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Time resolved alkali silicate decondensation by sodium hydroxide solution

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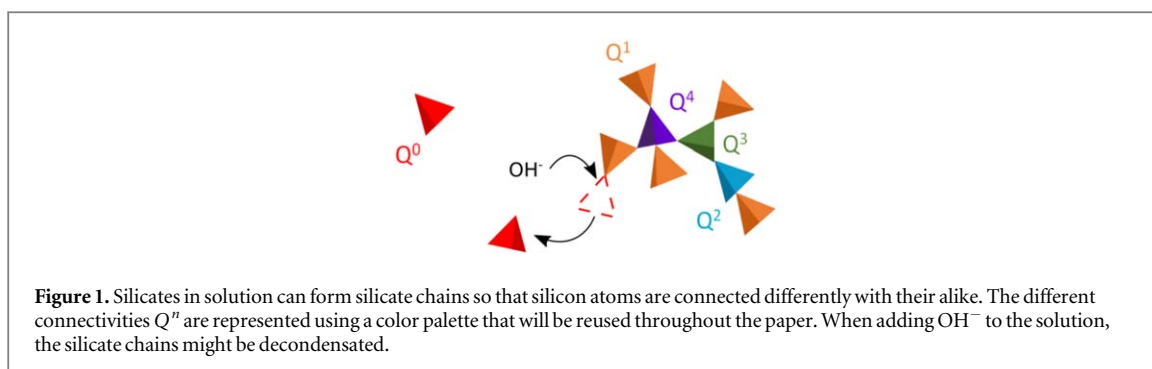
Abstract

Silica is by far the chemical compound the most widespread and used around the world: as a raw product in the buildings and roads industry, as concrete, or as a processed product in the manufacture of glass, ceramics or zeolites. In alkali silicate solutions—often used to synthesize those materials—a complex interplay of decondensation and condensation processes leads to the restructuring of silicate clusters at the atomic scale on a short time-scale. We were able to deconvolute these effects by combining time resolved small angle x-ray scattering, nuclear magnetic resonance, and parallel tempering simulations. We investigated the impact of a dilution by pure water or by a sodium hydroxide solution on the speciation and size of the dissolved silicates in solution. Herein, we show that the silicate clusters are not affected by dilution, suggesting that sodium cations protect the silicate clusters from hydrolysis. Decondensation is triggered by hydroxide ions that weaken and break Si–O bonds. Alongside the decondensation, the evolution of the computed protonation state of the silica species indicates a change in the interaction potential. Our results pave the way towards the investigation at the atomic scale of more complex systems implying alkali silicate solutions in condensation process by the addition of calcium or aluminum to synthesize aluminosilicate binders, hydrogels or zeolites.

Introduction

The chemistry of dissolved silica has been widely investigated for decades because of its relevance to various fields such as chemistry, geology, biology, and manifolds fields of application including construction, gas separation, ceramics and hydrogels [1–5]. For instance, to produce accessible and rock-like materials, mankind started making calcium silicate cement from limestone and pozzolan, and extracting aluminosilicate clays. Recently, the continuous growth of the concrete’s demand has been driven by the demographic change [6, 7]. This has motivated recent studies to assess the structure of cement at the nano-scale [8, 9] to maximize the durability of concrete [10, 11] and, thus, reduce its environmental impacts.

The rich and complex chemistry of silicate species motivates the study of the dissolution and polymerization of silica [12–14]. The role of ions, such as alkali, has long being studied [15] because it varies according to the type of material (glass, hydrated glass, gel, zeolite, mineral) and on the chemical environment [16–18]. In recent decades, silicates glasses or aluminosilicates binders have been widely studied in the construction industry and other specific areas. For instance, alkali silicate has been proposed to be used as binders in the nuclear industry to immobilize and store radioactive wastes in deep geological disposals [19, 20] as well as precursors to the formation of zeolites [21–23]. These materials are elaborated by mixing aluminosilicate mineral powders with solutions composed of a mixture of alkali silicate with sodium hydroxide. This mix leads to a hardened material by condensation reaction [24]. However, the presence of sodium hydroxide in silicate-based materials can profoundly alter their structure in a way that is difficult to control. For instance, glasses as they are formed in



presence of sodium will have more defects in their structure leading to complex effects that affects mechanical properties [25]. Colloidal solutions being out of the equilibrium phases, subsequent addition of cations may change the atomistic arrangement. Therefore, it is challenging to assess structural changes even though highly accurate nuclear magnetic resonance measurements can now be made. There is an understandable urge to investigate in details salt effect and concentration, the role of alkali (Na^+ , K^+) and pH on the stability of silicate species in solution in order to later control the dynamics of recondensation of aluminosilicates.

