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



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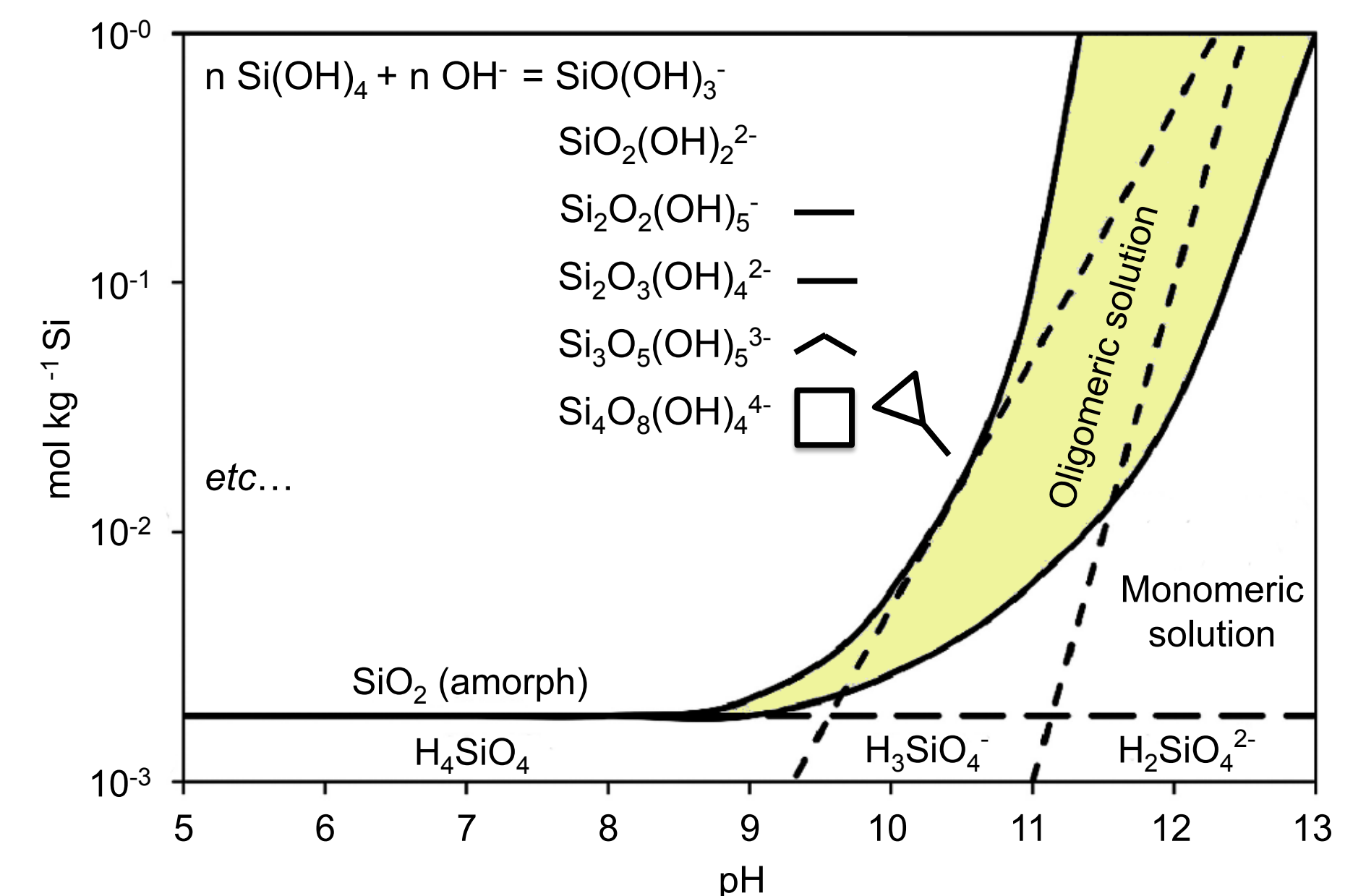
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Context



