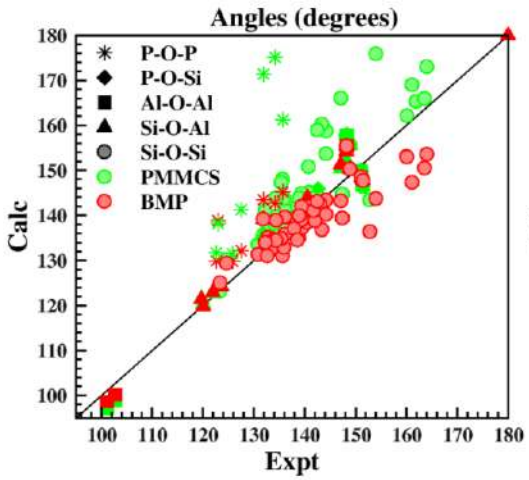
- Silicates (Si-O-Si, Si-Si)
- Aluminosilicates (Al-Si, Al-Al)
- Phosphates (P-O-P, P-P)
- Phosphosilicates (P-O-Si, P-Si)
- Borates (B-O*,B-O-B, B-B)
- Borosilicates (B-O*, B-O-Si, B-Si)

Fitting Strategy

PMMCS: Empirical Fitting on Structure and Elastic constants of binary oxide crystals



BMP: Empirical fitting on T-O-T angles and densities of crystals



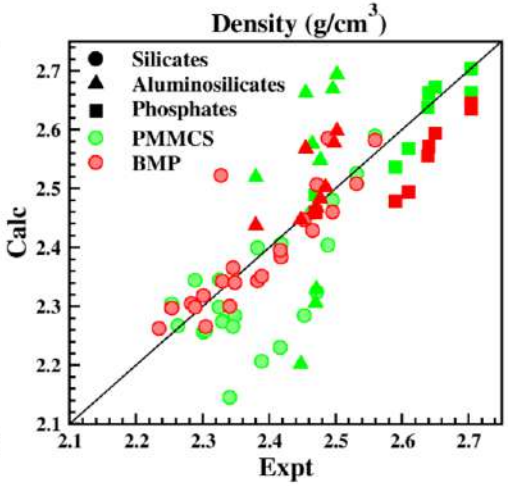
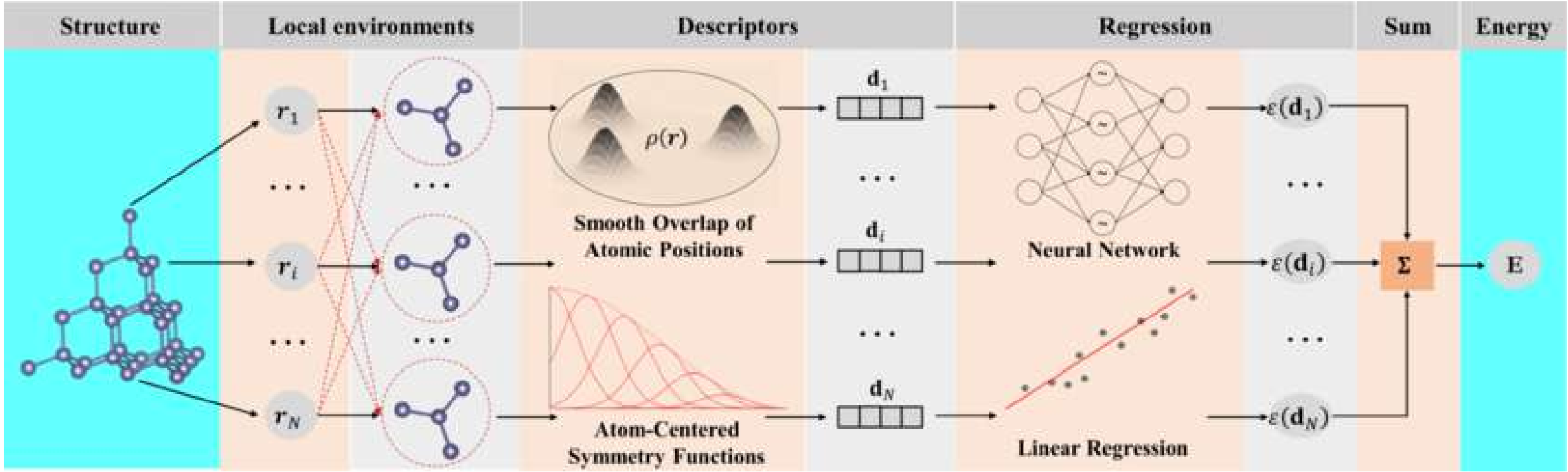
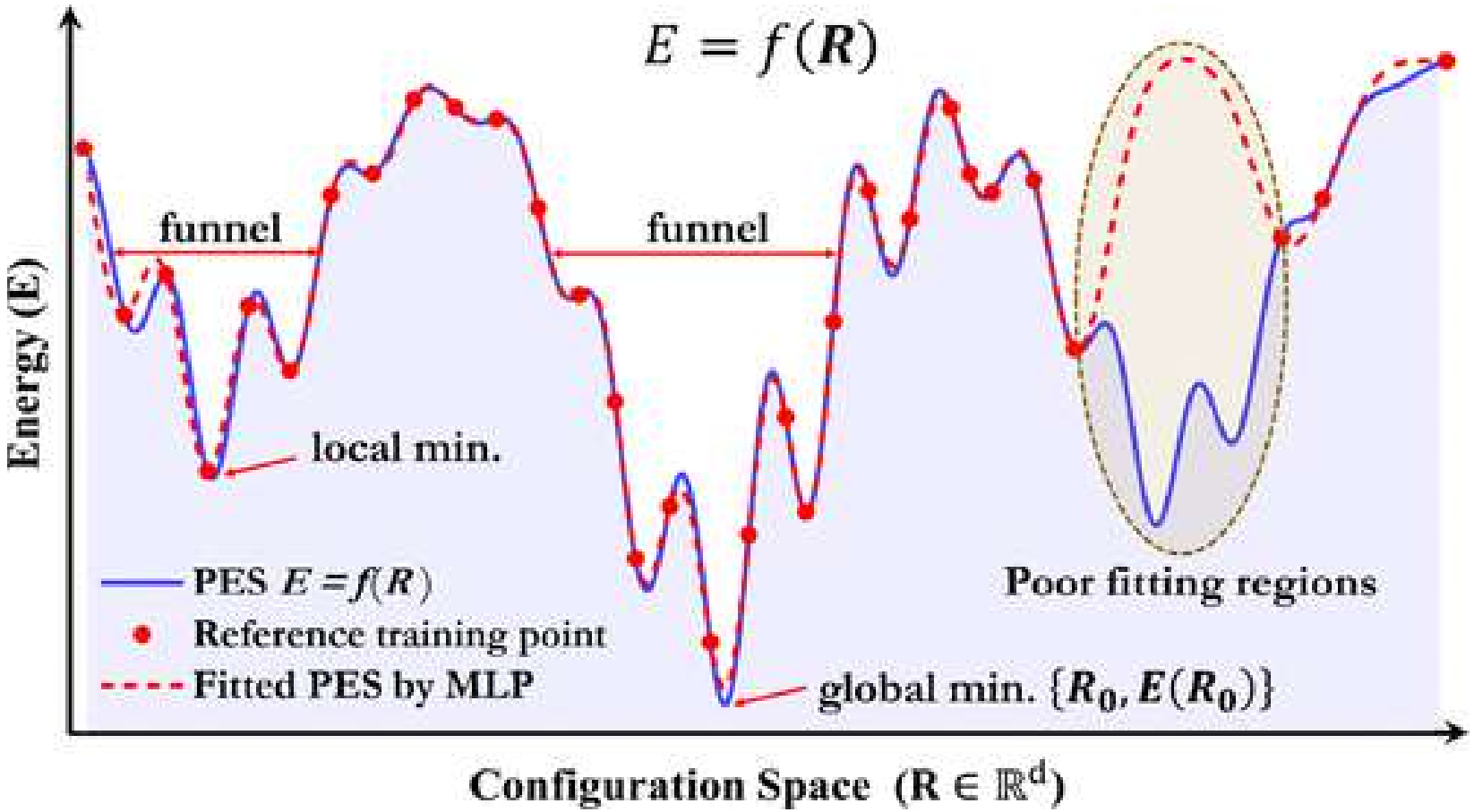


Illustration of descriptor-based machine learning potentials.

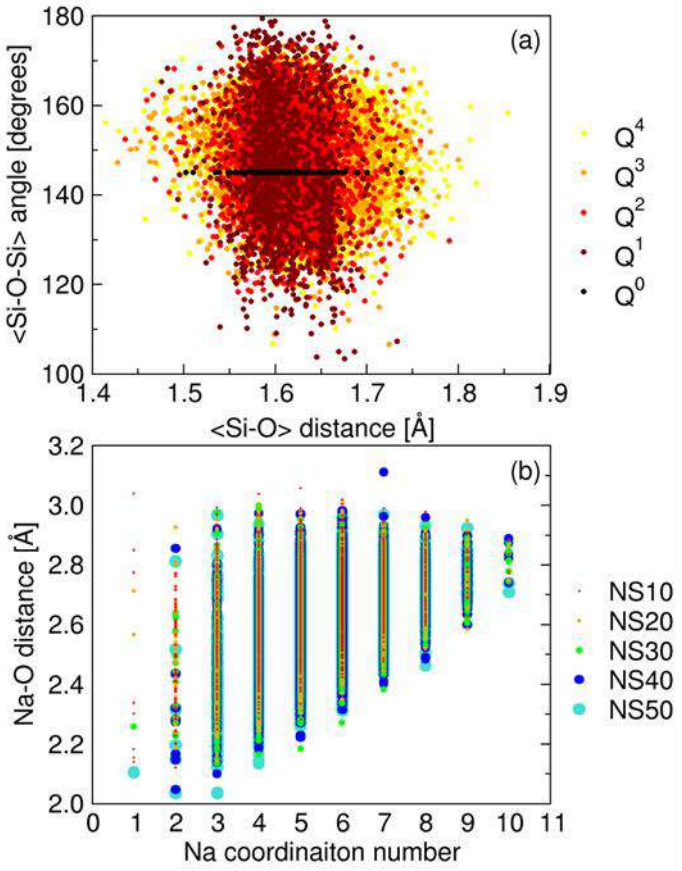


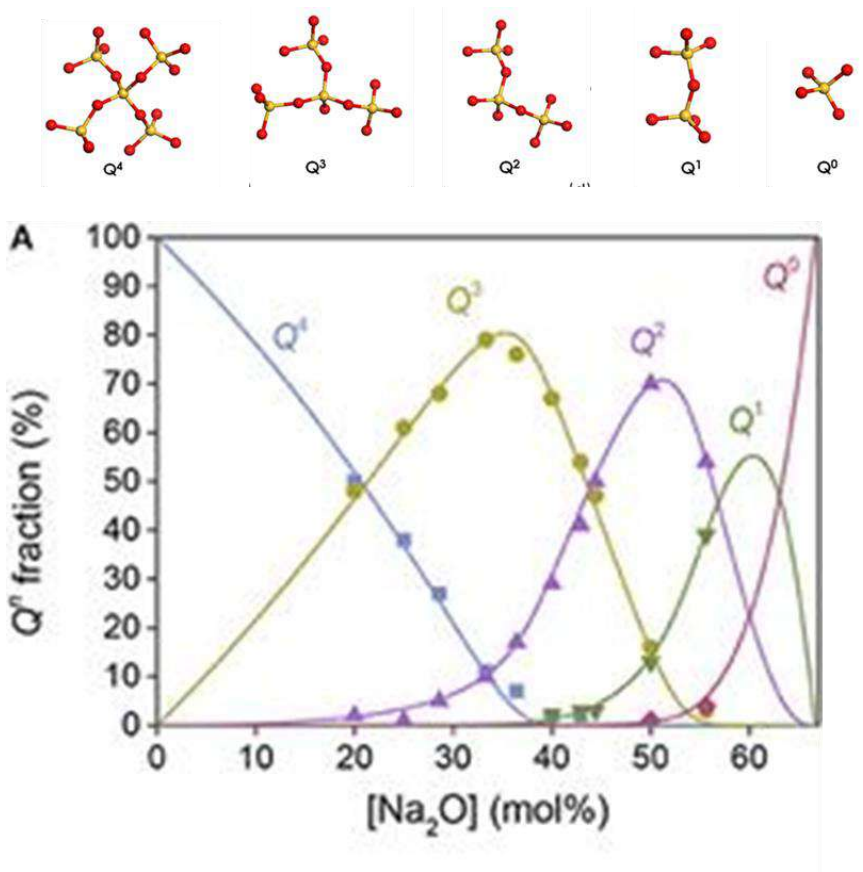
Taken from *J. Phys. Chem. Lett.* 2020, 11, 20, 8710–8720



ML techniques are not extrapolative so your dataset must contain all possible configurations that you can encounter during MD simulations

Problems with the generation of a dataset for oxide glasses

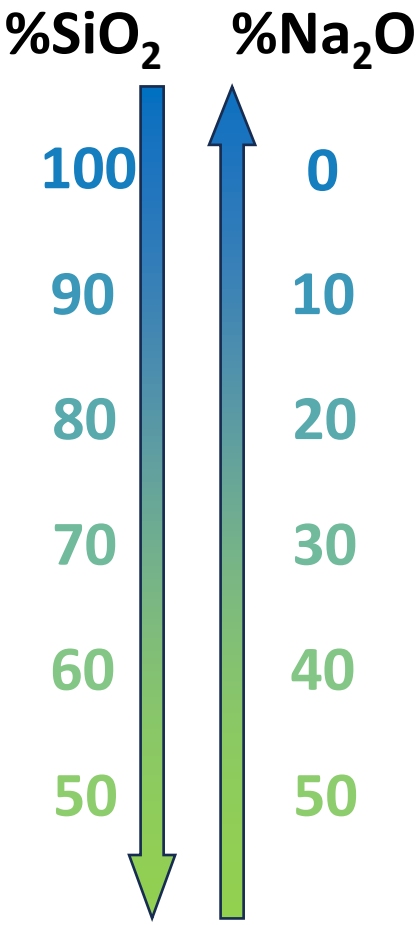




The dimesionality of the configurational and compositional space in multicomponent oxide glasses is enormous!

