DE LA RECHERCHE À L'INDUSTRIE

Molecular Dynamics simulation of glass structures

J.-M. Delaye[1]

with the contributions of

T. Charpentier[2], L.-H. Kieu[1], F. Pacaud[1], M. Salanne[3]

[1]Service d'Etudes de Vitrification et procédés hautes Températures (SEVT), CEA Marcoule, France

[2]Nanosciences et Innovation pour les Matériaux la Biomédecine et l'Énergie (NIMBE), CEA Saclay, France

[3]Physicochimie des Electrolytes et Nanosystèmes interfaciaux (PHENIX), Université Pierre et Marie Curie, France

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OUTLINE

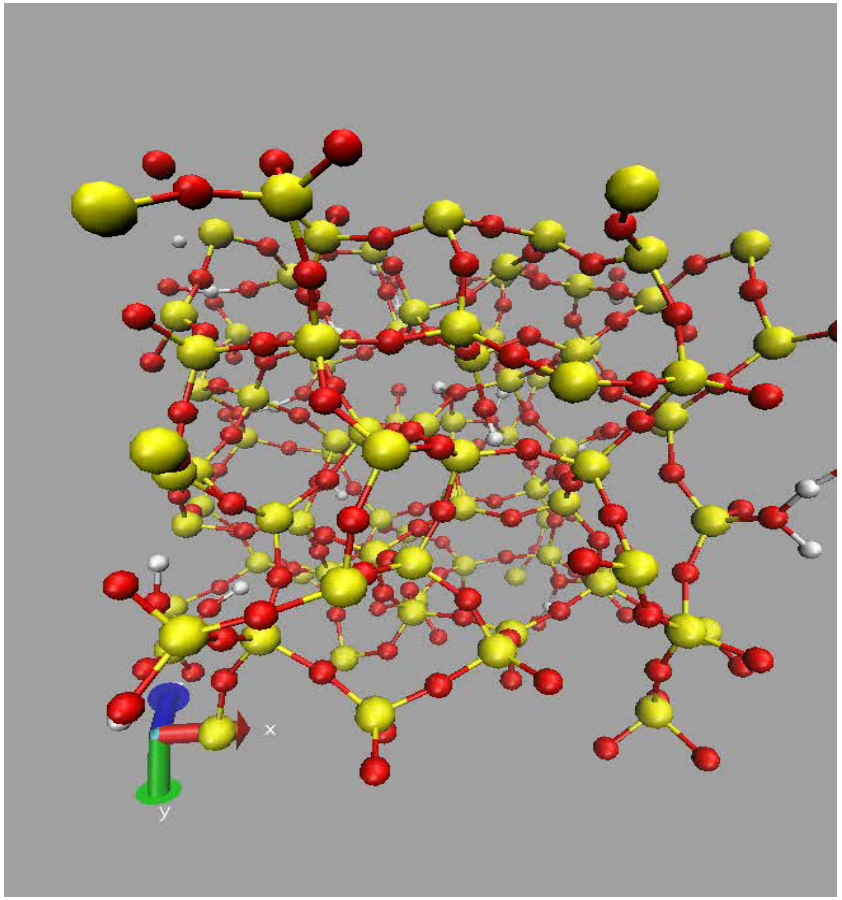
Objective of this lecture:

Describe the **state of the art** about simulation of **silicate glass** structure by **classical molecular dynamics**

- Some fundamentals about classical molecular dynamics (MD) and interatomic potentials (15')
- Alumino silicate glasses: three examples (10')
- Boro silicate glasses: two examples (10')
- Conclusions
- Perspectives: some words about very recent approaches (Reaxff, machine learning) (5')

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

- Classical molecular dynamics is able to represent the **dynamics** of **several thousands of atoms** (from 1000 to 10^6 or more) during **several picoseconds** (10ps - 1µs)



- Computers are more and more powerful.
- Larger systems are simulated giving access to new mechanisms: mechanical properties, longer relaxations …
- 10^6 atoms < > cubic box of 25 nm of side

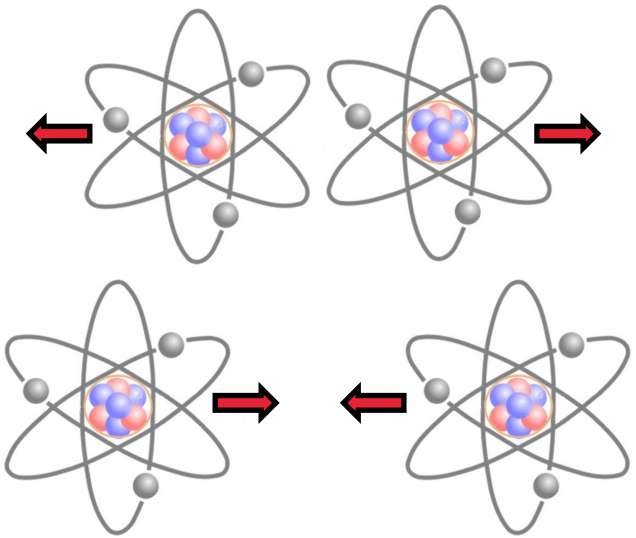
(SiO_2 with some water molecules)

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

- Representation of the atomic interactions →

INTERATOMIC POTENTIALS

- The first models were quite simple



At short distance, interpenetration of the electronic clouds: repulsion

At large distance, coulombic and dipolar attraction (dispersion term)

$$\phi(r_{ij}) = 4\varepsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right)$$

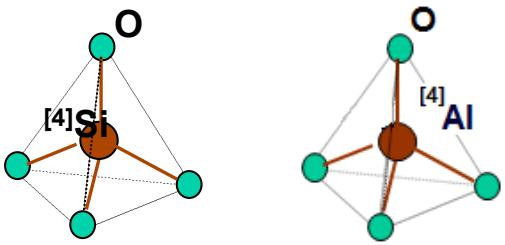
Lennard-Jones potentials

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + B_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

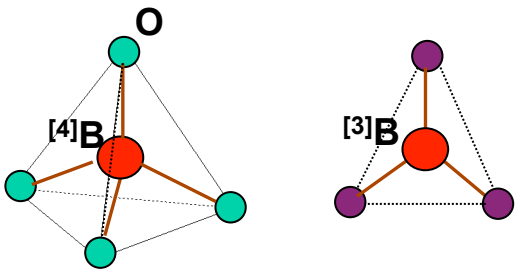
Buckingham potentials

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

- Oxide glasses are also subjected to covalent interactions
  → orbital hybridation, developed local angular order

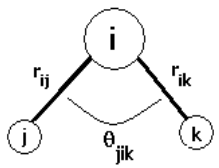


Tetrahedral order around the Si and Al ions (SiO_4 - AlO_4)



Tetrahedral or triangular order around the B ions (BO_4 or BO_3)

- This chemical property is taken into account using three body (angular) potentials



Triplet <jik>: r_{ij}, r_{ik}, θ_{jik}

$$E_{OSiO}(\theta) = \frac{1}{2} k_{3b} (\theta - \theta_0)^2$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp\left(\frac{\gamma}{r_{ij} - r_c} + \frac{\gamma}{r_{ik} - r_c}\right)(\cos\theta_{jik} - \cos\theta_0)^2$$

Energy associated to the triplet

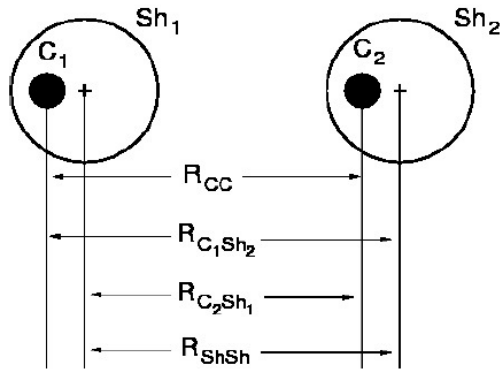
A. Tilocca, N.H. de Leeuw, A.N. Cormack, Phys. Rev. B 73 (2006) 104209
M.-T. Ha, S.H. Garofalini, J. Am. Ceram. Soc. 100 (2017) 563

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

- The ions can have dipolar momenta → the polarisation is treated via shell models or polarisation terms

Shell models

The ions are represented as cores (massive) connected to charged shells (very small mass) representing the valence electrons



The shift between the core and the shell creates a dipole.
The core and its shell are connected by an harmonic spring potential

$$E_{cs}(r) = \frac{1}{2} k_{cs} r^2$$

In the silicate glasses, the shell model is used only to represent the O ions because the polarisability is larger for this species compared to the other ones.

B.G. Dick Jr., A.W. Overhauser, Physical Review 112 (1958) 90

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

Polarizable potentials (PIM, AIM)

$$V_{tot} = V_{charge} + V_{disp} + V_{rep} + V_{pol}$$

- **Polarisation :**

$$V_{pol} = \sum_{i,j>i} \left[\frac{q_i r_{ij} \cdot \mu_j}{r_{ij}^3} g^{ij}(r_{ij}) - \frac{\mu_i \cdot r_{ij} q_j}{r_{ij}^3} g^{ij}(r_{ij}) \right] + \sum_{i,j>i} \left[\frac{\mu_i \cdot \mu_j}{r_{ij}^3} - \frac{3(r_{ij} \cdot \mu_i)(r_{ij} \cdot \mu_j)}{r_{ij}^5} \right] + \sum_i \frac{|\mu_i|^2}{2\alpha_i}$$

- **Charge :**

$$V_{charge} = \sum_{i,j>i} \frac{q^i q^j}{r_{ij}}$$

- **Répulsion :**

$$V_{rep} = \sum_{i,j>i} A^{ij} e^{-B^{ij} r_{ij}}$$

- **Dispersion :**

$$V_{disp} = -\sum_{i,j>i} \left[f_6^{ij}(r_{ij}) \frac{C_6^{ij}}{r_{ij}^6} + f_8^{ij}(r_{ij}) \frac{C_8^{ij}}{r_{ij}^8} \right]$$

At each time step, the dipolar momenta are determined by minimizing the polarisation energy V_{pol}.

