3rd Summer School on nuclear and industrial glasses for energy transition

Modeling Approaches

Short introduction

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What are the needs in glass alteration modeling?

NEEDS	NUMERICAL METHODS
Understanding **the elementary mechanisms** (hydrolysis, (inter)diffusion, structural relaxation, solvation of ions, adsorption, pH effect, …)	Atomistic scale (ab initio, ReaxFF, classical molecular dynamics)
Determining **characteristic quantities** (hydrolysis energies, diffusion coefficients, surface energies, …)	Atomistic scale (ab initio, ReaxFF, classical molecular dynamics)
Reproducing the **global alteration behavior**, the ripening of the gel … (and extrapolate for the long-term)	More macroscopic approach at the atomic scale (Monte Carlo), or a continuous scale (Phase Field method, GRAAL)

Presentation by J. Du

My 2nd presentation

Work conducted by T. Boutin / A. Cartalade

NUMERICAL METHODS	LIMITS
Atomistic scale (ab initio, ReaxFF, classical molecular dynamics)	**Size of the systems, duration of the calculations**, availability and precision of the force fields (currently no ReaxFF or classical force fields for hydrated borosilicate glasses but the dry ISG glass can be simulated)
More macroscopic approach at the atomic scale (Monte Carlo), or a continuous scale (Phase Field method, GRAAL)	Physics is simplified – Need to **validate the basic assumptions** - Need to ensure the robustness of long-term extrapolation

Presentation by P. Frugier

+ Global Descriptors + Machine Learning

Presentation by T. Charpentier

Four focuses on hot topics: New classical potentials
ReaxFF
Refined Monte Carlo approach
Machine Learning

A new tool for classical MD calculations

Coulombic potentials

$$U_{q_i-q_j}(r_{ij}) = \frac{q_i q_j}{r_{ij}} erfc\left(\frac{r_{ij}}{\beta}\right)$$

$$U_{q_{di}-q_j}(r_{ij}) = \frac{q_{di} q_j}{r_{ij}} erf\left(\frac{r_{ij}}{\sqrt{2}\xi_{ij}}\right) erfc\left(\frac{r_{ij}}{\beta}\right)$$

$$U_{q_i-q_{dj}}(r_{ij}) = \frac{q_i q_{dj}}{r_{ij}} erf\left(\frac{r_{ij}}{\sqrt{2}\xi_{ij}}\right) erfc\left(\frac{r_{ij}}{\beta}\right)$$

$$U_{q_{di}-q_{dj}}(r_{ij}) = \frac{q_{di} q_{dj}}{r_{ij}} erf\left(\frac{r_{ij}}{2\varepsilon_{ij}}\right) erfc\left(\frac{r_{ij}}{\beta}\right)$$

Repulsive and dispersive terms
Three body terms

$$U_{ij}^{rep}(r_{ij}) = A_{ij}^{rep} \frac{2 * \varepsilon_{ij}^{r}}{r_{ij}} erfc\left(\frac{r_{ij}}{2 * \varepsilon_{ij}^{r}}\right)$$

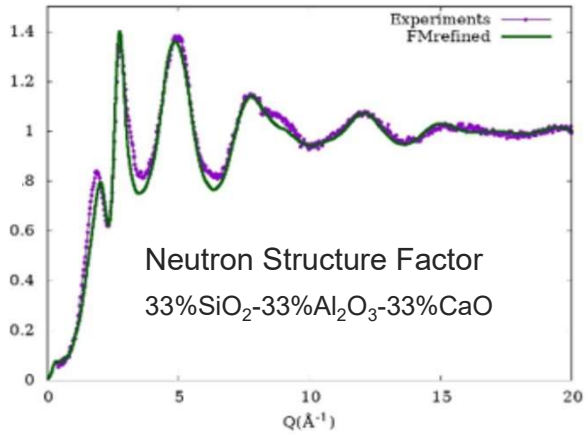
$$U_{ij}^{disp}(r_{ij}) = -\frac{C_{ij}^{6}}{r_{ij}^{6}}$$