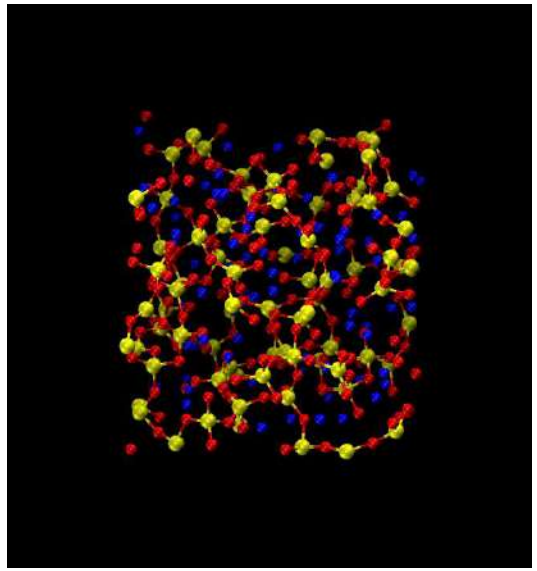
ML Potentials for Sodium Silicate Glasses: Dataset Generation

Composition

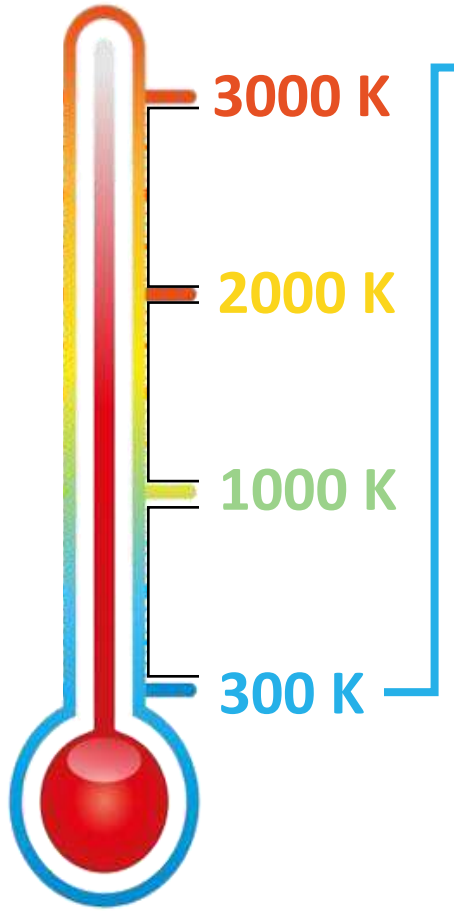


MD simulations

20 simulations for each composition (300 atoms)



Temperature

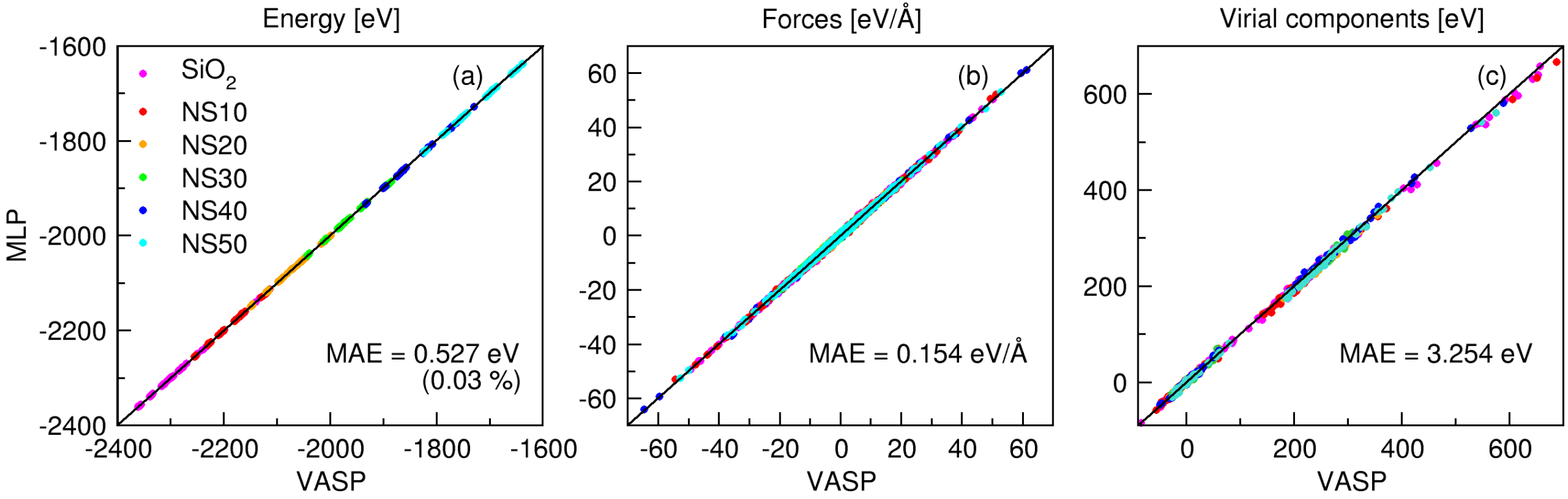


Modifications

½ DFT optimized (PBE)
½ Random distortion

TOTAL

1080 structures
324000 atoms



Scatter plot for (a) total energies, (b) forces on the x, y, and z, and (c) virials computed at the DFT level and predicted by the MLP for the test set.

Validating the glass structural models

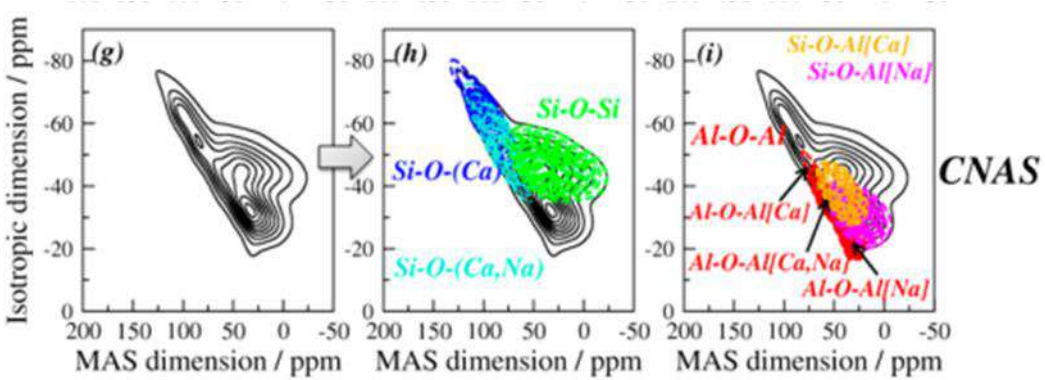
Real Space Correlation Functions

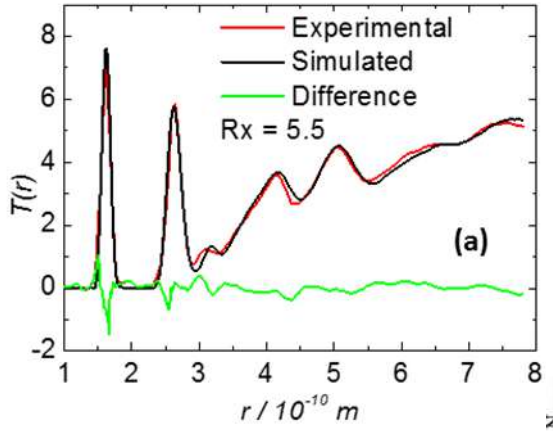
Neutron & X-Ray Structure Factors

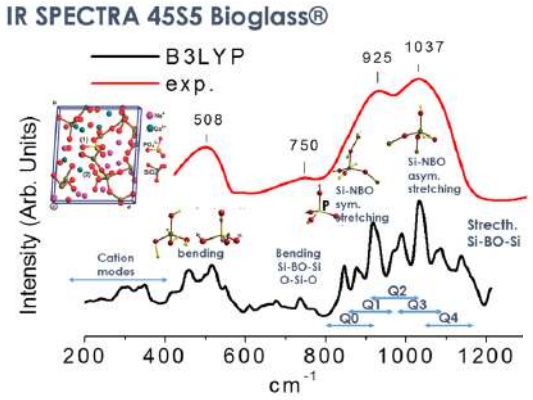
IR & RAMAN Spectroscopy

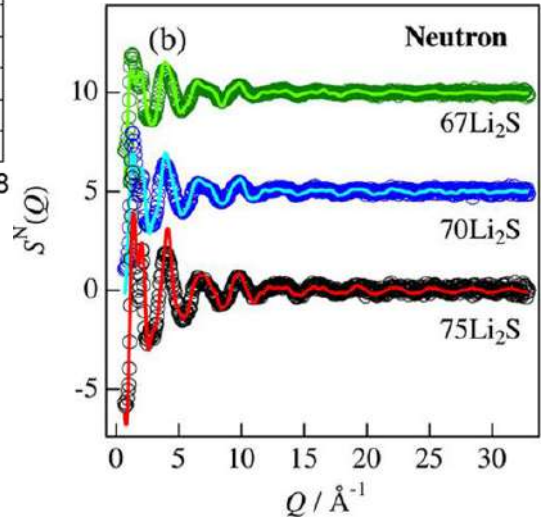
Phonon Dispersion Spectra

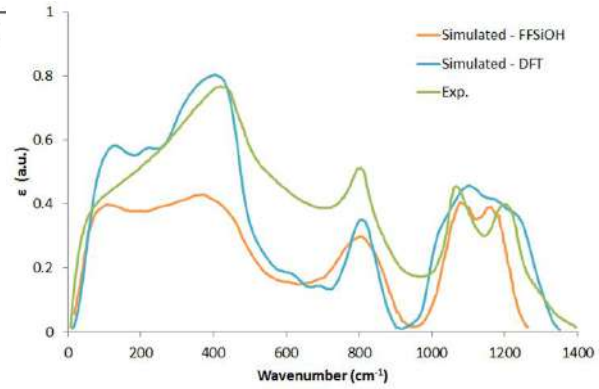
NMR Spectroscopy





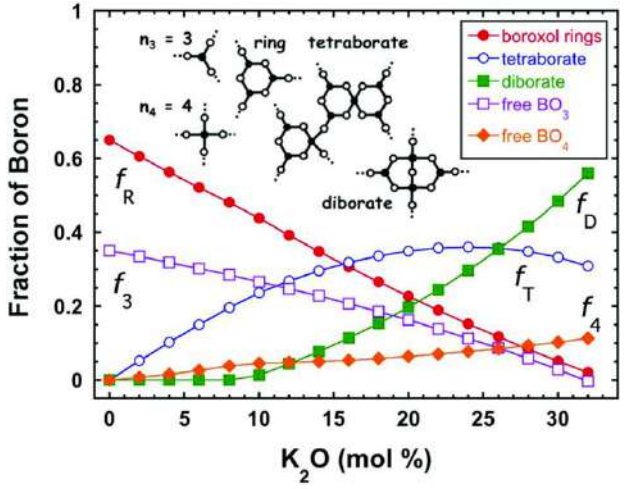




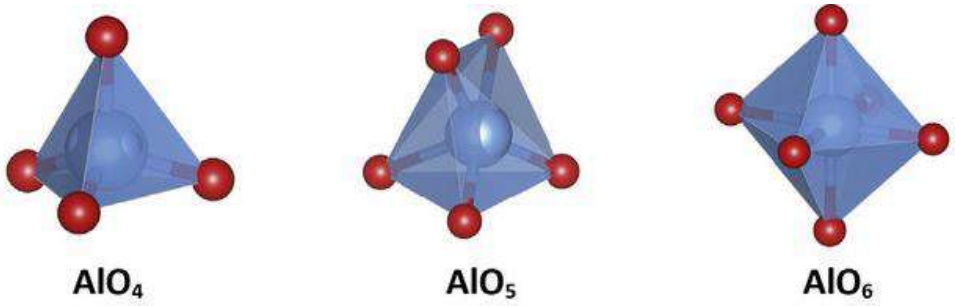


AI MD simulations: when it is mandatory

- When we want accurate and reliable results
- Reactivity
- For studying complex systems for which empirical force fields are not available or accurate (systems containing elements whose coordination changes with composition or it is difficult to reproduce because quantum mechanical effects are important, i.e. Jahn Teller effect).



