

## Multiscale Nature of Stress Corrosion Cracking

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Stress corrosion cracking (SCC) is an inherently multiscale process that requires a combination of experiment and simulation to understand. This talk will focus on the nature of stress corrosion cracking from atomistic to macroscopic length scales. Emphasis will be placed on the phenomenon of irradiation assisted stress corrosion cracking (IASCC) in austenitic stainless steels as an example of a process that can be understood only through combinations of techniques over a range of length scales. IASCC is believed to be driven by the combined action of localized deformation, grain boundaries and an aggressive environment. Using novel experimental techniques employing an in-situ capability, pre-determined and pre-characterized geometries for dislocation channel- grain boundary interaction, and molecular statics and molecular dynamics modeling of channel-boundary interaction, we are determining the basic processes and mechanisms by which IG cracking initiates in irradiated austenitic Fe-Cr-Ni alloys conducted in aggressive media at high temperature. A key aspect of this effort is that it embraces the essence of mesoscale science, providing the linkage from atomistic simulations of dislocation responses to the accommodation and emission of dislocations from grain boundaries, and direct observation of dislocations with irradiation defects and grain boundaries to macroscale experiments. A consequence of this combined effort has been the identification of the factors most likely responsible for establishing not only the local stress state at grain boundaries prone to failure but their location with respect to the macroscopic applied stress.

## Multiscale simulations of stress corrosion effects and surface response to charging

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Stress corrosion, tribochemical wear or the mechanical response of surfaces to charging are phenomena which require quantum mechanical treatment of the elementary physical phenomena but at the same time reveal their macroscopic consequences only by integration or interpretation on macroscopic scales.

As examples, I will address the dissociative chemisorption of H<sub>2</sub> molecules at the edges of hydrogen-induced platelet defects in silicon crystals which stabilizes the breaking up of highly strained silicon bonds. The resulting stress-corrosion fracture process yields atomically smooth cleavage of Si crystals along otherwise unstable (100) planes. Similar chemical reactions have a big influence on the tribological behaviour of diamond. Linear carbon chains that form during sliding of diamond surfaces undergo a fast degradation process upon exposure to air. This oxidative wear process is triggered by the chemisorption of O<sub>2</sub> molecules that lead to the splitting and to the shortening of such sp<sup>3</sup>-hybridized structures.

Direct electrical charging of metal surfaces alters the surface properties significantly. Electronic structure calculations allow assessing the effect of tangential strain on the work function and the change in surface stress as a function of charging. This is demonstrated on the 4d series of transition metals. They mostly follow a parabolic behavior, which is dependent on the d-band occupancy until we reach the noble metals, which show an s-band occupation dependency. The variation of the stress-charge coefficients is interpreted in terms of a bonding-antibonding orbital occupation.

## Multiscale modelling of materials chemomechanics: from catastrophic brittle fracture to stress corrosion cracking

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Fracture of oxides and semiconductors is the dominant failure process underlying many materials reliability issues, and is also relevant to mining, where huge amounts of energy are required to fragment thousands of tons of rock into fine powder raising ever more serious sustainability issues. At the same time, fracture remains one of the most challenging 'multi-scale' modelling problems: since crack propagation is driven by the concentration of a long-range stress field at an atomically sharp crack tip, an accurate description of the chemical processes occurring in the near tip region is essential, as is the inclusion of a much larger region in the model systems. Both these requirements can be met by combining a quantum mechanical description of the crack tip with a classical atomistic model that captures the long-range elastic behaviour of the surrounding crystal matrix, using a QM/MM (quantum mechanics/molecular mechanics) approach such as the 'Learn on the Fly' (LOTF) scheme [1], or more recently a novel information-efficient Machine Learning extension of LOTF, where the results of all QM calculations are stored in a database and used this to predict forces on new configurations whenever possible, thus calling upon QM only when it is strictly necessary [2].

Examples of the application of these techniques to 'chemomechanical' processes, where complex and interrelated chemical and mechanical processes that originate at the atomic scale go on to determine the mechanical behaviour of a material, include low-speed dynamical fracture instabilities in silicon [3], interactions between moving cracks and material defects such as dislocations or impurities [4], very slow crack propagation via kink formation and migration, and chemically activated fracture, where cracks advance under the concerted action of stress and corrosion by chemical species such as oxygen or water [5]. The mechanism underlying stress-corrosion cracking in silica forms the topic of ongoing work, enabled by an INCITE award from the US DoE and hosted at the Argonne Leadership Computing Facility [6]. An expansion of the modeling approach to metals is also underway, focusing on the mechanical properties of nickel-based superalloys, a class of materials that exhibit excellent strength and creep-resistance at high temperatures making them suitable for the construction of efficient turbines for energy generation and aerospace applications [7].

