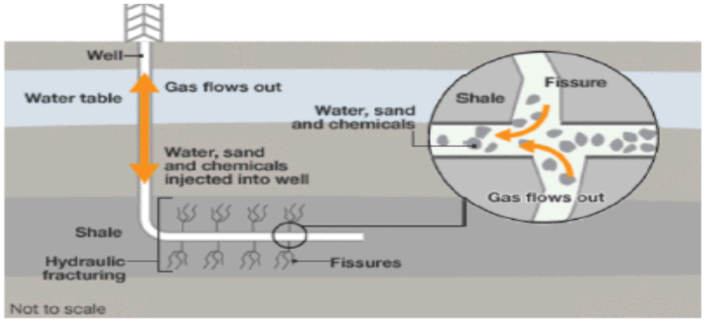
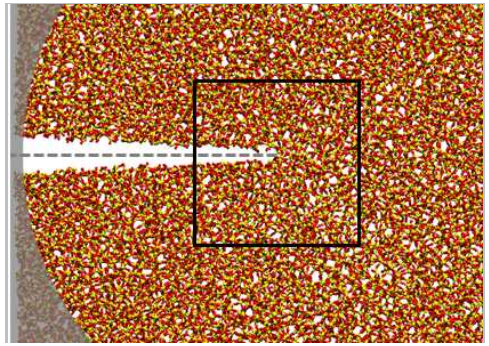
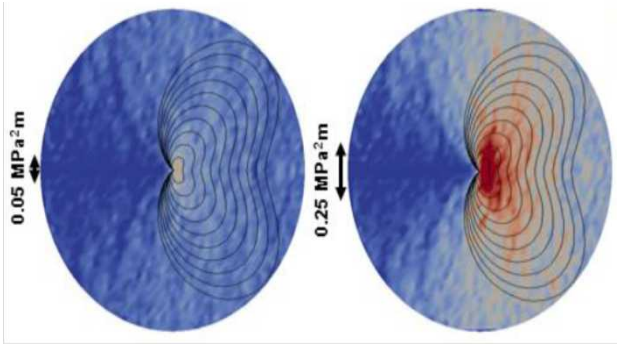
SAND2017-8333C







Nanoscale Stress-Corrosion of Silicate Glass in Aqueous Solutions

Louise J. Criscenti, Jessica M. Rimsza, Edward N. Matteo, and Reese E. Jones

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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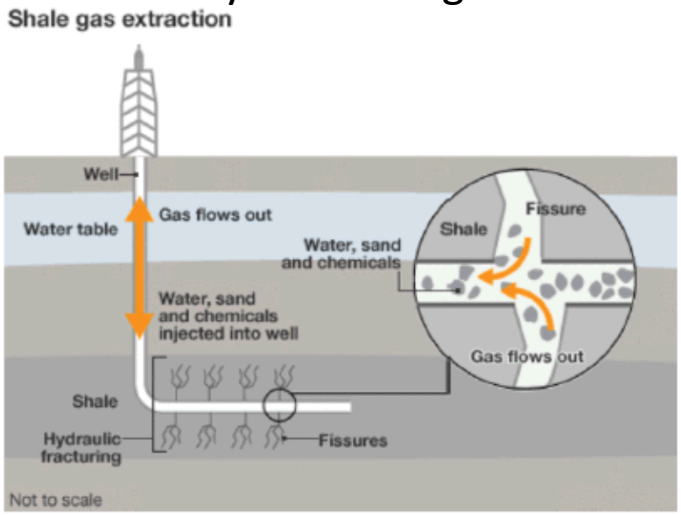
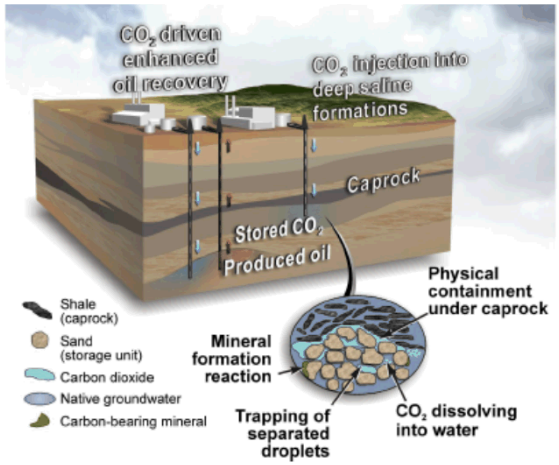
Motivation

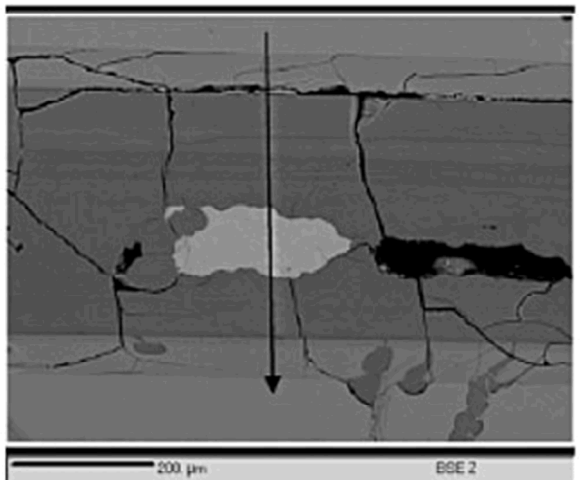
Hydrofracking



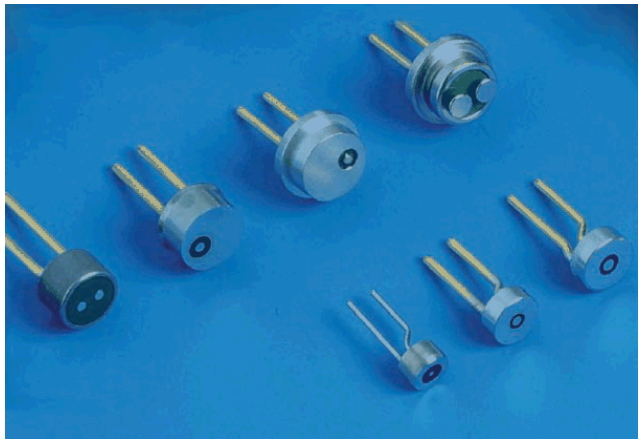
Sequestration



Crack in glass:
analog for glass waste form



Airbag feedthrough igniters



Overview

- To develop a fundamental atomistic-level understanding of the chemical-mechanical mechanisms that control subcritical cracks in low-permeability geomaterials.
- To link atomic-scale insight to macroscale observables and directly address how chemical environment affects mechanical behavior.
- **Why Atomistic Simulation?**
  - Cracks start at the atomistic scale – a crack tip will be initiated by the breaking of bonds (e.g., Si-O) at the rock-fluid interface.
  - Crack tip formation and crack propagation is impacted by interfacial fluid and surface chemistry (e.g., development of surface charge, impact of adsorbed species along fracture surface).

