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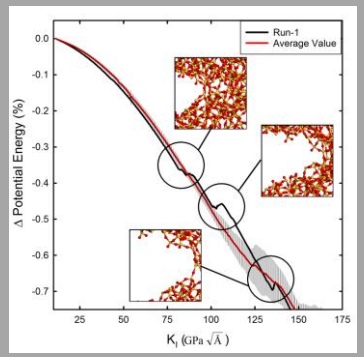

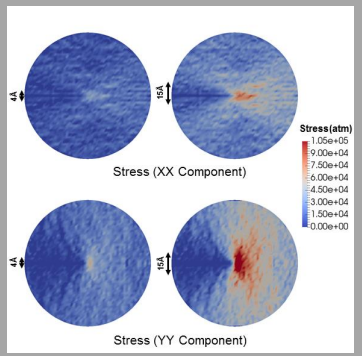

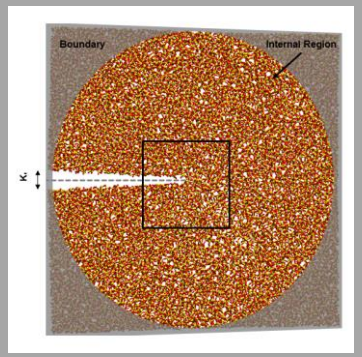

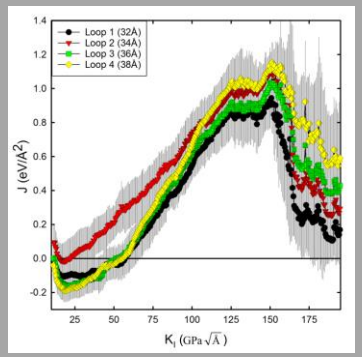

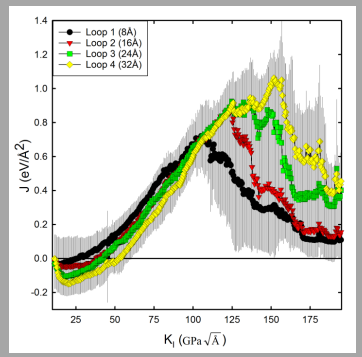

Atomistic-scale evaluation of the fracture toughness of silicates

J.M. Rimsza, R.E. Jones, L.J. Criscenti

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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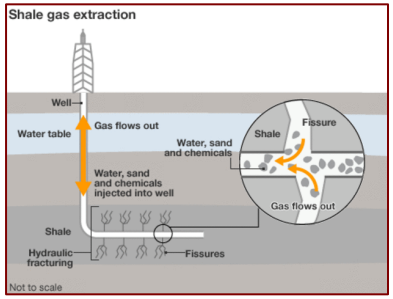
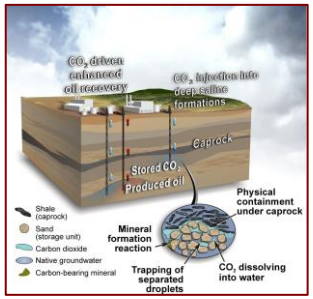
Technical Motivation

- Brittle fracture of silicates affect the stability and reliability of subsurface systems, making prediction of the mechanical response to fracking and carbon sequestration difficult

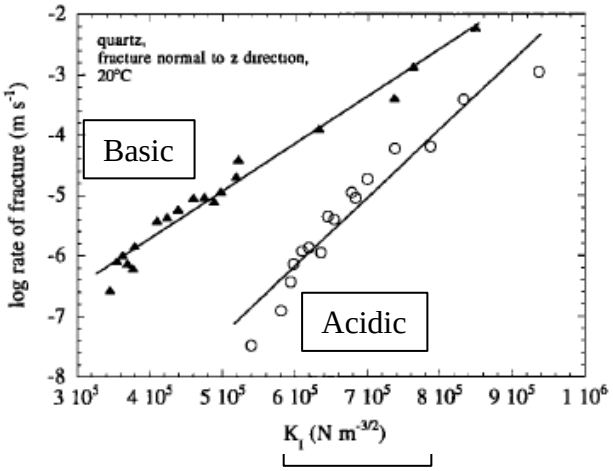




- Develop fundamental understanding of the chemical-mechanical mechanisms that control subcritical cracks in silicates.