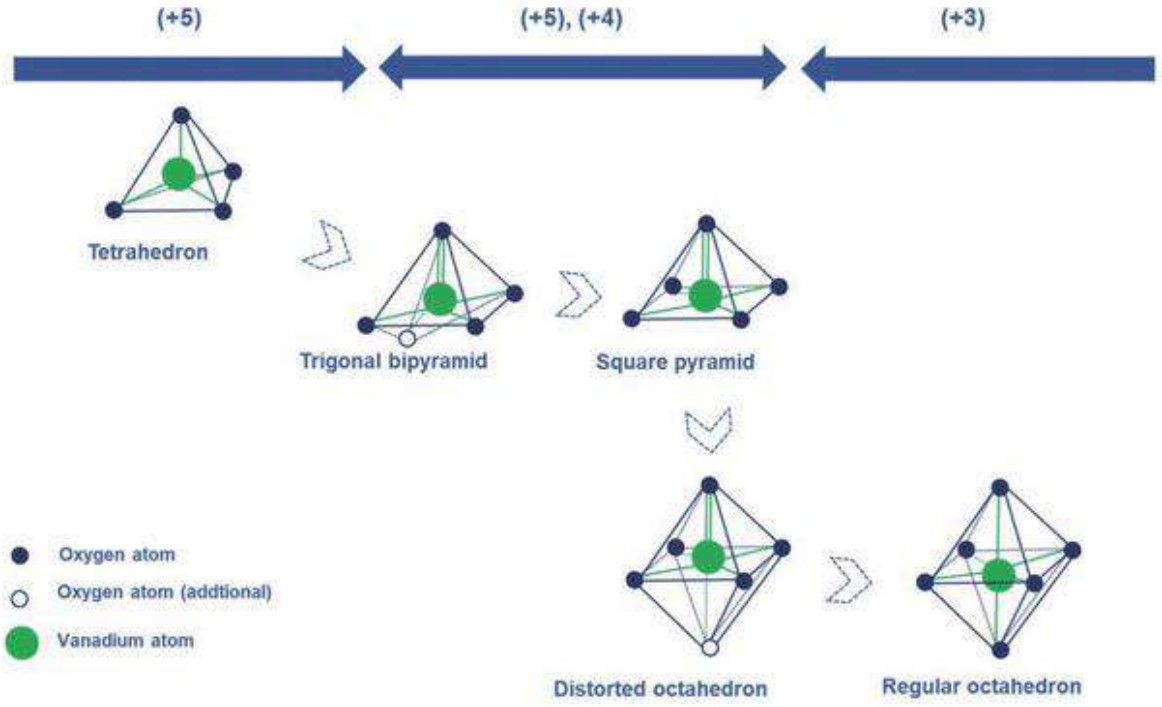
Boron-containing glasses



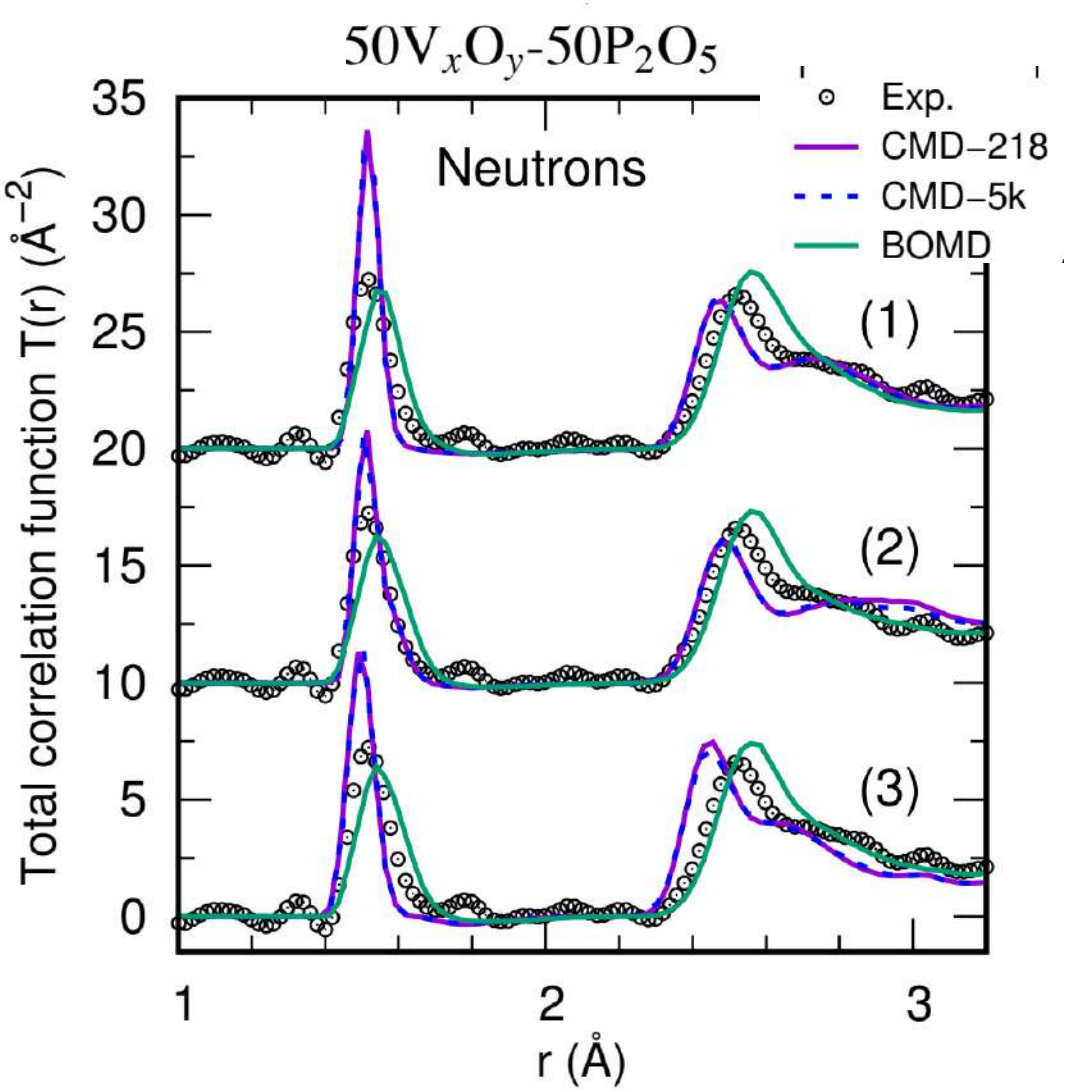
Aluminosilicate Glasses with peraluminous composition

Glasses containing transition metal elements: i.e. Vanadium

Coordination as a function of the oxidation state

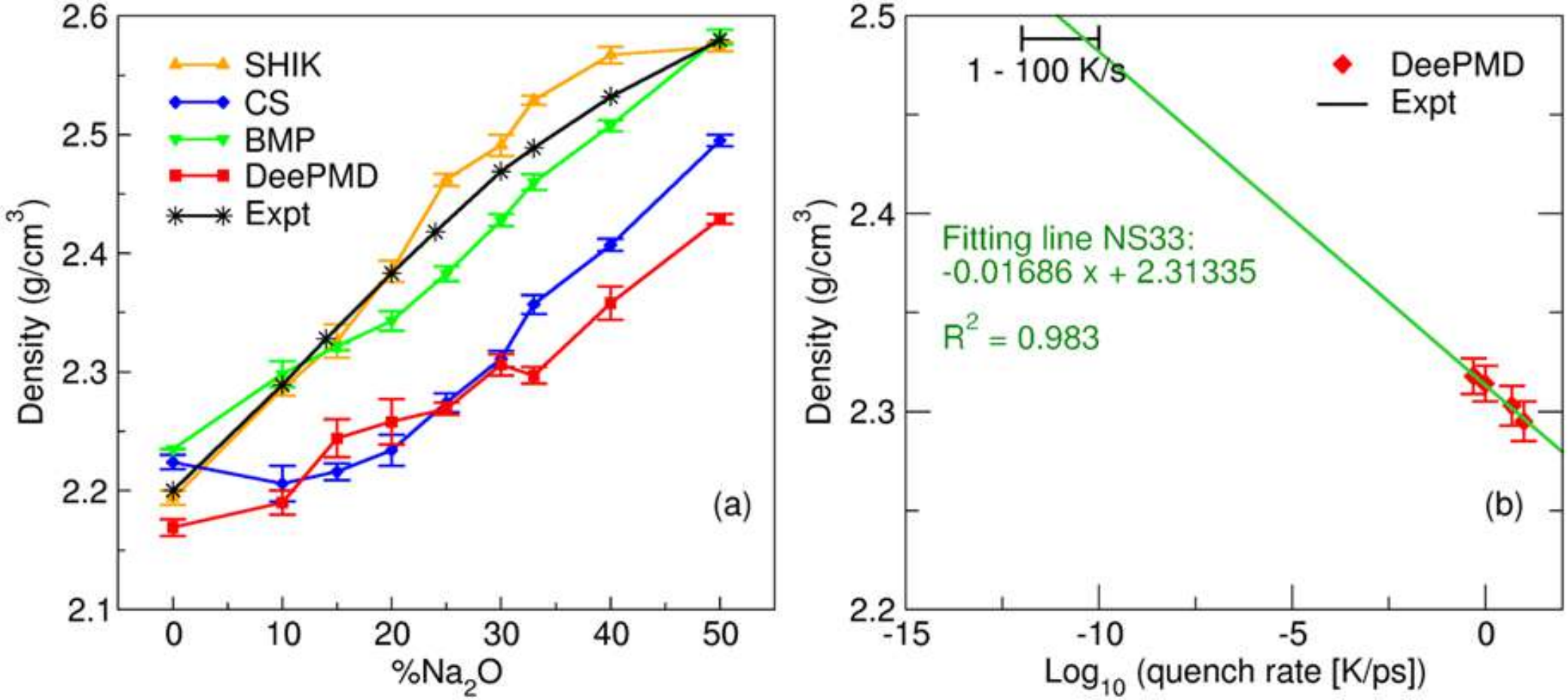


Taken from Song et al. Advanced Functional Materials 28, 2018,1802564



Wansi et al. JNCS 2023
https://dx.doi.org/10.2139/ssrn.4570126

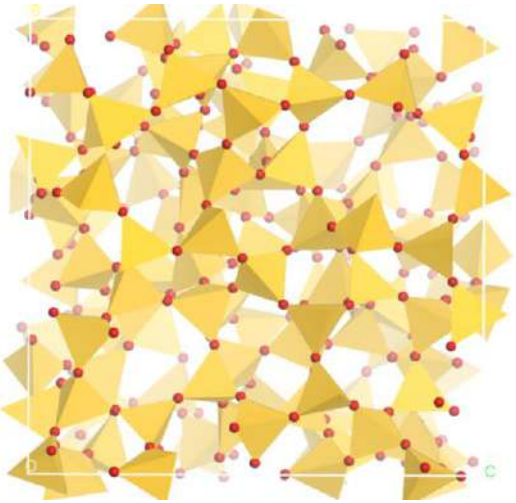
Performance of Empirical and ML-potentials: Sodium Silicate Glasses



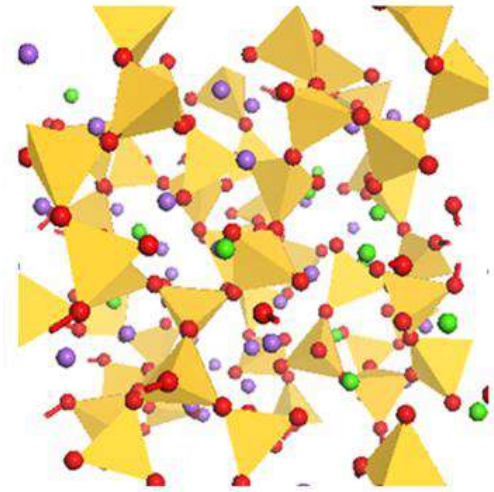
Bertani et al. J. Chem. Theory Comput. 2024, 20, 3, 1358–1370

Total Distribution Functions and Bond Angle Distributions

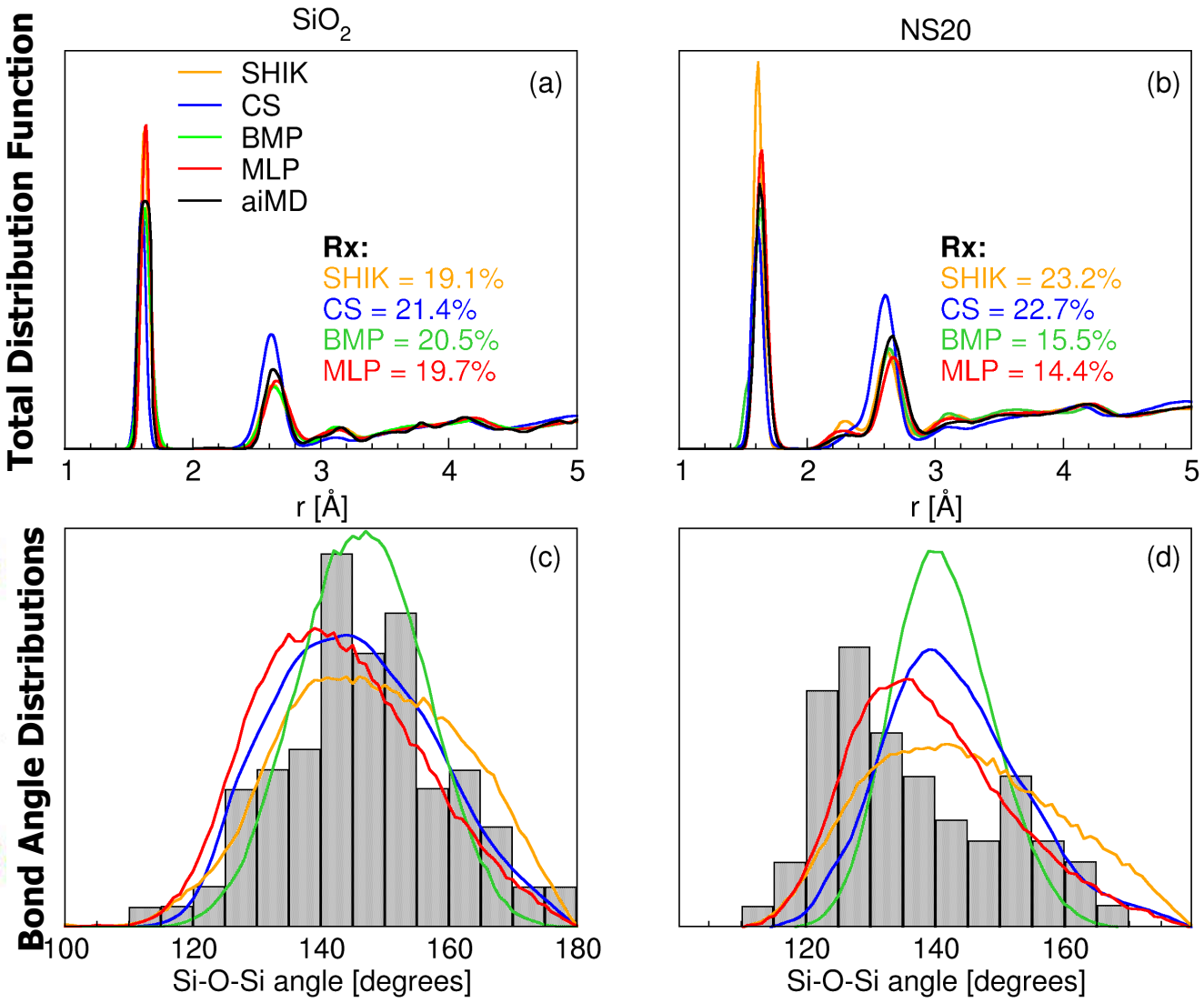
$$R_x = \left\{ \frac{\sum_{i=1}^{N} \left[T^{exp}(r_i) - T \quad (r_i) \right]^2}{\sum_{i=1}^{N} \left[T^{exp}(r_i) \right]^2} \right\}^{\frac{1}{2}} \cdot 100$$