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

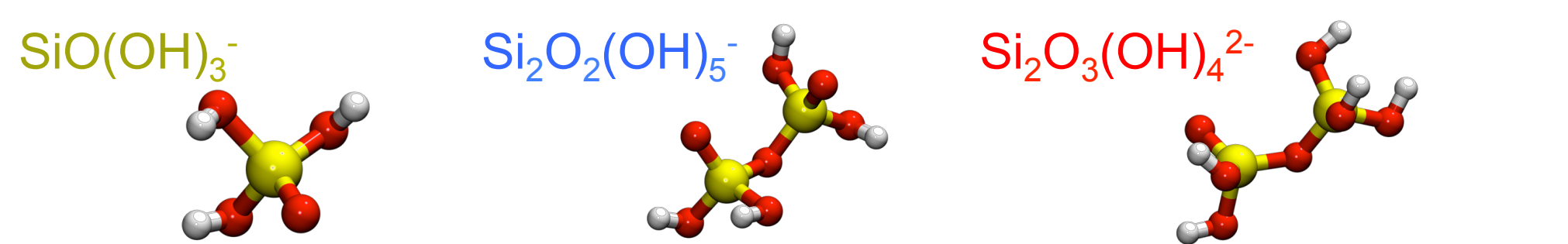
- Solutions of activation (= alkali media) of aluminosilicate are environmentally friendly and considered as green chemistry (used for ground stabilization, painting...)
- The formulation is complex since the parameters are various and numerous
- Understanding the ion-ion interactions for the oligomerization 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:



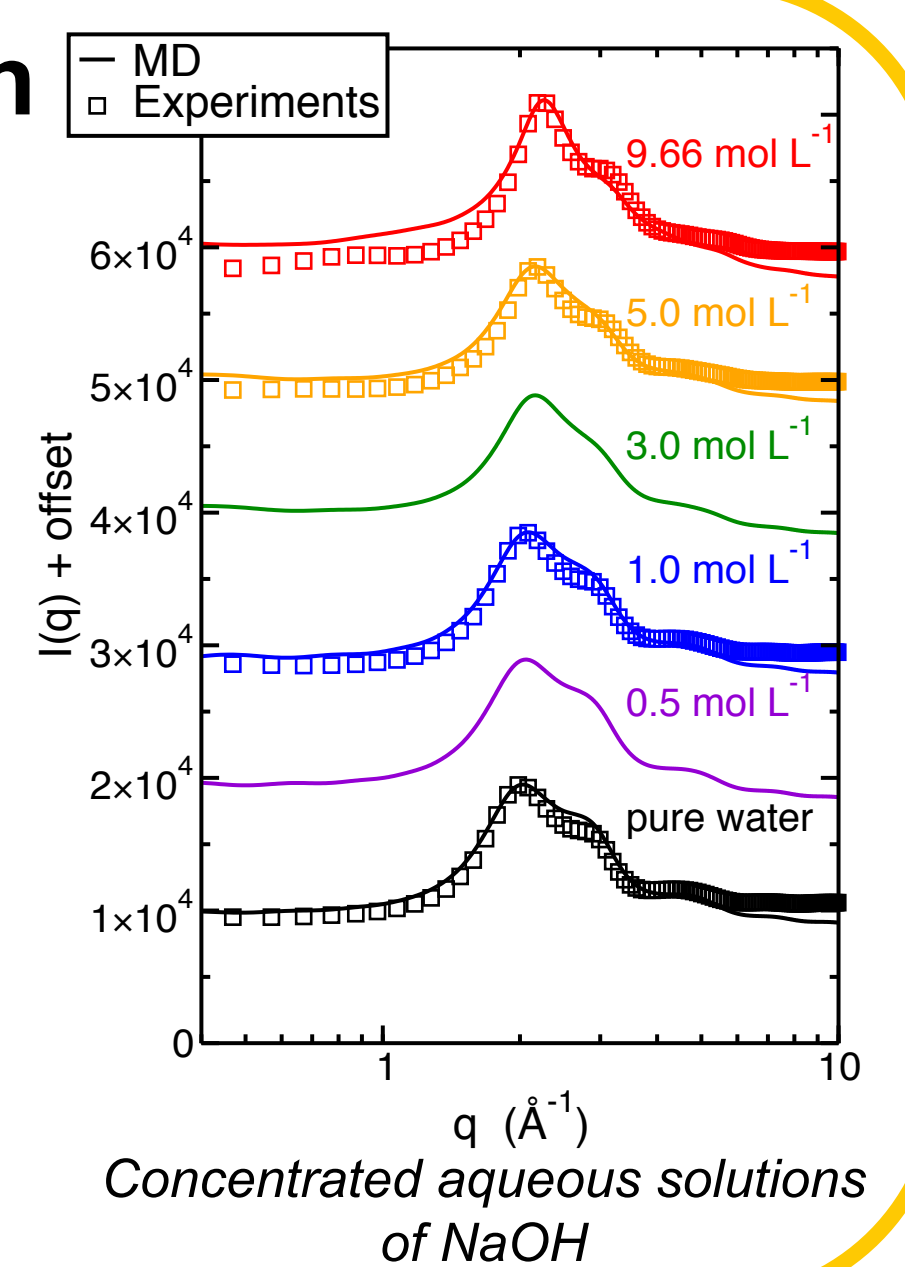
X ray scattering intensity from MD simulation