Herein, we are studying the effect of sodium hydroxide addition to a silicate solution by combining both an experimental and a simulation approaches. This is a step forward to understand and decorrelate the roles of sodium (Na^+), hydroxide (OH^-) or water on the stability of silicate chains. The combination of experiments and simulations to better understand the long-term stability of the silicate oligomers in solution, as schemed in figure 1, appears as an essential step for the synthesis of specific materials, particularly in the construction, ceramics and glass industries. These simulations were made possible by the recent developments of the brief parallel tempering technique [11] (brief-PT) and the reactive force fields ReaxFF (see Materials and Methods), allowing to make or break bonds, [26, 27] that have opened new pathways to study the stability of large systems in the long run—typically, ReaxFF opens the possibility to study systems of hundreds of thousands of atoms during a few ns using classical MD. At the same time, experiments now enable us to observe the evolution of the structural properties with a time-resolution of a few seconds, in order to observe the initial moments after a change of chemical conditions.

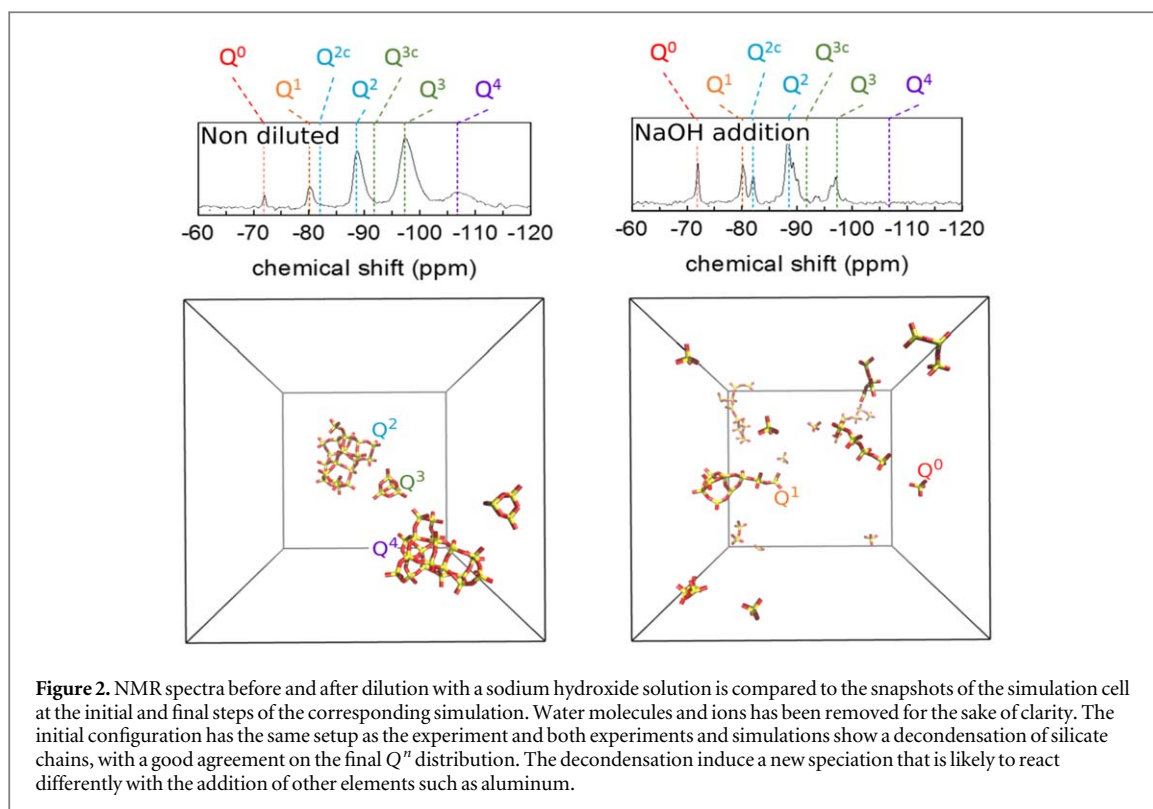
Results

Recently, several experimental and theoretical methods has been used to study the complexity of the structure of silica-based materials such as NMR [28–30], neutron diffraction [31], vibrational spectra [32–34] or molecular dynamics (MD) [35].

In this work, a sodium silicate solution (Woellner, Betol 39T: 27.8 wt% SiO_2 , 8.3 wt% Na_2O and 63.9 wt% H_2O) and deionized water were used to prepare the silicate solution with the desired concentration. The initial concentrations (before dilution or decondensation) are $[\text{Si}] = 2.25 \text{ mol.L}^{-1}$ and $[\text{Na}] = 1.31 \text{ mol.L}^{-1}$. It is known that the alkali silicate solutions are metastable, namely that they evolve over time. The manufacturer guaranties the stability of these solutions for a year. We studied the stability of these solutions by NMR and no evolution in the distribution of Q^n was noticed. From scattering data, we also observed that the radius of gyration does not evolve after 150–200 s. After the dilution and the decondensation $[\text{Si}] = 1.125 \text{ mol.L}^{-1}$ and $[\text{Na}] = 0.65 \text{ mol.L}^{-1}$, $[\text{Si}] = 1.125 \text{ mol.L}^{-1}$ and $[\text{Na}] = 1.31 \text{ mol.L}^{-1}$, respectively. The modulus (in weight) of the initial sodium silicate solution, $R = \text{SiO}_2/\text{Na}_2\text{O} = 3.33$. At the end of the decondensation step, $R = \text{SiO}_2/\text{Na}_2\text{O} = 1.665$.