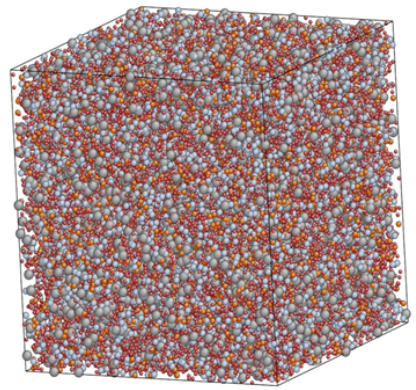
F. Pacaud, J.-M. Delaye, T. Charpentier, L. Cormier, M. Salanne, J. Chem. Phys. 147 (2017) 161711

QUICK INTRODUCTION TO THE CLASSICAL MOLECULAR DYNAMICS

- From the interatomic potentials to the forces:

$$E_{tot} = \sum_{i,j} \phi(r_{ij}) + \sum_{i,j,k} \phi_3(r_{ij}, r_{ik}, \theta_{jik}) \quad \Rightarrow \quad F_i = -\frac{\partial E_{tot}}{\partial r_i}$$

Total energy — Force exerted on an atom



- From the forces to the atomic displacements: discretization in time of the Newton's equation

$$F_i = \sum_j -\frac{\partial \phi(r_{ij})}{\partial r_i} = m_i \frac{d^2 r_i}{dt^2}$$

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{F(t)}{m}\frac{\delta t^2}{2} + \frac{b(t)}{6}\delta t^3 + O(\delta t^4)$$

$$r(t-\delta t) = r(t) - v(t)\delta t + \frac{F(t)}{m}\frac{\delta t^2}{2} - \frac{b(t)}{6}\delta t^3 + O(\delta t^4)$$

$$\Rightarrow \quad r(t+\delta t) = 2r(t) - r(t-\delta t) + \frac{F(t)}{m}\delta t^2 + O(\delta t^4)$$

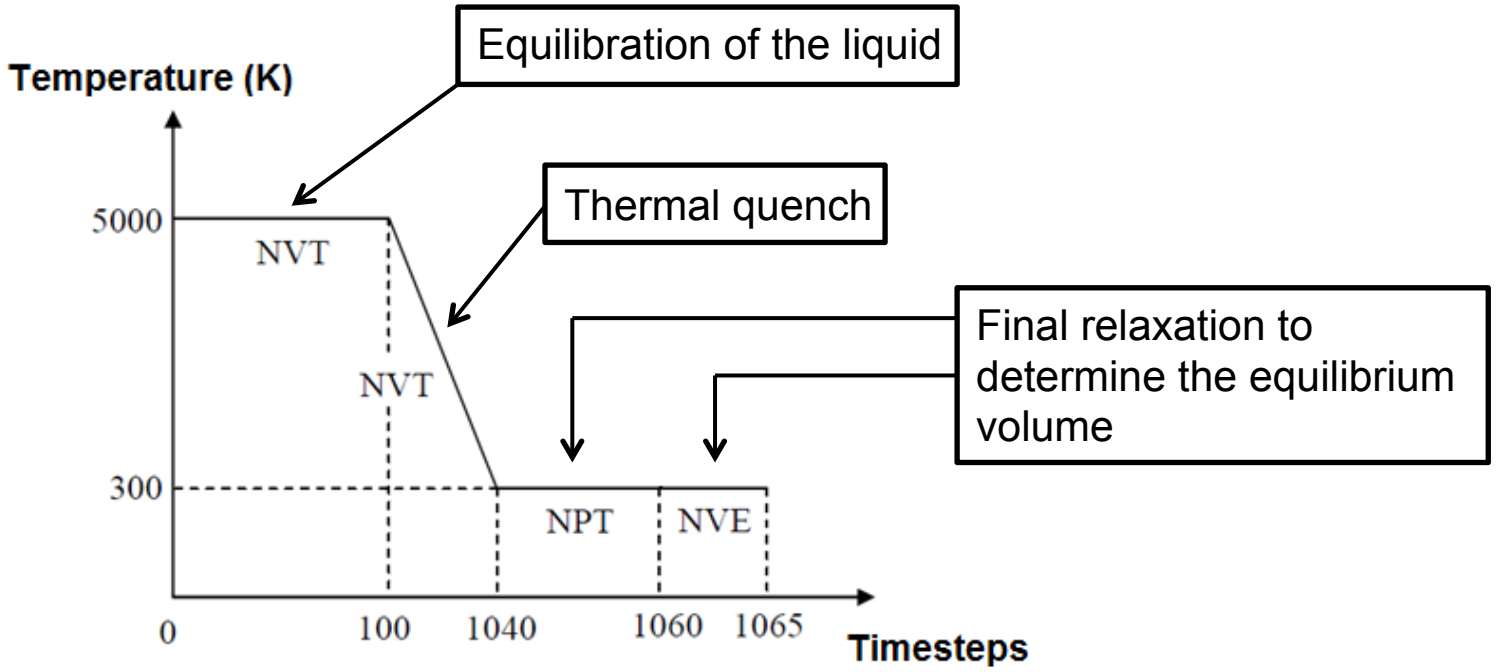
Timestep = 1fs typically

Positions are known at time t
Calculation of the forces

Calculation of the atomic displacements
Positions are known at time t+δt

GLASS PREPARATION

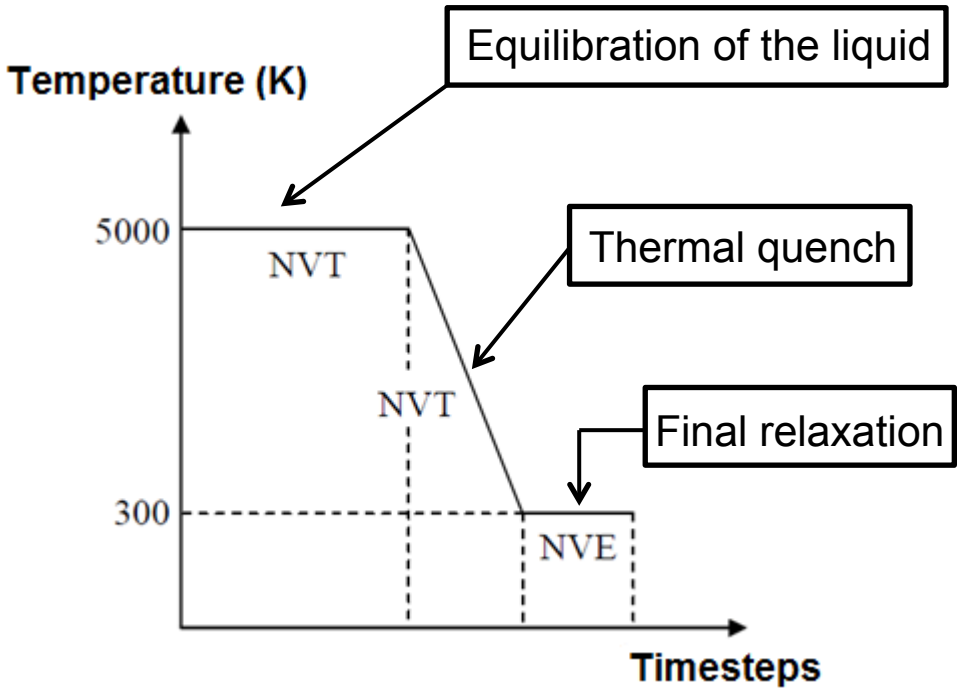
- A glass is prepared by equilibrating a liquid and by quenching it at ambient temperature

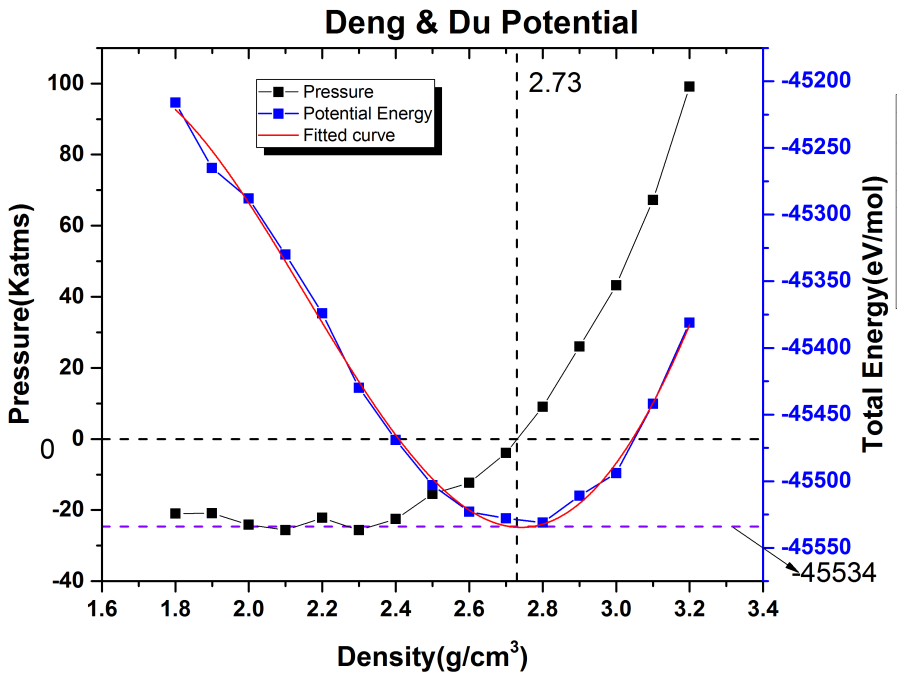


- The difficulty is to obtain a structure that corresponds to the minimum of the potential energy: one possibility is to prepare a glass in two steps

GLASS PREPARATION

First step: using different initial densities, the potential energy - density curve is plotted (no modification of the volume during the glass preparation)





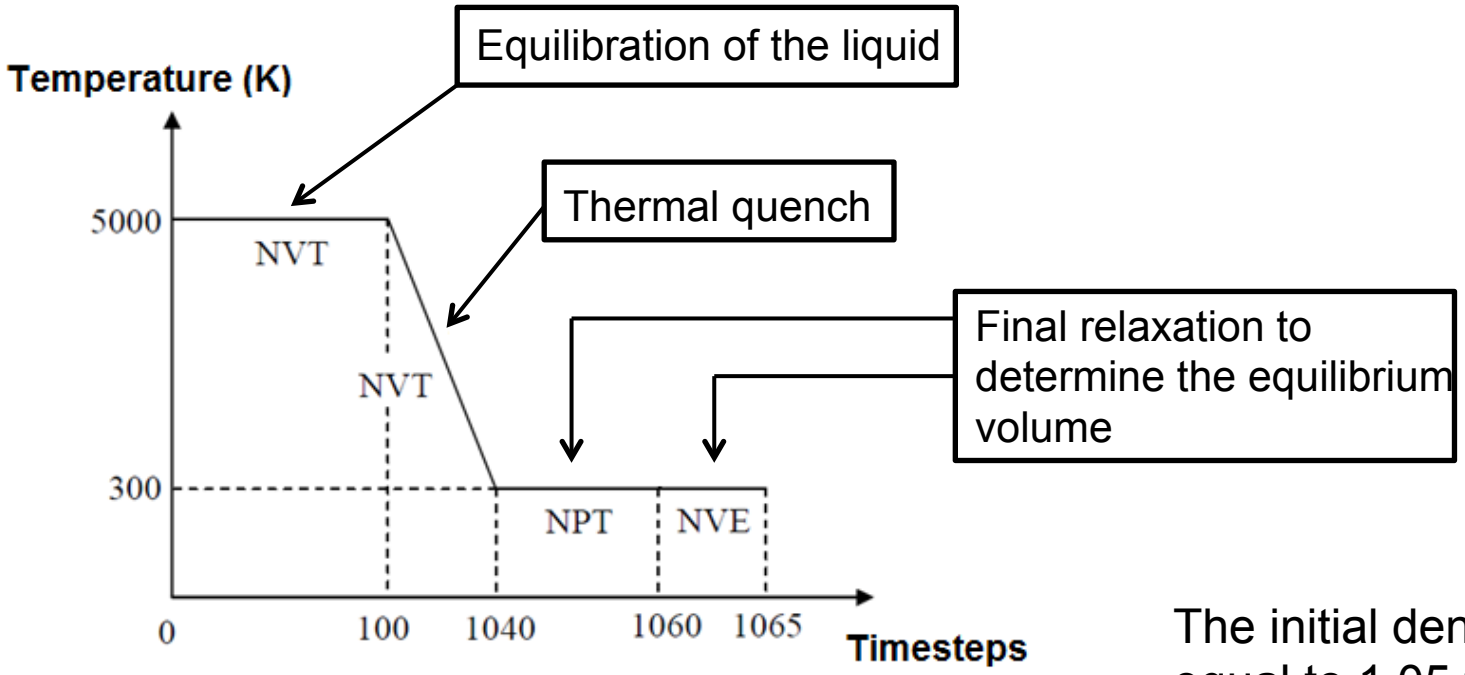
Glass: 67,73%SiO_2.18,04%B_2O_3.14,23%Na_2O (mol%)

The minimum of the potential energy and the corresponding density are determined

L. Deng, J. Du, Journal of Non-Crytalline Solids, 453 (2016) 177

GLASS PREPARATION

Second step: using the equilibrium density, a complete glass preparation is performed using the complete thermal scheme