Chemical Effects on Subcritical Rock Fracture

Stress-Corrosion Cracking

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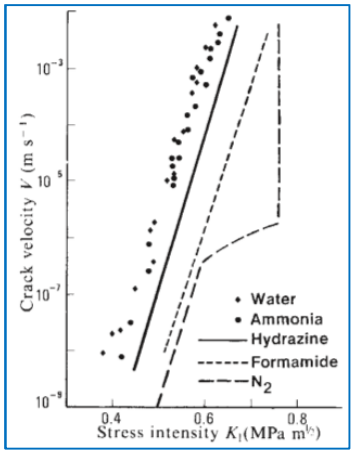
Silica Glass

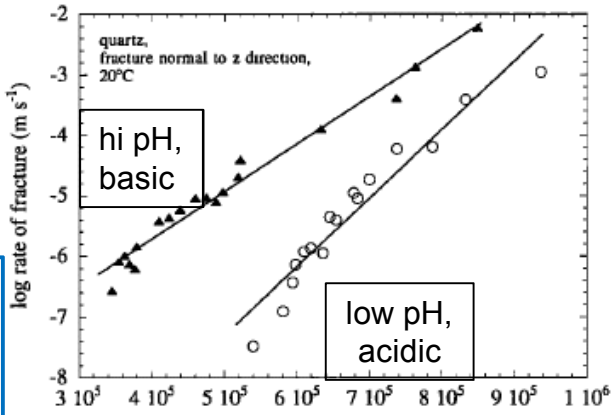


K_1 = measure of stress field at crack tip.

Orders of magnitude Difference in the rate of fracture with chemical environment

T.A. Michalske & S.W. Freiman, Nature (1982)

Quartz



K_I = stress intensity factor (N m$^{-3/2}$)

P. M. Dove, J. Geophys. Res. (1995)

Dove (1995) equation for rate of Si-O bond rupture

$$r_{Si-O} = \underbrace{A^*_{H2O}\left(exp\frac{-\Delta H_{H2O} + \boldsymbol{b_{H2O}K_1}}{RT}\right)\left(\theta^{H2O}_{Si-O}\right)}_{\text{>Si-O-Si< + } H_2O \text{ = * = 2>SiOH}} + \underbrace{A^*_{OH-}\left(exp\frac{-\Delta H_{OH-} + \boldsymbol{b_{OH-}K_1}}{RT}\right)\left(\theta^{OH-}_{Si-O}\right)}_{\text{>Si-O-Si< + } OH^- \text{ = *= >SiOH + >SiO}^-}$$

Without **bK_1** term, this expression would strictly describe quartz ***dissolution***

Objectives

- To calculate fracture toughness of dry silica glass from atomistic molecular simulation data
  - Start with a simple, well-studied isotropic material
  - Upscale atomistic data to macroscopic observable (fracture toughness)
- To calculate fracture toughness of wet silica glass from atomistic molecular simulation data
- To investigate the impact of different simple aqueous solution compositions on fracture propagation and toughness:
  - Cations: Li^+, Na^+, Ca^{2+}
  - Anions: OH^-, Cl^-
- To compare modeling and experimental results.

Fracture Mechanics Theory: Fracture Toughness

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Griffith Criterion:

$$\sigma_{cr} = \left(\frac{2E\gamma}{\pi c}\right)^{\frac{1}{2}}$$

Strain energy release rate (G) describes the energy stored in material prior to fracture

A linear elastic solution for a slit crack in plane strain mode I leads to:

$$G_{IC} = J_{IC} = \frac{K_{IC}^2(1-\nu)^2}{E} = 2\gamma_s$$

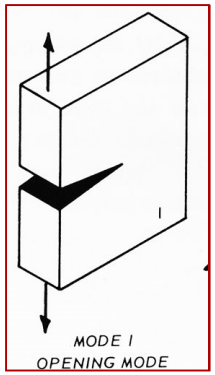
(brittle material)

$$G_{IC} = G_{diss} + 2\gamma_s$$

(material with inelastic behavior)

Fracture toughness (K_{IC}): **the energy required to propagate a crack in a material.**

σ_{cr} = critical stress
E = Young's modulus
c = crack length
γ = surface energy
K_I = stress intensity factor
ν = Poisson's ratio
G = strain energy release rate



J-integral: a path independent contour integral used to calculate *G* for monotonic loading

$$J = \int_{\partial\Omega} S \cdot dA$$

Eshelby stress field:

$$S = WI - H^T P$$

I is identity tensor

H = displacement gradient, measure of strain

P = stress

W = energy

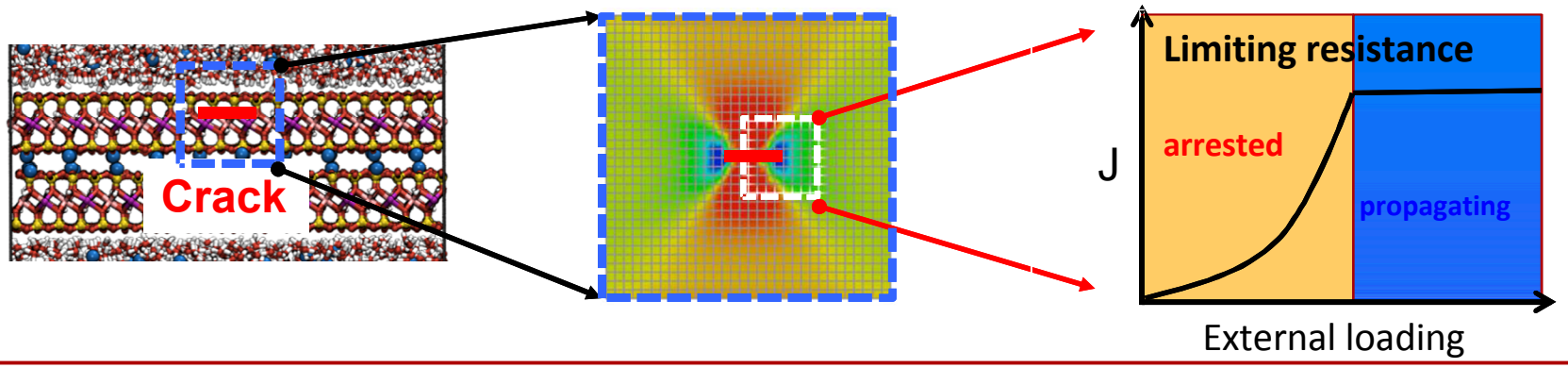
Mechanical Fracture Models

Upscaling Metrics: Atomistic to Continuum (AtC)

Molecular simulations sample atomic displacements, energies & forces

Eshelby stress fields use atomic data to characterize local energy available to move the crack (*in red*)

The J-integral is formed from the divergence of the Eshelby stress and determines if a crack will propagate

