Molecular Modeling and Design of Hybrid Glasses

Mark Oliver, Yusuke Matsuda and Reinhold Dauskardt

Materials Science and Engineering, Stanford University

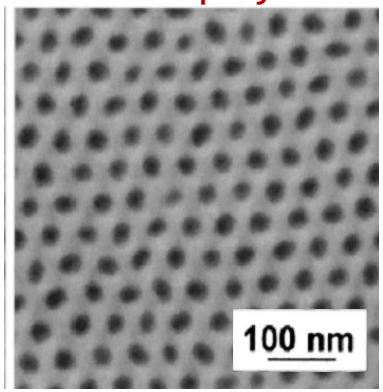
Collaborators (precursor synthesis):

Theo Frot and Geraud Dubois, IBM Almaden Research Center

Hybrid molecular materials work supported by the SRC for ULK'S, the Office of Basic Energy Sciences, DOE,, and the AFOSR.

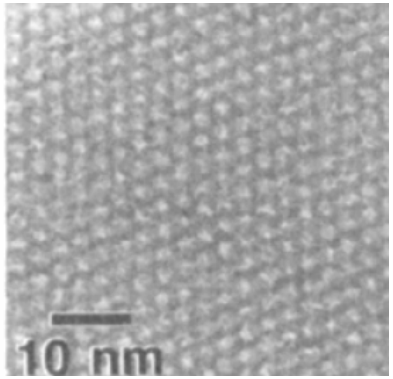
Nanoporous Hybrid Glass Films…

Block Copolymers



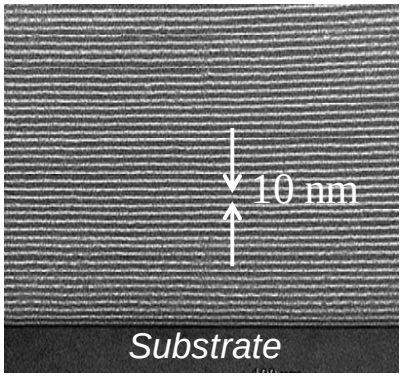
Guarini, et al. *J. Vac. Sci. Technol. B*, 2002.

Silica-Surfactant Structures



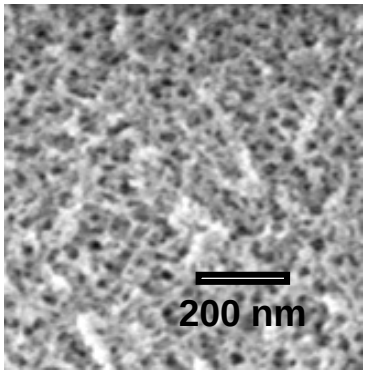
Beck, et al. *Journal Am. Chem. Soc*., 1992.

Nano-Laminates



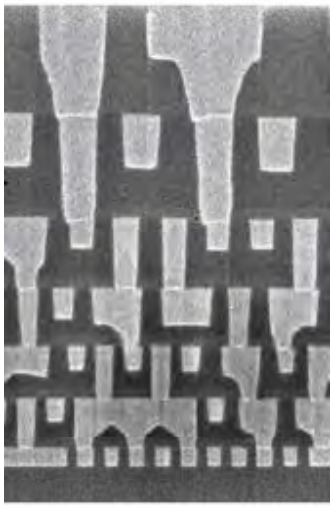
Dubois, et.al., 2008.

MSSQ Hybrids



Maidenberg and Dauskardt, Nature Materials, 2002.

Nanoscience Applications



microelectronic devices

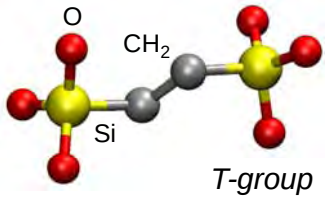
photovoltaics

… biosensors, molecular sieves, charge separation layers, anti-reflection coatings and ULK dielectrics…

…but hybrid glasses are mechanical fragile!