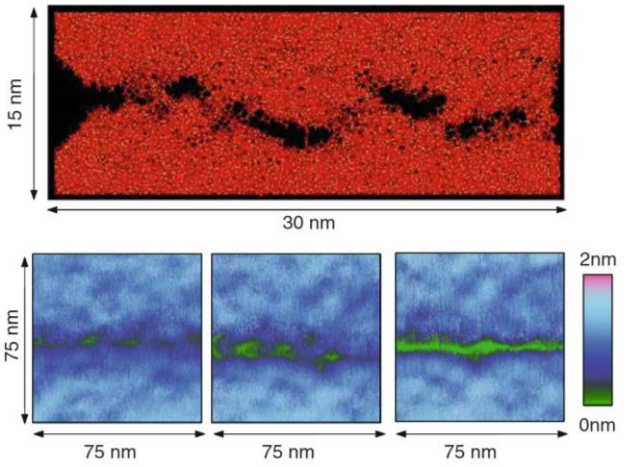
- Link atomic-scale insight to macroscale observables and directly address how chemical environment alter mechanical behavior.

- Why atomistic simulations?
  - Cracks start at the atomistic scale by the breaking of bonds at the solid-fluid interface.
  - Crack tip formation & crack propagation is influenced by fluid and surface chemistry (e.g., development of surface charge & adsorbed species along fracture surface).



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

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



Bonamy, Daniel, et al. *Int. J. Fract.* (2006)

Figures: Fracking (http://www.bbc.com/news/uk-14432401) carbon sequestration (https://www.arb.ca.gov/cc/sequestration/seq.htm)

Introduction to geomechanics

- Cracks propagate when the stress at the crack tip exceeds the strength of the material (Griffith criterion)

$$\sigma = \left(\frac{2E\gamma}{\pi a}\right)^{\frac{1}{2}}$$

A.A. Griffith, *Phil. Trans. R. Soc. A* (1921)

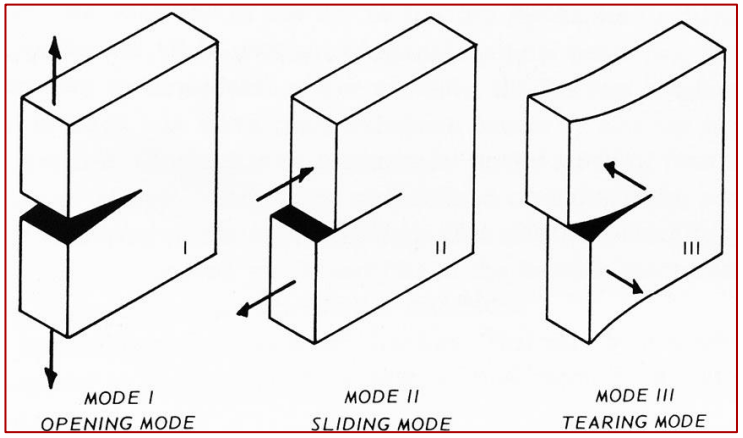
- Fracture toughness (K): the energy required to propagate a crack in a material

- Strain energy release rate (G): energy dissipated during fracture per unit of surface area

$$G = \frac{K_c^2(1-\nu)^2}{E} = 2\gamma_s \qquad \text{(brittle material)}$$

$$G = G_{diss} + 2\gamma_s \qquad \text{(material with inelastic behavior)}$$

- J-integral: method of calculating G for monotonic loading through a path independent contour integral
  - For a linear elastic (non-yielding) material G=J
  - Bulk material property
  - In Mode I: $J_{IC} = G_{IC} = K_{IC}^2\left(\frac{1-\nu^2}{E}\right)$
    - E: elastic modulus
    - ν: poission's ratio
- Modes of loading
  - Mode 1: Opening
  - Mode 2: Sliding
  - More 3: Tearing



http://thediagram.com/12_3/thethreemodes.html

Zhu, X, and J.A. Joyce. *Eng. Fract. Mech.* (2012)

Computational Methods

- Classical molecular dynamics for large scale simulation of silica fracture
- ReaxFF: bond order based forcefield including reactive water and silica bond breakage and formation