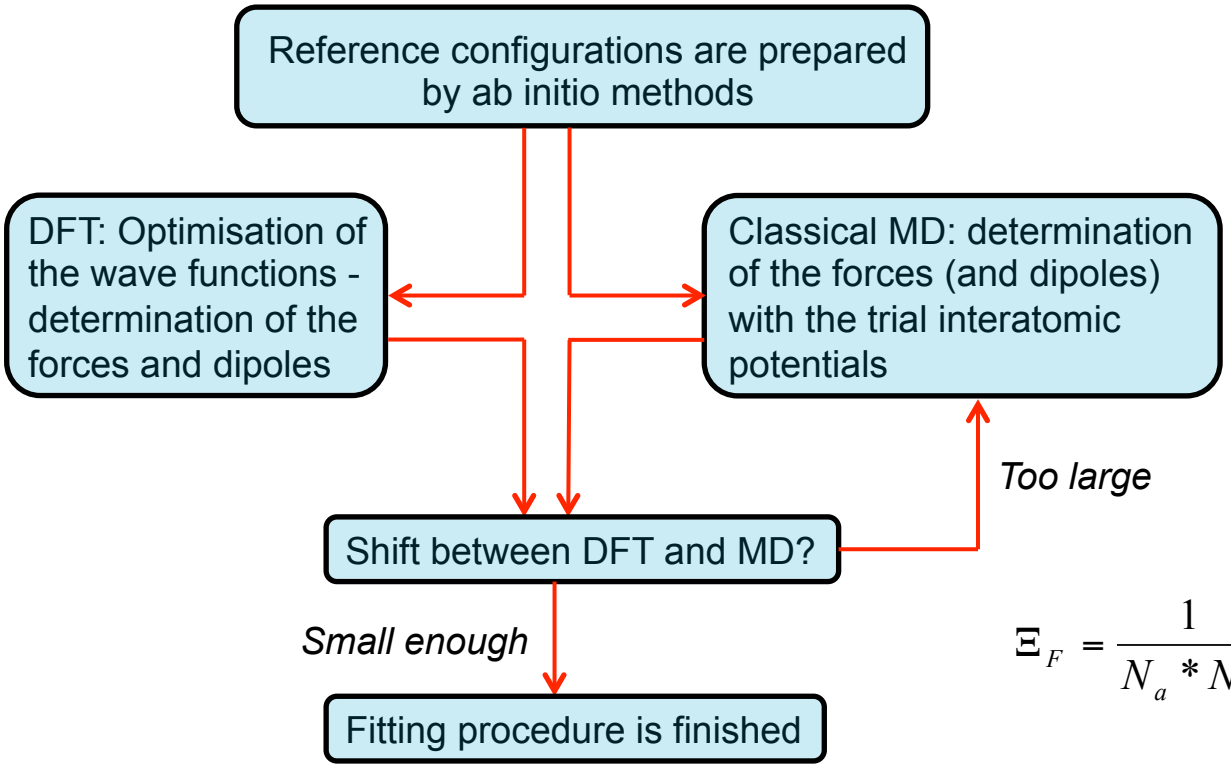
The initial density is taken equal to 1.05 the equilibrium density.

The final configuration is an equilibrated glass ready for the analysis

POTENTIAL FIT

- This step is very important: all the simulated glass properties (structural, dynamical, mechanical …) depend on the interatomic potentials

- Two main methods to fit the interatomic potentials
  → fit on experimental data
  → fit on ab initio calculations (more and more popular)



The adjustable parameters are determined by a convergence loop.

$$\Xi_F = \frac{1}{N_a * N_b} \frac{\sum_{k=1}^{N_a} \left| F^{classique} - F^{abinitio} \right|^2}{\sum_{k=1}^{N_a} \left| F^{abinitio} \right|^2}$$

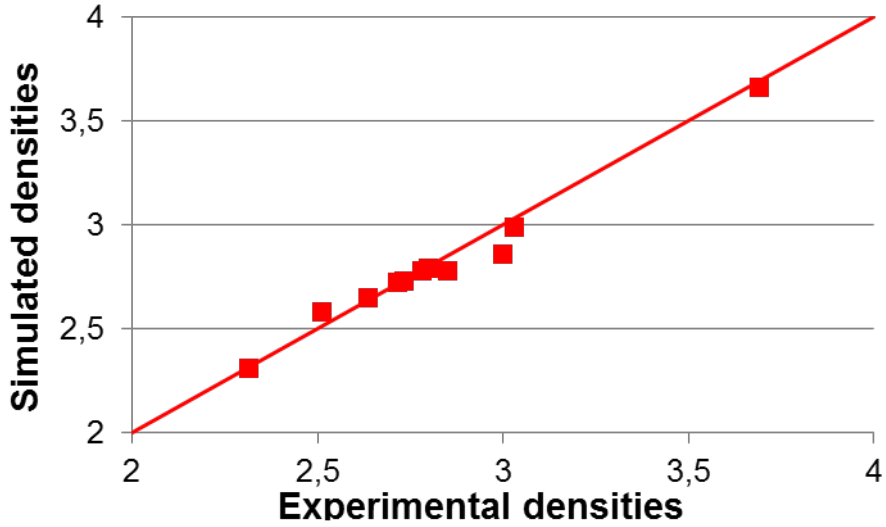
ALUMINO SILICATE GLASSES: GUILLOT AND SATOR'S POTENTIALS

- A work has been done to simulate complex systems that can be found in the Earth's mantle (SiO_2, TiO_2, Al_2O_3, FeO, Fe_2O_3, MgO, CaO, Na_2O, K_2O)

$$v(r_{ij}) = z_i z_j / r_{ij} + B_{ij} e^{-r_{ij}/\rho_{ij}} - C_{ij}/r_{ij}^6$$

Buckingham type potential

Silicate
Rhyolite (Ry)
Andesite (And)
Basalt(MORB)
Mars basalt (BM)
Green glass (LG15)
Black glass (LG14)
Komatiite (Ko)
Peridotite (Pe)
Olivine (Ol)
Allende m. (All)
Fayalite (Fa)



q_O = -0.945 (from Matsui's potential)

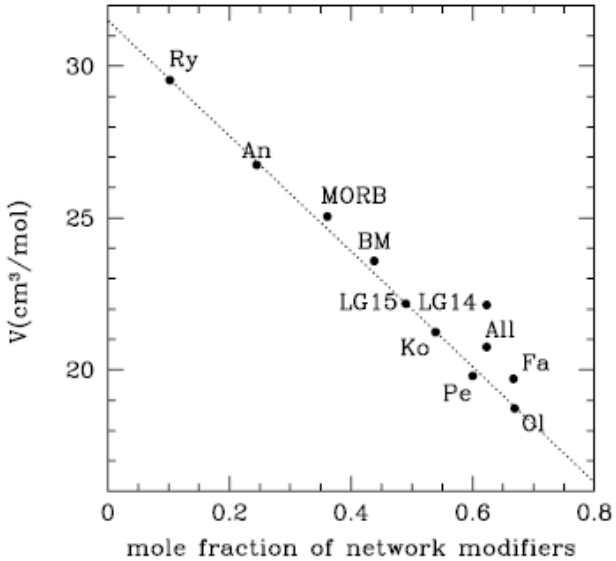
The adjustable parameters have been fitted in order to reproduce the densities of 11 natural silicate melts - $\Delta\rho/\rho = \pm 1\%$

B. Guillot, N. Sator, Geochim. and Cosmochim. Acta 71 (2007) 1249

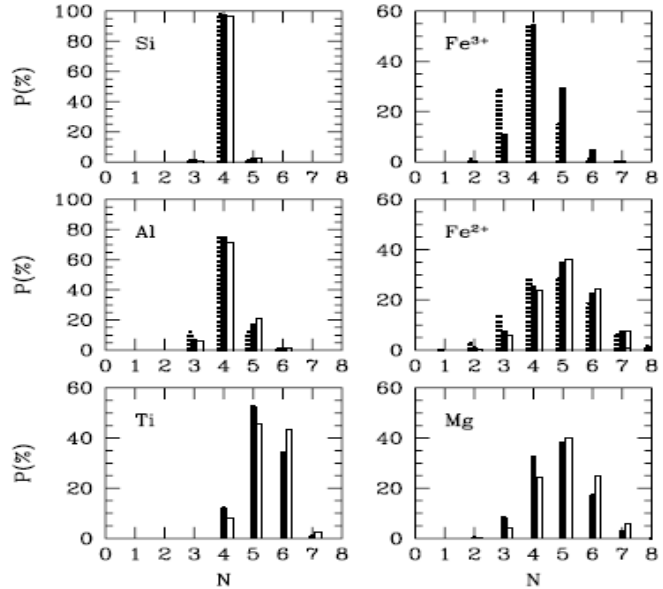
ALUMINO SILICATE GLASSES: GUILLOT AND SATOR'S POTENTIALS

- The interatomic potentials have been used to investigate other properties

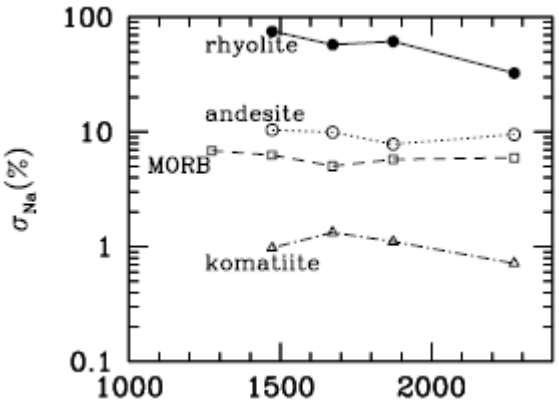
Molar volume vs. modifier concentration

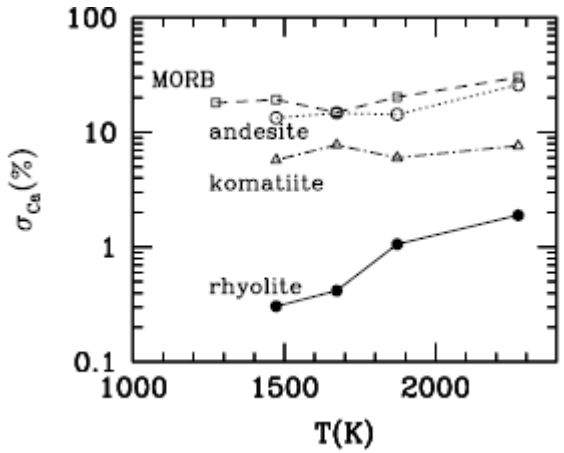


Distribution of local coordinations



Na and Ca contributions to the electrical conductivity





ALUMINO SILICATE GLASSES SIMULATED BY AIM POTENTIALS (Y. ISHII ET AL.)