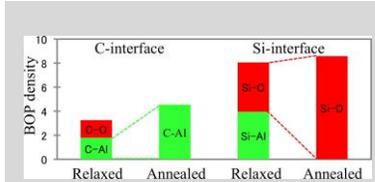
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# Self-Healing Materials and Damage from Shock Induced Nanobubble Collapse: Reactive Molecular Dynamics Simulations

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**Figure:** Purification of interfacial bonds by annealing. Total bond overlap populations of the C- and Si-interfaces are shown for both relaxed and annealed configurations. Bonds

Bonding and Structure of Ceramic-Ceramic Interfaces - Interfaces in multicomponent systems are critical in determining their material behavior. High-resolution TEM identified rich interfacial phases of thickness  $\sim 10 \text{ \AA}$ , which have distinct atomistic structures that do not exist in bulk phases. An archetypal ceramic/ceramic interface is formed between  $\text{Al}_2\text{O}_3$  and SiC, which is important for broad applications such as matrix-nanoparticle composites, high-power electronic devices, and self-healing nanocomposites that autonomously heal cracks and recover strengths. For better understanding and design of  $\text{Al}_2\text{O}_3/\text{SiC}$  interfaces, the central question is: What are the nature of interfacial bonding at the

atomistic level and its consequence on interphase structures?

Our quantum molecular dynamics (QMD) simulations of  $\alpha\text{-Al}_2\text{O}_3$  (0001)/3C-SiC (111) interfaces revealed profound effects of thermal annealing for producing strong interfaces consisting solely of cation-anion bonds. A Si-terminated SiC surface and  $\text{Al}_2\text{O}_3$  form a stronger interface (Si-interface) with a Si-O bond density of  $12.2 \text{ nm}^{-2}$ , whereas the C-interface has an Al-C bond density of  $9.46 \text{ nm}^{-2}$ . The interfacial bond strengthening is accompanied by the formation of an  $\text{Al}_2\text{O}_3$  interphase with a thickness of 2-8  $\text{ \AA}$ .

Damage on Silica Surface from Shock Induced Nanobubble Collapse - Despite a great deal of research on cavitation bubbles, several important questions about the mechano-chemistry of bubble collapse near a solid surface remain unanswered. In particular, an atomistic understanding is lacking. We have addressed these questions using billion-atom reactive molecular dynamics (RMD) simulations. These are the largest RMD simulations done on 163,840 processors IBM BlueGene/P at Argonne Leadership Computing Facility. The simulations revealed more chemical activity in water nanojets and vortex rings formed by collapsing nanobubbles, in cavitation pits on silica surface and around secondary shock waves. We found that the structural damage is intimately related to the chemical processes initiated by water nanojets, and can be mitigated by incorporating suitable gas in the nanobubble.

We examine chemical and mechanical damages due to shock-induced collapse of a nanobubble near a silica slab. We also performed two sets of simulations in which the nanobubble contained an inert gas at a density of 0.24 g/cc. The role of gas density in the stability of a single bubble is usually examined for gas densities around 0.5 g/cc. The simulated systems contained  $10^9$  and  $10^8$  atoms and the initial bubble radii in these systems were again 97.6 nm and 40 nm, respectively.

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# Mapping Strain Rate Dependence of Dislocation-Defect Interactions in Zirconium

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Probing the mechanisms of defect-defect interactions at strain rates lower than  $10^6 \text{ s}^{-1}$  is an unresolved challenge to date to molecular dynamics (MD) techniques. Here we propose a novel atomistic approach based on transition state theory and the concept of a strain-dependent effective activation barrier that is capable of simulating the kinetics of dislocation-defect interactions at virtually any strain rate, exemplified within  $10^{-7}$  to  $10^7 \text{ s}^{-1}$ . In particular, we investigate the interaction between an edge type dislocation and an irradiation induced self interstitial atom (SIA) cluster in Zr as a model system.

The resulting interaction paths, energy barriers and critical stresses are found to depend significantly on the strain rates and temperatures considered. We found that, at low strain rate and high temperature conditions, the SIA cluster is eventually absorbed by the dislocation forming a jog structure, and thus, assists the climb. However, at high strain rate and low temperature conditions, the dislocation passes through the cluster. Both the dislocation and the SIA cluster fully recover their original structures, and this process has no contribution to climb. Our predictions of a crossover from a defect recovery at the low strain rate regime to defect absorption behavior in the high strain-rate regime are validated against independent, direct MD simulations at  $10^5$  to  $10^7 \text{ s}^{-1}$ . Implications of the present approach for probing molecular-level mechanisms in strain-rate regimes previously considered inaccessible to atomistic simulations are discussed.