Fogarty, Joseph C., et al. *J. Chem. Phys.* (2010)
Yeon, Jejoon, and Adri CT van Duin. *J. Phys. Chem. C.* (2015)

$$E_{Total} = E_{Bond} + E_{Over} + E_{Under} + E_{LP} + E_{Val} + E_{Pen} + E_{Tors} + E_{Conj} + E_{VDW} + E_{Coul} \quad (1)$$

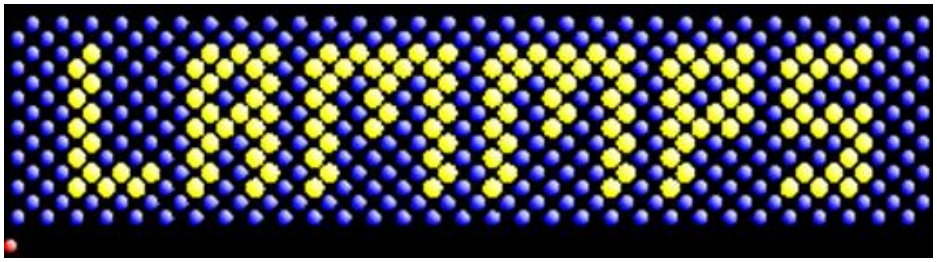
- J-integral and the fracture toughness from the stress, displacement and energy densities of atomistic system coarse grained onto a grid

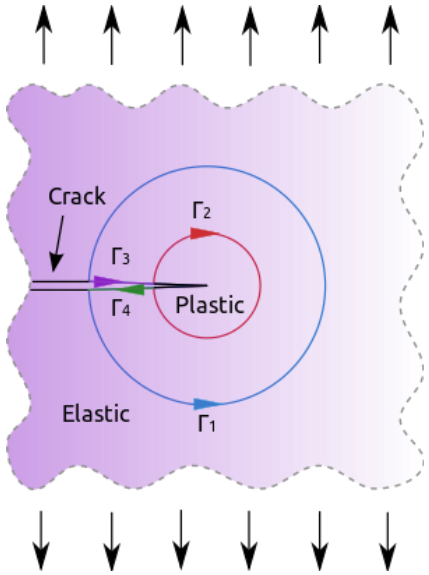
Jones, Reese E., et al. *J. Phys.: Condens. Matter* (2010)

- Eshelby stress (S) is calculated and the J-integral is evaluated around a loop around the crack tip

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

- Multiple loop sizes confirm that the in-elastic zone is completely enclosed and path independent
- Atoms-to-Continuum (ATC) package allows for calculation of the J-integral and the fracture toughness from atomic stresses and is available as a USER-ATC LAMMPS Package