SiO_2

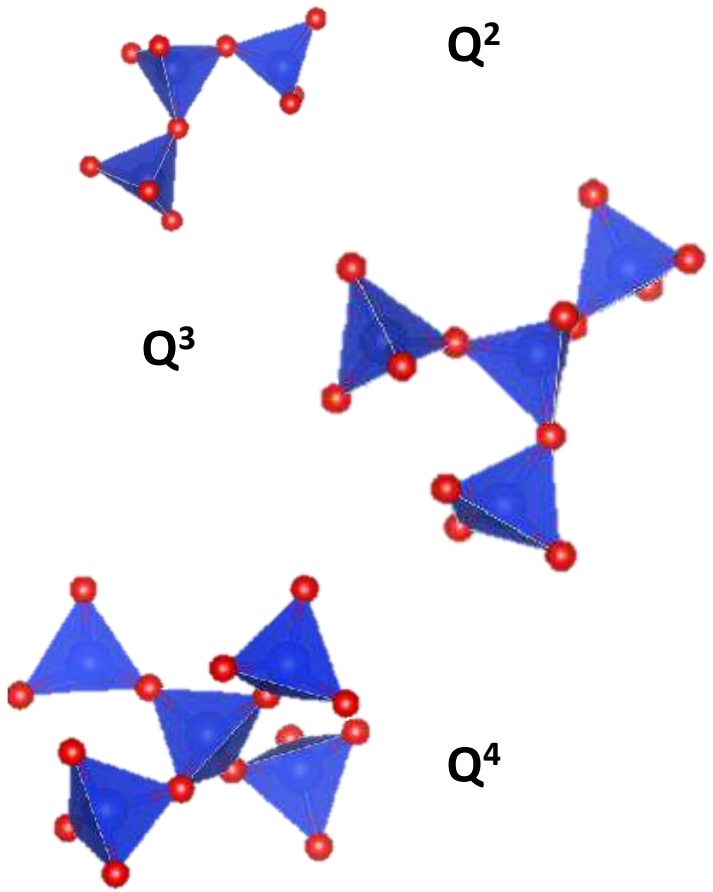


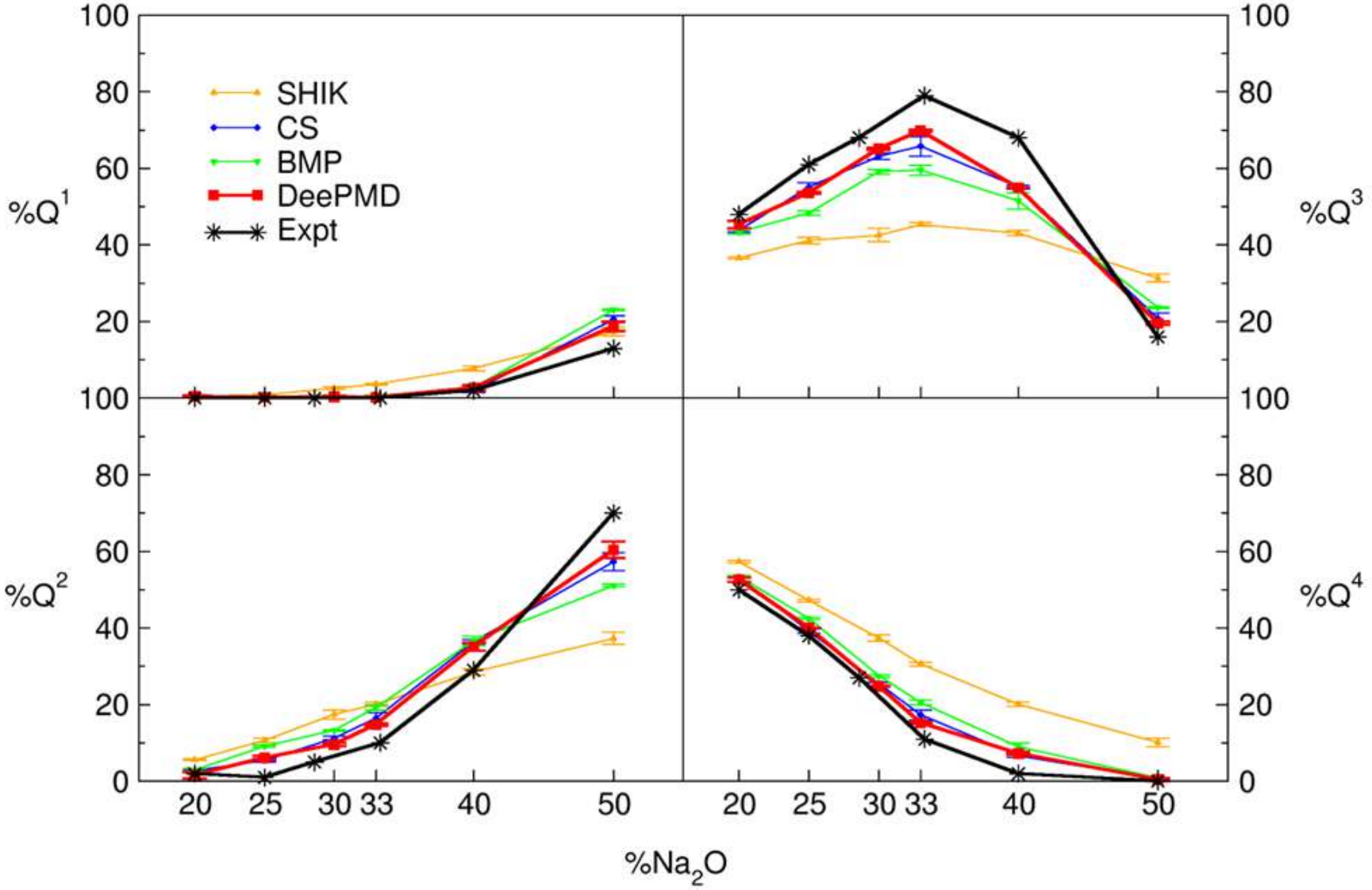
$20Na_2O\ 80SiO_2$



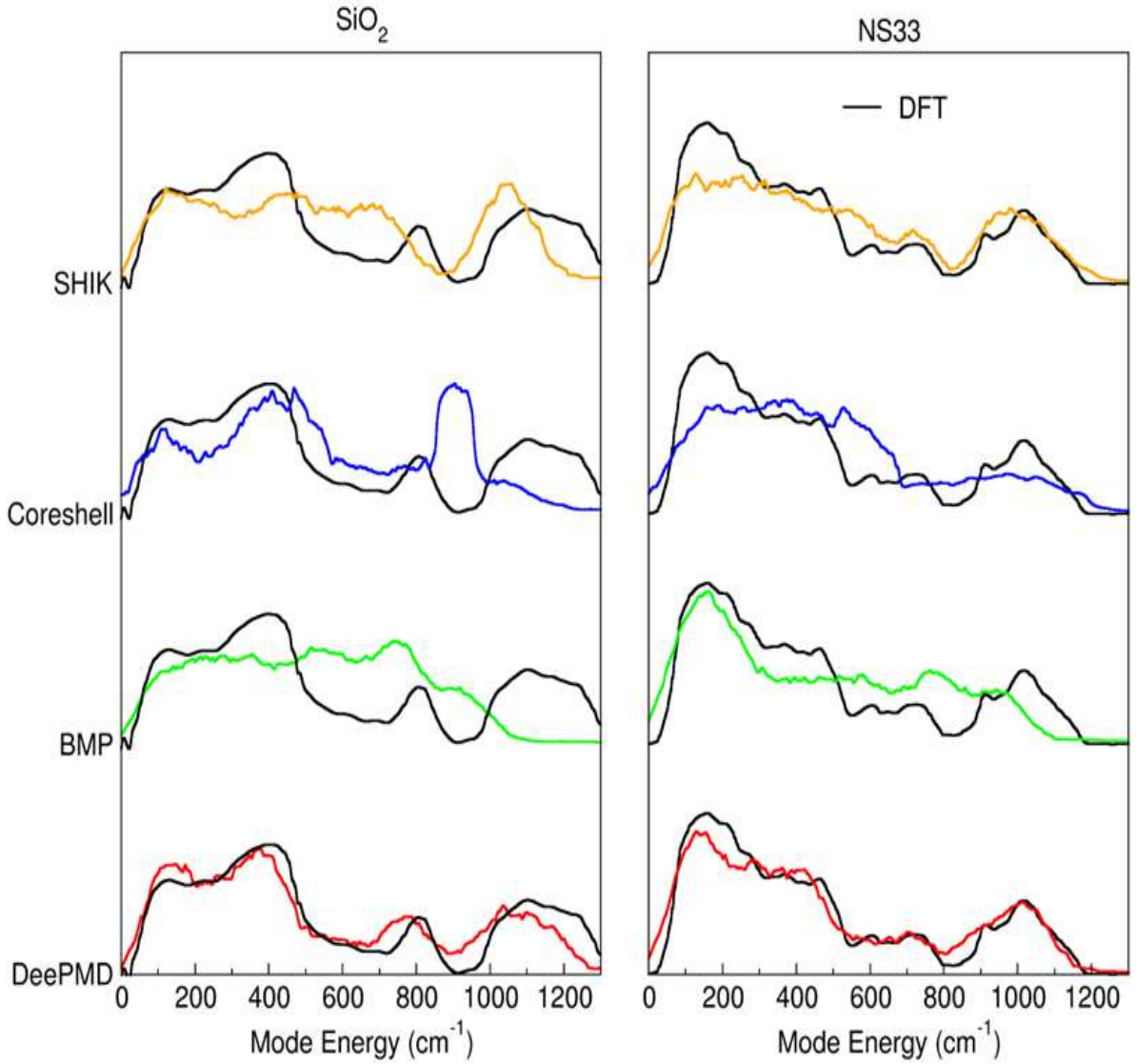
Q^n distributions

Si[Q^n] speciation



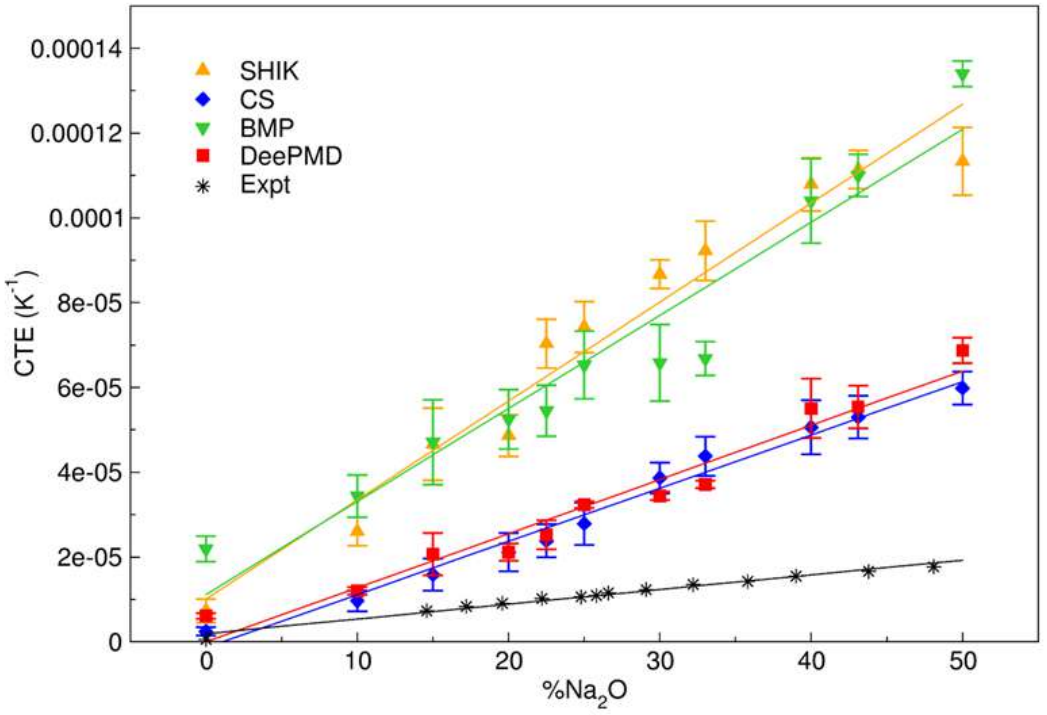


Vibration Density of States

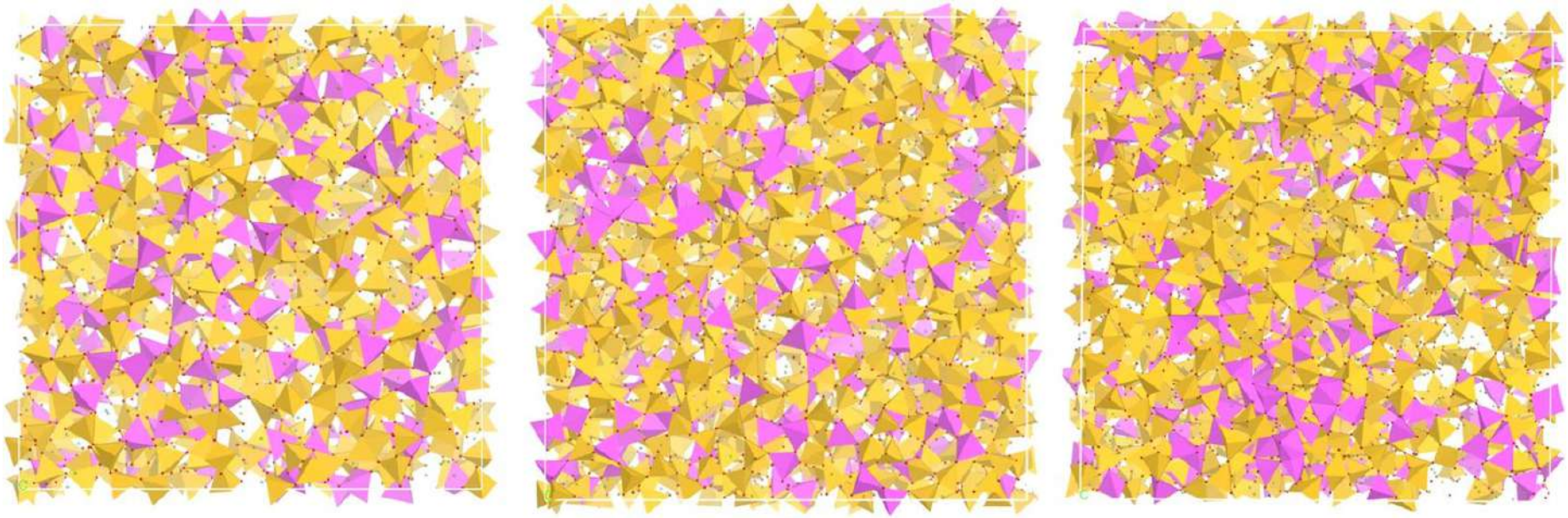


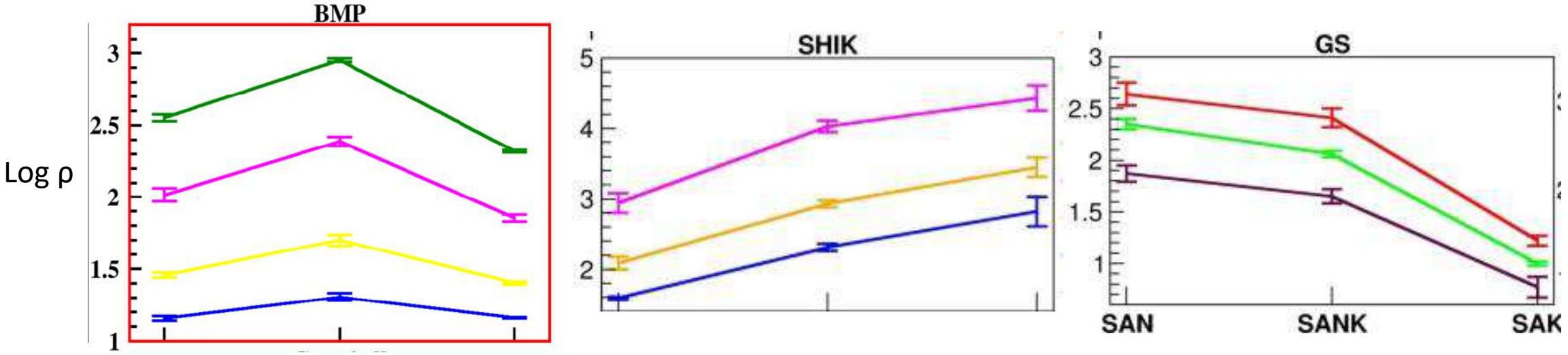
Coefficient of Thermal Expansion (CTE)

$$CTE = \frac{1}{V_0}\frac{dV}{dT}$$



Mixed Alkali Effects (MAE) in AluminoSilicate Glasses not observed with all empirical FFs