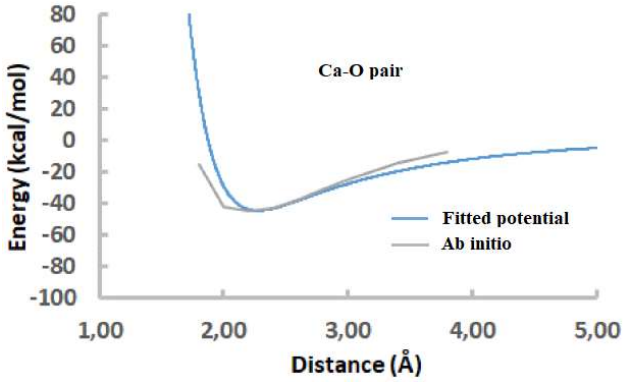
$$U_{ijk}^{thr} = \lambda_{ijk} exp\left(\frac{\gamma_{ij}}{r_{ij} - r_{ij}^{0}} + \frac{\gamma_{ik}}{r_{ik} - r_{ik}^{0}}\right)\left(cos\theta_{ijk} - cos\theta_{ijk}^{0}\right)^2$$

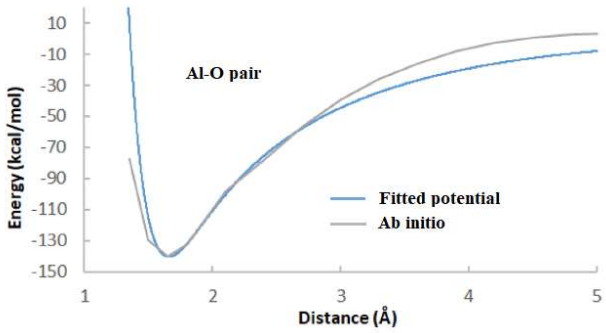
Diffuse Charge Reactive Potentials (DCRP)

T. S. Mahadevan and S. H. Garofalini, J. Phys. Chem. B, 2007, 111
T.S. Mahadevan et al., JNCS, 2022, 592

- Potentials developed for SiO_2+H_2O
→ Al_2O_3, CaO and Na_2O have been added.
- Fit on Structure Factors and ab initio calculations