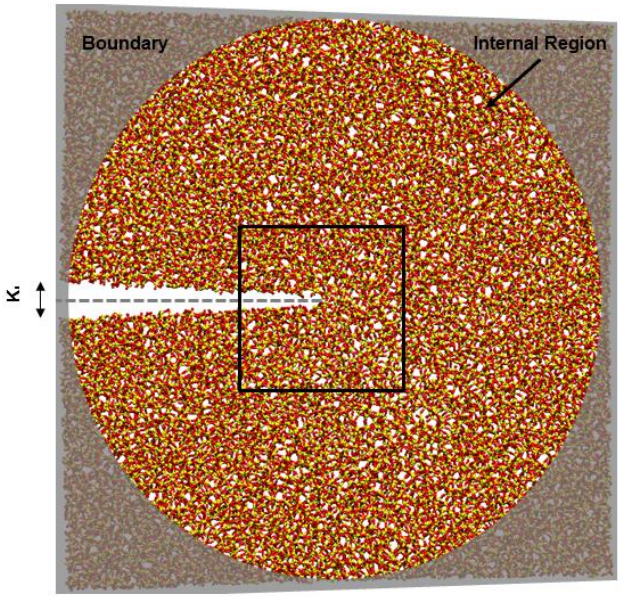


Bhanerje, "J-integral contours for an elastic material" 9/4/2013

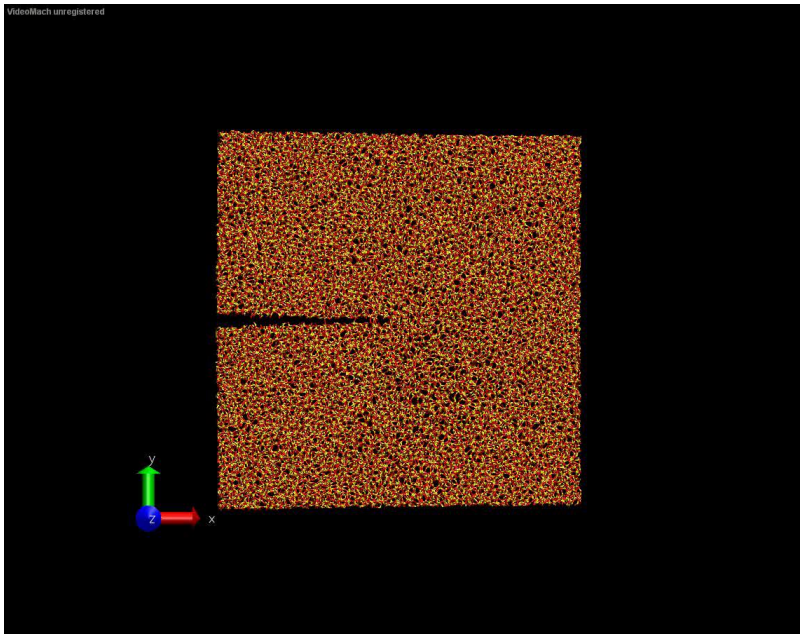
Schematic of J-integral demonstrating the inclusion of the plastic region inside an elastically responding matrix

Simulation set-up

- Amorphous silica, system size: 38400 atoms (143Åx143Åx28Å)
  - Melt and quenched from β-cristobalite system
  - 12 different cracks (three different silica structures with four different crack locations)
- Slit crack is formed by removing neighboring, creating a singular high stress condition
- Boundary atoms are fixed and atomic positions are adjusted to introduce far-field loading as a mode I fracture
- Interior atoms are allowed to freely move by integration with a microcanonical (NVE) ensemble
- Atomic positions adjust to accommodate the added stress
- Stress is introduced iteratively by increasing the crack width



Schematic of silica slit crack, crack width, as well as boundary and internal regions. Atoms: oxygen (red), silicon (yellow)



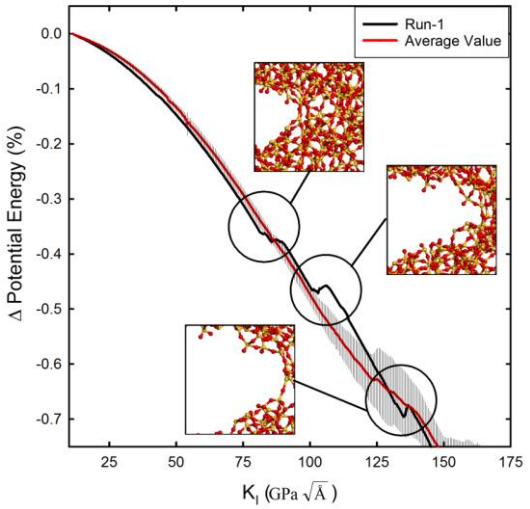
Opening of silica slit crack
Atoms: oxygen (red), silicon (yellow)

