

# Hybrid quantum-classical simulation of the reaction of breaking bond by water molecules in silica glass

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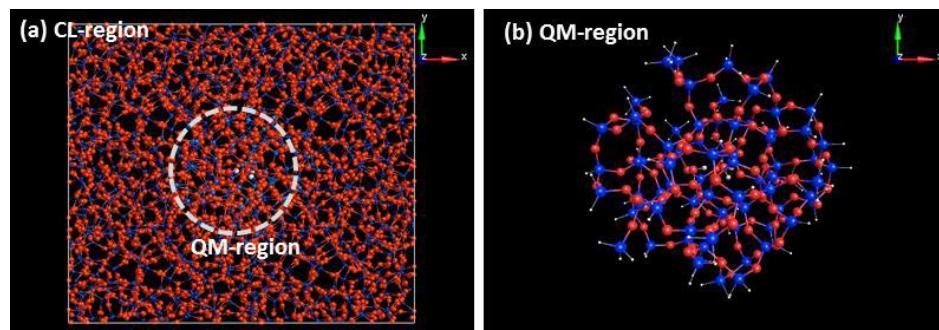
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The silica glass is a fundamental of various kinds of glasses and is widely used, e.g., in the optical fibers. Due to the brittleness of the silica glass, the micro-cracks and impurities contained in it influence sensitively its strength and lifetime. It is experimentally well known that the water molecules, which migrate into the silica glass from the moisture environment, react with the silica atoms to break the stretched Si-O bond, resulting in accelerated breakage of the glass. The reaction mechanism of the bond breakage has been believed to follow the Michalske-Freiman reaction model ( $\text{H}_2\text{O} + \text{-Si-O-Si-} \Rightarrow \text{-Si-OH} + \text{HO-Si-}$ )[1].

We propose a novel reaction model between the water molecules and silica glass by performing reaction-dynamics simulation using the hybrid quantum-classical method. In the hybrid method, the quantum region treated with the electronic density-functional theory (DFT) is embedded in a large classical system: the quantum and classical regions couple mechanically with each other. We perform the hybrid simulation of a silica glass system (about four thousand atoms) with water molecules inserted in it (Figure 1 (a)). We set the quantum region as that composed of the water molecules and their surrounding atoms (Figure 1 (b)). For fast computation we use the real-space grid based implemented of the Kohn-Sham DFT (RGDFT) code.

In the cases where a single water molecule in highly stretched or expanded systems contrary to the Michalske-Freiman reaction model mentioned above. In the cases where two molecules are placed initially at neighboring sites, they attract each other to form a water-dimer in a relatively large site of the silica glass. Those self-dimerized water molecules react quite sensitively with the silica atoms to break the Si-O bond. Detailed analyses about the reaction mechanisms are presented.



**Figure 1:** Hybrid Quantum-Classical simulation of  $\text{SiO}_2$ . (a) Classical (CL)-region. (b) Quantum (QM)-region. Si is shown in blue, O in red, and H in gray.

[1] T. A. Michalske and S. W. Freiman, J. Am. Ceram. Soc. **66** (1983) 284.

## **Simulation of impurity atom segregation formation kinetic in the vicinity of dislocations and crack tips**

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Elastic fields, generated by defects of the structure, influence the diffusion processes. To describe the stress influence on diffusion flows in interstitial alloys, we use an approach, developed earlier for the case of vacancy mechanism. This approach is in contrast to most other known takes into account atomic structure in the vicinity of the impurity atom and the structure changes under strains not only on rest position but also at the position of the saddle point. Stress fields alter the surrounding atom configuration and, as a consequence, the height of the activation barrier is changed. In contrast to our works [1,2], we consider, that in inhomogeneous systems, the barrier height depends on the two coordinates: rest position and saddle-point position and hence jump rate also depends on these two coordinates. Knowing the changes of the activation barriers it is possible to calculate the jump rates. The rates of atom jumps in different directions define the flux density of the defects, the explicit form of which can be derived by calculating the balance of different jumps and their contribution to the flux. We obtain the expressions for the interstitial diffusion fluxes in FCC and BCC structures for different kinds of atom jumps. In these nonlinear equations, influence of deformation tensor component on diffusion flux is determined by coefficients depending on atom interaction and atomic structures in the vicinity of the saddle point and rest position. New equations are differed sufficiently from the equations obtained in [2]. Our approach gives the possibility to use the equations at low temperatures, in conditions where the strain influence on the diffusion fluxes is manifested in maximal degree.

We use new equations for studying of interstitial impurity atom redistribution kinetics in the vicinity of crack tips or dislocations taking into account the strain generated by mentioned defects. Two levels of simulation are applied. First one is evaluation of mentioned coefficients that determine the influence of strain tensor component on diffusion flux. For this purpose we have developed a model into the framework of molecular static method taking into account an atom environment as near the interstitial site as for the saddle-point configuration. The second level is modeling of interstitial segregation formation based on nonlinear diffusion equations taking stress fields generated by defects. The results of simulation show, that the distribution of the interstitials near the crack tip has a quite complicated character and the hydrogen distribution has qualitatively different character as compared with carbon distribution.

[1] A.V. Nazarov and A.A. Mikheev, J. Phys.: Condens. Matter **20**, 485203 (2008).

[2] Andrei Nazarov, Alexander Mikheev, Irina Valikova and Alexander Zaluzhnyi, Solid State Phenomena, **172-174**, 1156 (2011).

# **Understating pitting in the passive layer of carbon steel starting from first principles study of its point defects**

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In a CO<sub>2</sub>-rich anoxic aqueous environment as in some oil fields, a layer of siderite (FeCO<sub>3</sub>) grows on carbon steel as a byproduct of steel corrosion. This layer acts as a resistive barrier that kinetically slows down further corrosion of steel. A safe and economic employment of carbon steel in such oil fields strongly relies on the coherence of this siderite layer. However, under certain conditions, yet to be discovered, siderite suffers pitting corrosion. The pitting is believed to initiate at weak spots in the siderite layer and proceed by the dissolution of the layer into the surrounding aqueous environment [1]. The weak spots, at which pits are initiated, are suggested to be weak due to the accumulation of point defects [2]. The purpose of this study is to understand the defect equilibria in siderite under various thermodynamic conditions as a first step to understand pit initiation.

We use density functional theory (DFT) with an on-site Coulomb interaction (U) for d electrons, to study iron, carbonate and electronic defects in FeCO<sub>3</sub>. By applying charge neutrality condition, we compute the concentration of these defects as a function of the thickness of the siderite layer starting from the iron rich region (steel/siderite interface) to the carbonate rich region (siderite/water interface).

A multi-scale approach that links our atomic scale modeling with a rate-equations model such as the point defect model [2] provides a potentially predictive paradigm for pitting in carbon steel. A discussion of the capabilities and challenges of this paradigm will be discussed.

[1] J. Han, S. Nesic, Y. Yang, B. N. Brown, *Electrochim. Acta*, **56**, 5396, (2011).

[2] D. D. Macdonald, *Pure Appl. Chem.*, **71**, 951, (1999).