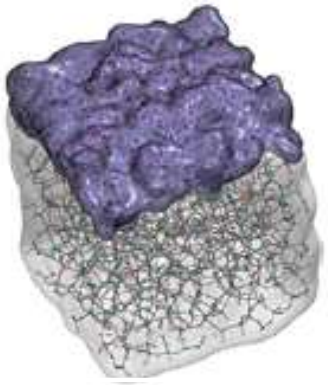


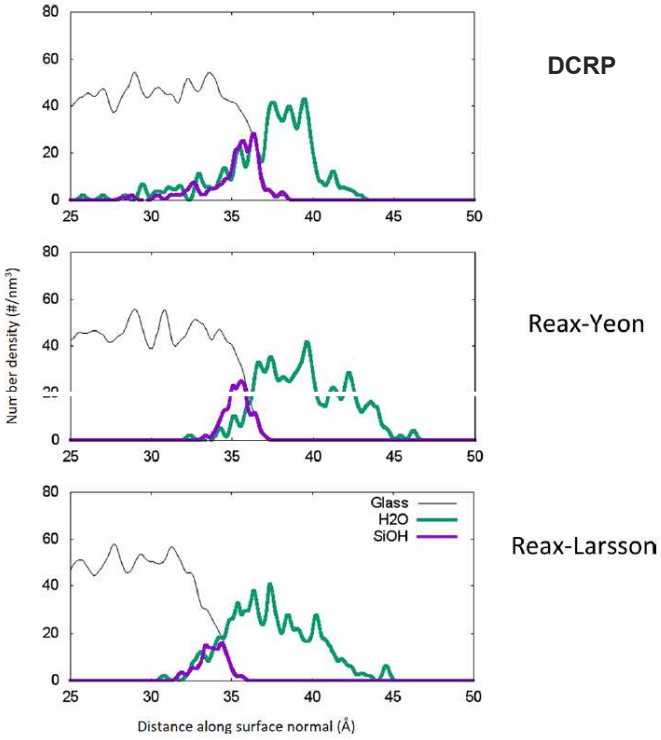


SiO_2-Al_2O_3-Na_2O-CaO + H_2O systems can now be simulated

A few examples of usage

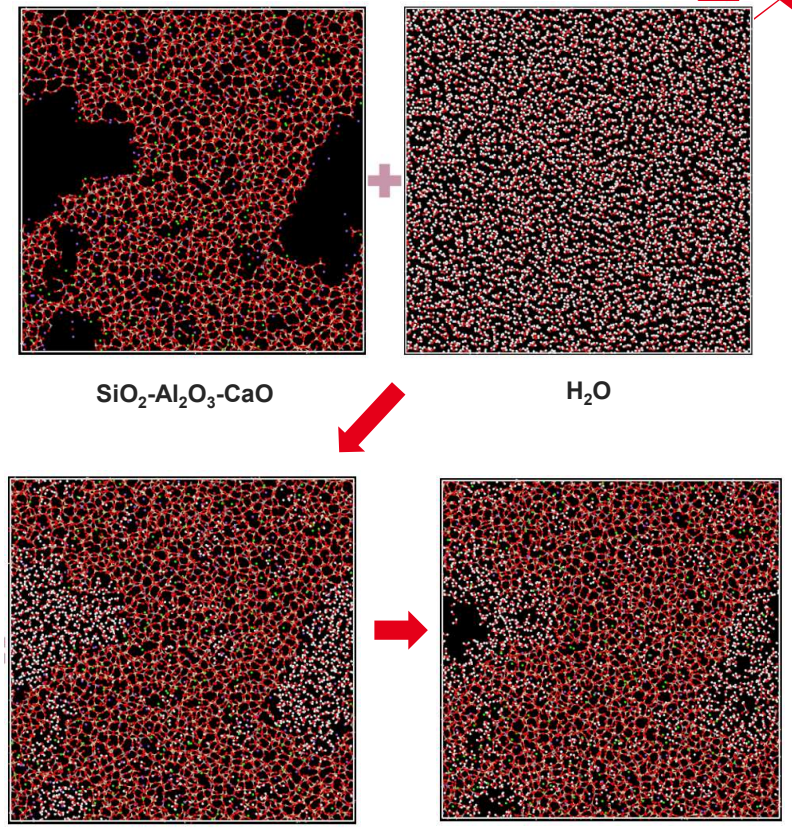
- A silica – H_2O interface is built *(T. Mahadevan, JPCC, 122 (2018) 9875)*
- The water penetration is studied





Water molecules and protons can penetrate within the bulk near the surface (it is not just a surface reaction)

- Possibility to build a model of gel
(M. Taron, PhD, Univ. Montpellier, 2022)