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

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

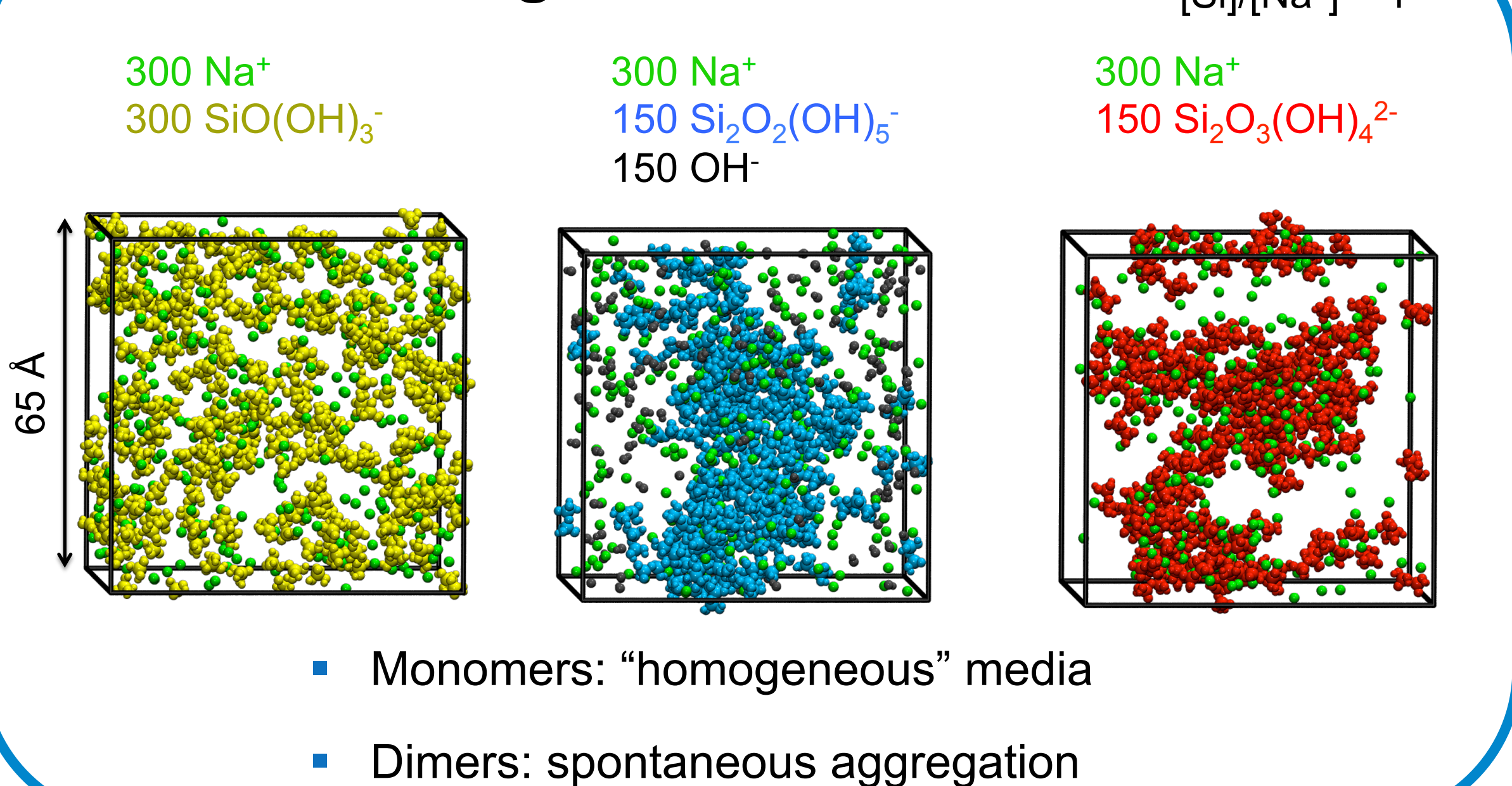
$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \sqrt{\rho_{\alpha} \rho_{\beta}} \text{FT}_{3D}(g_{\alpha\beta}(r) - 1)$$