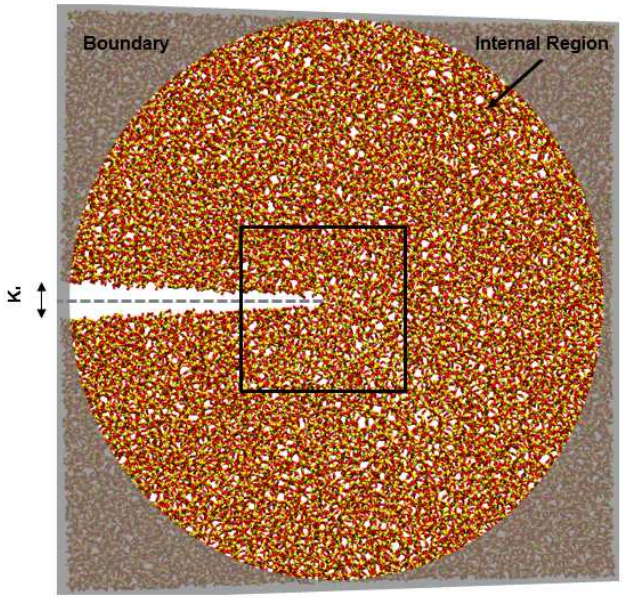


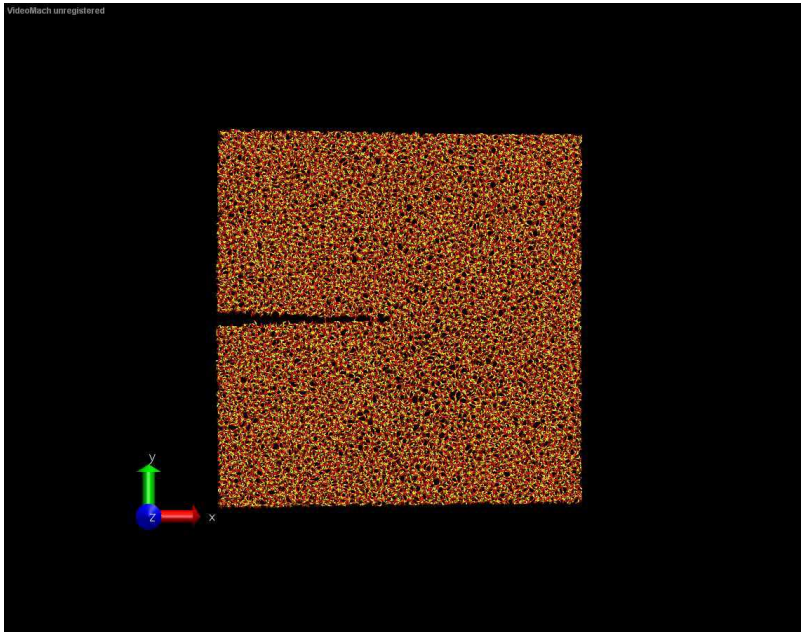
Jones & Zimmerman: First to successfully apply continuum fracture theory to atomistic systems to estimate fracture toughness

- The J-integral provides the characteristic crack tip driving force regardless of system configuration.
- **When J reaches the material's fracture toughness (J_c) , crack propagation begins**.
- J/J_c can be measured experimentally using geometries and procedures specified in standards (e.g. ASTM E1820 - Standard Test Method for Measurement of Fracture Toughness)

Simulation Set-Up for Dry Silica System

- ReaxFF Force Field, LAMMPS MD code (Plimpton, XXXX)
- Amorphous silica, system size: 38,400 atoms (143 Å x 143 Å x28 Å); Melt and quenched from β-cristobalite system; 12 replicas
- A slit crack is formed creating a singularity with highly concentrated stress
- Boundary atoms are fixed; Far-field loading as Mode I fracture
- Interior atoms are allowed to move freely
- Stress is introduced iteratively by increasing the crack width
- Atomic positions adjust to accommodate the added stress





Silica Fracture and Energy Dissipation

- Fracture propagates in distinct steps when the stress at the crack tip exceeds the strength of the material
- Perfectly brittle fracture will have no dissipation energy, with all energy used to propagate the fracture
- Dissipation energy calculated from change in energy of the system over the added surface area

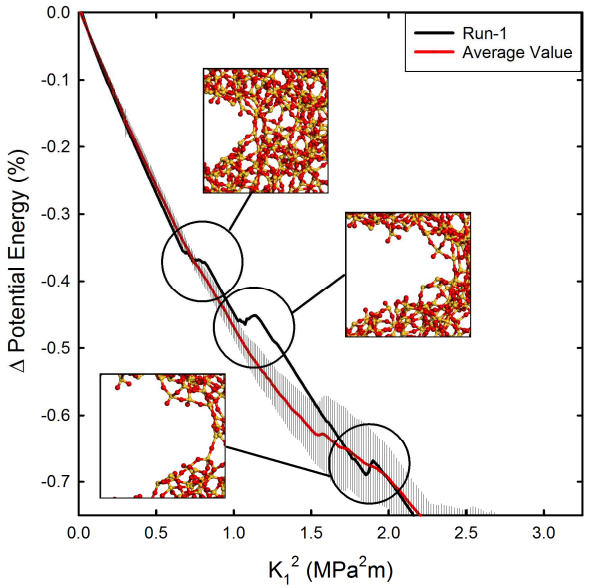
$$\frac{\Delta U}{\Delta S_A} = G_{diss}$$

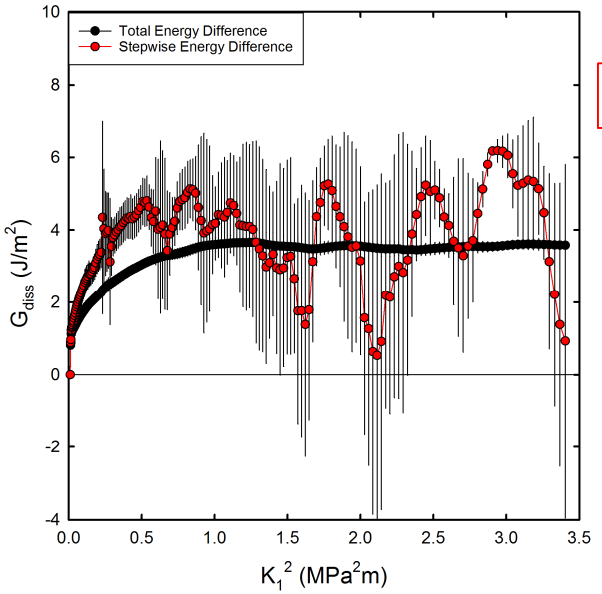
- Local inelastic behavior as energy is introduced into the silica during loading and not completely dissipated once fracture occurs

$$J_{IC} = G_{IC} = G_{diss} + 2\gamma_s$$

- Surface energies (γ_s): 1.2-2 J/m^2

Rimsza, J. M. et al. *Langmuir* (2017).



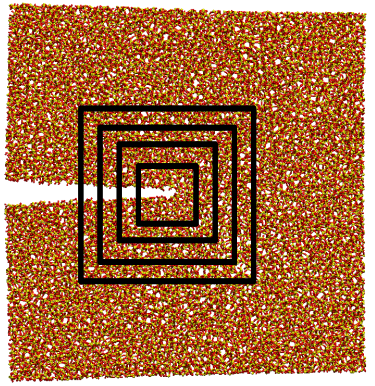


$G_{diss} = 3.5$ J/m^2

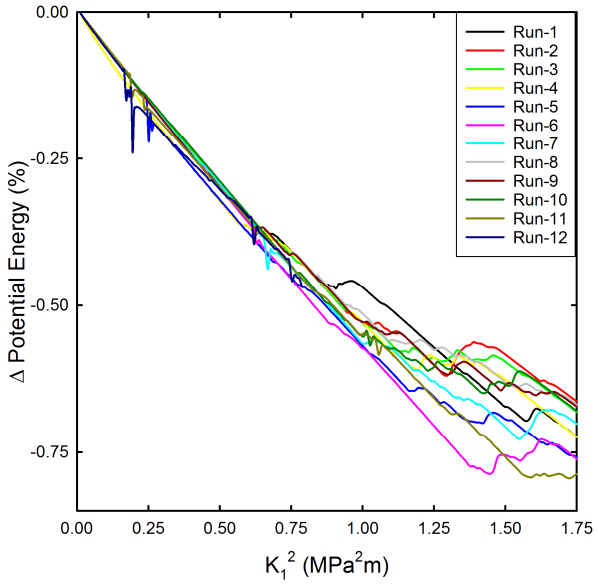
Estimated J_{IC} values are ~5.9-7.5 J/m^2