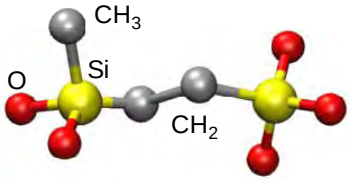
Molecular Modeling of Hybrid Glasses

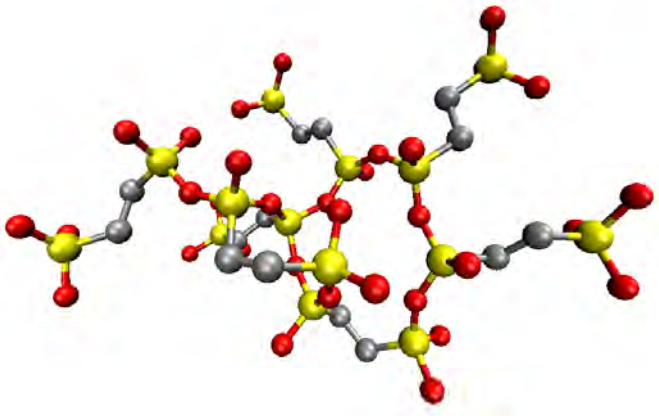
Organosilane Precursors



Et-OCS

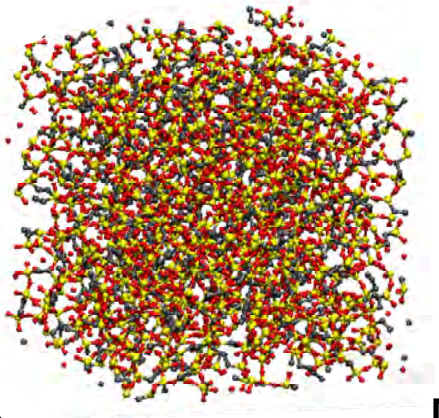
Et-OCS(Me)

