



HAL
open science

Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study

Amaury Coste, Olivier Diat, Arnaud Poulesquen, Jean-François Dufrêche, Magali Duvail

► To cite this version:

Amaury Coste, Olivier Diat, Arnaud Poulesquen, Jean-François Dufrêche, Magali Duvail. Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study. 7th EuCheMS Chemistry Congress, Aug 2018, Liverpool, United Kingdom. <hal-02142629>

HAL Id: hal-02142629

<https://hal.science/hal-02142629v1>

Submitted on 28 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization



Investigation of the role of alkali cation in early stage of oligomerization in silicate fluids: a molecular dynamics study



amaury.coste @cea.fr

Amaury Coste^a, Olivier Diat^a, Arnaud Poulesquen^b, Jean-François Dufrière^a and Magali Duvail^a

^a Institute for Separation Chemistry in Marcoule (ICSM), UMR 5257 CEA – Université Montpellier - CNRS - ENSCM, BP 17171, F-30207 Bagnols-sur-Cèze

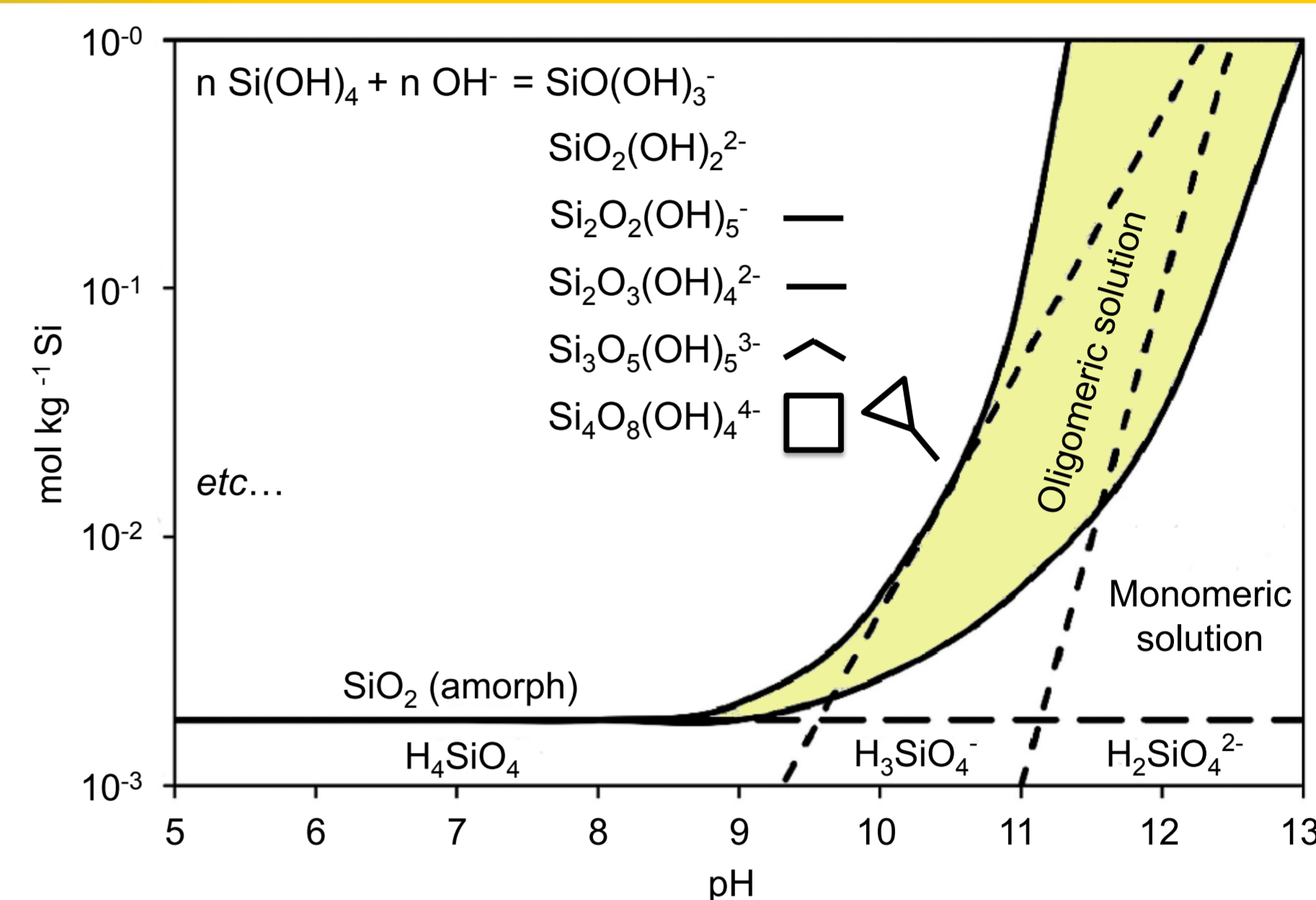
^b CEA, Nuclear Energy Division, Research DE2D (SEAD, LCBC) BP 17171, F-30207 Bagnols-sur-Cèze