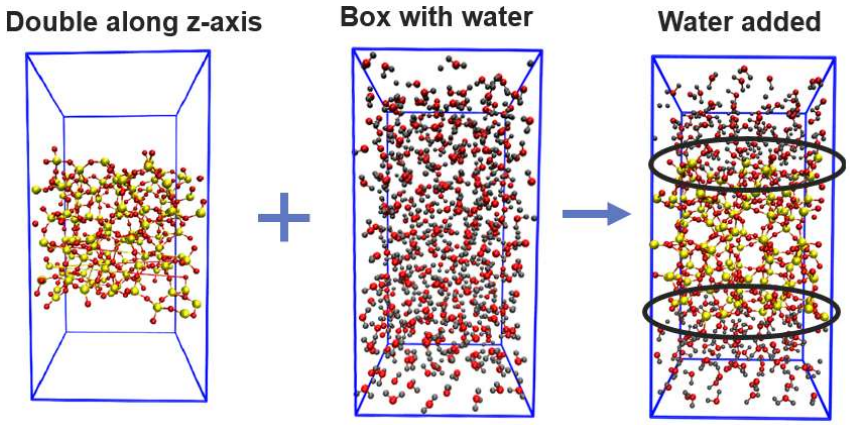


Water molecules migrate inside the bulk leaving empty spaces in the porosity

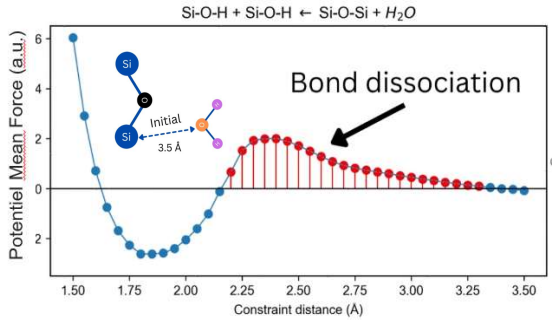
A few examples of usage

- A SiO_2-Al_2O_3-CaO – H_2O interface is built

(K. Damodaran, Acta Materialia 225 (2022) 117478)

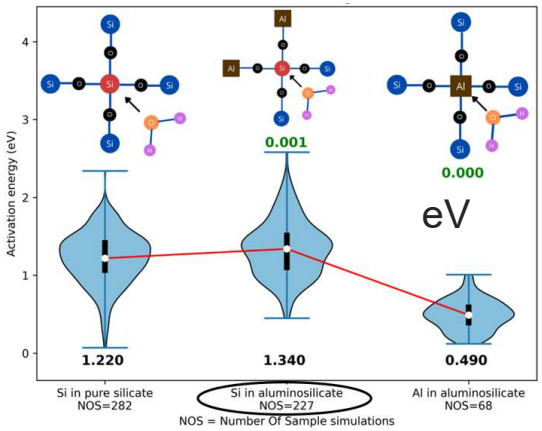


- Potential Mean Force method is used to estimate the hydrolysis energies



Glass name	SiO_2	Al_2O_3	CaO
Pure silica	100	-	-
Aluminosilicate	63.7	23.8	12.5

(wt%)



- Al is the easiest element to dissociate
- Si hydrolysis energy in SiO_2 < Si hydrolysis energy in SiO_2-Al_2O_3-CaO

(Strengthening effect of Al)

ReaxFF is increasingly being employed for simulating glass corrosion

- ReaxFF : Reactive Force Field
  - Many different energetical terms are considered

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}$$

$$BO_{ij} = \exp\left[p_{bo,1}\left(\frac{r_{ij}}{r_0}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3}\left(\frac{r_{ij}}{r_0}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5}\left(\frac{r_{ij}}{r_0}\right)^{p_{bo,6}}\right]$$ Bond order

  - The parameters are fitted on ab initio calculations and experiments (thermodynamic data, state equations, structures, diffusion …)

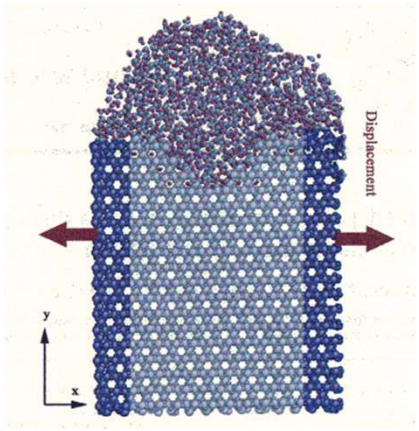
  - Meaning of the energetical terms
    - E_{over} : energy penalty in case of over coordination
    - E_{under} : energy penalty in case of under coordination
    - E_{val} : energy associated to the angular strains
    - E_{pen} : additional term to stabilize some specific bonds
    - E_{tors} : energy associated to the torsion
    - E_{conj} : energy associated to connexion between bonds
    - $E_{vdWaals}$: Van der Waals term
    - $E_{Coulomb}$: Coulombic term