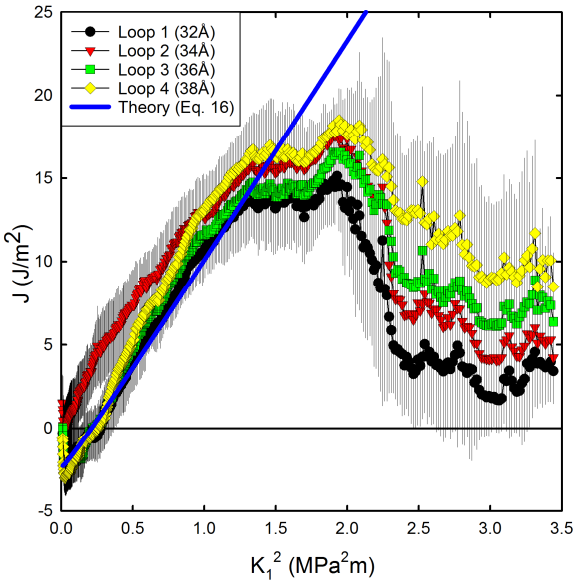
J-Integral Calculation for Dry Silica

- Calculated via the AtC method through coarse graining energy, displacement, and stress *Jones, Reese E., et al. J. Phys.: Condens. Matter (2010)*
- J-integral converges at loop sizes of ~3 nm approximates the size of the inelastic zone