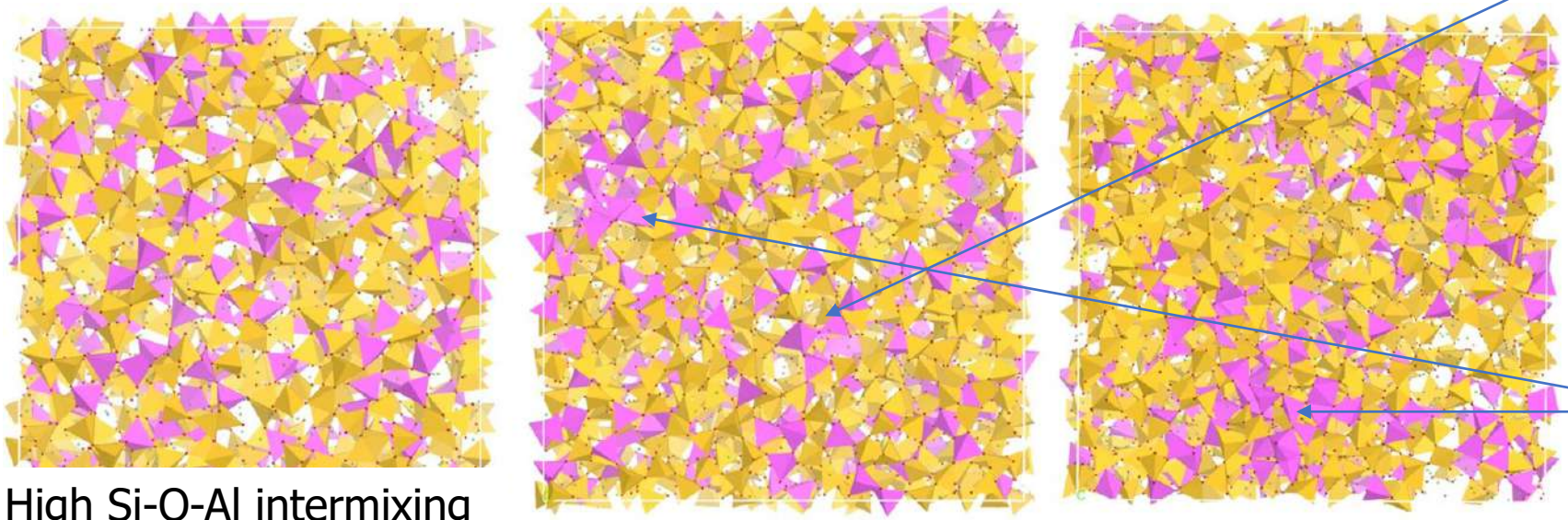




Wrong Structural Models – No Mixed Alkali Effect observed

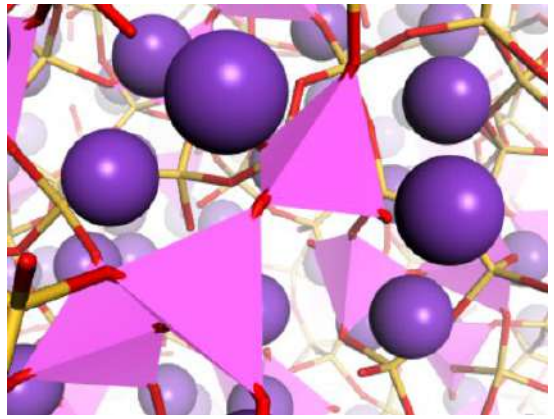
… Effect of the structural models

Clusterization

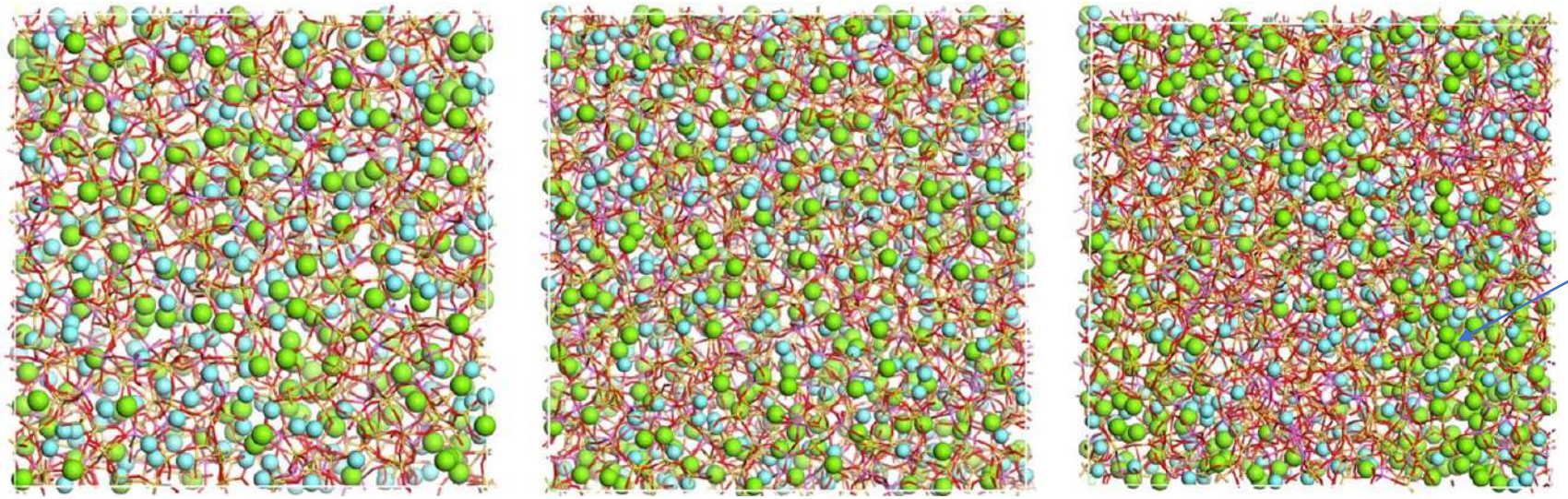


High Si-O-Al intermixing

Strong Al-K interaction
Low K mobility



Al clusterization

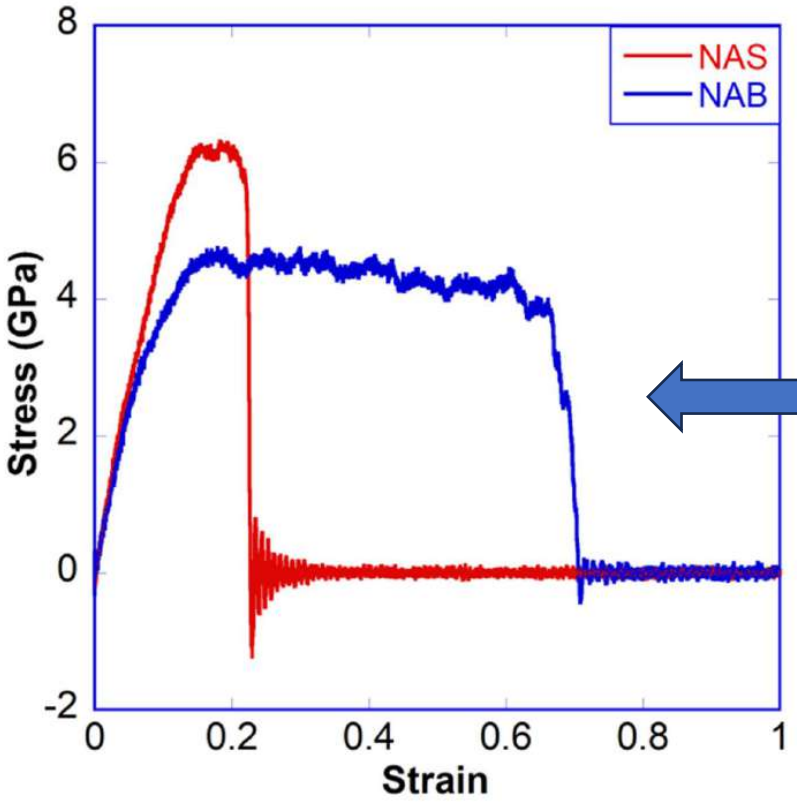


K clusterization

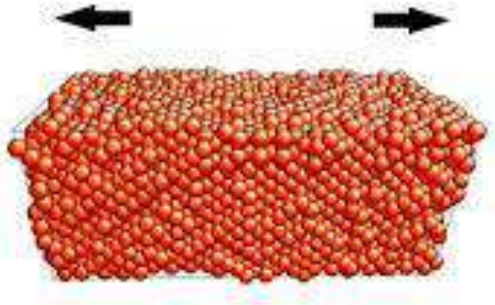
High K mobility

BMP **SHIK** **GS**

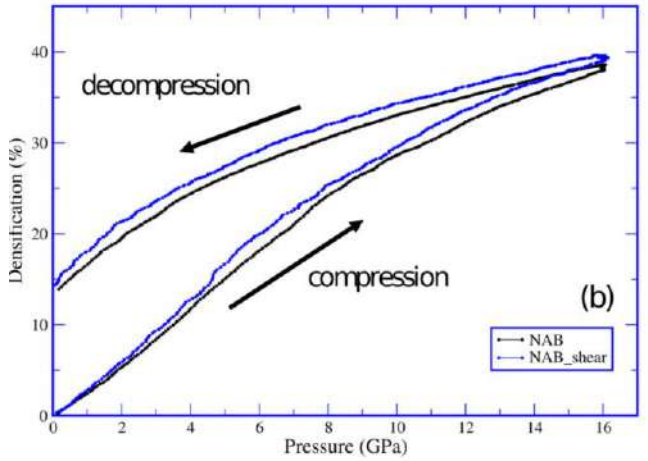
Mechanical Tests and Properties

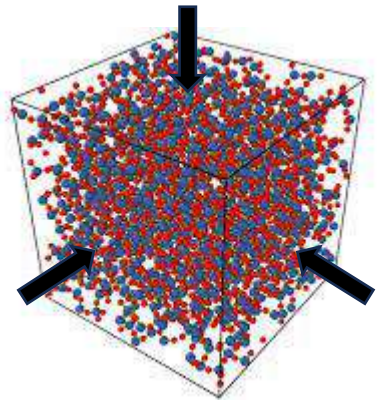


Elastic moduli, strength, fracture mechanims

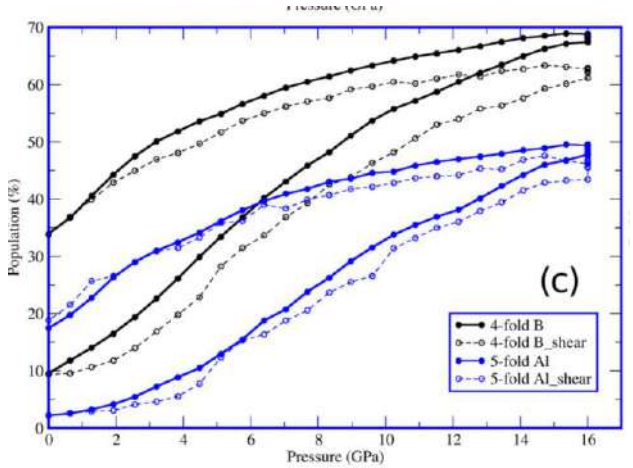


Uniaxial Tensile Tests





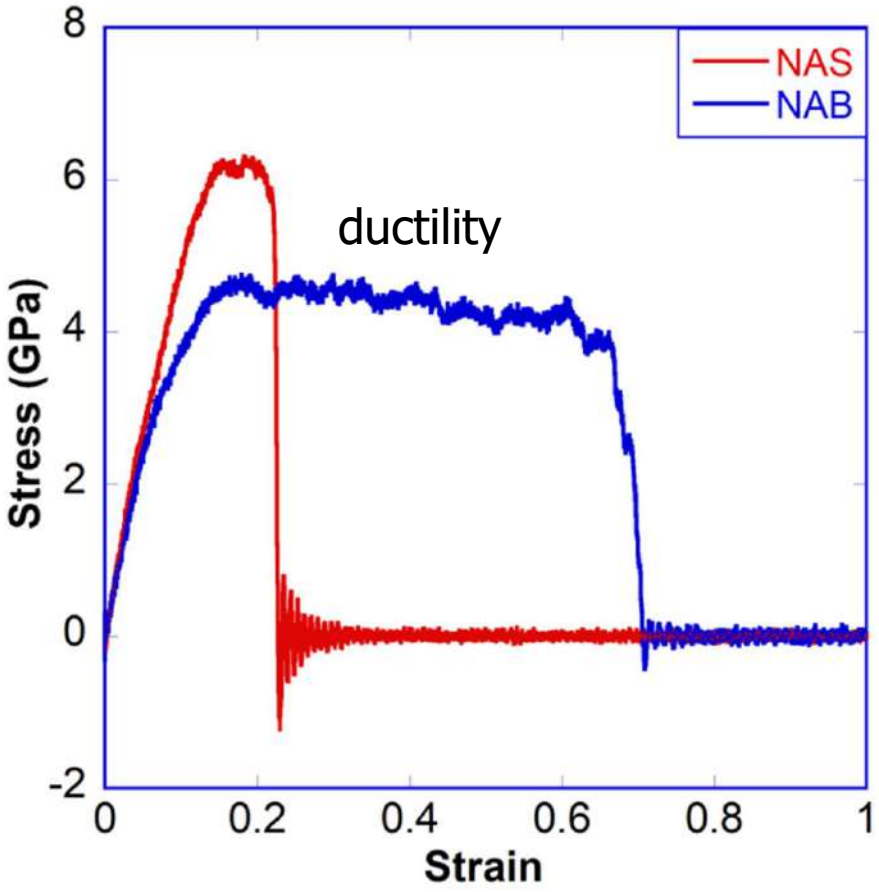