A.C.T. van Duin, J. Phys. Chem. A, 105, 2001, 9396

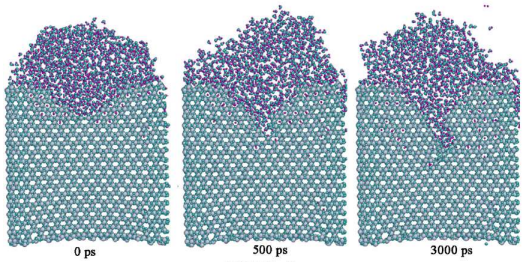
A few examples of usage

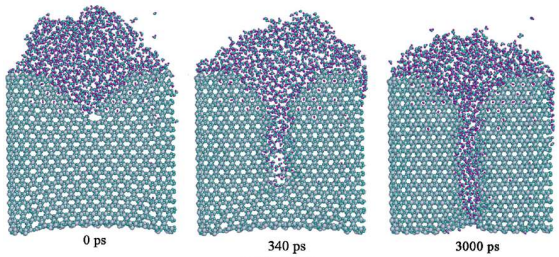
- ReaxFF : crack propagation in SiO_2 in the presence of water

Y.-A. Zhang, Comp. Mater. Sc., 82, 2014, 237

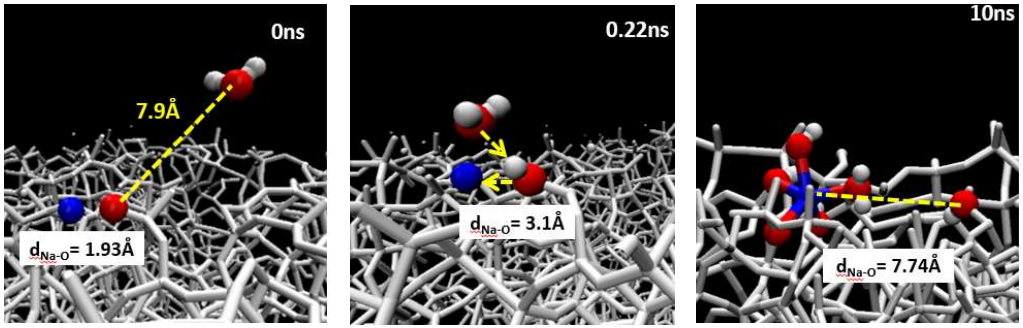


- The crack propagation is easier in the presence of H_2O
- Transition from stress corrosion behavior to brittle fracture behavior as the strain rate increases.



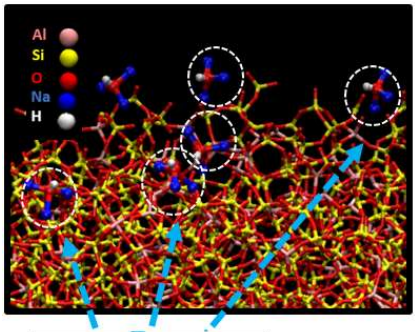


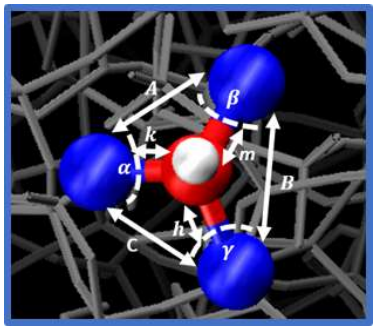
- ReaxFF: exchange mechanisms at a SiO_2-Al_2O_3-Na_2O glass - water interface