From NMR experiments, we have firstly extracted the number of Si–O–Si bonds per Si atom (Q^n). At the top of the figure 2, NMR spectra are plotted. From these spectra, it is clearly evidenced that sodium hydroxide addition to alkali silicate solutions is strongly affecting the integrity of the silicate oligomers [36–39]. Having done this, we have devised methods to build the initial simulation structure: initially, we manually drew several structures having the correct Q^n distribution but we quickly found out that these were dissociating at room temperature—due to the presence of weak Si–O–Si bridges. Later, we have decided to extract a chunk of the gel structures produced by Dupuis *et al* 2019 [11]—these chunks, as shown in figure 2, are highly connected and stable. Altogether, this indicates that the Q^n distribution is far from being restrictive and strengthen our interest for conducting atomistic simulations.

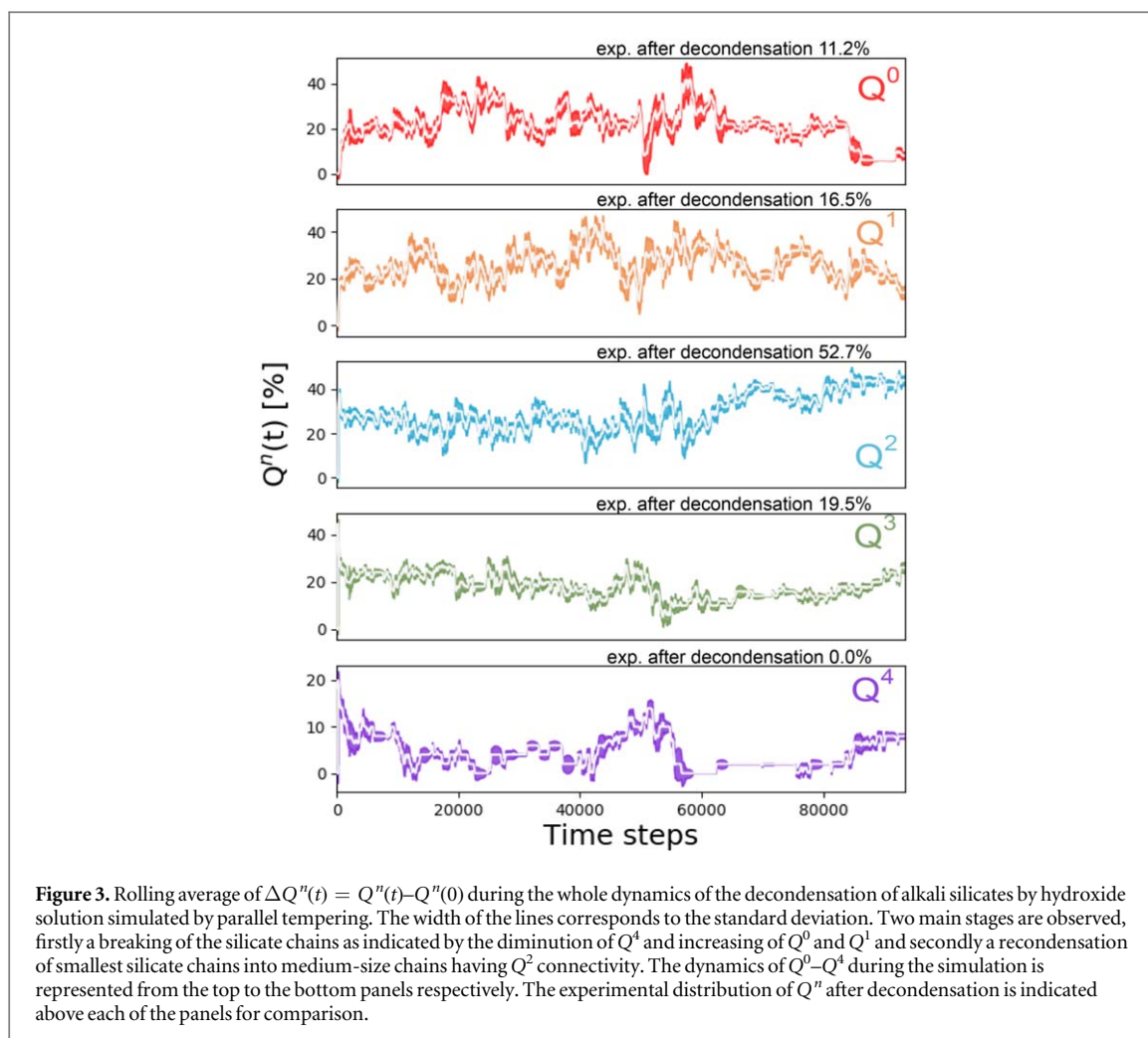
The effect of adding a solution containing NaOH to the silicate solution mentioned above was reproduced by atomistic simulations using brief-PT method as described in the section Materials and Methods. The method has been proven to efficiently reproduce the formation of amorphous structures such as the silica solutions we