Hydrostatic Compressive Tests



Densification mechanism, bulk modulus

Liu et al. J. Appl. Phys. 128, 035106 (2020)

- NAB glasses more crack resistance than NAS
- NAB glasses show ductility compared to NAS
- Shear strain taken up by B in NAB glasses



Atomic Shear Strain

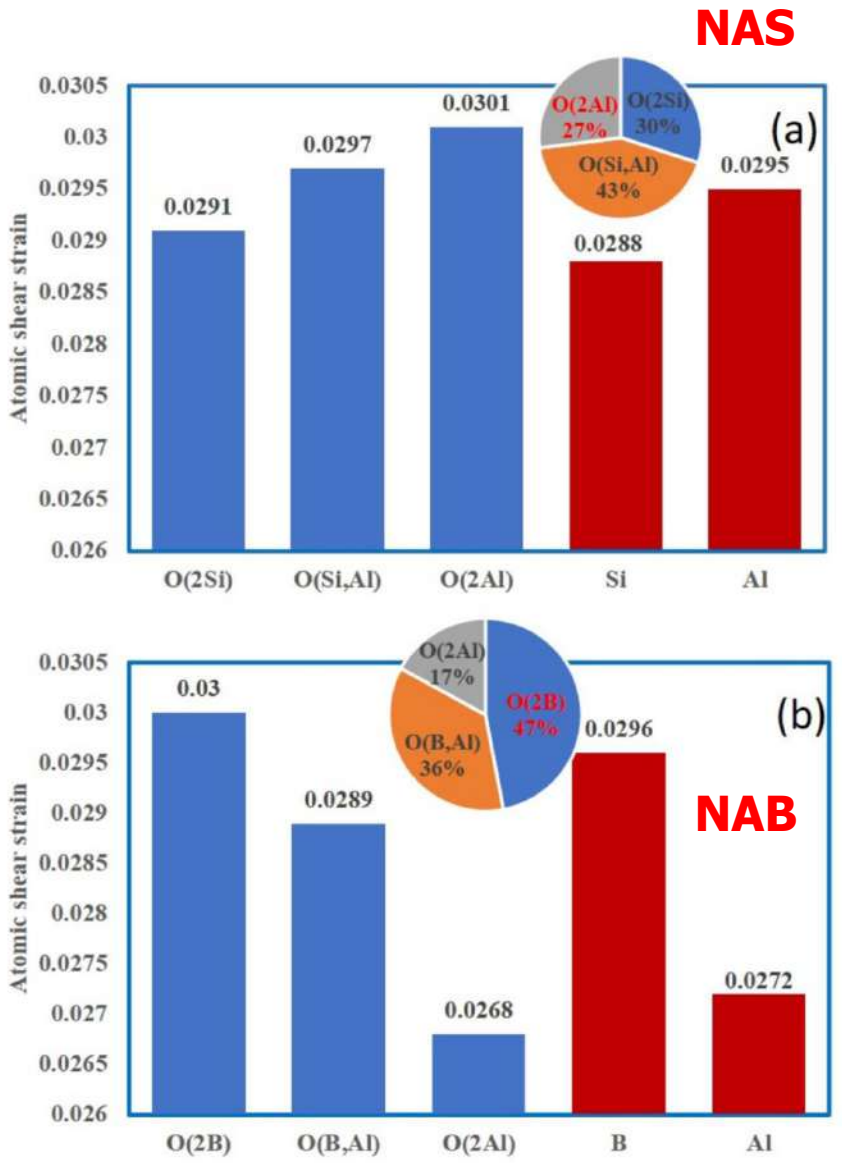


FIG. 6. Local shear deformation propensity in the NAS (a) and the NAB (b) at 300 K. Population of O with two neighbors of Si, Al, and B in different combinations are shown in the pie chart insets.

Indentation tests

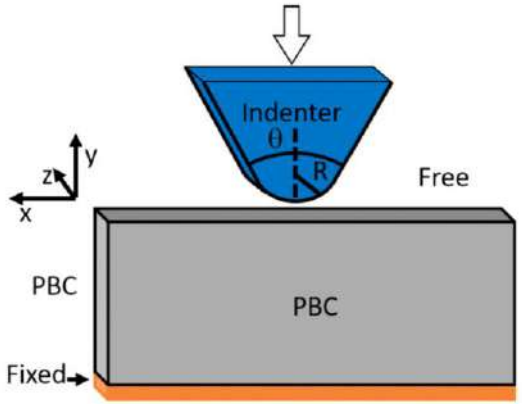
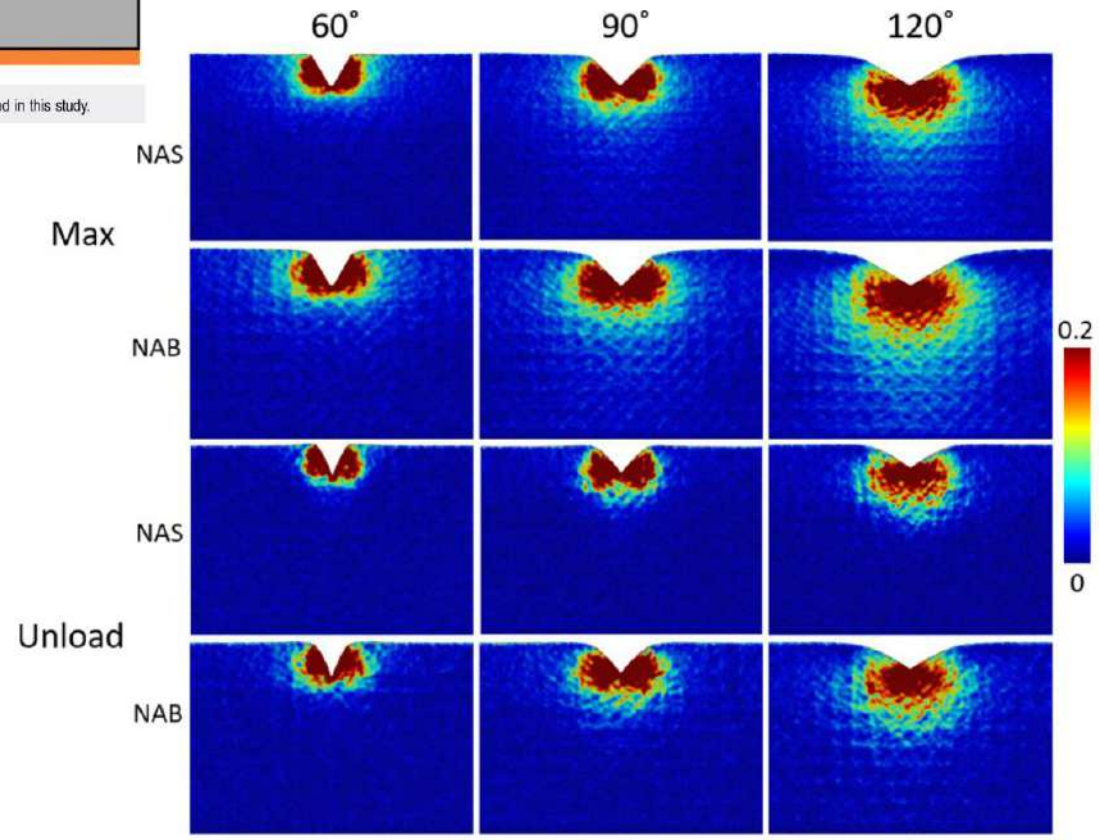
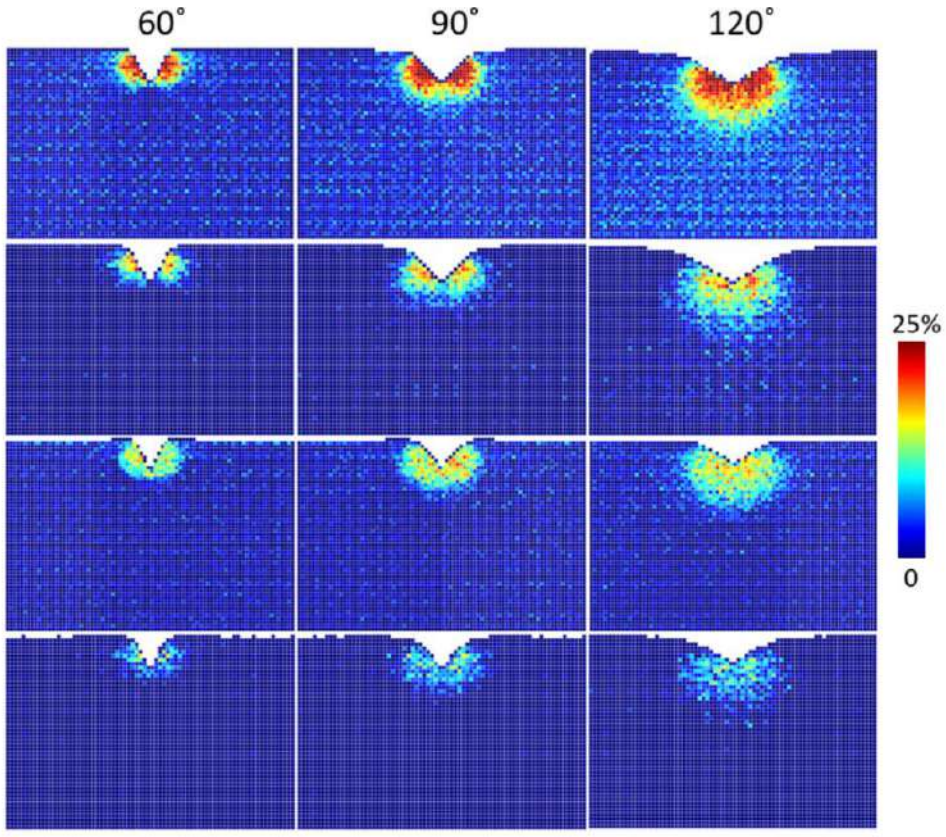


FIG. 1. Schematic of the nanoindentation setup used in this study.