Na – H_2O interactions

H. Jabraoui et al., JPCC, 125, 2021, 27170



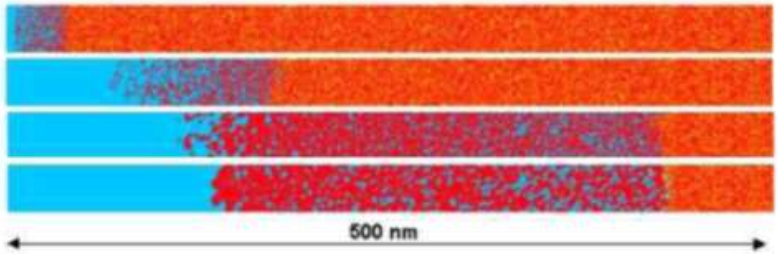


Na_3OH clusters with tetrahedral shape are observed

Improved Monte Carlo methods since the 1990s

SCK-CEN (M. Aertsens) : a solid network (SiO_2-Na_2O) in contact with a solution (diffusion in solution is considered)

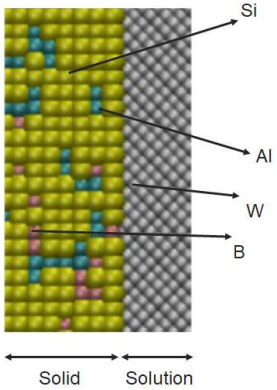
CEA (F. Devreux, A. Ledieu, C. Cailleteau): a solid network (SiO_2-B_2O_3-Na_2O) in contact with a solution (diffusion in solution is not considered)

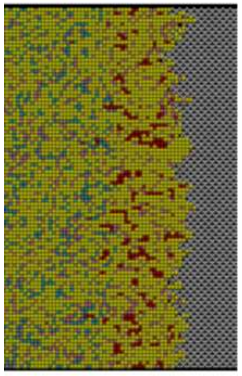


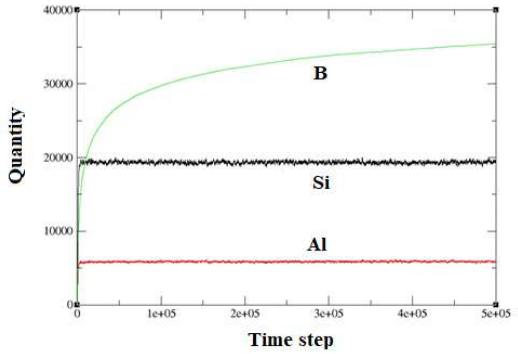
PNNL (S. Kerisit) : complexification of the solid network (SiO_2-Al_2O_3-B_2O_3-Na_2O) in contact with a solution (role of Al, role of boroxol rings)

CEA (J.-M. Delaye): two intertwined networks for the solid and the solution

- Possibility to simulate
  - gel ripening
  - residual alteration rate

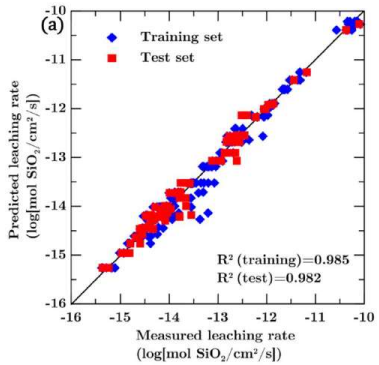




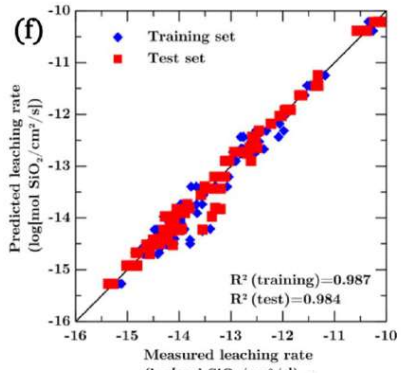


Machine Learning and global descriptors are increasingly employed for predicting glass corrosion