## **Measurements and Observations on Adhesion to Brittle Materials**

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Bonded systems between different material families (metals, ceramics, and polymers), and within each family are widely used. A few examples include: polymer coated dielectrics, encapsulated electronic packages, brazed and soldered assemblies, glass to metal seals, plated and coated electrical contacts, coatings on tribological materials, and arc-sprayed components. The performance of such multi-materials systems is often limited by the adhesion between the layers. Experimental observations and measurements of interfacial properties in ceramic-polymer/metal systems are described. Spherical shaped indenters have been used to induce delaminations at the interface. The load for initial delamination is used to measure the interfacial strength, while the load-crack length relationships are used to estimate interfacial toughness. In the ceramic-polymer system used for dielectric protection, surface chemical modifications led to enhanced interfacial toughness, and various modelling approaches needed to properly characterize the system are discussed. In the ceramic-metal cases described, the interfacial microstructure changes during processing or use (high temperature sealing, and solid-oxide fuel cell applications). Here we will highlight the reasons why multi-scale models are necessary for accurate descriptions of performance, and how experimental techniques can help in building these models.

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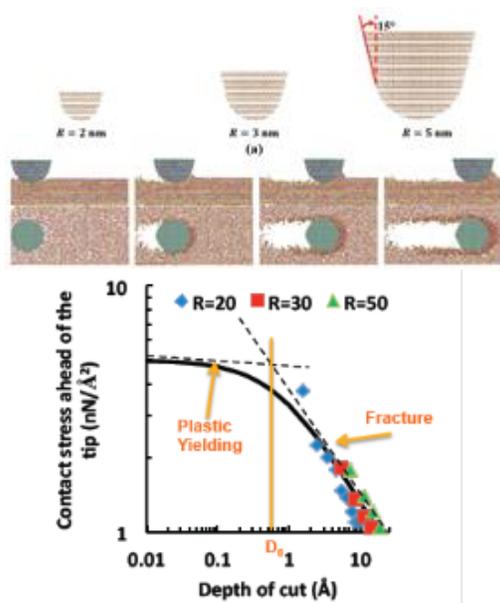
# Decoding the chemomechanics of friction and scratch in complex granular hydrated oxides

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Calcium-Silicate-Hydrate (C-S-H) is a structurally complex material that is the primary binding phase of all Portland cement concrete materials. C-S-H is typically considered as an assemblage of discrete nanoscale particles whose interactions are governed by nano-scale friction and interfacial cohesion. Despite the critical role of interparticle forces on mechanics of granular materials such as C-S-H, there is currently no unified understanding on the atomistic mechanisms governing the nanoscale friction, scratch and cohesion in C-S-H; a lack of knowledge, which presents a major barrier to decode the interplay between chemistry, structure and mechanics of various C-S-H systems. Here, we develop a molecular dynamics framework, coupled to a set of re-defined classical continuum relations, aimed at filling this gap. The normal force is calculated by relaxation of two C-S-H particles at various distances and crystallographic orientations. The effect of watery environment is studied by immersing the particles in water molecules, and the friction and scratch forces are calculated by sliding the tip over the substrate in various directions. Our study identifies the distinct contribution of van der Waals and electrostatic forces to the interfacial behavior of C-S-H particles. While the electrostatic forces govern the interaction of particles at short and large distances, the van der Waals forces are responsible for variations in the normal force at intermediate distances. We find that normal force varies sub-linearly with nanoscale contact area between the tip and substrate, while the friction force shows a linear trend. Our results demonstrate to what extent atoms of particular type contribute to the total interfacial forces. Due to large electronegativity, Si atoms (vs Ca, O and H)



**Figure 1.** Typical scratch test in C-S-H (top). Classical fracture size-effect of quasi-brittle materials does not hold for nanoscale scratch test in C-S-H.

contribute most to the friction and normal forces. Finally, we probe the effect of pile-up and show that the nanoscale scratch test does not follow the classical laws of size-effect in fracture of quasi-brittle materials (**Figure 1**). Our findings, for the first time, provide an “atomistic lens” on nanoscale friction and contact phenomena in particulate C-S-H systems. This has a significant impact on understating of C-S-H and modulation of its behavior, thus impacting the mechanics of granular cementitious materials.

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