(a) Shear strain



(b) Densification

Liu et al. J. Appl. Phys. 128, 035106 (2020); doi: 10.1063/5.0013555

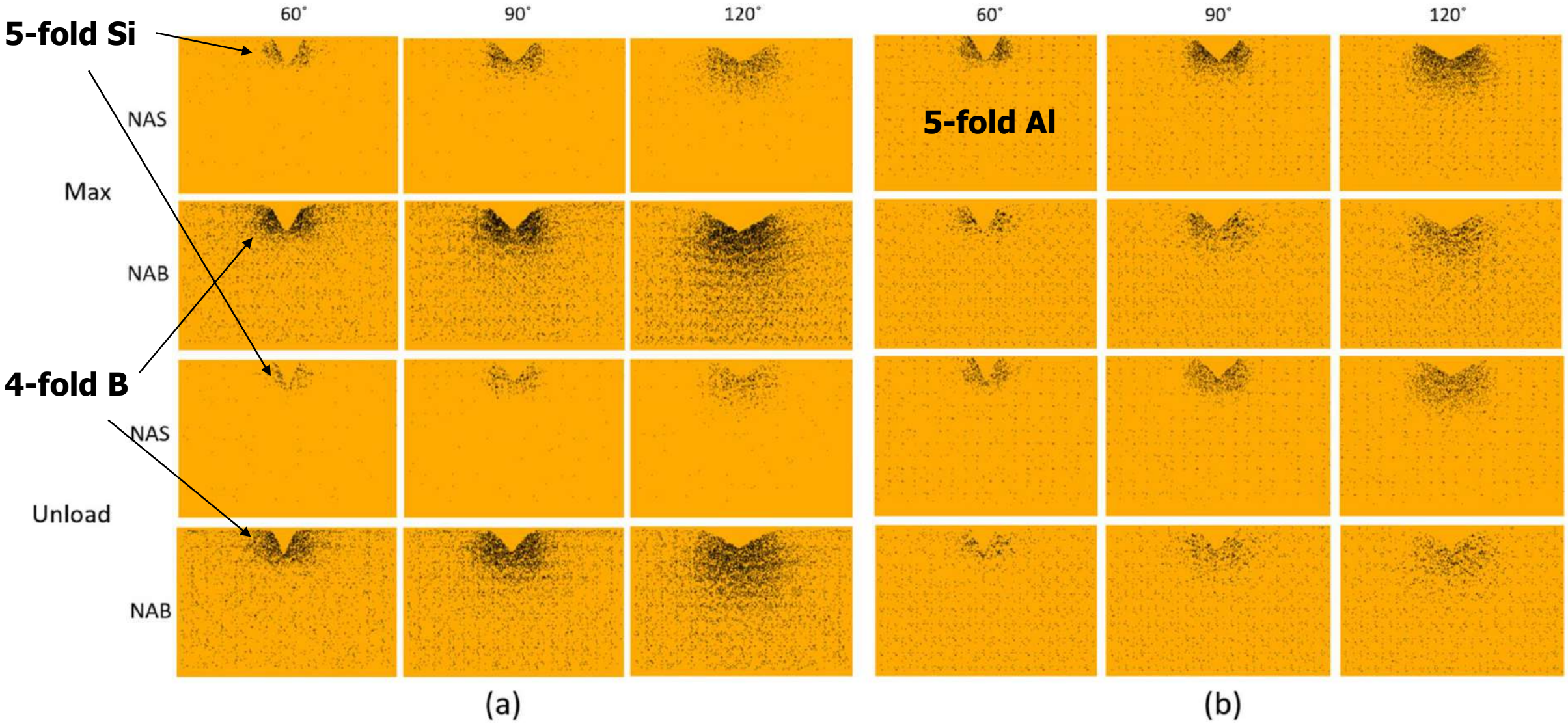


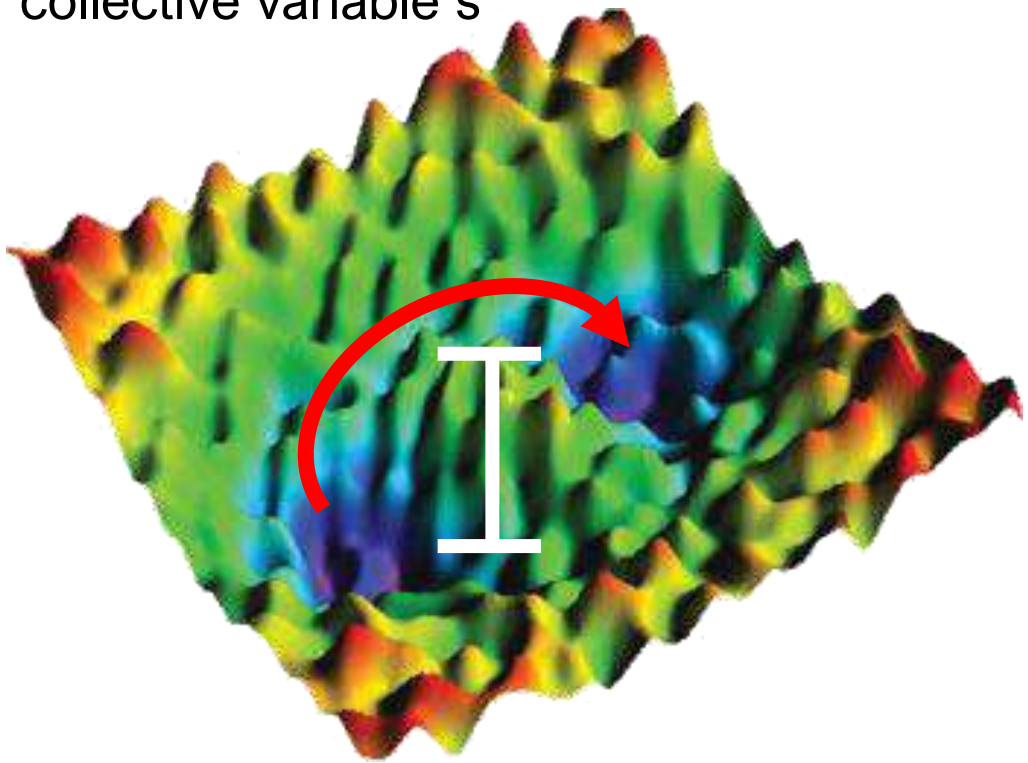
FIG. 12. (a) Distribution of fivefold coordinated Si atoms (indicated as black dots) in the NAS and fourfold coordinated B atoms (indicated as black dots) in the NAB at the maximum indentation depth (top two rows) and after unloading (bottom two rows) tested with different indenter angles (60°, 90°, and 120°) and a tip radius of 1 nm at 300 K. (b) Distribution of fivefold coordinated Al atoms (indicated as black dots) in the NAS and NAB at the maximum indentation depth (top two rows) and after unloading (bottom two rows) under the same indentation conditions.

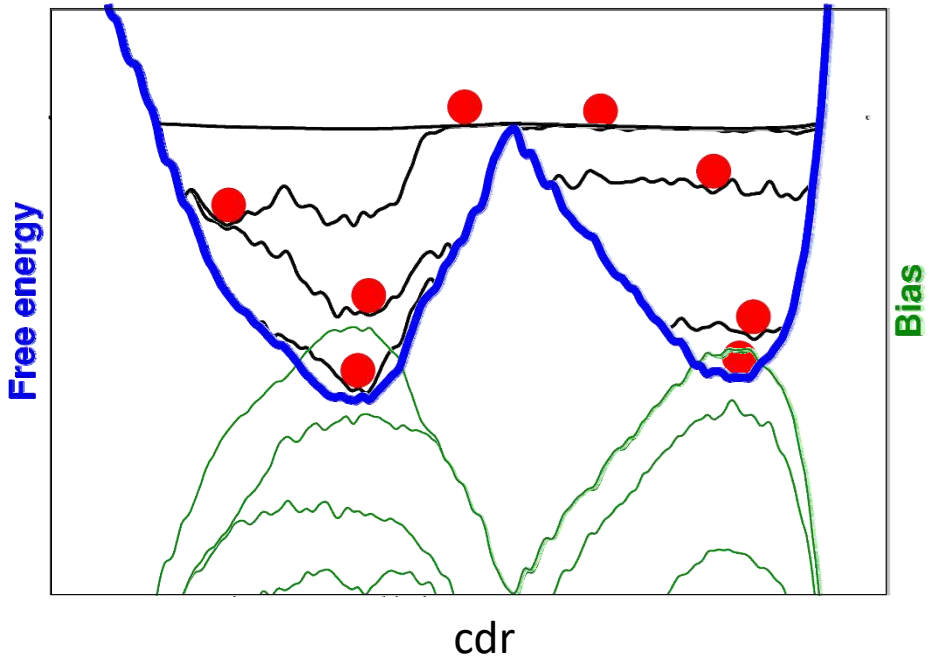
Studying Crystallization in glasses: Metadynamics

- **Enhanced Sampling Techniques**

Add **bias potential** in the explored space along a collective variable s

$$U(\vec{r}) \rightarrow U(\vec{r}) + V_{BIAS}(s(\vec{r}))$$





Reconstruct the **Free Energy Surface** (FES)

$$F(s) = -\frac{\gamma}{\gamma - 1} V(s,t) - c(t)$$

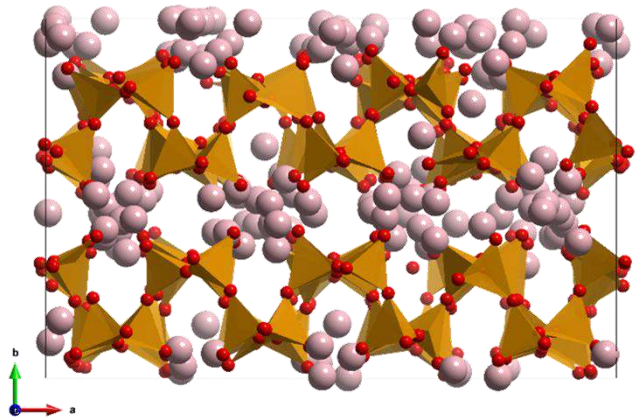
Laio, A., & Parrinello, M. (2002). *PNAS*, *99*(20), 12562-12566

Barducci, A., Bussi, G., & Parrinello, M. (2008). *PRL*, *100*(2), 020603.