Fracture and Energy Dissipation

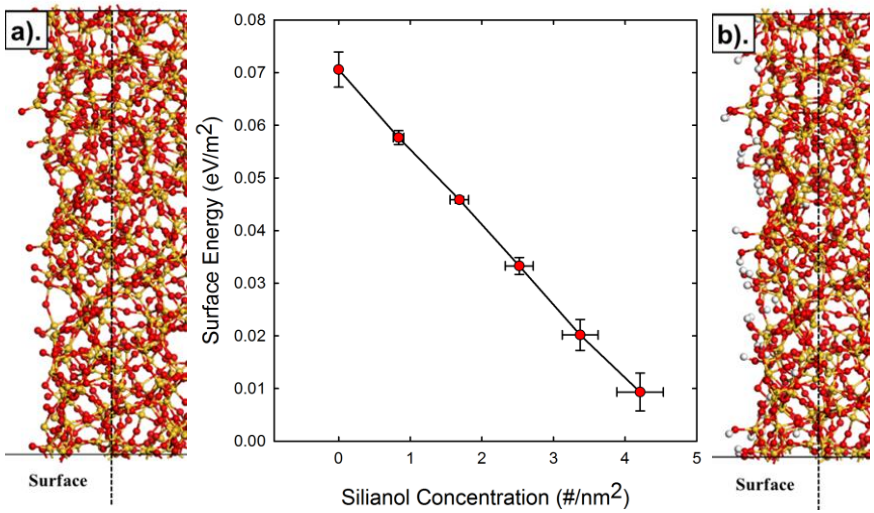
- Fracture propagates in distinct steps when the stress at the crack tip exceeds the strength of the material
- Perfectly brittle fracture will have no dissipation energy, with all energy used to propagate the fracture
- Dissipation energy calculated from the total energy of the system and the predicted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

$$E_{system} = SA * \gamma_s + E_{diss}$$

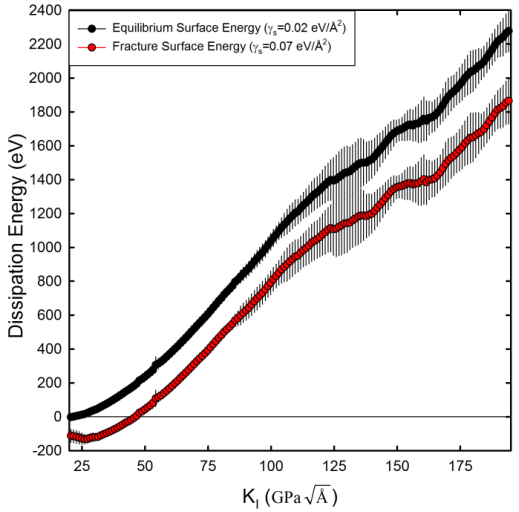
- Surface energy from atomically flat "fracture" surfaces (un-annealed, un-hydroxylated, 0.07 eV/Å^2) or equilibrium values (0.02 eV/Å^2)
- Some inelastic behavior as energy is introduced into the matrix during loading and not completely dissipated once fracture occurs



Potential energy with loading for a single simulation (Run-1) and averaged. Snapshots: (25Åx25Å).



Decreasing surface energy with hydroxylation on silica surfaces with two different classical MD forcefields.



Energy dissipation during crack propagation in silica calculated with equilibrium and fracture surface energies.

Surface Energies: J.M. Rimsza et al. *Langmuir* (2017), A.K. Varshneya, Fundamentals of inorganic glasses, Elsevier 2013

Crack Tip Blunting

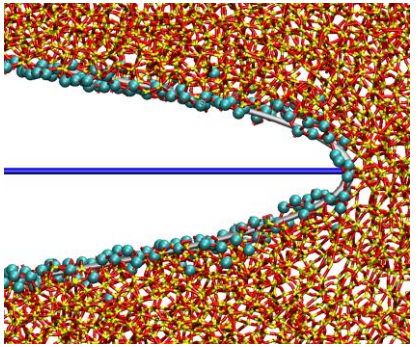
- Crack tip blunting indicates an even stress distribution and the development of local inelastic behavior
- Strength of a material is proportional to the radius of curvature of the crack tip (ρ):

$$\sigma_{max} \propto \sqrt{\frac{1}{\rho}}$$

C.E. Inglis, Spie Milestone series MS (1997)

- To calculate ρ the internal atoms of the crack tip are fit with a parabolic function, from which ρ is calculated: *A. Howard, Calculus: With analytic geometry, John Wiley 1988.*