- AIM (Aspherical Ion Model) potentials are used to simulate sodium alumino silicate glasses: ion shapes are introduced in the potentials

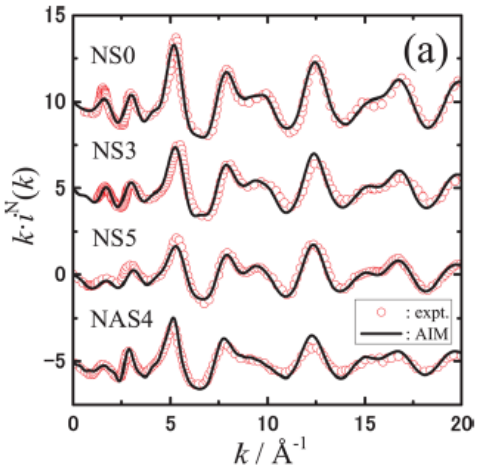
$$\phi^{\mathrm{rep,AIM}} = \sum_{i\in\mathrm{cation}} \sum_{j\in\mathrm{O}} [A^{ij} \exp(-a^{ij}\rho_{ij}) + B^{ij} \exp(-b^{ij}\rho_{ij})] + \sum_{i\in\mathrm{cation}} \sum_{j\in\mathrm{O}} C^{ij} \exp(-c^{ij}r_{ij}) + \sum_{i\in\mathrm{O}} \sum_{j\in\mathrm{O},i<j} A^{ij} \exp(-a^{ij}r_{ij}) + \sum_{i\in\mathrm{O}} [D\{\exp(\beta\delta\sigma_i) + \exp(-\beta\delta\sigma_i)\} + \{\exp(\zeta^2|\nu_i|^2) - 1\}]$$

$$\rho_{ij} = r_{ij} - \delta\sigma_i - \delta\sigma_j - \frac{1}{r_{ij}}\mathbf{r}_{ij}\cdot(\boldsymbol{\nu}_i - \boldsymbol{\nu}_j)$$

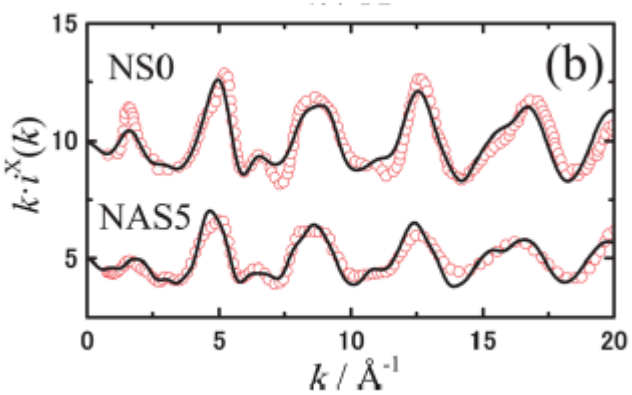
With $\delta\sigma_i$ a deviation from the ionic radius and v_i the distorsion of the dipolar shape

- Validation of the potentials on different structural characteristics: S(Q)

Neutron structural factors



X-Ray structural factors

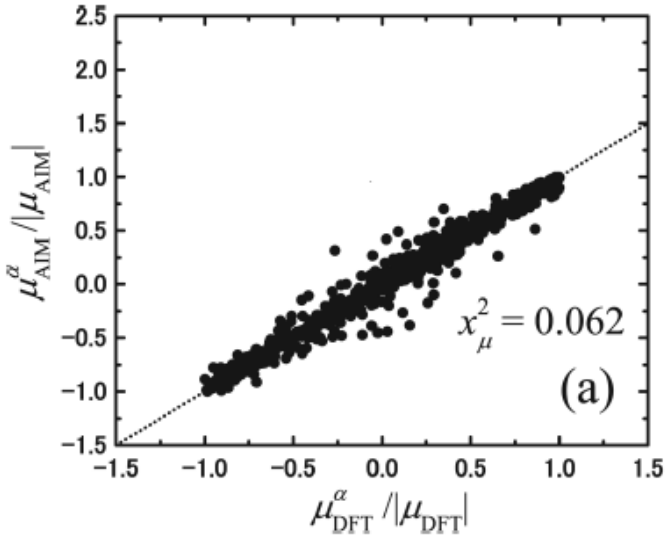


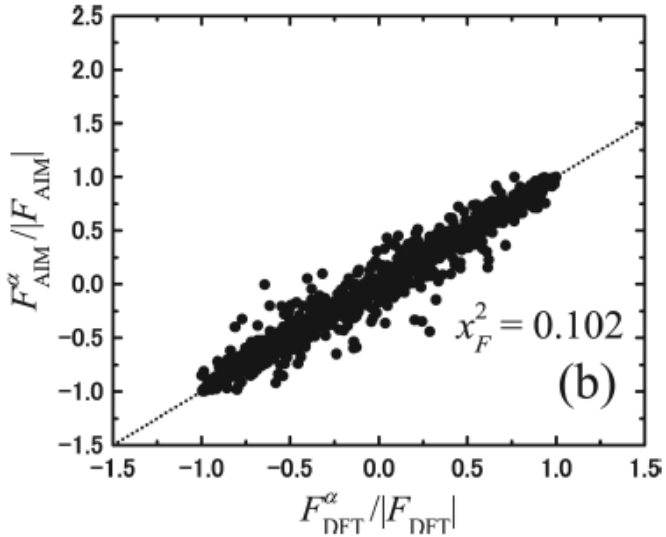
Y. Ishii, M. Salanne, T. Charpentier, K. Shiraki, K. Kasahara, N. Ohtori, J. Phys. Chem. C 120 (2016) 24370

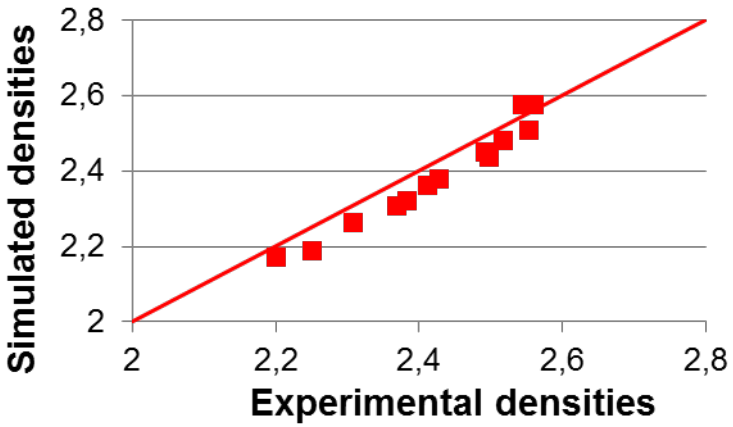
ALUMINO SILICATE GLASSES SIMULATED BY AIM POTENTIALS (Y. ISHII ET AL.)

- Validation of the potentials on different structural characteristics

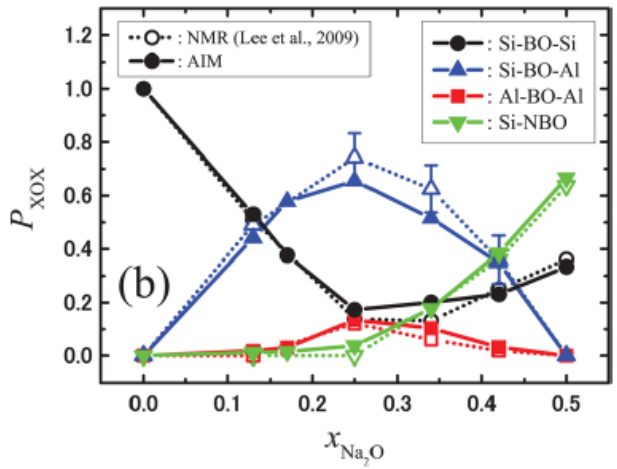
Comparison between MD and ab initio







Distribution of the X-O and X-O-Y bonds

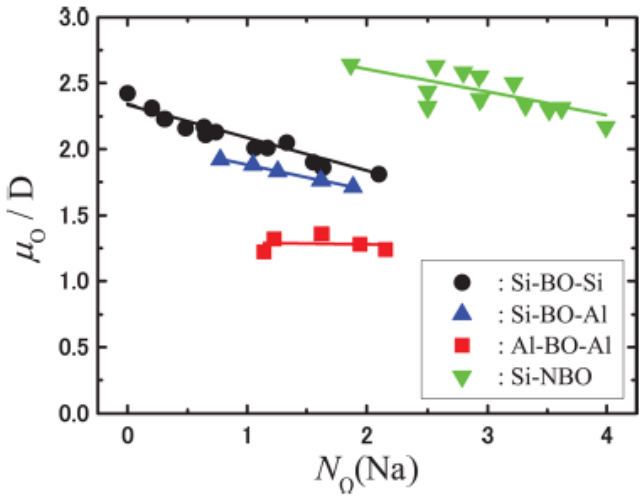


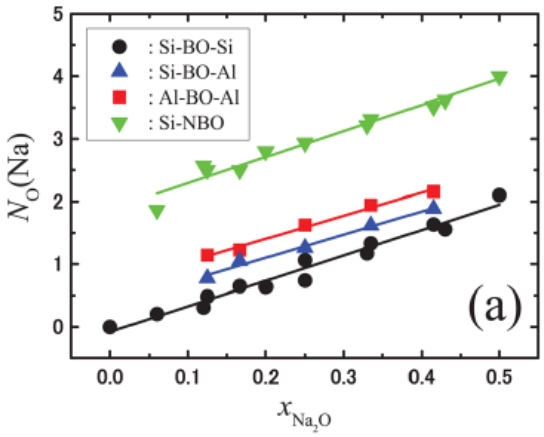
Y. Ishii, M. Salanne, T. Charpentier, K. Shiraki, K. Kasahara, N. Ohtori, J. Phys. Chem. C 120 (2016) 24370

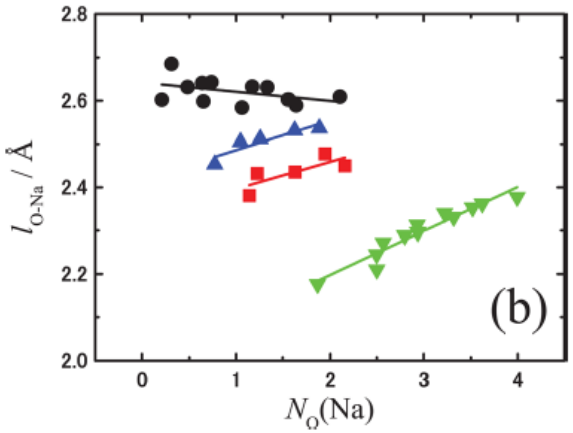
ALUMINO SILICATE GLASSES SIMULATED BY AIM POTENTIALS (Y. ISHII ET AL.)

- The AIM potentials can be used to investigate the glassy structures

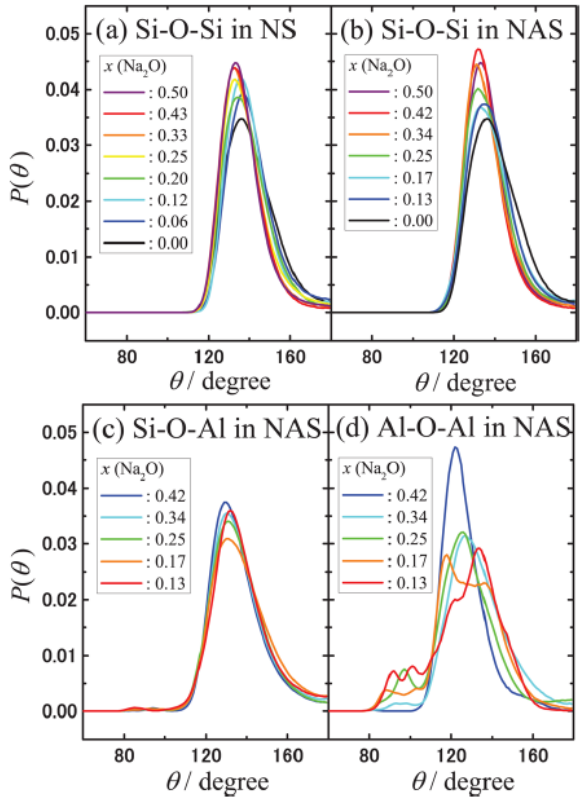
Dipole moments on O







Local environments around Na



Distribution of local angles

Y. Ishii, M. Salanne, T. Charpentier, K. Shiraki, K. Kasahara, N. Ohtori, J. Phys. Chem. C 120 (2016) 24370

SIO_2-AL_2O_3-NA_2O-CAO: COMPARISON OF DIFFERENT POTENTIALS

- Different interatomic potentials have been compared (Buckingham type + three body terms): Guillot-Sator, Matsui, Deng-Du, Pedone, Ha-Garofalini