Schematic of increasing loop sizes for J-integral convergence test



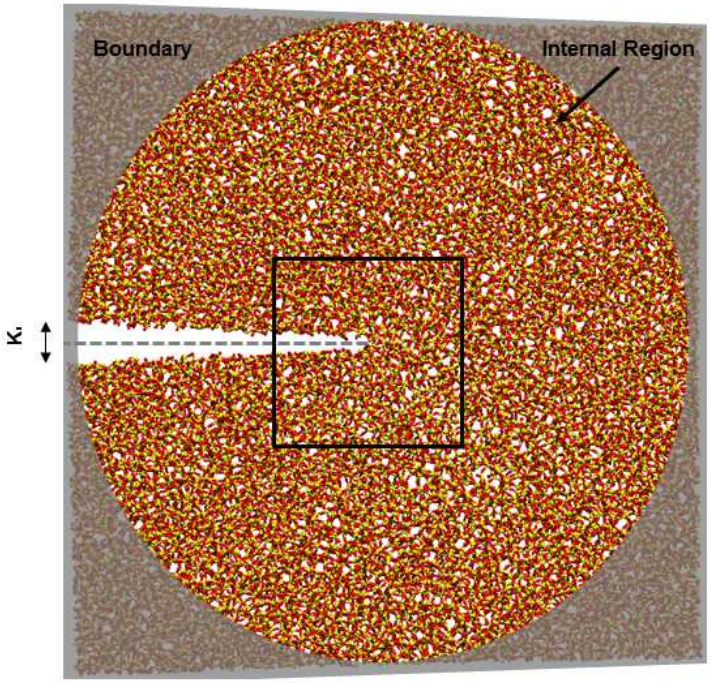


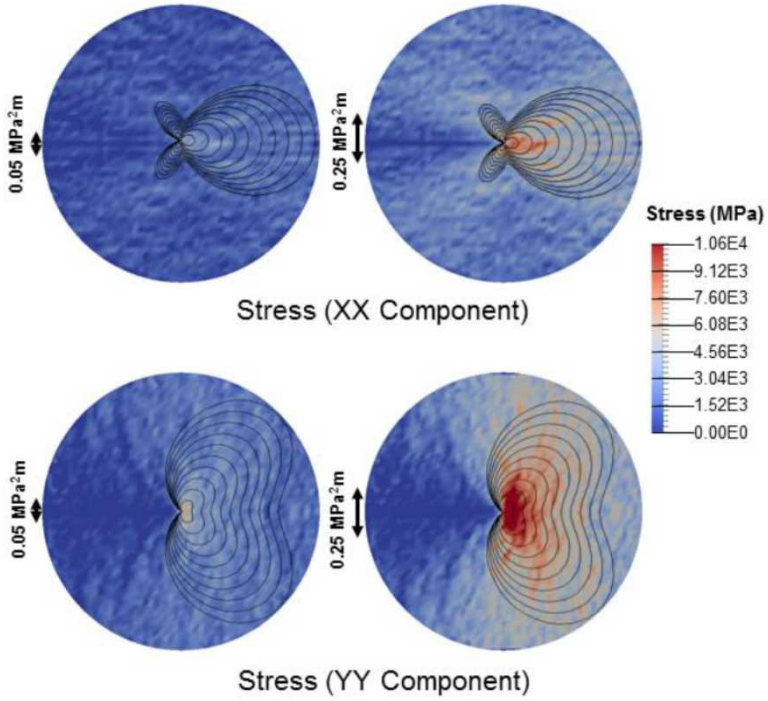
J-integrals with converged loop sizes

Calculated
K_{IC}=0.76±0.16 MPa√m
J_{IC}=6.16±4.34 J/m^2

Experimental
K_{IC}=0.78±0.04 MPa√m

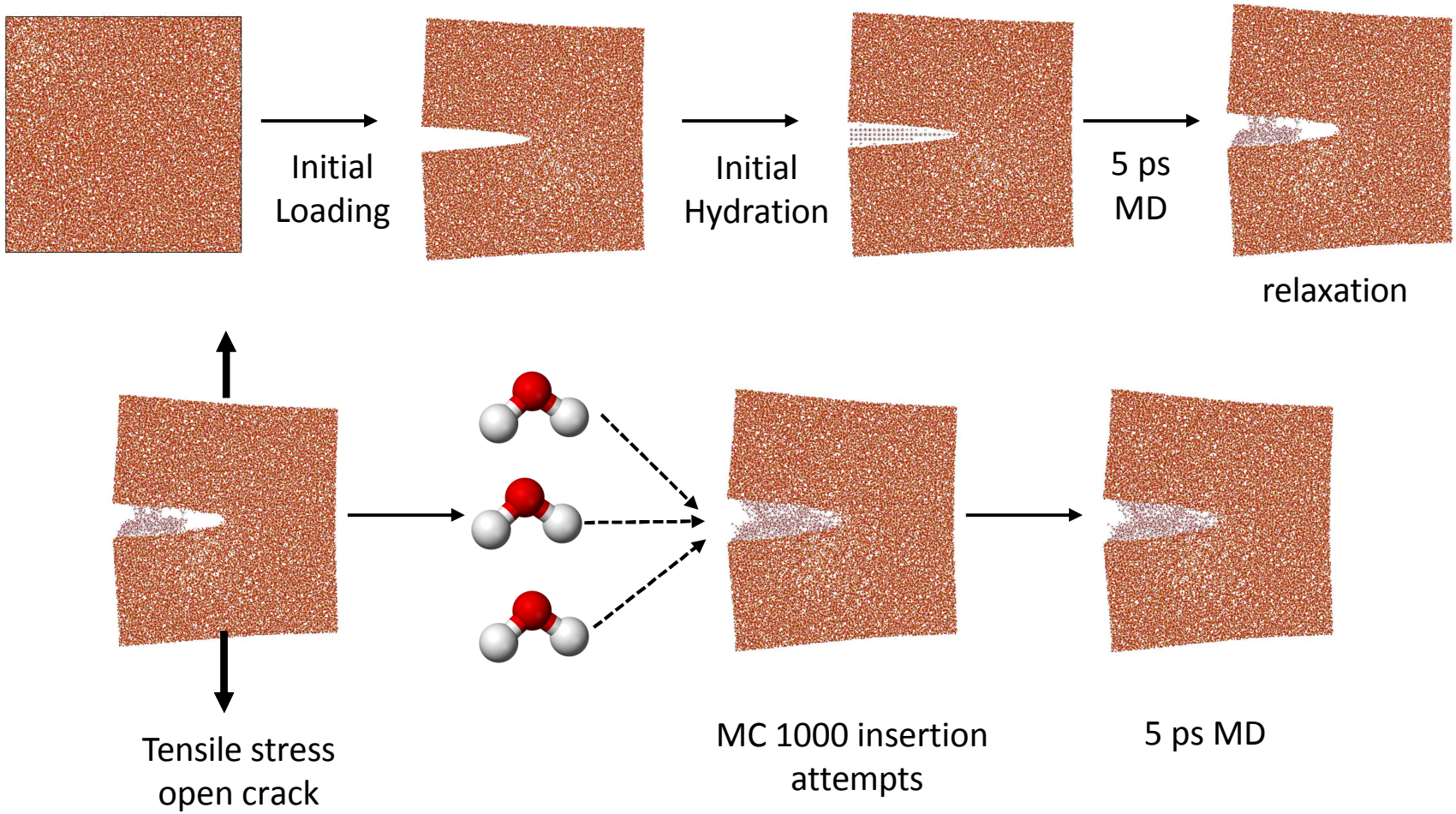
Simulated Stress Fields for Dry Silica





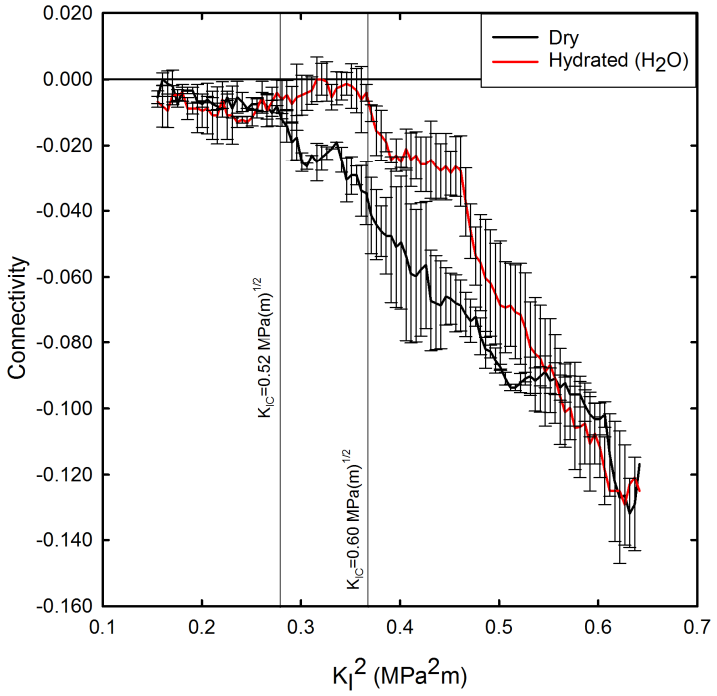
Crack tip stress fields in amorphous silica at two loading levels (K_I^2 ~ 0.05 and 0.25 MPa^2m). Black contours are from linear elastic solution.

Silica Fracture in Water: Methodology

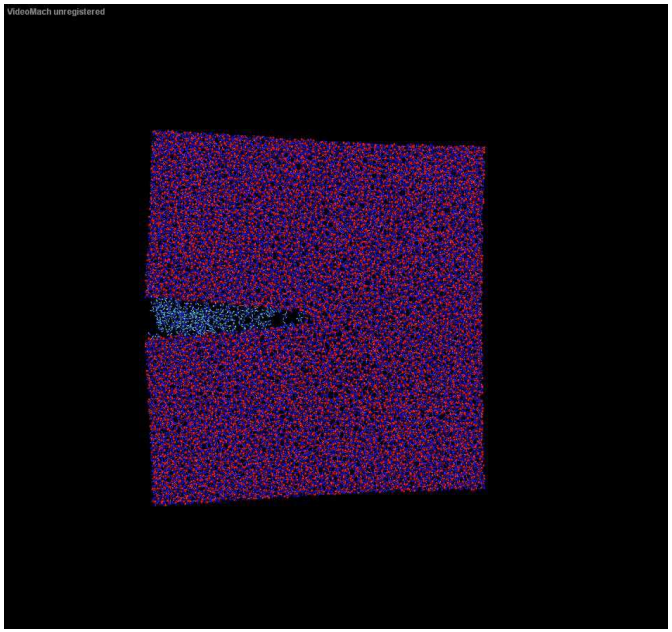


ReaxFF: Fracture of Hydrated Silica

- Water placed inside the crack followed by far field loading
- Dry silica fractures with less loading (~0.52 MpaVm) compared with wet systems (~0.60 MPaVm)