Context



Ground stabilization on building site (Wöllner GmbH&Co.KG)

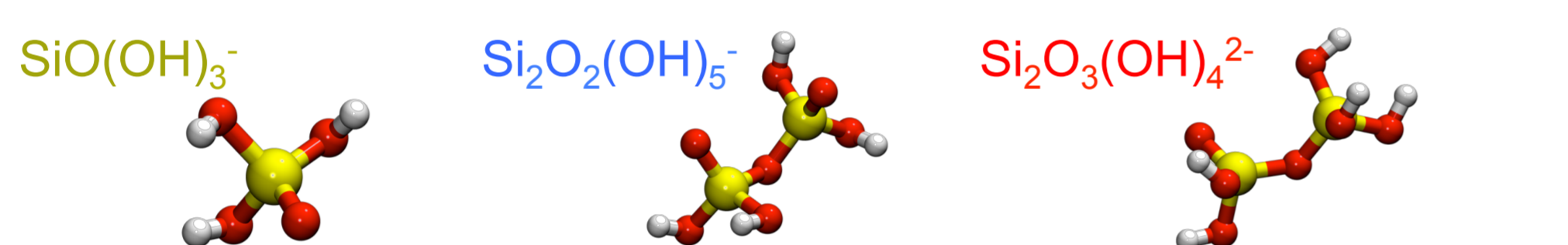
- Solutions of activation (= alkali media) of aluminosilicate are environmentally friendly and considered as green chemistry (used for ground stabilization, painting...)
- The formulation is complex since the parameters are various and numerous
- Understanding the ion-ion interactions for the oligomerization process where the nature and concentration of alkali drives the final properties of the gel [1]
- Molecular dynamics is a useful tool to fill the gap between theoretical and experimental studies
- Molecular dynamics allows the calculation of the structural and dynamical properties of the solutes in solution
- Effect of water, alkali and hydroxide are explicitly taking into account



Method

Classical Molecular Dynamics (MD)

- Molecular dynamics simulations using explicit polarization with AMBER14 [3]
- Development of a polarizable silicate force field for describing all the silicate oligomers by assembling neutral and anionic fragment (10 types of atom)
- MD simulations focused on 3 species:



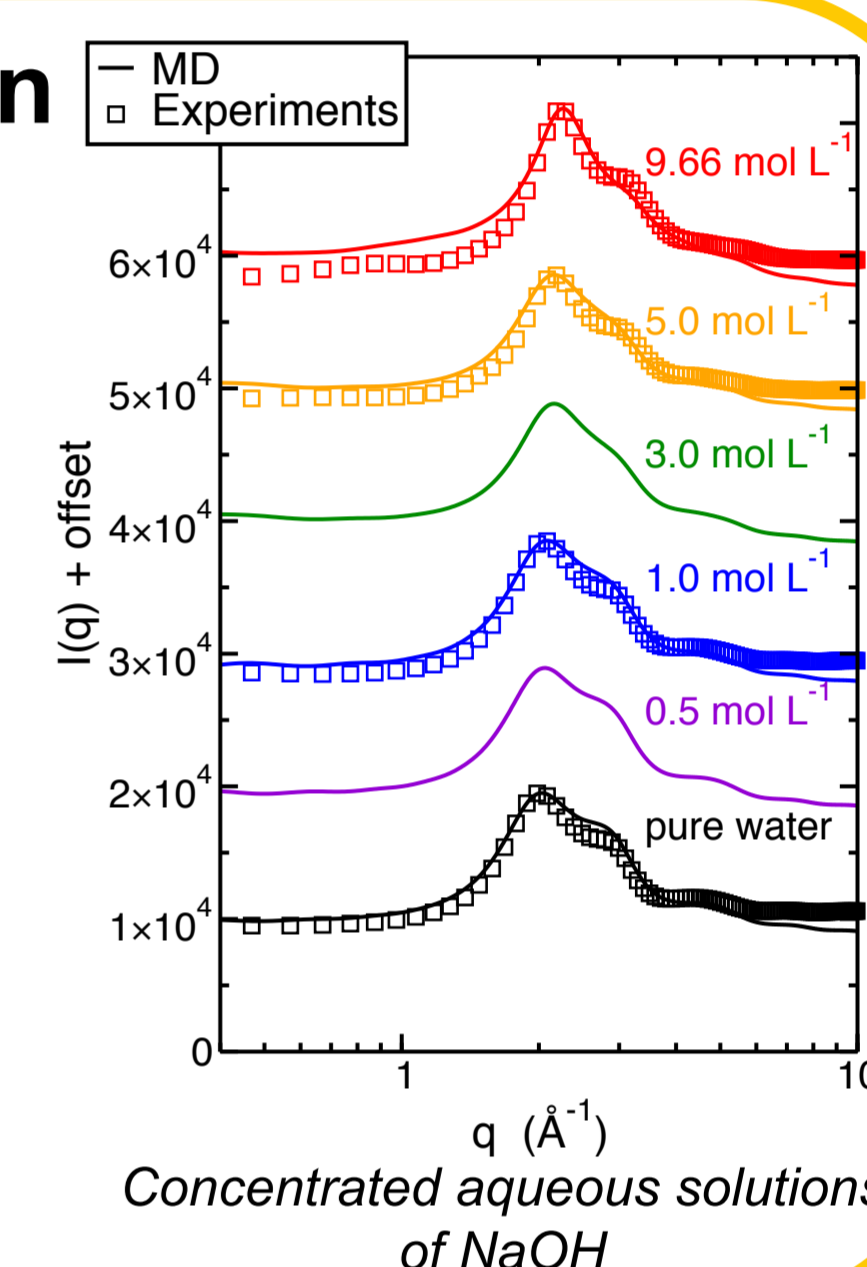
X ray scattering intensity from MD simulation

- Calculation of $I(q)$ from radial distribution functions

$$I(q) = \sum_{\alpha} \sum_{\beta} f_{\alpha}(q) f_{\beta}(q) \sqrt{N_{\alpha} N_{\beta}} S_{\alpha\beta}(q)$$