- Nine different glass compositions have been simulated

Series	Notation	du verre	SiO_2	Na_2O	Al_2O_3	CaO
	VP-3	CNA 58.36.6	65.6	27.1	7.4	0.0
1	VP0	CNA 58.22.6	59.9	19.8	6.6	13.7
	VP1	CNA 58.10.6	58.0	9.1	6.5	26.4
	VP2	CNA 58.0.6	56.5	0.0	7.4	36.1
	VP-NBO10	CNA 55.21.10	55.6	20.3	10.3	13.9
2	VP-NBO20	CNA 49.19.20	48.7	18.0	20.7	12.6
	VP-NBO28	CNA 44.17.28	43.9	16.5	28.3	11.3
	VP-NBO32	CNA 42.16 .32	41.4	15.3	31.8	11.3
3	CASN	CASN 60.10.10	60	10	10	20

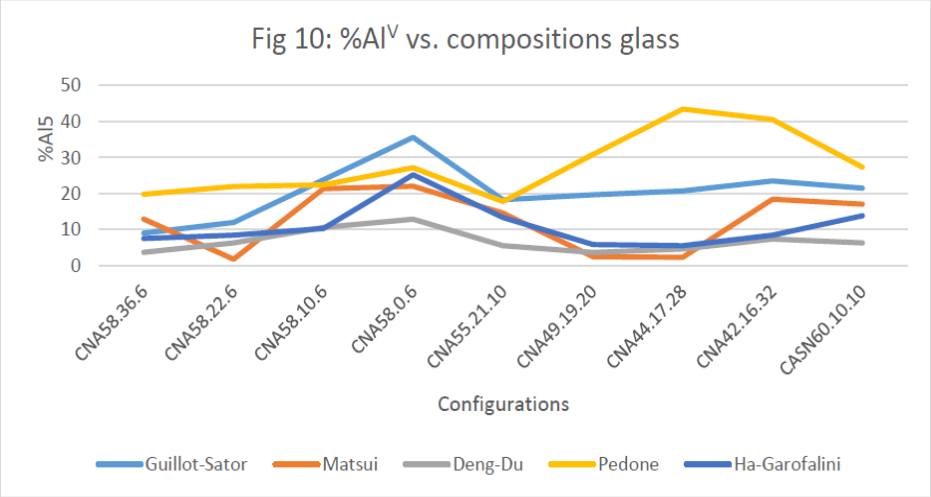
- The potentials have been tested on different criteria:
  - Densities
  - Presence or absence of Si^V and Al^V (not expected in these glasses)
  - NMR spectra on one composition
  - X-Ray S(Q) on one composition
  - Relative attraction between Si-Al:NBO and Na-Ca:Al

SIO_2-AL_2O_3-NA_2O-CAO: COMPARISON OF DIFFERENT POTENTIALS

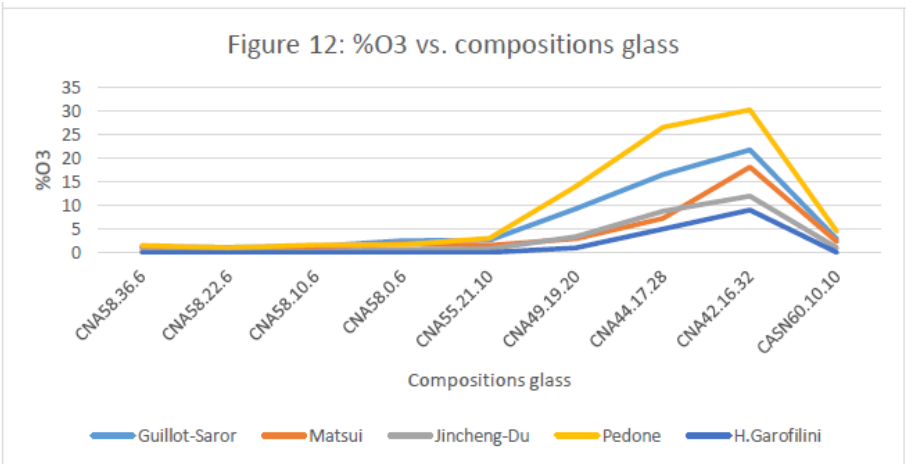
- Densities:

Glasses	Guillot-Sator	Matsui	Deng-Du	Pedone	Ha.Garofalini
R_x (%)	10.65 %	7.36 %	4.46 %	12.04 %	-11.30 %

- 5 coordinated Al

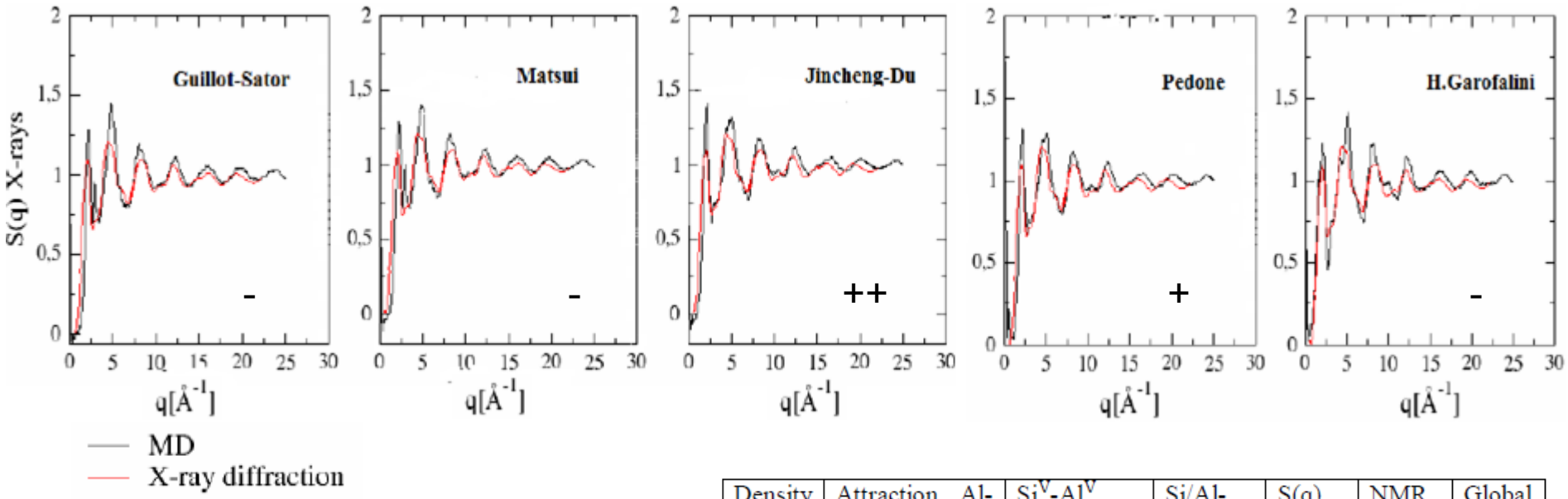


- 3 coordinated O



SiO_2-AL_2O_3-NA_2O-CAO: COMPARISON OF DIFFERENT POTENTIALS

- X Ray S(Q) for $0.67SiO_2 – 0.08Al_2O_3 – 0.18Na_2O – 0.07CaO$:



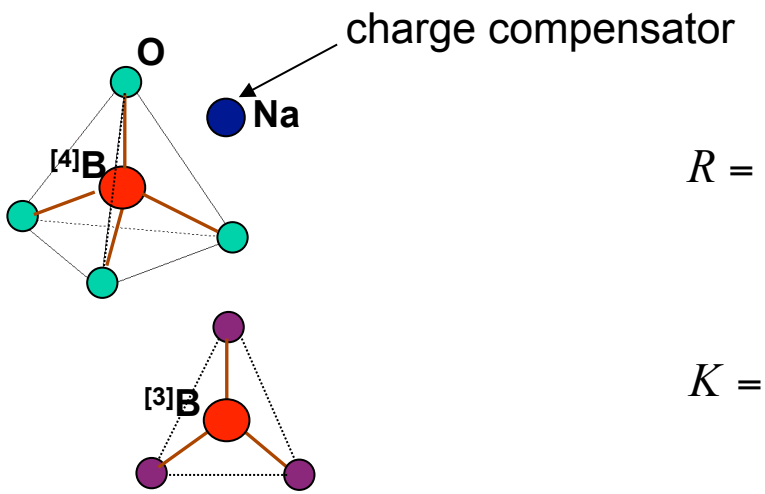
Significant differences can be observed between the potentials depending on the composition

	Density	Attraction Al-Na/Ca	Si^V-Al^V	Si/Al-NBO	S(q)	NMR	Global
Guillot-Sator	- -	-	- -	+	-	-	-
Matsui	+	+ +	- -	+	-	-	0
Deng-Du	+ +	+	+ +	+	+ +	+	+ +
Pedone	- -	- -	- -	+	+	- -	-
Ha-Garofalini	- -	+ +	+ +	+	-	+	+

BOROSILICATE GLASSES

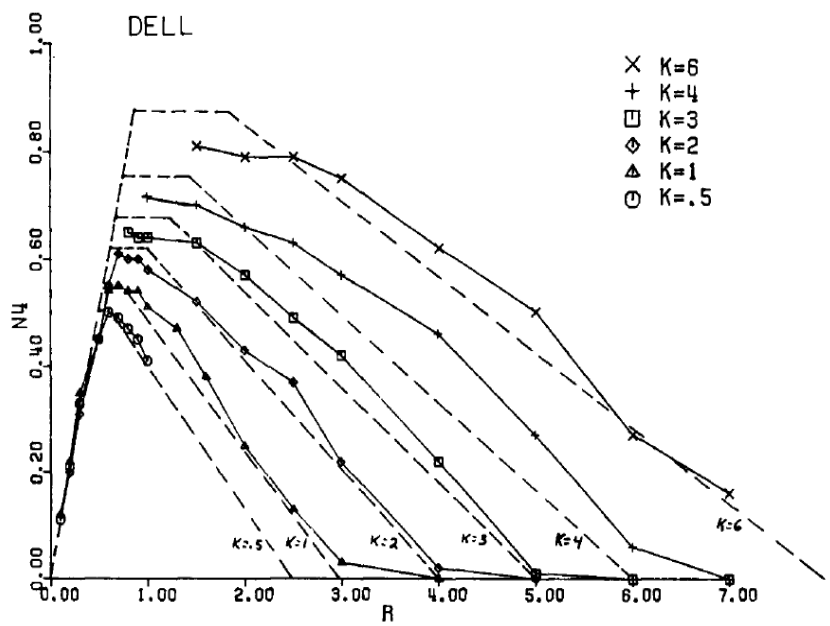
- Currently, several teams are working to develop precise potentials for borosilicate glasses