$$\rho = \frac{(1 + f'(x)^2)^{\frac{3}{2}}}{f''(x)}$$

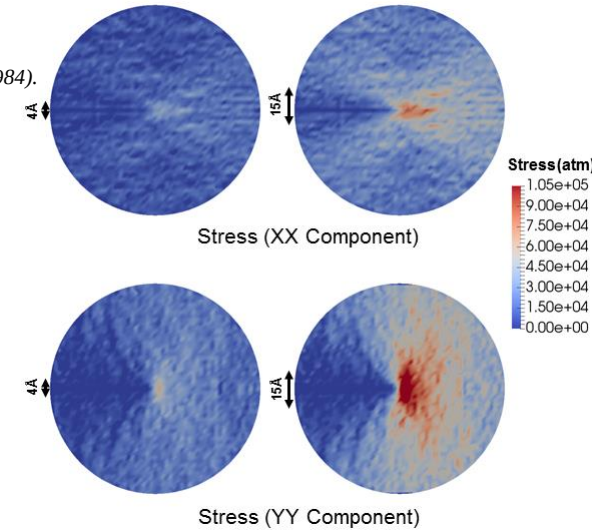


Silica structure (red and yellow) atoms in quadratic fit (turquoise), parabola estimating the shape of the crack tip (silver), and horizontal axis (blue)

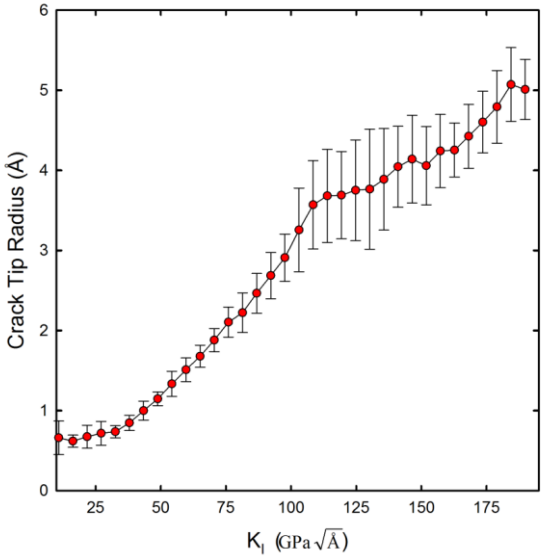
- Radius of curvature: 0.1Å-5Å, experimental value: 15Å

Bando et al. J. Amer. Cera. Soc. 67.3 (1984).

- Increasing ρ with increasing load, changing distribution of stress around the crack tip
- Stress fields indicate increasing stress around the crack tip prior to fracture, due to incorporation of stress around the crack tip
- Highlights the size of the inelastic zone and some development of a high stress conditions ahead of the crack tip



Stress fields calculated from individual atomic stresses. Averaged over twelve different trajectories.



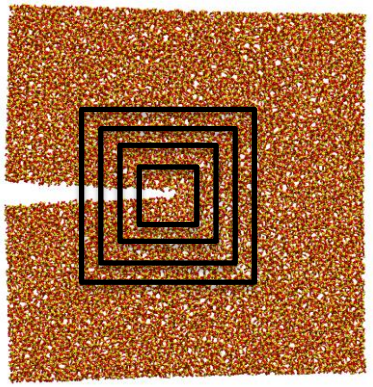
Radius of curvature and crack length during brittle fracture in silica . Error bars are the standard deviation

J-Integral

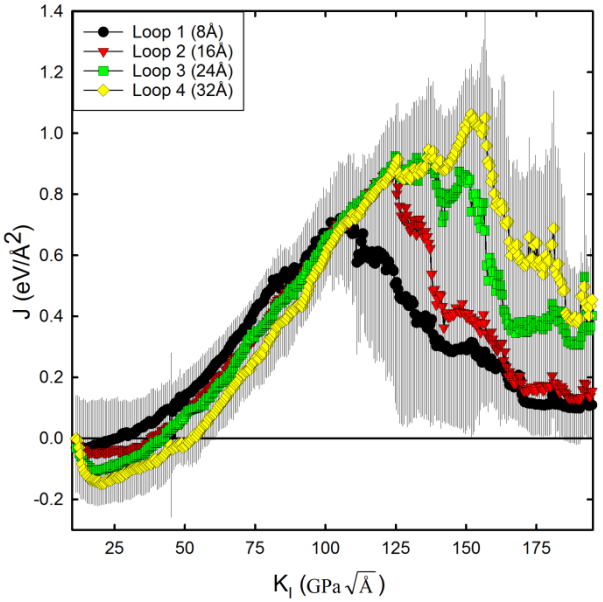
- Calculated via the AtC method through coarse graining energy, displacement, and stress
  Jones, Reese E., et al. *J. Phys.: Condens. Matter* (2010)
- J_{IC} value = J-integral when the crack begins propagating