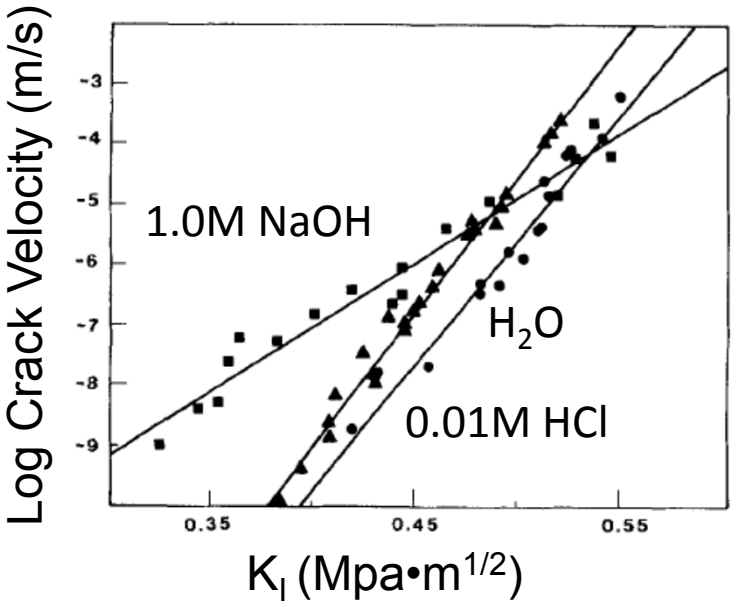


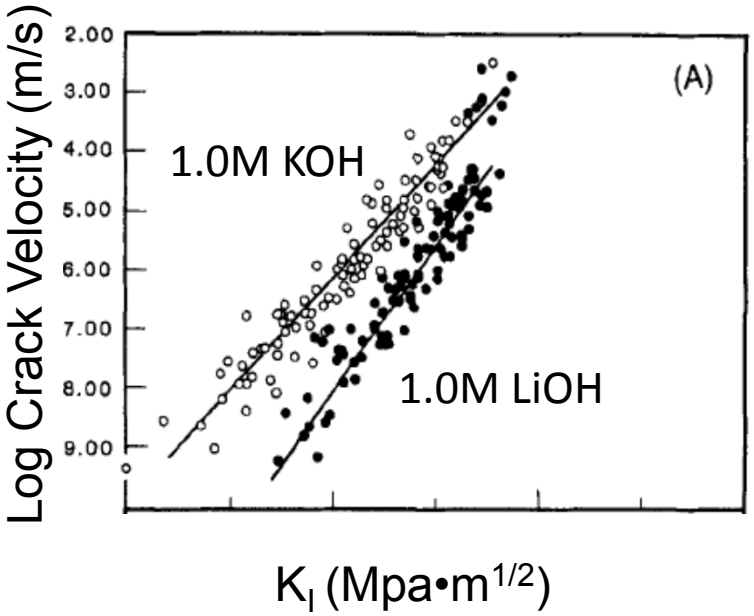
Changing connectivity with loading to identify when a fracture propagation event occurs in dry and hydrated systems



Fracture of hydrated silica
Colors: water (blue), silica (pink and purple)

Effect of Counterions on Crack Growth in Vitreous Silica





- The chemical activity of hydroxide is affected by the nature of the cation due to ion association.
- Hydroxide can penetrate the solvation shell of molecules.
- LiOH association decreases OH^- activity in solution more than NaOH association.
- Dependence of applied stress on cation identity: NaOH ~ KOH ~ CsOH > LiOH

0.1M NaOH	pK = -0.7
0.1M LiOH	pK = -0.08

1M NaOH	9% Associated
1 M LiOH	26% Associated

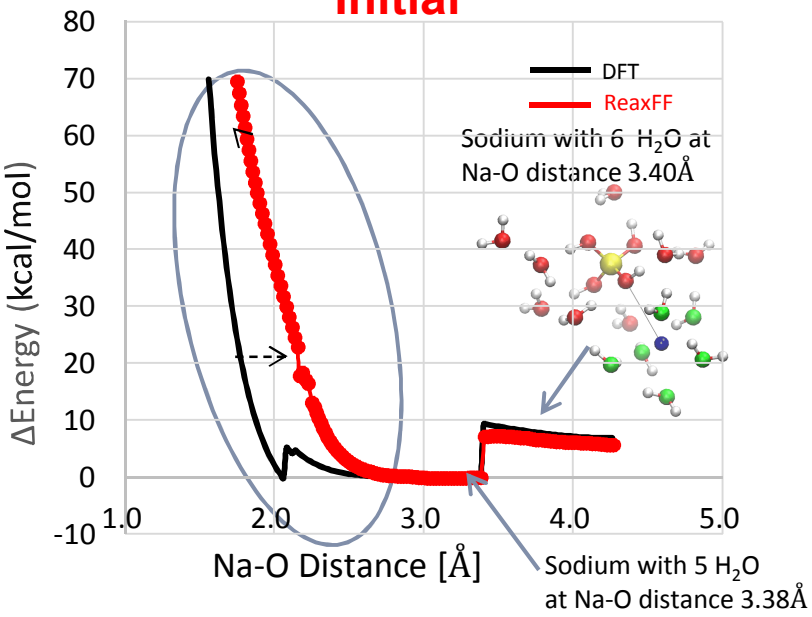
White et al., 1987

REAXFF Development

Adri van Duin, Penn State

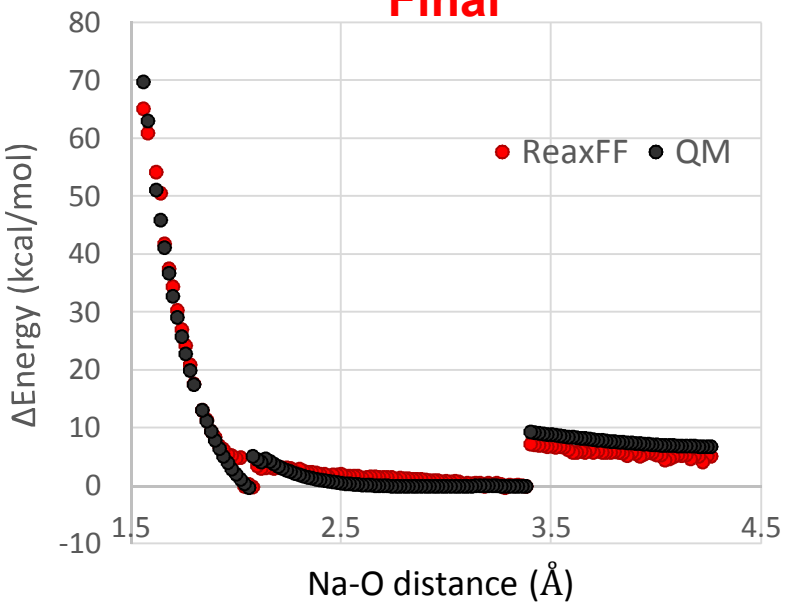
- Parameters for aqueous electrolytes under development at PennState
- NaOH, KOH, LiOH: Exhibits differences in association constants that are observed experimentally
- Collaboration between PennState and Sandia to develop parameters for Na^+-H_2O-SiO_2, Li^+-H_2O-SiO_2

Initial



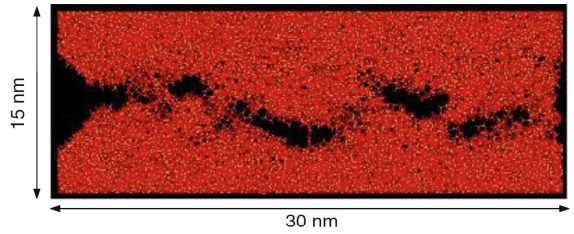
- Good agreement in 2.5-4.5 Å range
- ReaxFF is too repulsive below 2.5 Å

Final

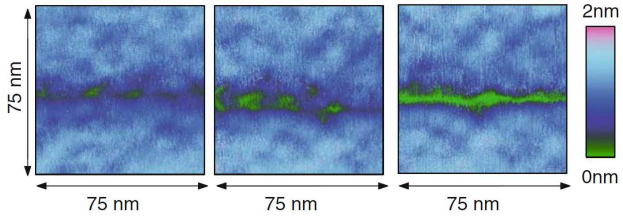


- Excellent agreement through the entire range, including energy jumps around 3.38 Å and 2.1 Å associated with H-bond configuration changes