are interested in [11]. The evolution of Q^n due to dilution of the initial alkali solution by a sodium hydroxide solution, keeping the sodium concentration constant, was subsequently obtained and is plotted in figure 3. Interestingly enough, we have found that dilution with pure water had no effect on hydrolysis of the silicate centers (the evolution of the structural properties are given in the supplementary material). The same passivation effect was observed in the literature for dry silica gels due to the formation of high-density clusters containing many silica rings [11, 40]. This was later verified in our experiments that the decondensation of silicate chains is not triggered by the addition of pure water. This confirms that our choice for the initial structure was reliable to study this system. In the following, we examine whether passivation effect ceases to occur when diluting with a NaOH solution.

Before adding the solution containing Na^+ and OH^- ions, we have substituted half of the protons that were protonating the silicate chains by Na^+ as the initial silica solution already contains 1.31 mol l^{-1} of sodium hydroxide. In this system, all the Na^+ are compensating the charge of a silanol group. Then, we have equilibrated the system in the NVT ensemble during 10 ps. Later, NaOH solution has been added to the simulation cell using a GCMC approach and a new equilibration of 10 ps has been simulated. In order to have the same chemistry in the simulation as the one measured experimentally, the simulated structure with the addition of the NaOH solution contains 50 Si atoms, 2200 H_2O molecules and 56 Na^+ (the initial structure corresponds to the left snapshot in figure 2). The number of silicon atoms has been defined to 50 in order to have a representative simulation cell and keep the total number of atoms reasonably low. The instability introduced by the addition of the NaOH solution, leading to the decondensation of the silicate chains, is splitted in two stages during the dynamics. First, as shown in figure 3, the decondensation starts with a prompt loss of Q^3 and Q^4 in favor of the production of Q^0 and Q^1 . In other words, clusters are firstly divided into smaller pieces. The number of Q^2 and Q^3 remains relatively stable during the first steps of the simulation. In a second time, after about 50 000 steps, a further decondensation of the silicate chains will produce more Q^2 and some Q^0 will recondensate into Q^2 by connecting at the end of an already formed silicate chain—if Q^0 were to form dimers and therefore new silica chains, we would have observed an increase of Q^1 . At the end of the dynamics, the Q^n distribution is in excellent agreement with the experiments (see figure 3). In particular the distribution of Q^2 , that remained stable along the first stage of the dynamics, has reached a new plateau at about 40% which is close to the 52% found experimentally. The final snapshot is shown on the right side of figure 2. This shows that the number of silicate chains has changed and that the size of the chains has been reduced together with the condensation.

In terms of performance, the brief-PT method has enabled fast crossing of high-energy barriers. For the first time, we have the possibility to compare the method to experiments the experiments resolved in time. After only 20 000 steps, more than half of the Q^4 has disappeared. In the experiments, the equilibrium is obtained after about 3 min, as shown in figure 4 representing the silicate clusters' size determined by adjustment of the Guinier model on TR-SAXS data. In the simulation, similar Q^n distribution was obtained after about only 85 000 steps.