- Borosilicate glasses are more difficult to simulate than alumino silicate glasses because of:
  - Boron speciation
  - Non linear dependence of the B coordination versus the $K=[SiO_2]/[B_2O_3]$ and $R=[Na_2O]/[B_2O_3]$ ratios
  - When Al and B are present, the Na ions compensate Al in priority before B



$$R = \frac{[Na_2O]}{[B_2O_3]}$$

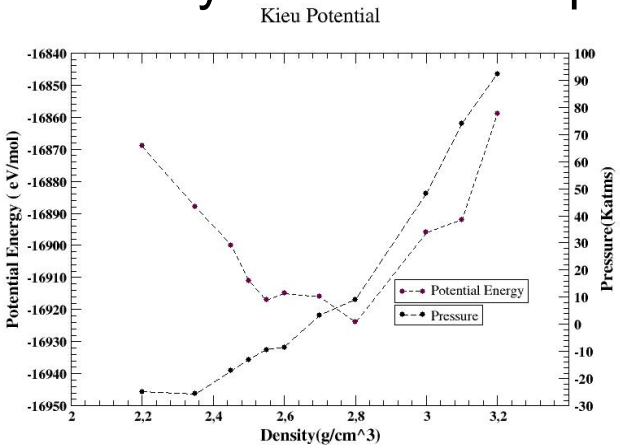
$$K = \frac{[SiO_2]}{[B_2O_3]}$$

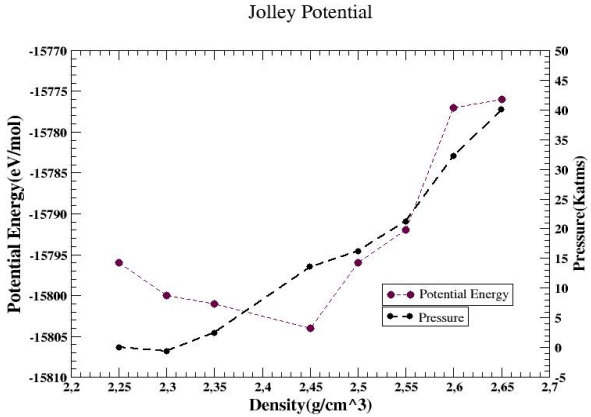


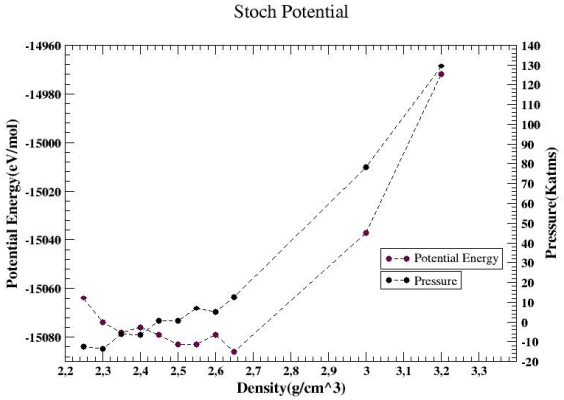
W.J. Dell, P.J. Bray, S.Z. Xiao, J. Non-Cryst. Solids 58 (1983) 1

BOROSILICATE GLASSES: SEVERAL BUCKINGHAM TYPE POTENTIALS ARE AVAILABLE

- We have recently compared three different Buckingham type potentials found in the literature to simulate a SiO_2-B_2O_3-Na_2O glass: Kieu's, Jolley's and Stoch's potentials

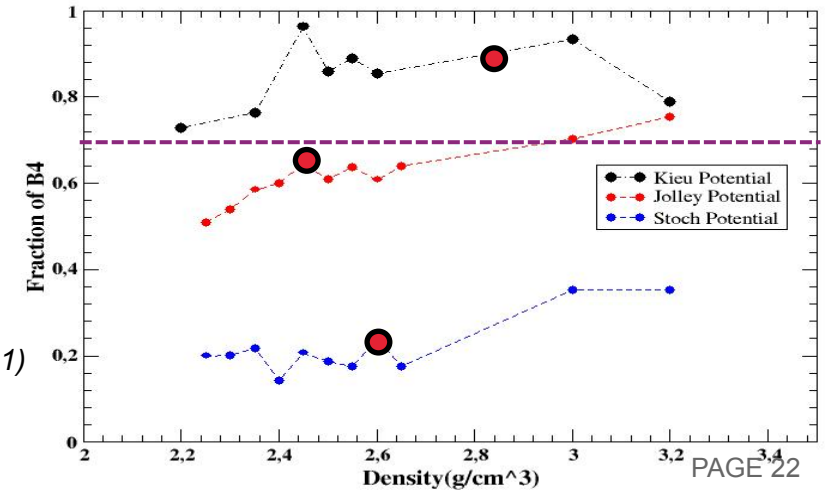






70%SiO_2 – 15%B_2O_3 – 15%Na_2O

The predicted B coordination is equal to 3.72 (Dell & Bray model)



L.-H. Kieu, J.-M. Delaye, L. Cormier, C. Stolz, J. Non-Cryst. Solids 357 (2011) 3313

A.F. Alharbi, K. Jolley, R. Smith, A.J. Archer, J.K. Christie, NIMB 393 (2017) 73

P. Stoch, A. Stoch, J. Non-Cryst. Solids 411 (2015) 106

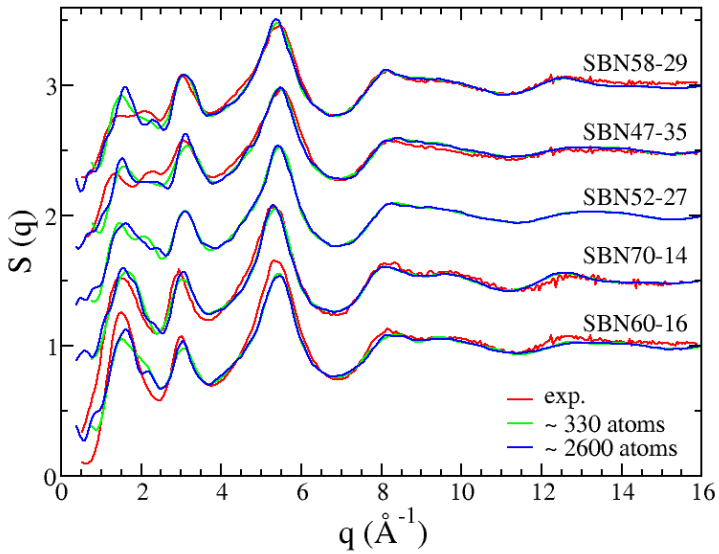
DEVELOPMENT OF A PIM POTENTIAL FOR SiO_2-B_2O_3-NA_2O SYSTEMS

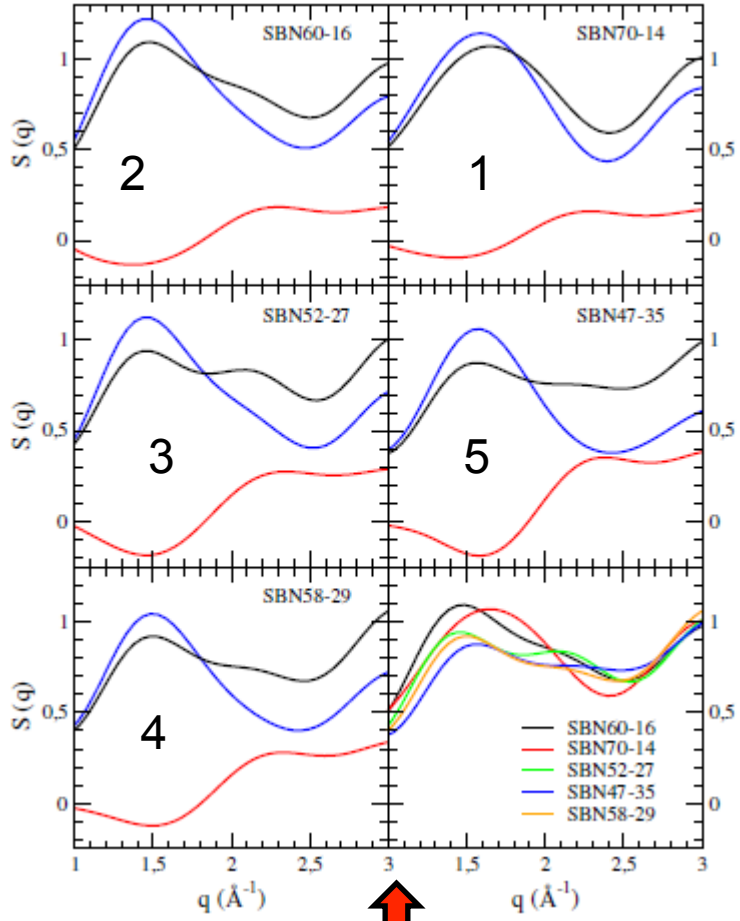
F. Pacaud, J.-M. Delaye, T. Charpentier, L. Cormier, M. Salanne, J. Chem. Phys. 147 (2017) 161711

- A PIM type potential has been developed to simulate SiO_2-B_2O_3-Na_2O in the liquid and glassy states

Simulated glasses

% mol.	SiO_2	B_2O_3	Na_2O	R	K
SBN60-16	59,6	23,9	16,5	0,69	2,49
SBN70-14	70,0	15,5	14,4	0,93	4,52
SBN52-27	52,5	20,7	26,8	1,29	2,53
SBN47-35	47,0	18,5	34,5	1,86	2,54
SBN58-29	58,0	13,0	29,0	2,23	4,46