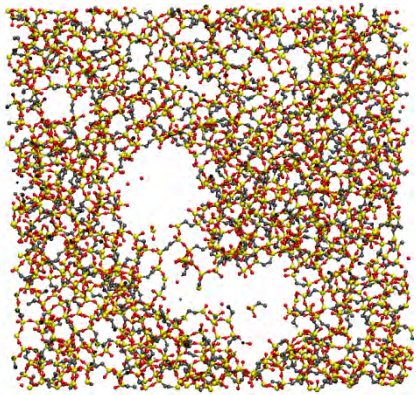


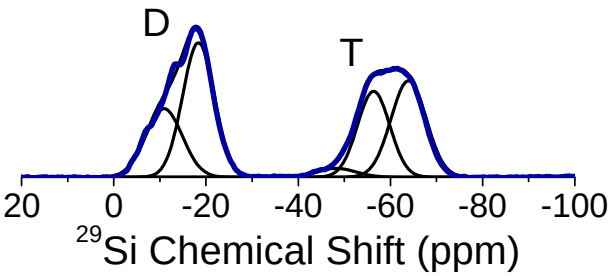


simulated anneal to create distortion free glass

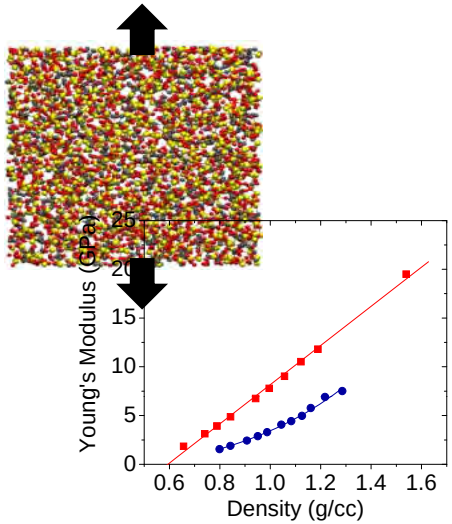
3-D glass Model



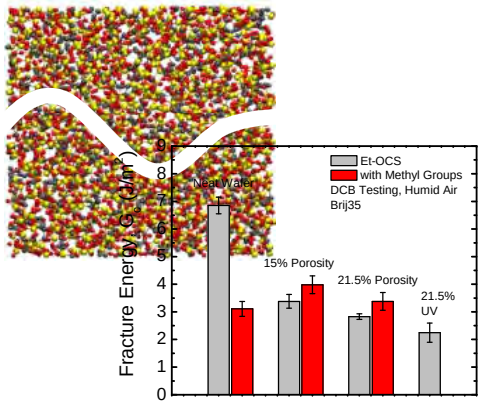




Elastic Properties



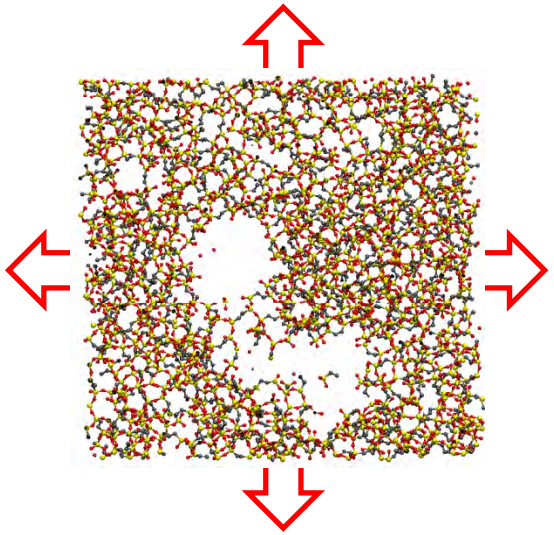
Fracture Properties



Outline

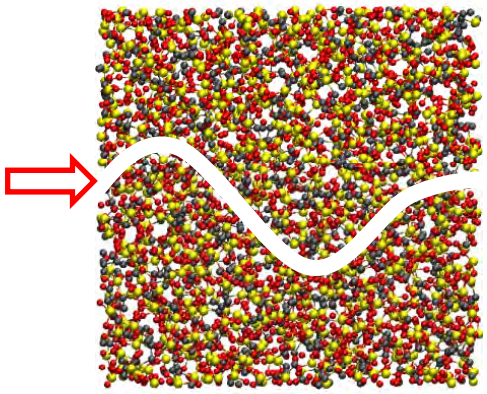
Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

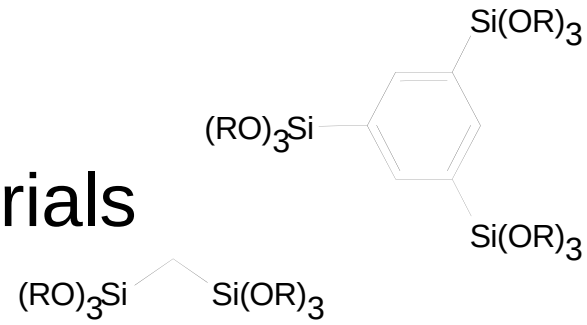


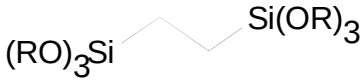
Fracture Energy

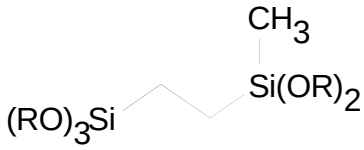
- network connectivity
- scaling relations



New Materials







STANFORD ENGINEERING

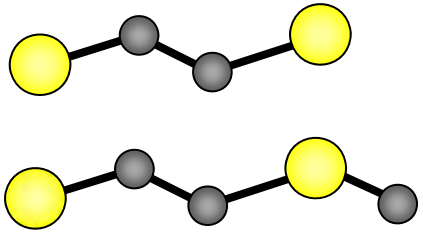
MD Modeling of OCS/OCS(Me)

Simulation Elements

Oxygen:

OCS:

OCS(Me):



H atoms are modeled implicitly
(united atom approach)

Bonded Interactions

$$U(r) = k \cdot (r - r_o)^2$$

$$U(\theta) = k \cdot (\theta - \theta_o)^2$$

$$U(\phi) = \frac{1}{2}K_1[1+\cos(\phi)] + \frac{1}{2}K_2[1-\cos(2\phi)]$$

$$+\frac{1}{2}K_3[1+\cos(3\phi)] + \frac{1}{2}K_4[1-\cos(4\phi)]$$

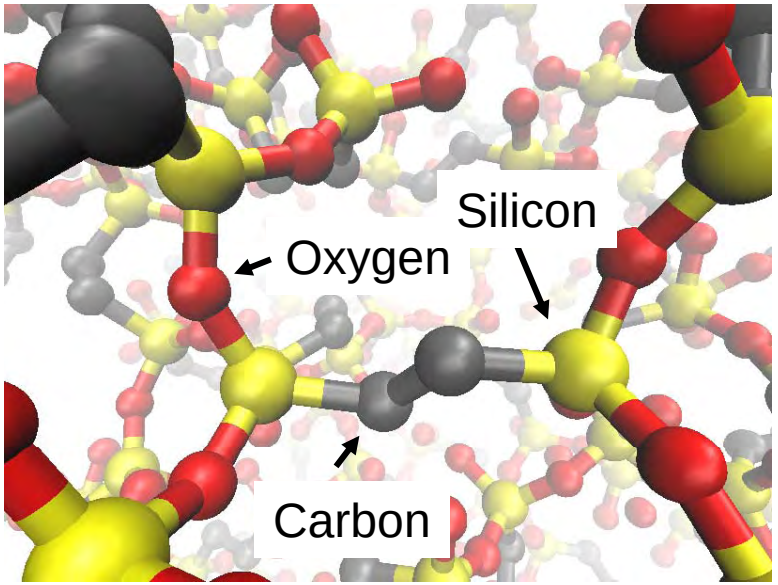
enforce all bond lengths, angles and dihedral angles