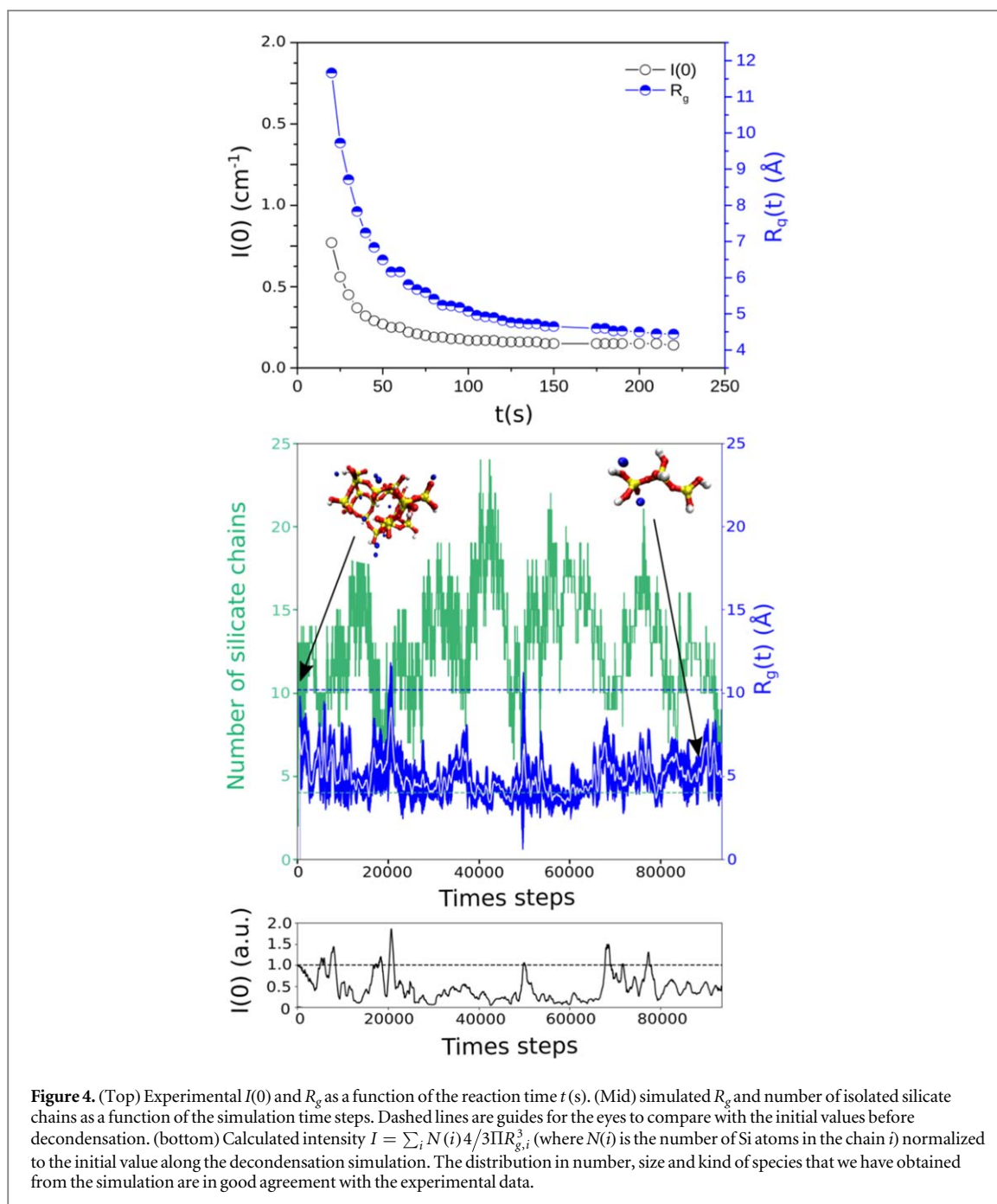
Therefore, in this simulation we have been able to simulate, by accelerated dynamics, the evolution of the silicate solution over an equivalent of few minutes. This represents an important step toward the study of long-time processes with atomistic simulations.

Discussion

Decondensation

Both the simulations and experiments that have been performed show a similar decondensation of the silicate oligomers due to the addition of the NaOH solution. Further discussion will focus on the structural changes and on the effect of hydroxide on the stability of silicate oligomers.

As a matter of facts, a change in the condensation state will impact the geometry of the silicate clusters. Two different cases can be expected: an opening of dense structures to make long silica chains; or a division of the silica clusters into smaller pieces. Using time resolved SAXS experiments, one can determine the intensity of the Guinier plateau $I(0)$ and the radius of gyration (R_g) as a function of time by adjustment of experimental data with the Guinier law where $I(0)$ is relative to the amount of scatterers and their size [41]. Besides, the species characteristics are fully defined and can be traced during the molecular simulation. As shown in figure 4, the gyration radius and the scattering intensity at low scattering vector are divided by a factor 2.5 and 4 respectively within 3 min. This is due to the splitting of larger clusters into smaller pieces of smaller gyration radius. Similarly, in the simulation, the gyration radius has been divided by 2 during the decondensation. This indicates that in both cases, the decondensation scenario is the one showing the breakage of the silicate clusters. We have calculated that the number of silicate species is increase by 3 after adding the NaOH solution. This is also indicated by the increase of Q^0 and Q^1 in the first steps of the MD. As mentioned previously, we have distinguished two stages in the decondensation of the silicates leading to the dissociation of silicate clusters. This result is comforted by the agreement between the variation in the calculated reflected intensity I (bottom panel in figure 4), that depends on the number of species and the volume of the scattering entities through the radius of