$$J_{IC} = \frac{K_{IC}^2}{E^*} \qquad E^* = \frac{2\mu}{1-\nu}$$

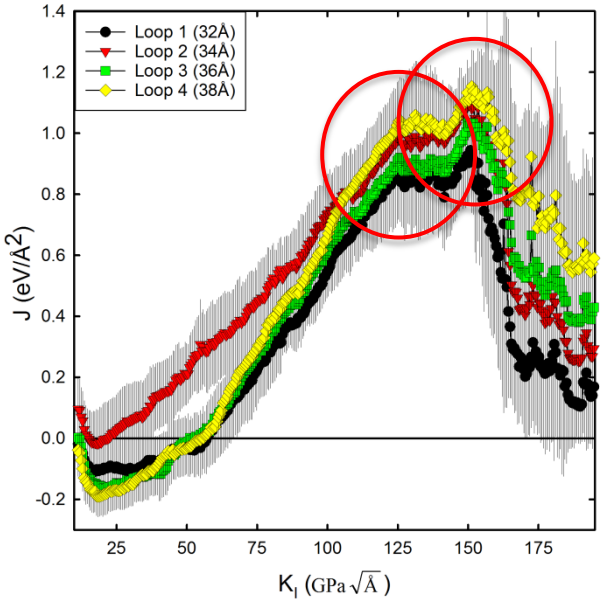
- J-integral converges with loop sizes of ~3nm, indicates the size of an inelastic zone
- J_{IC} value: 1.108±0.179 MPa√m (from just before complete fracture)
  1.042±0.156 MPa√m (from initial loss of linearity in K_I v.J plot)



Schematic of increasing loop sizes for J-integral convergence test



Convergence test of increasing loop sizes for J-integral calculation. Error bars are the standard deviation.



J-integrals with converged loop sizes. Error bars are the standard deviation.

Fracture: Aqueous Conditions

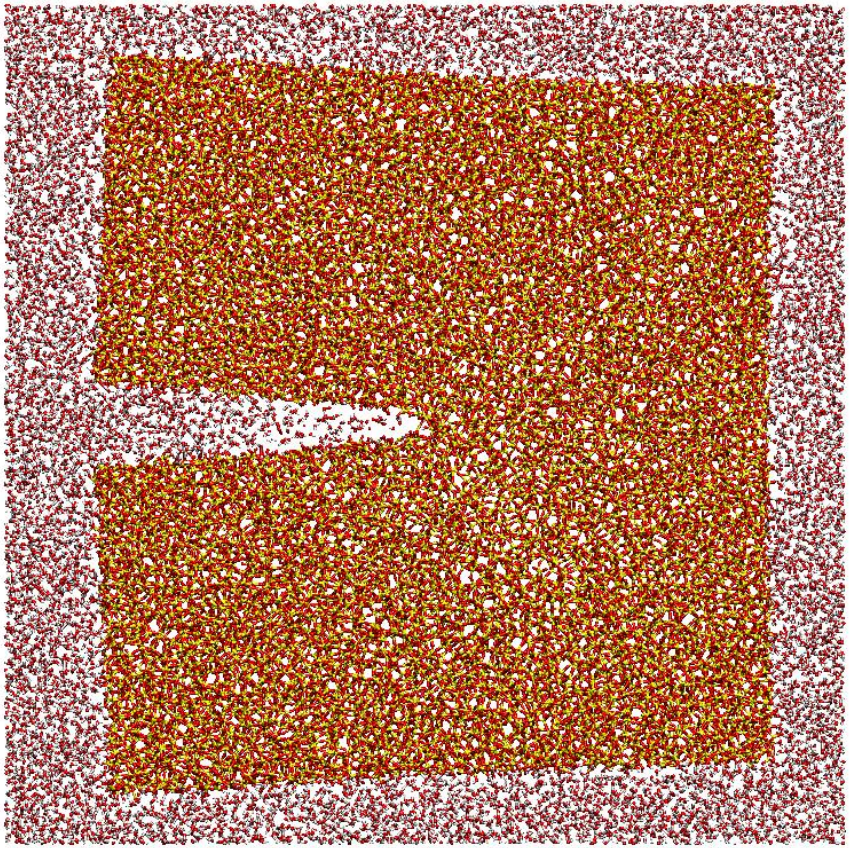
- Coupled chemical-mechanical processes inside the crack affects the propagation rate of cracks in silicates