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

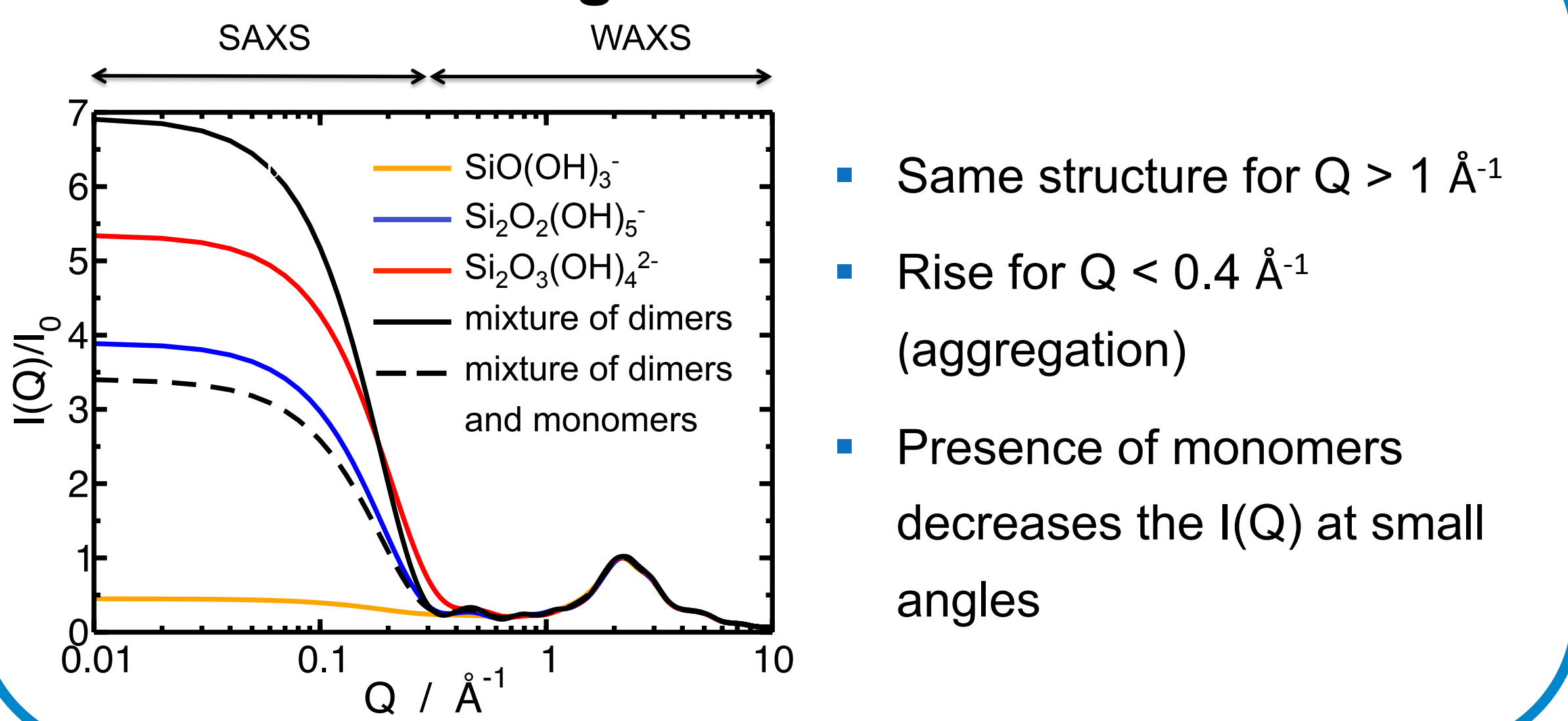


Silicate in NaOH concentrated media

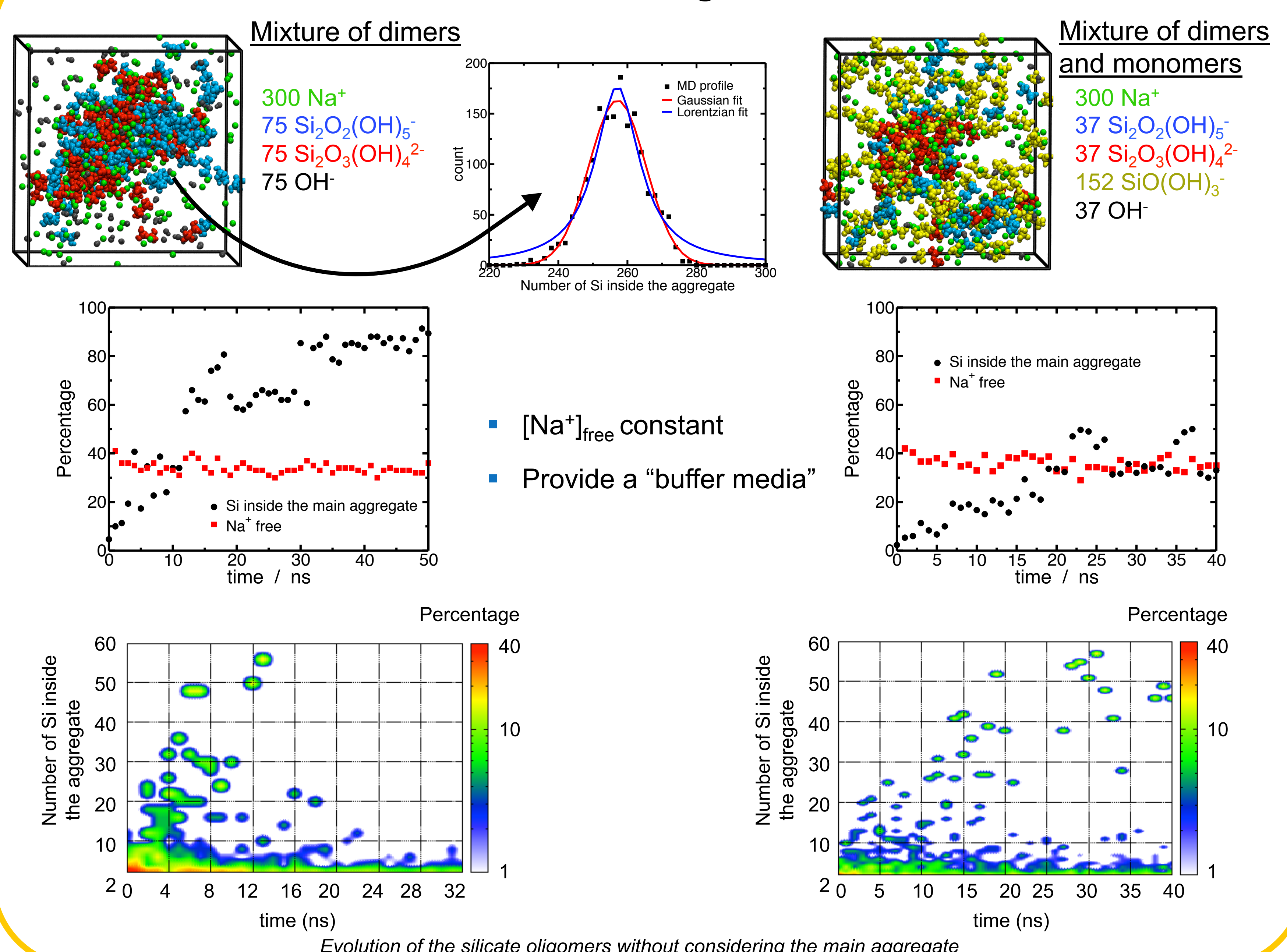
Pure oligomer solutions



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 Si₂O₃(OH)₄²⁻ interact strongly with Na⁺
 - Monomers SiO(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 [Si]/[Na⁺] ratios with respect to NMR experiments
 - Influence of the alkali nature on the aggregation

Acknowledgements

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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)