

# modelling & theory

## From explosive volcanism to semiconductors: structural and dynamical properties of hydrous silica(tes)

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The presence of water drastically alters the physical properties of silica and silicates. For example, the decrease in viscosity plays a decisive role in explosive volcanic eruptions [1]. Water is also used to passivate defects in  $\text{SiO}_2$  in semiconductor devices [2]. In silicates, water can dissolve to form  $\text{SiOH}$  groups but molecular water may also be present. To date the water-induced microscopic mechanisms leading to the modification of the macroscopic properties of silicates, like viscosity and electric conductivity, are not well understood. We have combined first-principles molecular dynamics computer simulations with neutron scattering techniques in order to understand the influence of water on mass transport in silica(tes) as well as their electronic properties.

**It is well known that**, due to the different scattering lengths of hydrogen and its isotope deuterium, neutron scattering is one of the most suitable experimental techniques for investigating water containing systems. Structural and dynamical properties like the static structure factor  $S(q)$  and the vibrational density of states are accessible with this experimental probe. On the other hand, exactly these quantities can be extracted from molecular dynamics computer simulations. Classical molecular dynamics are not able to give a realistic description of hydrous silicate systems since reliable potentials for water and the dissolution products  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  do not exist. Therefore, a quantum-mechanical treatment of the electrons, as in the Car-Parrinello method, must be used. Since this type of *ab initio* calculation is computationally demanding (CPU time as well as memory), we have used parallel supercomputers extensively. Our calculations were per-

formed using the "CPMD" code, developed by Prof. Parrinello's group [3].

Exploring mechanisms associated with explosive volcanism requires a clear understanding of the liquid state. Considerable progress was made recently for sodium silicate systems [4], also by combining molecular dynamics computer simulations and neutron scattering. Due to the chemical similarity of the systems  $(1-x)\text{SiO}_2+x\text{H}_2\text{O}$  and  $(1-x)\text{SiO}_2+x\text{Na}_2\text{O}$  ( $0 \leq x \leq 1$ ), it can be assumed that both systems have similar mechanisms for mass transport. However, hydrous silicates are much more challenging to investigate:

**Experiments** are currently limited to the glassy state. Pressures of several kbar and temperatures in excess of 1000 K are required to bring water-silicate mixtures into equilibrium. Since such pressure equipment is not currently available on neutron scattering instruments, experimental data

can only be obtained below temperatures where water is released from the silicate.

**Simulations** are in principle limited to the liquid state. Today's computer power puts clear limits on the *ab initio* equilibration of viscous liquids. For a system size of about one hundred atoms, the time limit is some tens of pico-seconds (these are six orders of magnitude less than in the classical approach used for sodium silicates). The lowest temperature at which equilibration can be achieved is 3000 K. Information on the glass can only be obtained from samples based on ultra-rapid quenches.

The set-up and the main results of the CPMD simulation for the liquid state of a system with the composition  $\text{SiO}_2+11.8\text{mol}\%\text{H}_2\text{O}$  were recently described in references [5,6]. Also structural information on quenched samples has been obtained from experiments [7]. Figure 1 shows a snapshot of the computer simulation of hydrous silica at a temperature of 3500 K.

Apparently all hydrogen atoms are attached to the silica matrix in the form of  $\text{SiOH}$  groups. It can be seen that the structure of the hydrous liquid exhibits other states whose appearance is not *a priori* evident. In particular  $\text{SiO}$  dangling bonds highlighted in yellow and oxygen tri-clusters (highlighted in blue) are present. The contribution of these defects to the diffusion process of hydrogen was also revealed in reference [6].