- Machine learning applied on a series of Na_2O-Al_2O_3-SiO_2 glasses (299 data points): alteration at 25°C, pH between 1 and 12, S/V between 1.4 and 2 cm^{-1}, Si release is followed
- Different methods tested: linear regression, support vector machine regression, random forest, artificial neural network
- Artificial neural network gives the best results



- Separating the data into low pH and high pH sets leads to better results

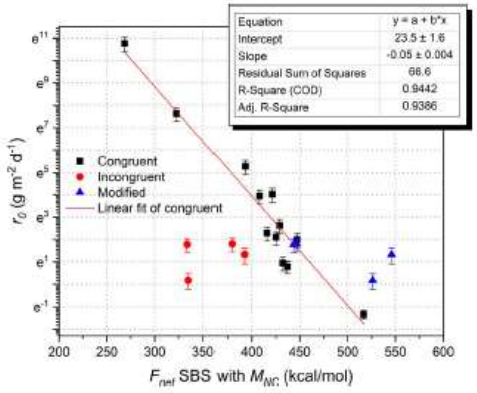


A. Krishnan et al., JNCS 487 (2018) 487

- Descriptors like TCT (Topological Constraint Theory) or Fnet have been tested to predict glass alteration
- Database : 20 borosilicate and aluminosilicate glasses: initial dissolution rates measured in a static mode at 90°C, pH=9

J. Du et al., JACS 104 (2021) 4445

$$F_{net} = \frac{1}{N} \sum_{X}^{cations} n_X \cdot CN_{XO} \cdot SBS_{XO} \cdot m_X$$

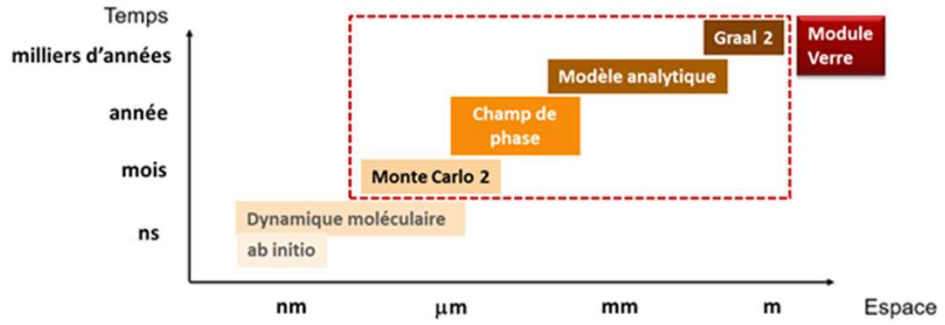


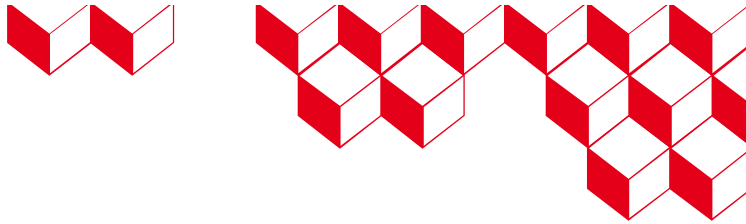
Conclusions

- Glass alteration can be simulated at the atomic scale (ab initio, classical molecular dynamics, Monte Carlo)
- Glass alteration can be simulated at a continuous scale (phase field approach, GRAAL)
- Machine learning and global descriptors can be used to predict the alteration behavior

But a coupling between these methods for the integration of the elementary mechanisms into a continuous scale modeling is missing → objective of the **TANGRAM** project: multi scale modeling of glass alteration

Toward an Integrative **A**pproach of **N**uclear **G**lass alteration in a **R**eactive environment from MultiscA**A**le **M**odelling





Thank You for

Your attention