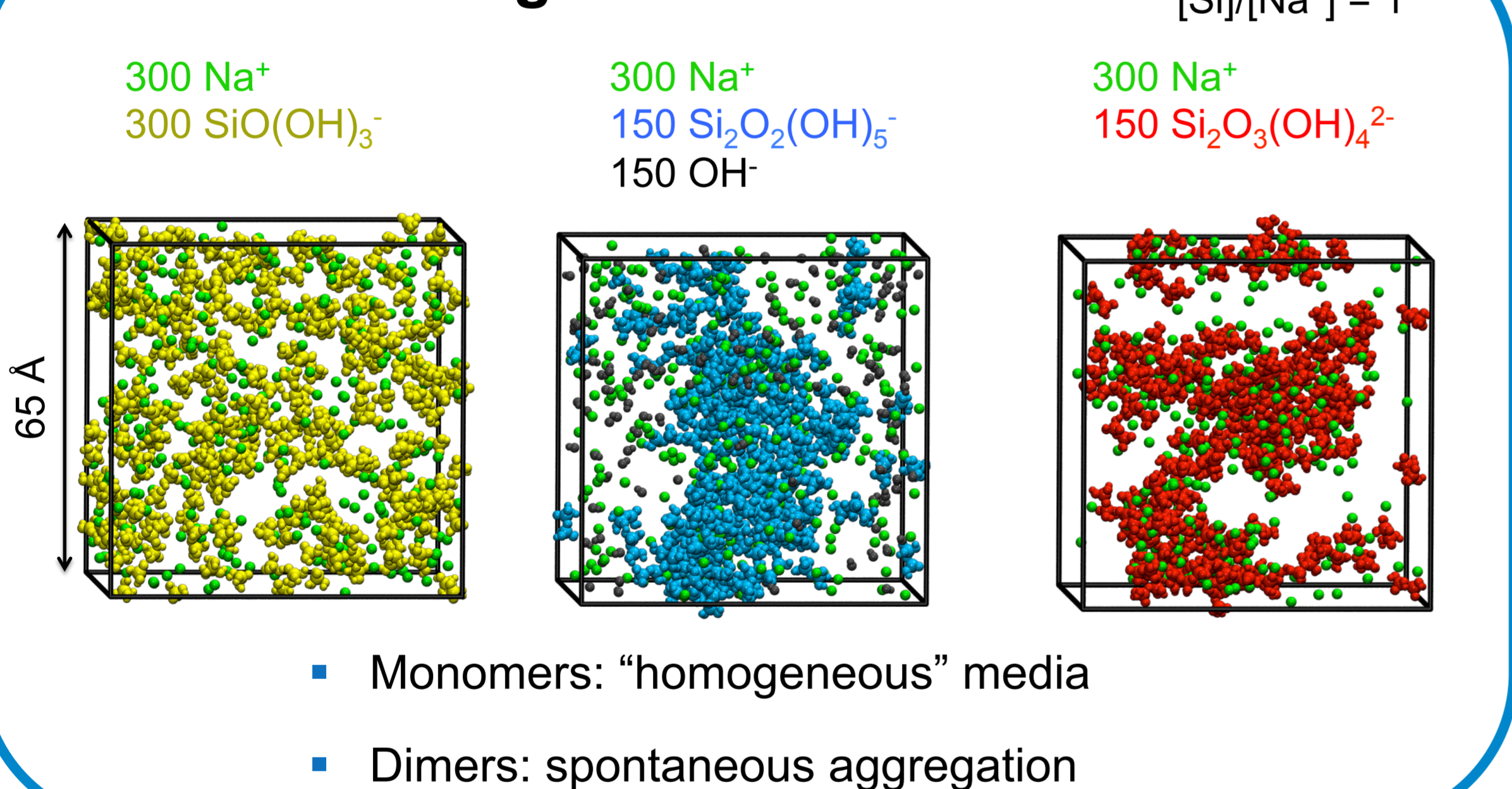
$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \sqrt{\rho_{\alpha} \rho_{\beta}} \text{FT}_{3D}(g_{\alpha\beta}(r) - 1)$$

- Theoretical $I(q)$ directly comparable to experimental one
- Efficient method for describing alkali media [4] → study of silicate oligomers in such media