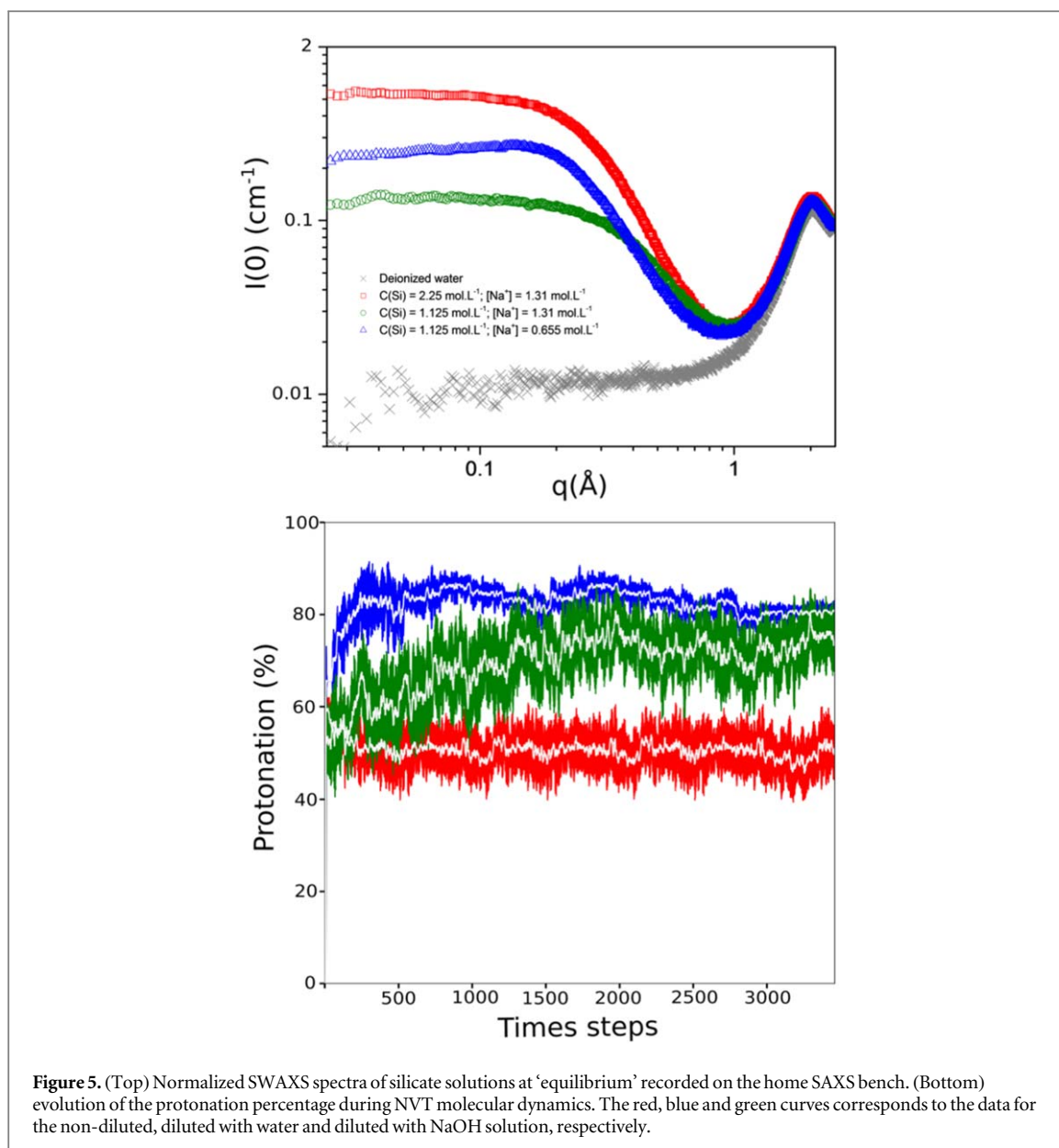


gyration, and in the experimental one. The decreasing in the simulation is about $1/3$, which is in agreement with the experiments (about $1/4$) considering that in the simulation the volume of the silicate clusters is considered as a simple sphere of radius R_g .

These findings can be regarded as important insights to understand the more complex phenomena of silicates' restructuring due to the addition of elements such as Ca^{2+} or aluminate ions. Indeed, reactivity of such elements on silicates species might be enhanced by a prior decondensation due to sodium hydroxide, which will thus favor a different type of reconcondensation. More generally, in silicates, different arrangements can be found depending on the chemistry. For instance, in calcium silicate hydrates gels that can be found in cement, the Ca/Si ratio and the hydration ratio, or Al/Si ratio, are drastically changing the structural and mechanical properties of the gels [42–44]. A decondensation of silicate chains by the NaOH solution could reduce the energy barriers necessary to go from one structure to the other.

Protonation of the silicate chains

A change in the gyration radius indicates a decondensation that in the simulation is followed by a change in the protonation state. As indicated before, half of the initial non-bridging oxygen atoms are protonated and the



other half has the charge compensated by Na^+ . During the decondensation, we observed that the number of protonated oxygen atoms increases (see figure 5). According to the pK_a [45] of monomers and dimers this is consistent that short silicate chains are more likely to be protonated than silicate chunks. For these simulation cells, the pH can not be precisely calculated because adding or removing a single proton from the simulation will correspond to a large variation of $[\text{H}^+]$. From an experimental point of view, pH measurements can be misleading at high pH in presence of alkali silicates. Firstly, at high pH values, the proton activity is very low and activity of small alkali ions is high, leading thus to alkaline error. Moreover, silicates are likely interacting with the pH probe glass membrane. Such a difficulty can be circumvented by assessing acidity function measurements and using spectrophotometry [46, 47].