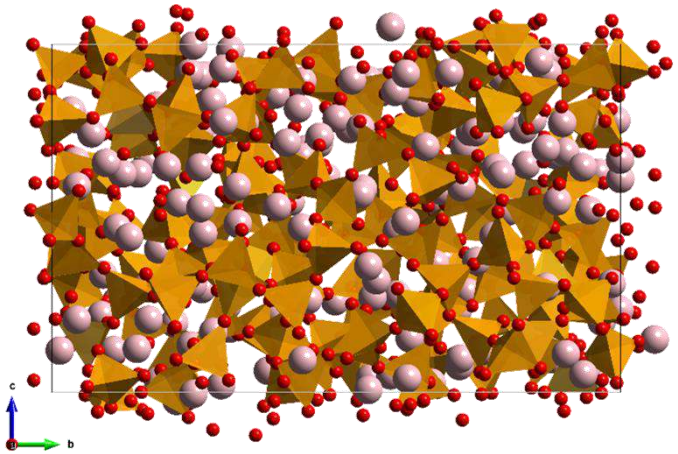
Lithium Disilicate

Collective Variable

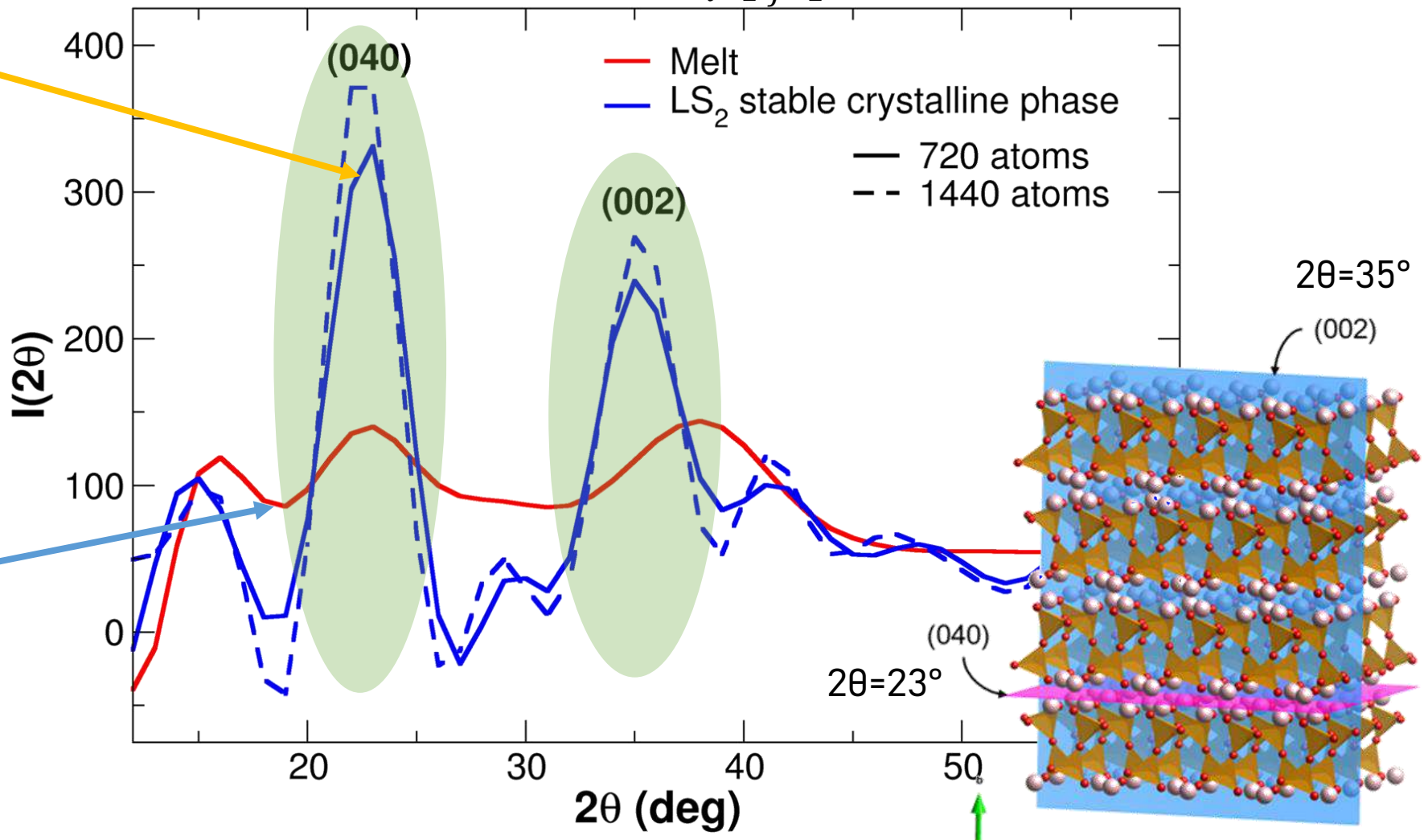
Crystalline



Glass



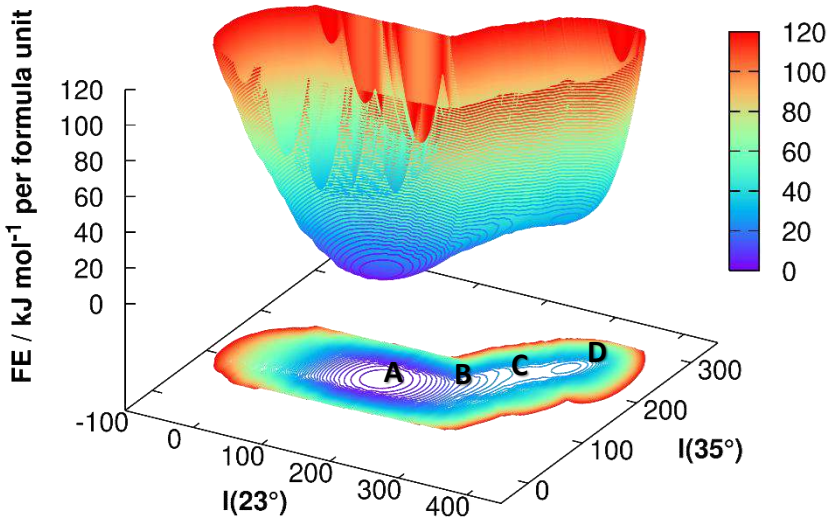
X-ray diffraction: $$I(Q) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} f_i(Q) f_j(Q) \frac{\sin(Q \cdot R_{ij})}{Q \cdot R_{ij}} W(R_{ij})$$

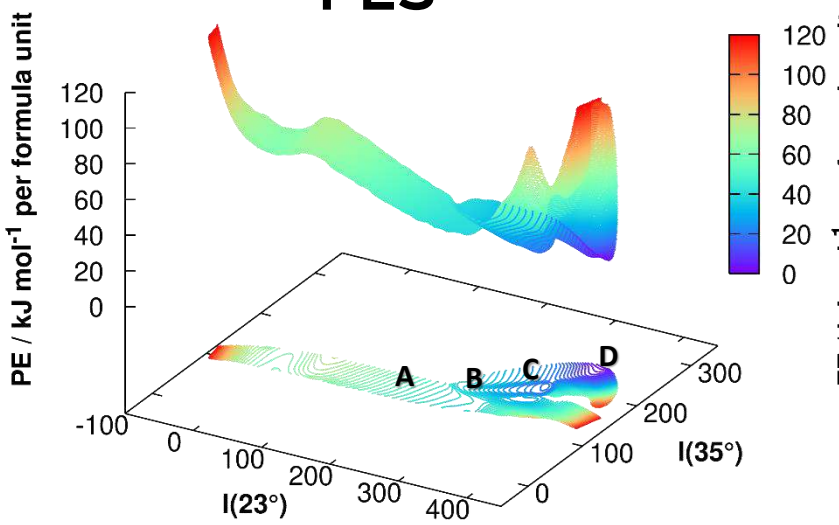


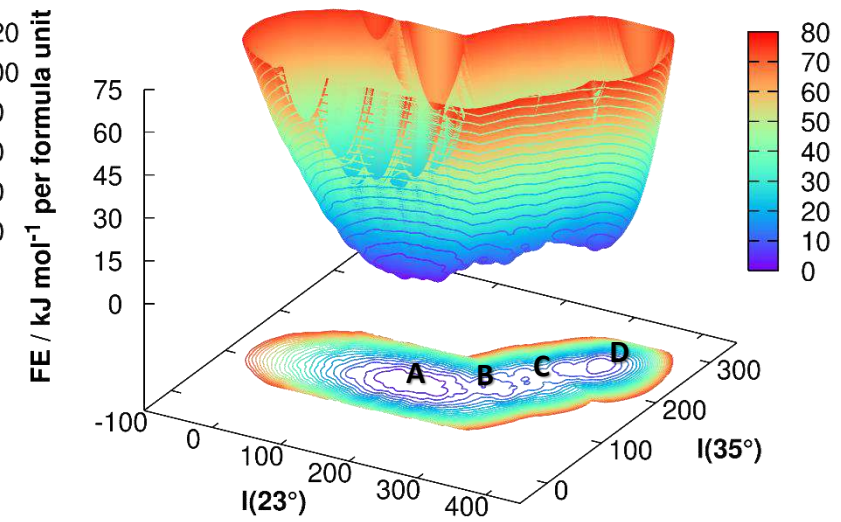
Niu, H., Piaggi, P. M., Invernizzi, M., Parrinello, M. (2018). *PNAS*, *115*(21), 5348–5352

Free Energy Surface of Lithium Disilicate Crystallization

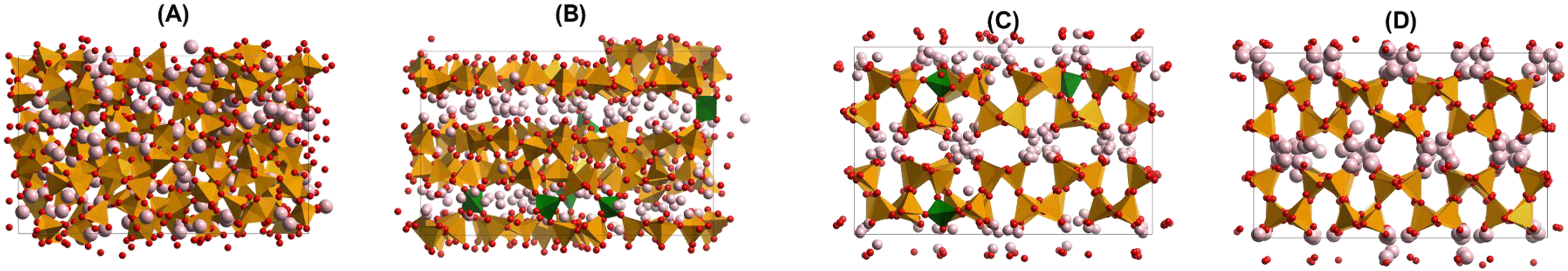
PES







FES at 1800 K → **Temperature rescaling** $P_T(R,t) = P_{T'}(R)e^{-(\beta-\beta')H(R,t)}$ → **FES at 1200 K**



Step mechanism:
intermediate phase made of disordered layers

Lodesani, F. et al. (2021). *Phys. Rev. Mat.*, *5*(7), 075602

Conclusions

Molecular Dynamics Simulations allow to study the structure, properties and behaviour of multicomponent oxide glasses.

Some Challenges remain:

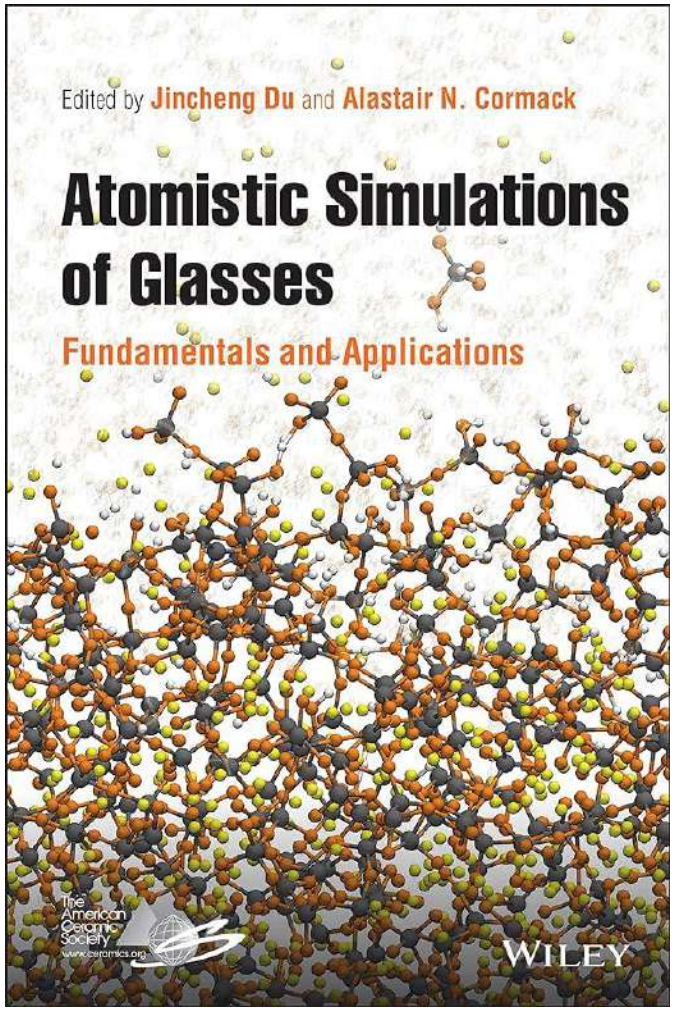
Developing accurate Force-Fields (machine learning and empirical)

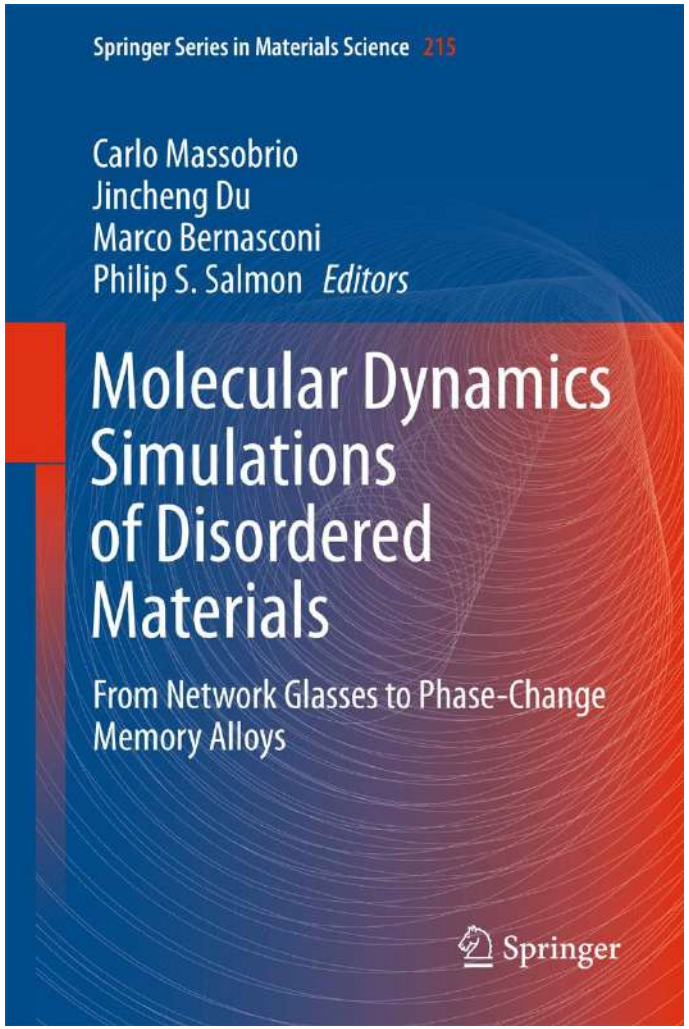
Time scale problem (too high quenching rates)

Methods and protocols for simulation of properties

Reactivity for large systems and for long time

Books





Reviews

Pedone, A. *Properties Calculations of Silica-Based Glasses by Atomistic Simulations Techniques: A review*. **J. Phys. Chem. C**, (2009), 113, 20773-20784. DOI:10.1021/jp9071263

Pedone, A.; Bertani, M.; Brugnoli, L.; Pallini, A. *Interatomic Potentials for oxide glasses: Past, present, and future*. **J. Non-Cryst. Solids: X** (2022) 15 100115. https://doi.org/10.1016/j.nocx.2022.100115

Urata, S.; Bertani, M.; **Pedone, A.** *Applications of Machine-Learning Interatomic Potentials for modeling Ceramics, Glass, and Electrolytes; a review*. **J. Am. Cer. Soc.** (2024)

Acknowledgments

Collaborators

Dr. Thibault Charpentier (Center for Atomic Energy, France)
Prof. Francesco Faglioni (UniMORE)
Dr. Marco Bertani (UniMORE)
Dr. Luca Brugnoli (UniMORE)
Dr. Federica Lodesani (UniMORE)
Dr. Annalisa Pallini (UniMORE)
Prof.ssa Maria Cristina Menziani (UniMORE)
Dr. Shingo Urata (AGC)
Dr. Wolfgang Mannstadt (SCHOTT)

NVIDIA

2 NVIDIA Academic Grants

AGC

Ashai Glass Company, Japan

SCHOTT
glass made of ideas

Thank you all for your attention!