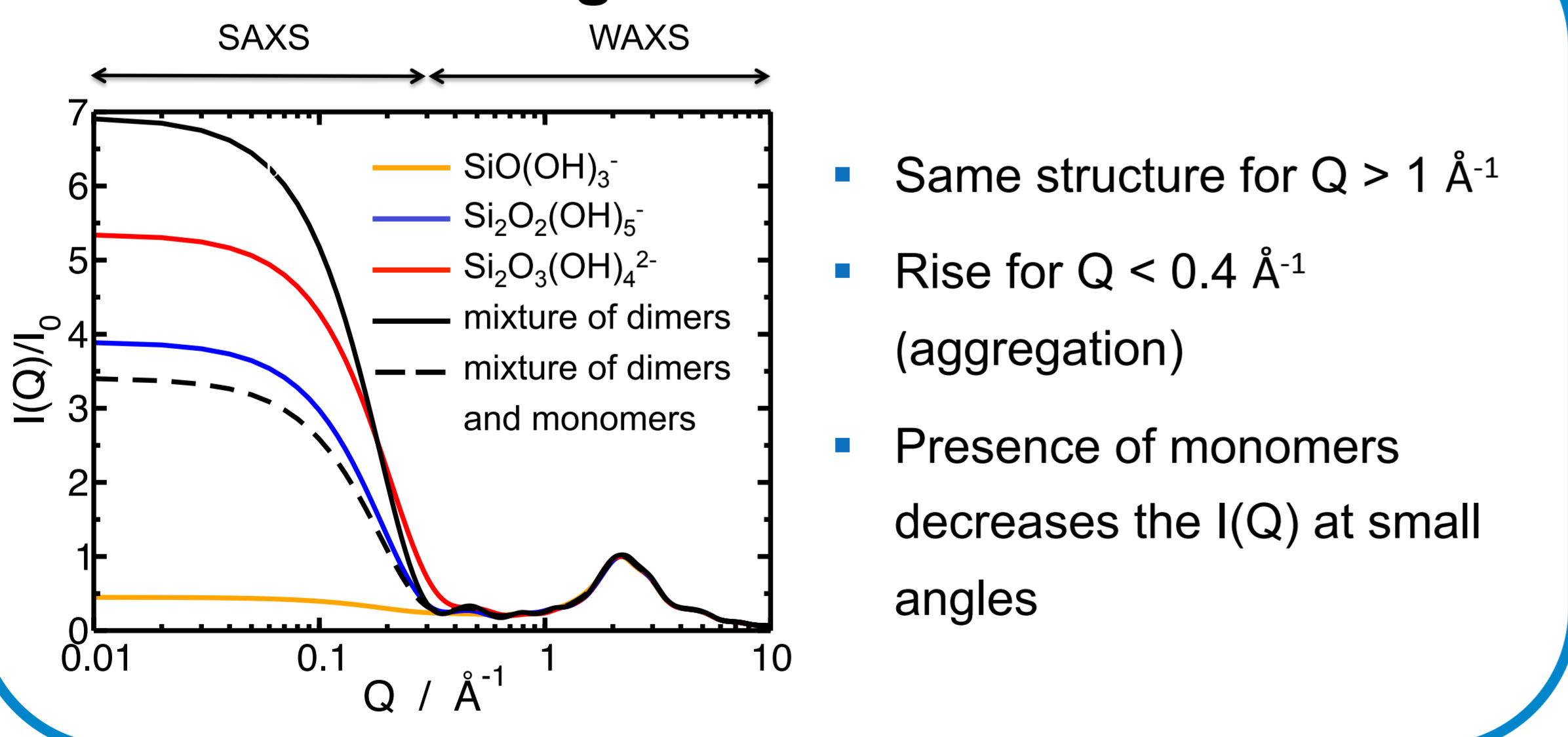


Silicate in NaOH concentrated media

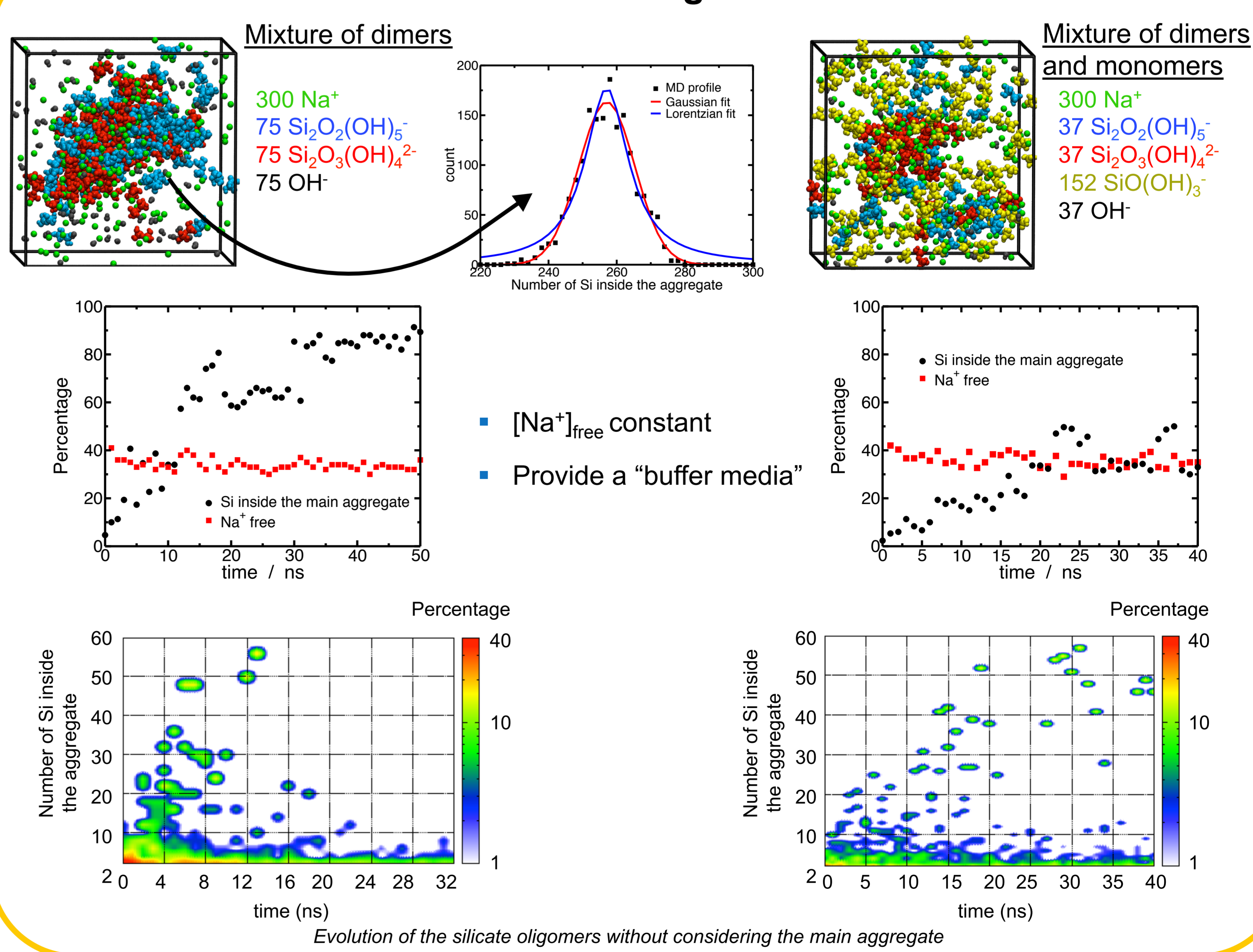
Pure oligomer solutions



Scattering intensities from MD



Mixtures of oligomers



Conclusions and Outlooks

- Structure of the solution depends on the oligomer composition and nature:
 - Spontaneous aggregation of dimers in solution: aggregates composed of silicates and Na^+
 - Dimers $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ interact strongly with Na^+
 - Monomers $\text{SiO}(\text{OH})_3^-$: small aggregates, and destabilize the aggregation (entropic effect)
- Similar behaviours of Na^+ : "buffer media" with the hydroxide anions
- MD simulations of "real" solutions:
 - Different $[\text{Si}]/[\text{Na}^+]$ ratios with respect to NMR experiments
 - Influence of the alkali nature on the aggregation

Acknowledgements

This work was made possible thanks to the financial support of the ANR DYNAMISTE (ANR-15-CE07-0013-01) and high performance computing facilities of TGCC/CCRT and the computing center of CEA Marcoule.

References

- [1] L. Provis *et al.*, *Ind. Eng. Chem. Res.* 2005, **44**, 8899
- [2] C. T. Knight and S. D. Kinrade, *Silicon in Agriculture*, Elsevier, 2001, vol. 8, chap. 4
- [3] D.A. Case *et al.*, *Computat. Chem.*, 2005, **26**, 1668
- [4] A. Coste *et al.*, *J. Chem. Phys.*, submitted (2018)