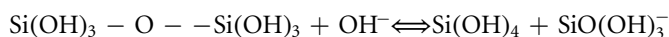
As we did a measurement of the SWAXS for non-diluted, diluted, and diluted with NaOH solutions, we found that the length of silicate chains were reduced by NaOH addition, as discussed previously and shown in figure 5. Interestingly, we observed that the curve for the water diluted solution shows a correlation bump at q equals 0.2 \AA^{-1} . This indicates that the silicate chains or cluster of chains, instead of being attracted the one with the other, are slightly repulsed. The origin of this repulsive behavior is seemingly due to a change in the protonation state of the silica chain, since no variation was observed in the Q^n ratios. In order to investigate that, we have simulated the non-diluted and diluted structures (before addition of NaOH) in the NVT ensemble by MD and we have calculated the protonation states (see figure 5). After leaving enough time for the silicate chains to diffuse and for H^+ and Na^+ to be exchanged (i.e. the average value of the protonation degree does not vary more than 1% during 1000 steps), about half of the non-bridging oxygen atoms are protonated in the non-diluted solution whereas after dilution, about 3/4 of the sites are occupied by a proton. Consequently, the

proportion of free sodium in the solution is higher when the solution is diluted. An increase of protonation can lead to a higher chemical shift in the ^{29}Si NMR signal—although that effect can be screened by the presence of other counterions such as Na^+ [48]. In the NMR signal, presented in supporting information, the diluted solution shows a shift of all peaks towards higher chemical shifts. The protonation due to the dilution could stem from the repulsive effect that is observed in the SWAXS signal due to the interaction between silanol groups from different silicate chains. The release of Na^+ into the solution, due to the protonation of the silicate chains, might also have a repulsive effect on the cluster–cluster interaction at larger scales. In gels, water will have an effect for both the diffusion properties of ions and possibly the screening effects due to the solvation of ions or molecules. To investigate all these effects, multi-scale approaches will require large simulations that go beyond the scope of this study. Nonetheless, our work paves the way towards the investigation of atomic scale effects on nanoscale arrangements that can be simulated with, for instance, coarse grained model [10, 49]. At different scales, alkali type (Na, K) could affect the setting time of gels and their mechanical properties (shear, strength, ...) as well as salt concentration [50, 51].

Role of hydroxide and sodium ions

In glasses, the presence of Na^+ , as other cation such as Ca^{2+} and Li^+ , is considered to be a glass modifier because the ion can compensate a charge near a non-bridging oxygen—which will modify locally the Si–O–Si angular distribution [25] and vibrational properties [32]. Other cations such as aluminum are glass former and form chains together with silicon atoms [31, 32, 52]. Similarly, in zeolites, Na^+ and NaOH modify the structure and can reduce the connectivity of silicates [53]. In gels or solutions, cations can be both in a charge compensation scheme, like in glasses, or solvated. Moreover, the combined effect of different ions is not well known. If Na^+ tends to reduce the connectivity in silicate glasses [53], it may have a different role in solutions due to the presence of water.

In the literature, pure silica solutions with high water to silicon ratio have lower connectivity than the one measured for the non diluted solution in figure 2 [54]. Therefore, the role of Na^+ in the initial solution favors higher connectivity of silicate chains compared to a pure silica gel. Cations in silicate solution, like sodium, can be either in a charge compensator near a non-bridging oxygen O^- or solvated. Before the addition of sodium hydroxide, almost all sodium ions are considered to be charge compensators. During the decondensation, we observe that most of the silicate chains become protonated. Therefore, Na^+ does not play the same charge compensation role as in glasses but it will be highly solvated. The role of Na^+ in the decondensation should be minimal. On the contrary, the effect of pH, or OH^- , is important because these groups can directly dissociate a Si–O–Si bond. For instance, for a dimer dissociation:



Aluminate is often used to make silica-based materials having longer silicate chains. It may be provided either from the alkaline dissolution of minerals like metakaolin or by-products such as slags or fly-ash, or directly added in the form of an alkali-aluminate solution. In these two cases, when these aluminum sources are mixed with alkali-silicate solutions, two antagonist effects, happening on the same time-scale, occur since Al tends to connect with silicates clusters whereas sodium hydroxide favors their decondensation. One implication of this work is that, adding an aluminate solution that contains sodium hydroxide will most likely dissolve large silicate clusters into small silicate chains that can later be recombined due to the presence of reactive aluminate monomers. Therefore, instead of having aluminates added to the surface of large clusters, the aluminate could be at the center of an aluminosilicate chains with multiple branches. This raises the question of how the addition of sodium hydroxide can modify the initial stages of the aluminosilicate formation and play a role in the final gel structure that is a key point in the synthesis of aluminosilicate binders or zeolites [13, 14, 55]. A benefit of our approach is that we are able to decouple the effect of adding different kind of ions and to study specifically the addition of the NaOH solution. In the experiment, having both $\text{Al}(\text{OH})_4^-$ and sodium hydroxide, the effects are arduous to separate because the decondensation happens too quickly. Using atomistic simulations, the addition of only $\text{Al}(\text{OH})_4^-$ into the solution can be investigated in further studies.