Experimental Validation of K_{IC}

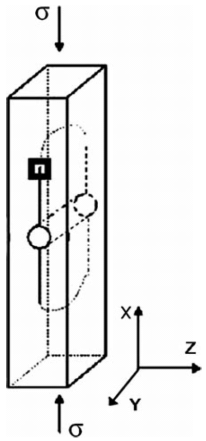


MD



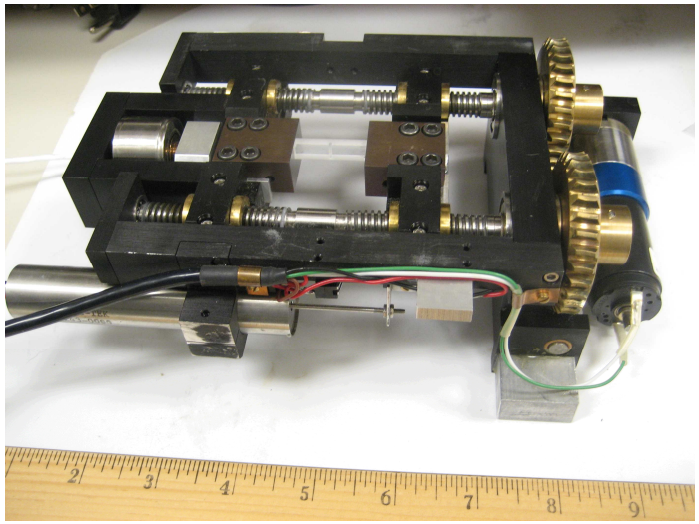
AFM

Bonomay et al. Int. J. Fract. 2006



DCDC = Double Cleavage Drilled Compression

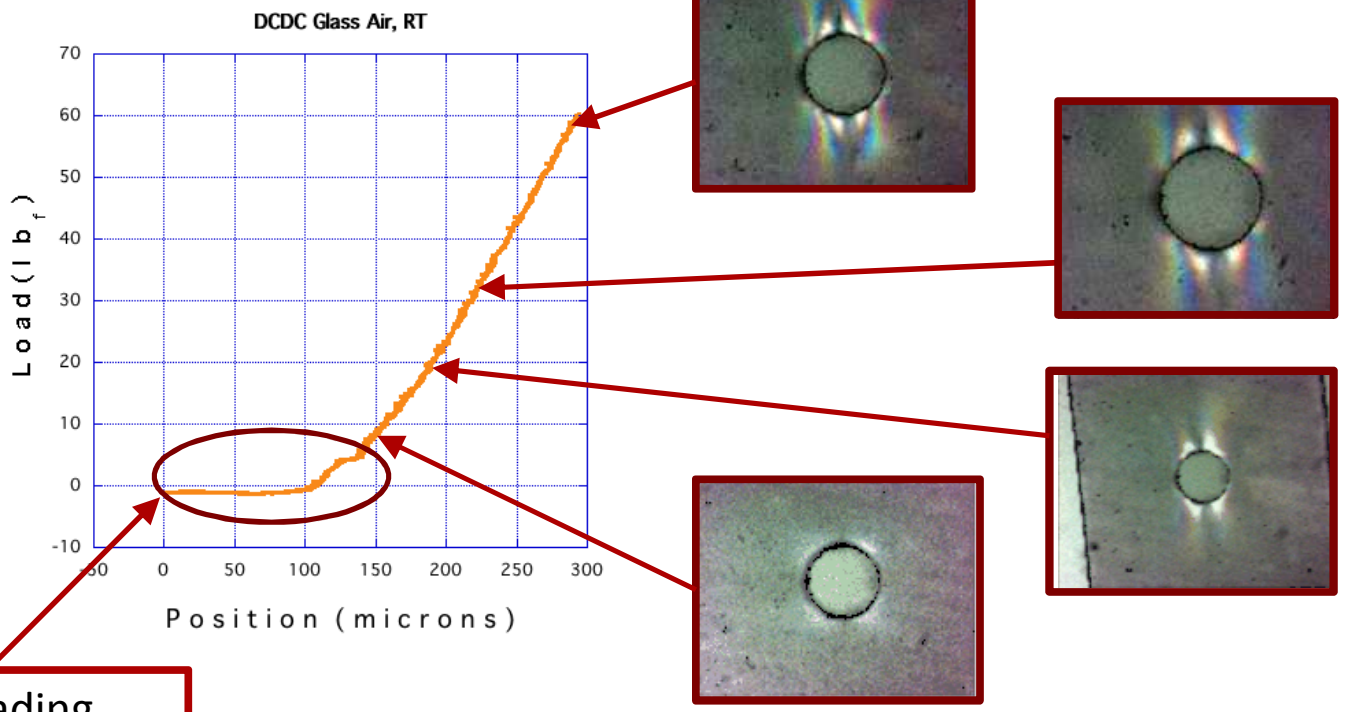
Technique may also be implemented with confocal microscope.



Load Frame

Review articles: Ciccotti, J. Phys. D 2009, Ciccoti et al. JNCS 2008

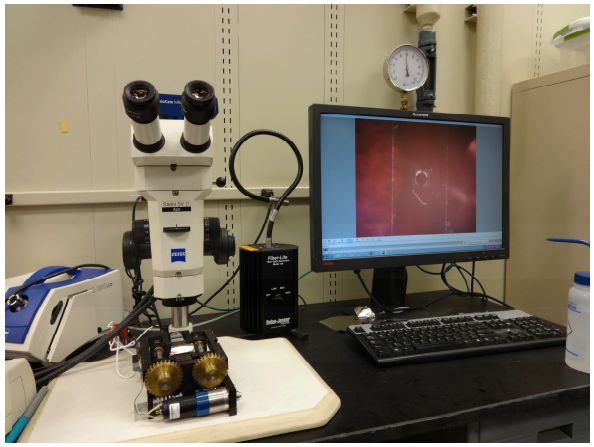
Imaging Capabilities and Preliminary Results for Dry Silica

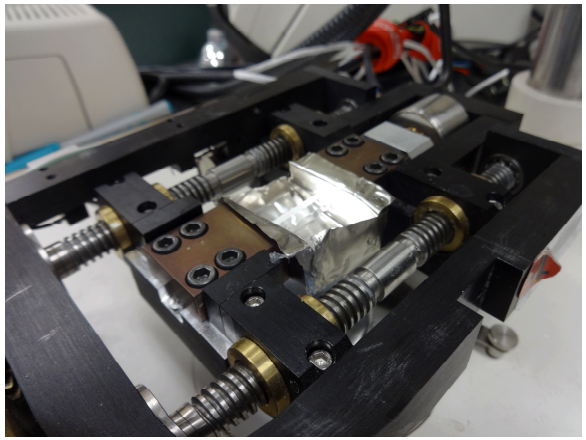


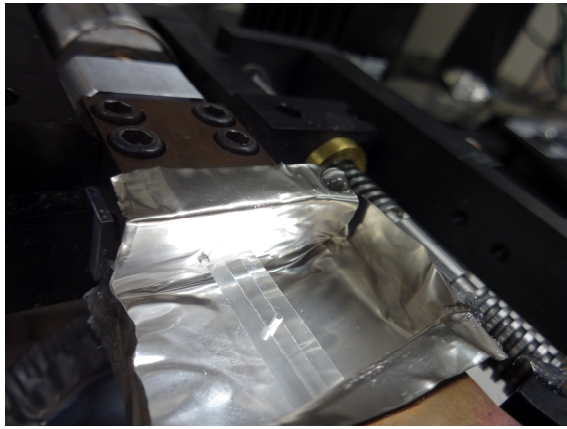
Sample loading and compliance of nickel foil