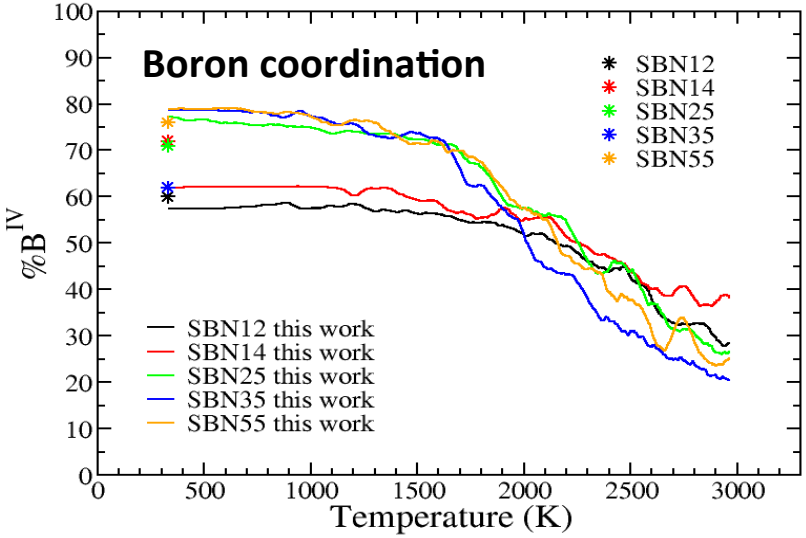


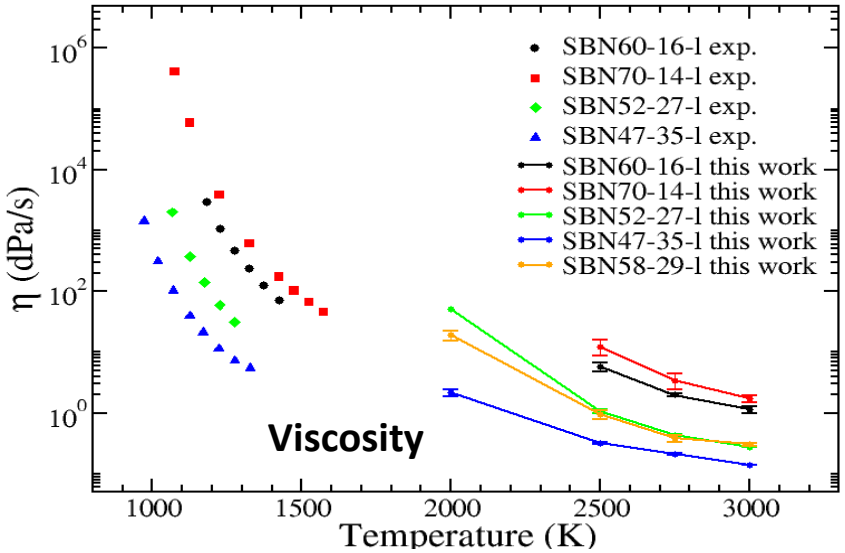


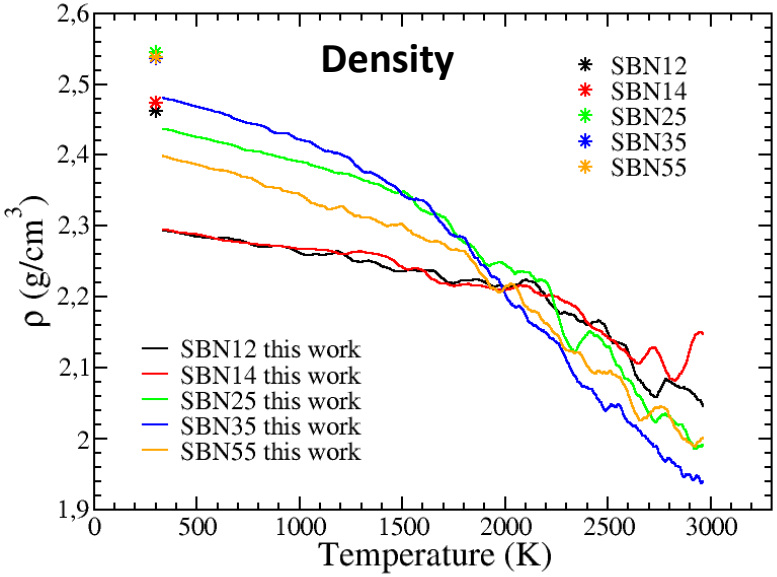
Partial structure factors

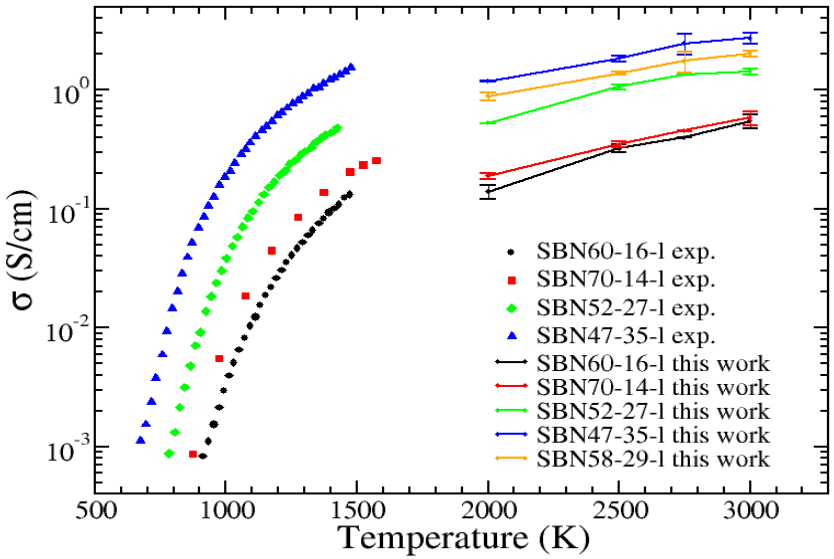
Total neutron structure factors

DEVELOPMENT OF A PIM POTENTIAL FOR SiO_2-B_2O_3-NA_2O SYSTEMS: LIQUID STATE





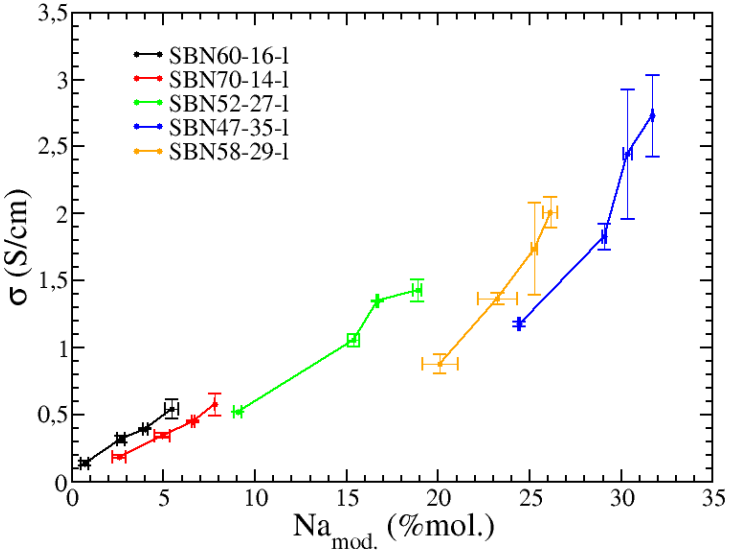




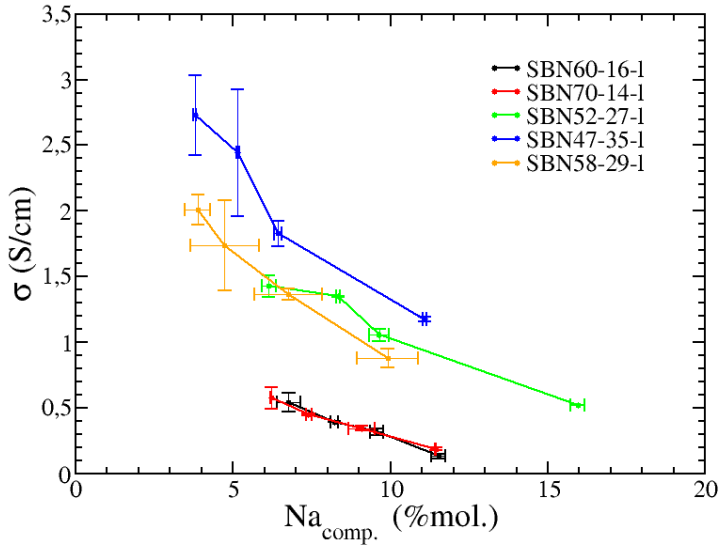
Electrical conductivity

DEVELOPMENT OF A PIM POTENTIAL FOR SiO_2-B_2O_3-NA_2O SYSTEMS: NA DIFFUSION

Electrical conductivity



vs. Na in a modifier role



vs. Na in a charge compensator role

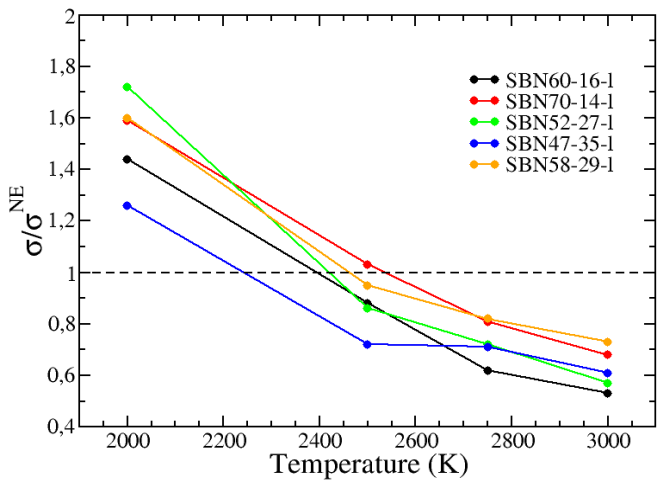
Nernst-Einstein formulae

$$\sigma^{NE} = \frac{\beta e^2}{V} \lim_{t\to\infty} \frac{1}{6t} \sum_{\alpha} N_\alpha q_\alpha^2 \left\langle \left| \delta r_{i,\alpha}(t) \right|^2 \right\rangle$$

Complete formulae

$\sigma / \sigma^{NE} > 1$ → cooperative mechanisms

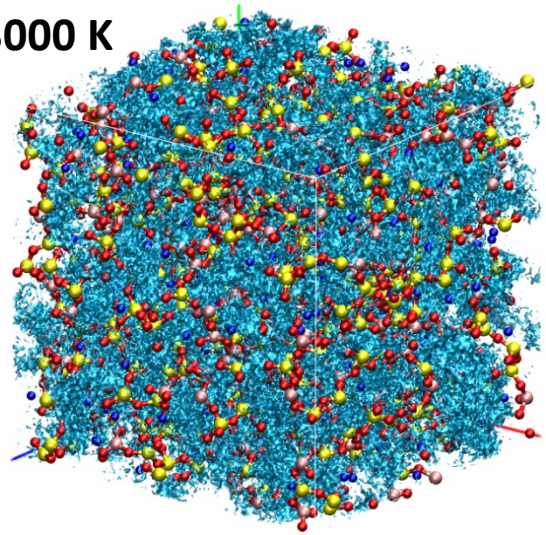
$$\sigma = \frac{\beta e^2}{V} \lim_{t\to\infty} \frac{1}{6t} \left\langle \left| \sum_{\alpha} q_\alpha \sum_{i\in\alpha} \delta r_{i,\alpha}(t) \right|^2 \right\rangle$$



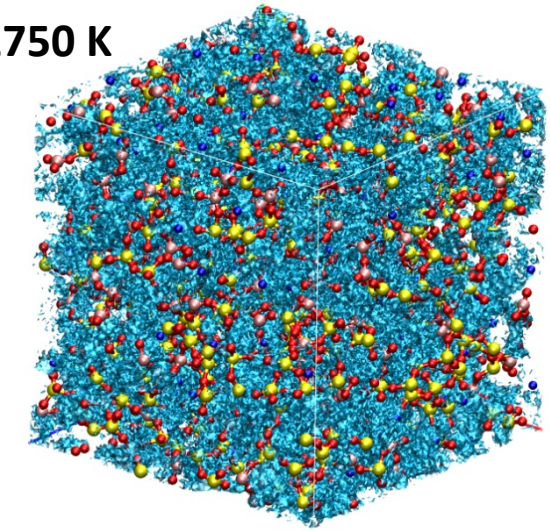
DEVELOPMENT OF A PIM POTENTIAL FOR SiO_2-B_2O_3-NA_2O SYSTEMS: NA DIFFUSION

Glass $70SiO_2 – 15.5B_2O3 – 14.4Na_2O$

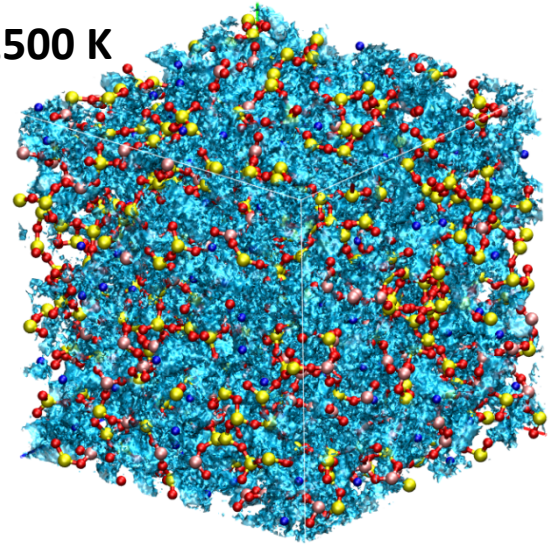
3000 K



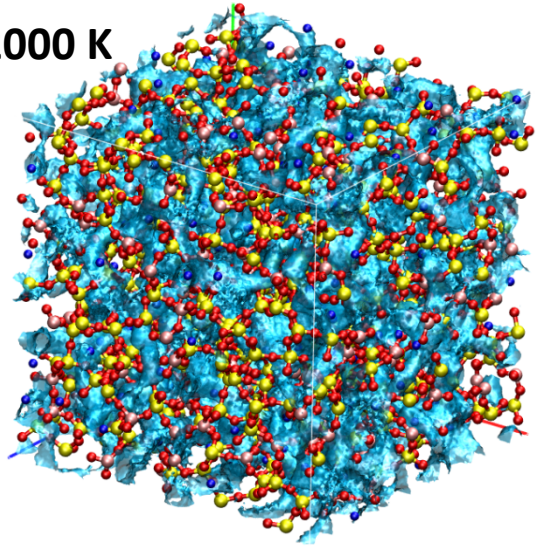
2750 K



2500 K



2000 K



O

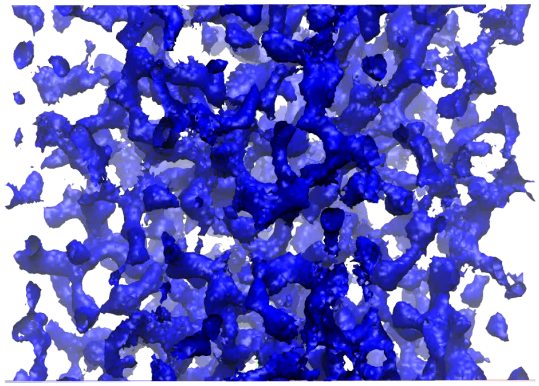
Si

B

Na

Crossed regions

Diffusion pockets emerged when the temperature decreases



CONCLUSIONS - PERSPECTIVES

- A large activity around silicate glass simulations: several new potentials have been proposed recently