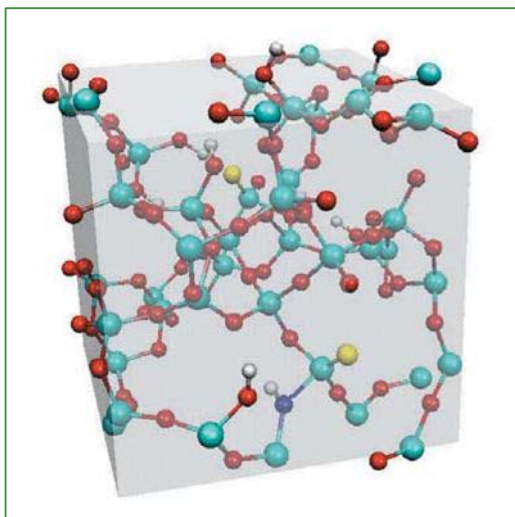
It is remarkable that even at temperatures of 3500 K and 3000 K the silica tetrahedral

network is preserved. Also during an ultra-fast quench, with a quench rate of the order of  $10^{14}$  K/s, the tetrahedral network is not destroyed (in agreement with other studies [8]) and hence the structure at ambient temperature obtained from the computer simulation should be realistic. Indeed this can be demonstrated for the neutron scattering structure factor. Figure 2 shows the simulated neutron scattering structure factor for dry and hydrous silica at ambient temperature, compared with the same quantity recorded on D20. Generally the experimental and simulated curves are in rather good agreement. Deviations occur only for very low  $q$  and between  $9 \text{ \AA}^{-1}$  and  $12 \text{ \AA}^{-1}$ . At low  $q$  the deviations from the simulation to the experiment can be ascribed to the rapid cooling

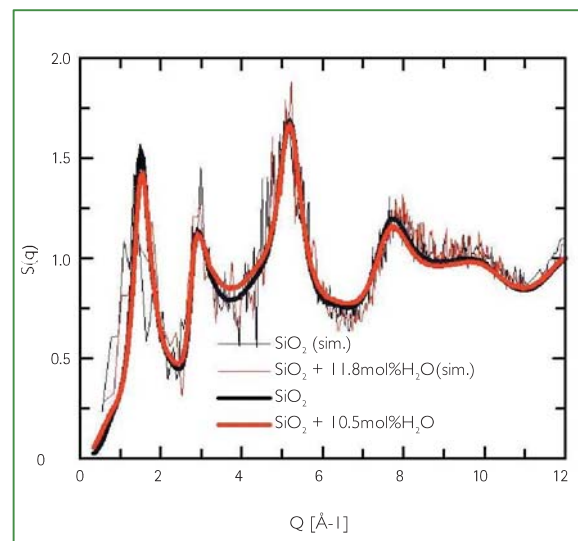
rate in the simulation. The deviations between  $9 \text{ \AA}^{-1}$  and  $12 \text{ \AA}^{-1}$  most probably arise from the corrections made to the experimental data. Experiment and simulation therefore clearly demonstrate that water does not significantly affect the silica tetrahedral network. Comparison with studies of sodium silicates, shows that the influence of sodium oxide on the structure of silica is much greater than the influence of water. This effect is predominantly related to the different sizes of the hydrogen and the sodium atom [6].

The neutron scattering structure factor  $S(q)$  is one of the few ways to calibrate simulation with experiments and thereafter microscopic information can be extracted with greater confidence from the simula-

tion. Due to the *ab initio* character of the simulations, they are able to reveal electronic features of the system [9]. In particular our simulations were able to confirm predictions made many years ago on states in the electronic band gap that lead to electronic conductivity [10] and may be responsible for the breakdown of semiconductor devices. Proton conductivity, associated with the different states of hydrogen in the silicate network, remains to be investigated by quasi-elastic neutron scattering. Finally this work demonstrates that the combination of neutron scattering and *ab initio* molecular dynamics simulations allow problems to be investigated in detail, which are relevant to the semiconductor industry and other fields where silica and silicates are important.



**Figure 1:** Snapshot of  $\text{SiO}_2 + 11.8\text{mol}\% \text{H}_2\text{O}$  at 3500 K. Silicon (green spheres), oxygen (red spheres), and hydrogen (white spheres) and the defect states, SiO dangling bonds (yellow spheres) and O bridging hydroxyl groups (blue spheres).



**Figure 2:** Neutron scattering structure factor of pure and hydrous silica at 300 K as obtained from the experiment (bold lines) and the simulation (thin lines).

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