Conclusion

Understanding the behavior of alkali silicate solution with the addition of sodium hydroxide or water is of great importance from theoretical and practical standpoints. In this work, we have investigated the role of water, hydroxide and sodium ions on the dissolved silicates by combining theoretical and experimental approaches. The methodology and results we have obtained open new pathways to better understand the chemistry of silica-based materials. We have shown that not only the silica clusters decondensate in presence of sodium hydroxide but also that the protonation state is modified by the dilution in pure water. The comparison with the experiments shows a good agreement which comforts the use of accelerated atomistic simulations for studying liquids, gels, reactional intermediates, and phase transitions. Alkali–silicate solutions are precursors of the formation of aluminosilicate binders or zeolites obtained from hydrogel systems [56]. The presence of cations

(Na^+ , K^+ , Ca^{2+}) or aluminates in the solution is key to control the shape and the properties of the final products [47, 57]. One of the main challenges is to understand the stages of the formation of zeolites or amorphous aluminosilicate binders at the atomic scale [58] starting from a liquid or pasty solution until the formation of the solid materials through a phase transition. The speciation of silicate centers, which is affected by the presence of alkali such as Na^+ , that we have provided gives insights on the possible chemical paths for aforementioned processes. It also provides information on the energetic properties of the solution that can be used to compute phase diagrams.

Material and methods

Sample preparation and simulation cell details

Silicate solutions were prepared by dilution of commercial water glass solutions with deionized water. Sodium concentrations were adjusted by addition of sodium hydroxide (NaOH). The simulation cell is a $42 \times 42 \times 42 \text{ \AA}^3$ cube that contains 7350 atoms. (More information on the sample preparation and simulation details can be found in SI.)

Nuclear magnetic resonance of silicon-29 (^{29}Si NMR)

^{29}Si NMR spectra were recorded on a Bruker 400 Avance III spectrometer using a 4 mm zirconia rotor. Chemical shifts are reported with respect to tetramethylsilane (TMS) reference. NMR spectra were analysed with DMFit software for the determination of connectivity proportions. NMR experimental results can be compared to simulations [34, 59].

Small and wide angle x-ray scattering (SWAXS) on lab bench

For equilibrated solutions characterizations SWAXS measurements were performed on a Xenocs lab bench using a Mo radiation. More details are provided in SI Material and Methods. Each spectra was preprocessed using Fit2D program.

Time resolved small angle x-ray scattering (TR-SWAXS) on SWING beamline

For decondensation kinetic experiments, time resolved measurements TR-SWAXS were recorded on the SWING beamline at the SOLEIL Synchrotron facilities (Saint Aubin, France) which integrates a syringe pump to allow an *in situ* mixing. A preprocessing was performed for all spectra using the local dedicated program Foxtrot [60]. More details are provided in SI Material and Methods.

Reactive force field

Calculations has been performed using the reactive force field ReaxFF [26] and the parameters provided for Si/O/H/Na [61, 62]. ReaxFF allow bond formation/breaking due to a multi-functional scheme in which the charge, coordination number and other parameters influencing on the bond-energy are recalculated every steps. These parameters has been extensively tested for silica gels, zeolites and other silicate structures [11, 61–64] and give good agreement compared to experiments. In the S.I., the potential is tested against the $g(r)$ of Si–O distances, the angular distribution distribution of water and the water dipole distribution.

Brief-parallel tempering

The formation of oligomers is a slow process compared to times reachable by MD due to the energy barrier to form Si–O bonds [44, 65]. We have used a recent accelerated simulation method which is based on the parallel tempering method (PT, also called replica exchange) [11, 27]. In PT, the system is replicated several times and each replica run at a different temperature—high-temperature replica having higher probability of crossing high energy barriers. After a given time, two configurations can be exchanged. The difference in brief-PT, is simply that the PT is often interrupted, leading to low temperature states periodically repopulating the ensemble of simulations [11]. The simulation is hastened by several orders of magnitude compared to MD.

Statistic analysis

In the manuscript, we have used the concept of chains to define an ensemble of silicates connected together. The connectivity, defined by Q_n and obtained in the simulations is compared to the NMR experiments. In order to define which silicon atoms belongs to a chain, we have used an algorithm that seeks for closest oxygen atom neighbors to a silicon atom in a radius of 2.0 Å, which corresponds to the first minimum in the Si–O radial distribution function.

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