- Several methods to fit the interatomic potentials: on experimental or on ab initio data

- Potentials are more and more complex: Buckingham type, Polarizable Ion Model, Aspherical Ion Model

- Difficult to find transferable potentials validated on large composition domains or thermodynamic conditions: the fit has to be done depending on the target of the study

CONCLUSIONS - PERSPECTIVES

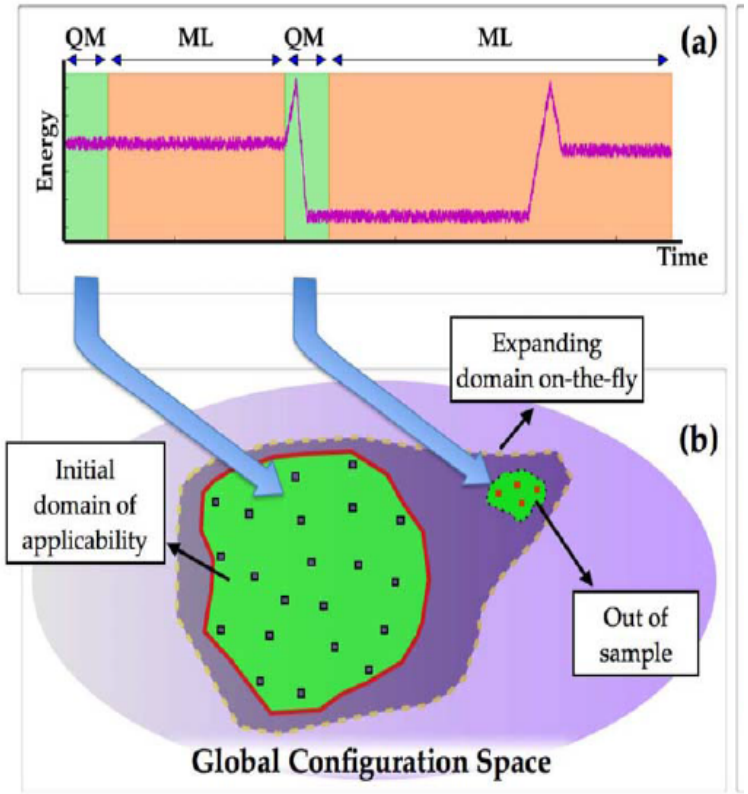
- Future developments

Machine learning

During a typical MD trajectory, a system is largely exploring similar configurations, and new features or events are encountered rarely,

It is fair to assume that similar configurations will have similar properties (such as energies, atomic forces, etc.). If a robust numerical representation of the configurations can be developed, a quantitative measure of (dis)similarity of configurations can be defined, which can then be mapped to (dis)similarities between properties via a learning algorithm.

When a completely new configuration or event is encountered, a decision has to be made to switch back from ML to QM.



V. Botu, R. Ramprasad, Int. J. Quantum Chem. 115 (2015) 1074

For each local environment around an atom, a set of fingerprints is calculated and the forces is evaluated from the available dataset

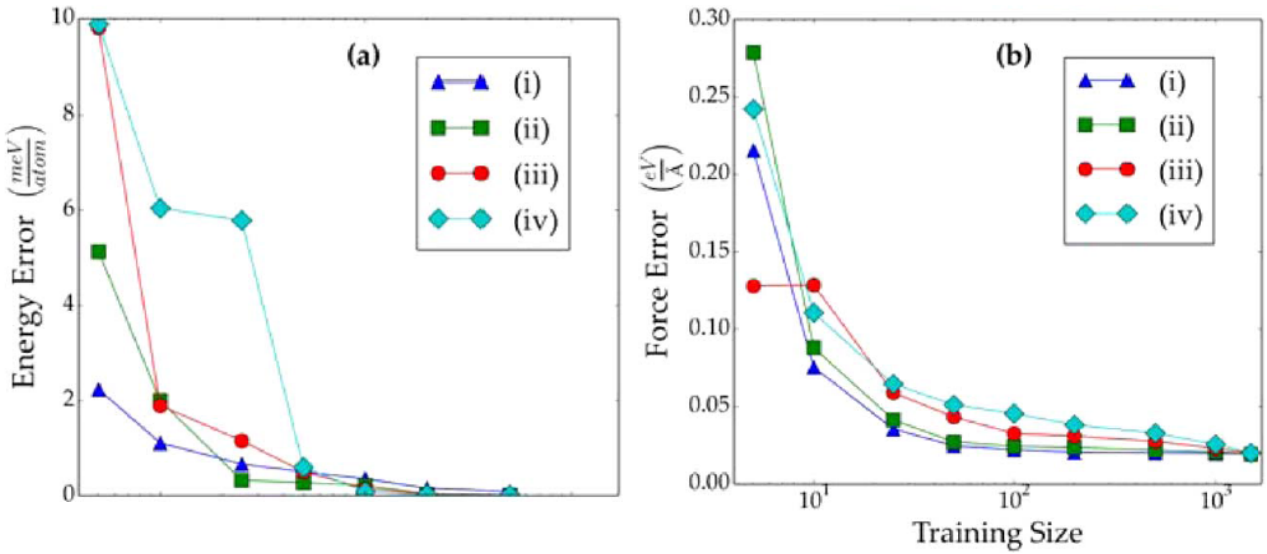
$$P_u = \sum_v \alpha_v e^{-\frac{1}{2}\left(\frac{|d_{uv}|}{\sigma}\right)^2}$$

If a new local environment is met, the dataset is completed by an ab initio calculation

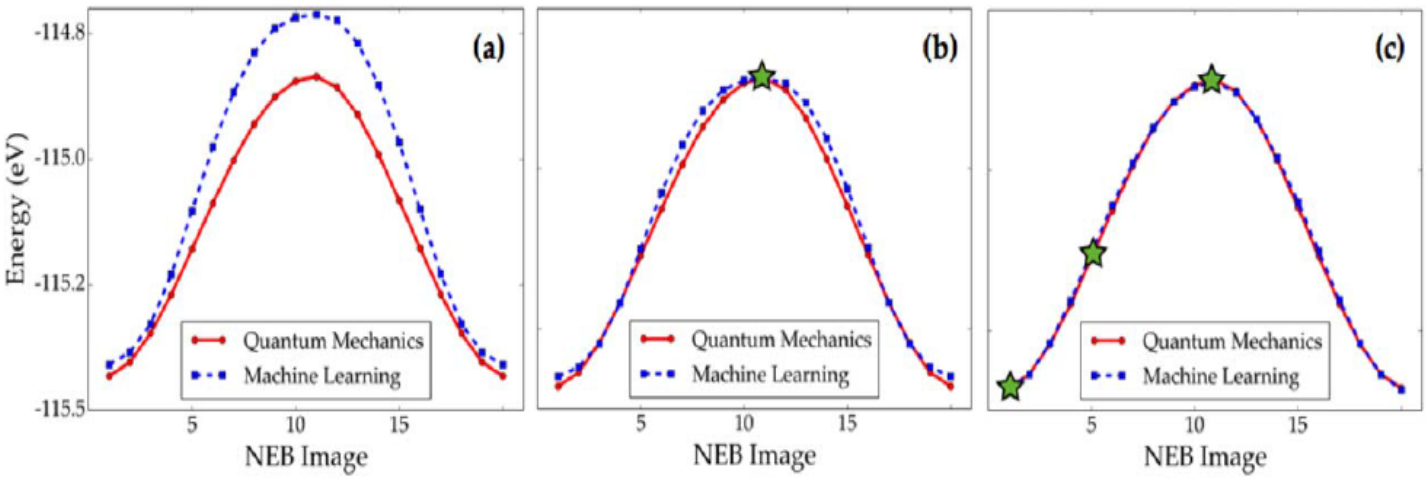
CONCLUSIONS - PERSPECTIVES

- Example on Al

V. Botu, R. Ramprasad, Int. J. Quantum Chem. 115 (2015) 1074



Error on the energy and forces vs. the training size



Comparison between MD and ab initio for the migration of an Al atom towards a vacancy

CONCLUSIONS - PERSPECTIVES

- Future developments

Y. Yu, B. Wang, M. Wang, M. Bauchy, Int. J. Appl. Glass Sci. 8 (2017) 276

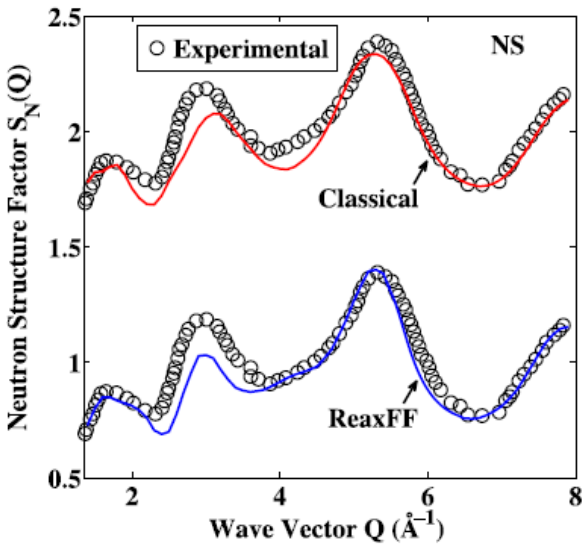
ReaxFF

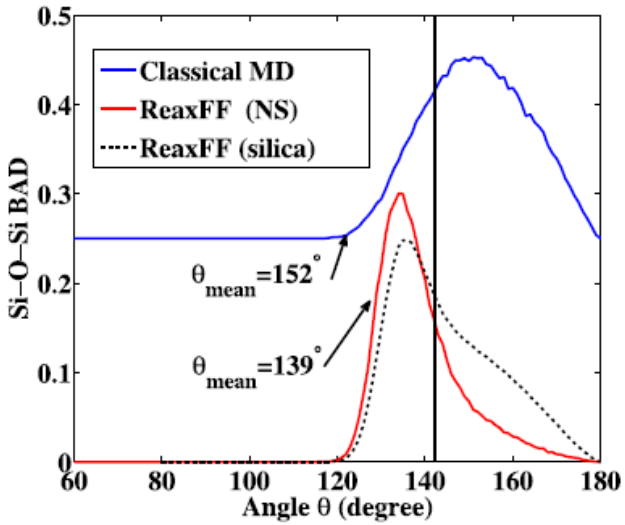
ReaxFF method is slower than classical MD but can predict more precise glassy structures

The calculation of the ionic forces is based on the computation of bond orders

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{under}} + E_{\text{over}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{torsion}} + E_{\text{conj}}$$

For the $30Na_2O - 70SiO_2$ glass, the ReaxFF structure is more precise than the MD structure (Teter potential)





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