Table I. Surface Energy Lowering of Quartz and Fracture Strength of Silica Glass Rods in Various Saturated Vapors

Saturated vapor	Exposure time (min.)	Surface free energy lowering (ergs/cm²)	Average fracture strength (psi)	Number of tests	Standard deviation of the mean (psi)
Vacuum	10	0	13,200	19	700
Benzene (dried)	10	52	13,600	8	1000
Ethyl alcohol	10		12,600	8	1350
Acetone	10	85	11,900	8	600
Butyl alcohol	10		11,600	8	1050
Benzene ("with less than 0.02% water")	10		10,200	8	1000
Ethyl acetate	10		9,900	8	390
Propyl alcohol	10	110	9,600	8	1000
Water	10	244	8,000	7	570
Water	100	244	6,600	6	700

Hammond, M. L., and S. F. Ravitz. *J. Amer. Ceram. Soc.* (1963)

- Method:
  - Surrounding system in water controls the fluid pressure inside and around the crack
  - Temperature (400K) and pressure (750 atm) consistent with subsurface conditions
  - Focus on the water molecules at the crack tip, rather than kinetic infiltration



Representative system of water infiltration of a crack

$$r_{Si-O} = A^*_{H2O}\left(exp\frac{-\Delta H_{H2O} + \boldsymbol{b_{H2O}K_1}}{RT}\right)\left(\theta^{H2O}_{Si-O}\right) + A^*_{OH-}\left(exp\frac{-\Delta H_{OH-} + \boldsymbol{b_{OH-}K_1}}{RT}\right)\left(\theta^{OH-}_{Si-O}\right)$$

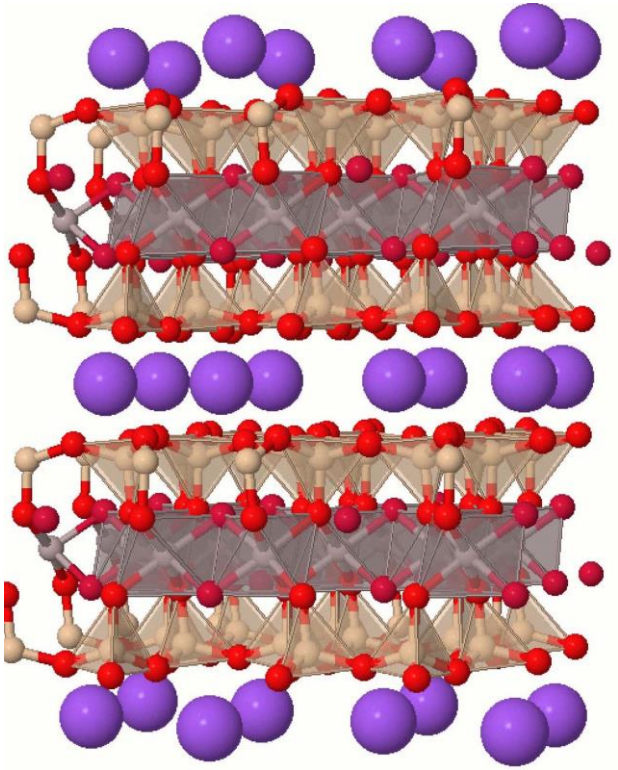
>Si-O-Si< + H_2O = * = 2>SiOH >Si-O-Si< + OH^- = *= >SiOH + >SiO^-

Conclusions

- Dry silica fracture:
  - Development of localized high stress inelastic region prior to fracture
  - Inelastic zone estimated with a radius between 3-3.2 nm
  - J-integral of ~1 MPa√m consistent with experimental results
- Atoms-to-Continuum methods appropriate for evaluating macroscopic fracture properties from atomistic scale information

Current Work

- Reacting fluids and pH effects on silica fracture
  - Varying brine compositions
  - Temperature and pressure effects
- Layered mineral and clay structures



Montmorillonite

Acknowledgements

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