- Optical profilometry for post-test analysis and preliminary imaging of load frame tests of DCDC samples
- Polarized light microscopy for visualizing stress fields; will use Moiré analytical methods for stress field quantification

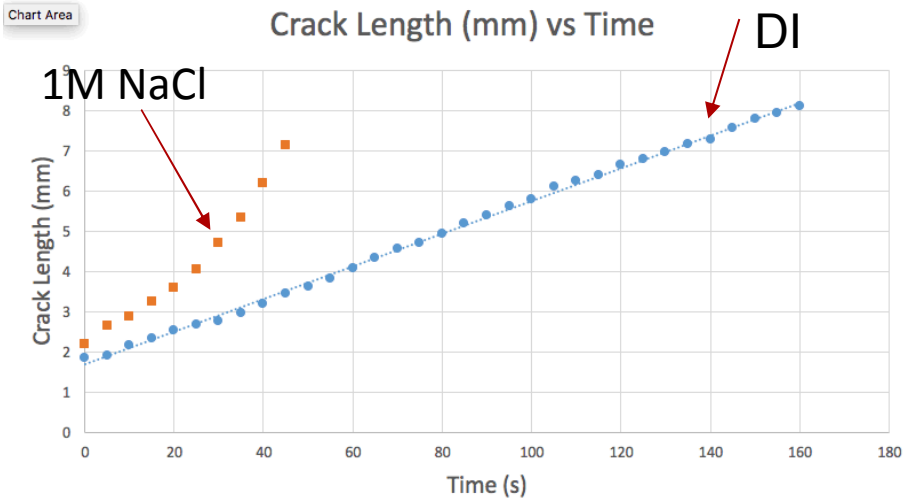
Experimental Results in Solution







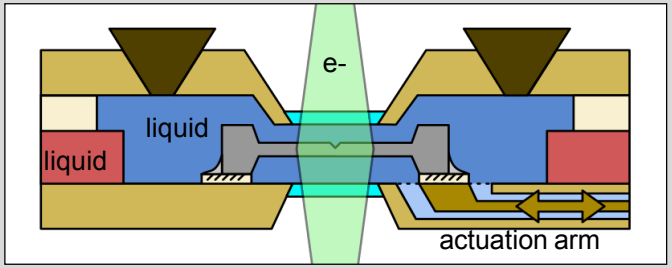
- Tested design for loading in liquids
- Repeatable loading of DCDC glass samples in DI water
- Air, DI, and 0.5 NaCl tested
- Upgraded test equipment for load frame and imaging
  - Software, updated laptop (Windows 10)
  - Time lapse software
  - Upgraded USB microscope



Different SNL Project
Developing Liquid-Mechanical TEM Platform

- First-of-its-kind MEMS device for quantitative testing the mechanical properties of materials within a controlled (chemical and temperature) liquid environment that is coupled with high-resolution real-time imaging
- Through BES support at CINT, this capability will be available to the international research community

Generation 1 Concept

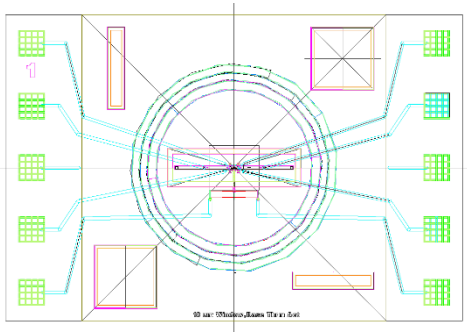


- Buried movable arm attached to sample
- Sample suspended over large pads
- Heating of liquid seal-ring
- Prevention of sample/window stiction
- SAM in movable arm and liquid seal-ring
- Low and high force actuators

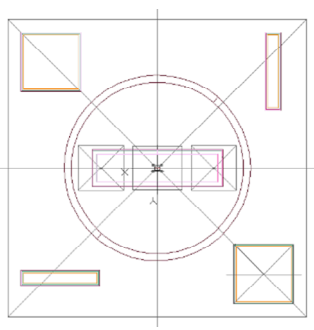
Liquid-Mechanical MEMS Device

- Nano Fracking TEM Base: 15 modules, 11 different designs, 240 usable die per wafer
  - 11 designs for testing of heaters, window dimensions, window thickness, sample placement, actuation strength, single vs. dual actuation, and capacitive sensing
- Nano Fracking TEM Lid: 25 modules, 4 different designs, 400 usable die per wafer
  - 4 different designs based on window dimensions and thickness

Base



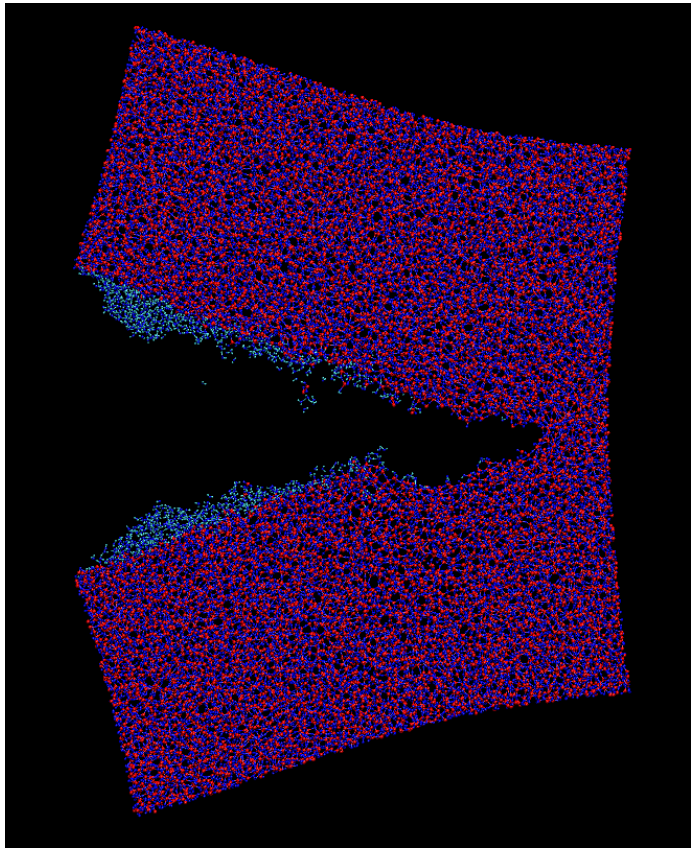
Lid



Summary and Conclusions

- First time atomistic simulation data has been used to calculate the macroscopic J-integral and crack stress fields from atomistic data for an oxide.
- First time ReaxFF has been used to investigate subcritical crack propagation using a slit crack and Mode I tension.
- First time that a molecular-scale simulation method has been developed for stress-corrosion cracking in DI water.
- First time that DCDC experiments have been conducted in environmental chambers – new experimental design

- In simulations for dry silica, a localized high stress inelastic region develops prior to fracture with an estimated radius between 3-3.2 nm.
- The calculated K_{IC} of ~0.76 MPa√m is consistent with experimental data reported in the literature.
- Preliminary data is consistent with conceptual models and previous experimental data.



Snapshot of fracture silica in a hydrated environment

Acknowledgements

This work was fully supported by the Laboratory Directed Research and Development (LDRD) program of Sandia National Laboratories.