Non-Bonded Interactions: Stillinger-Weber Type Potential

$$U = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r) = A\varepsilon\left[B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q\right]\exp\left(\frac{\sigma}{r - a\sigma}\right)$$

$$\phi_3(r,s,\theta) = \lambda\varepsilon[\cos(\theta) - \cos(\theta_0)]^2 \exp\left(\frac{\gamma\sigma}{r - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{s - a\sigma}\right)$$



STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Oliver, Dubois, Sherwood, Gage, Dauskardt, Adv. Funct. Matls, 2010. In press.

Simulations Reproduce Local Chemical Structure

Characteristics of simulation with 750 OCS molecules and 2800 O atoms
Variable condensation

Si atoms are fully coordinated

- 99.5 % have oxygen CN of 3
- 0.05 % have oxygen CN of 2

Few free oxygen defects

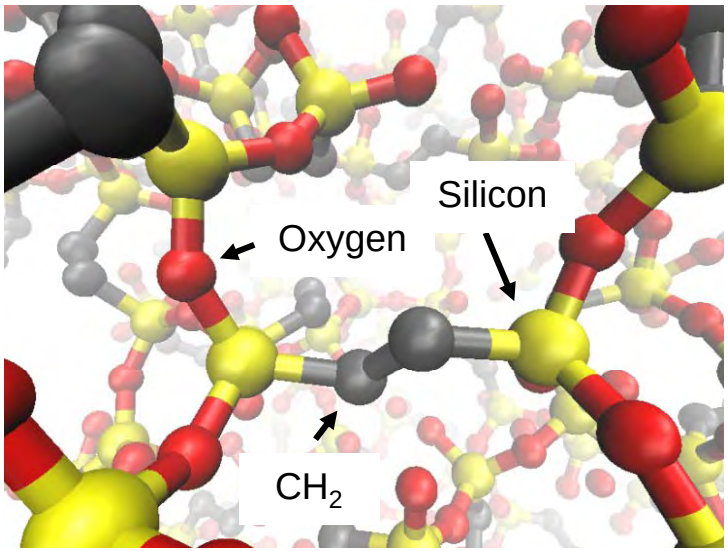
- only 1% O atoms are unbound

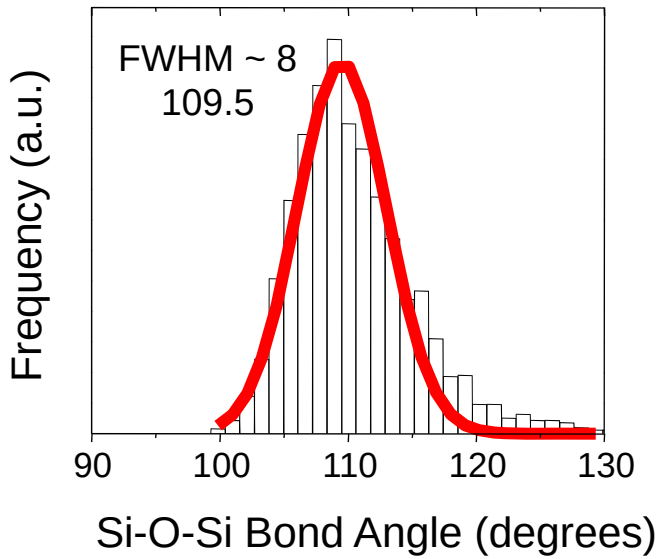
Correct density

- Model density = 1.596 g/cc
- Real density = 1.539 g/cc

Correct Si-O-Si bond angle distribution

FWHM of ~ 8 degrees consistent with 7 degree FWHM reported for silica
[Feuston and Garofalini *J. Phys. Chem.* 1988]



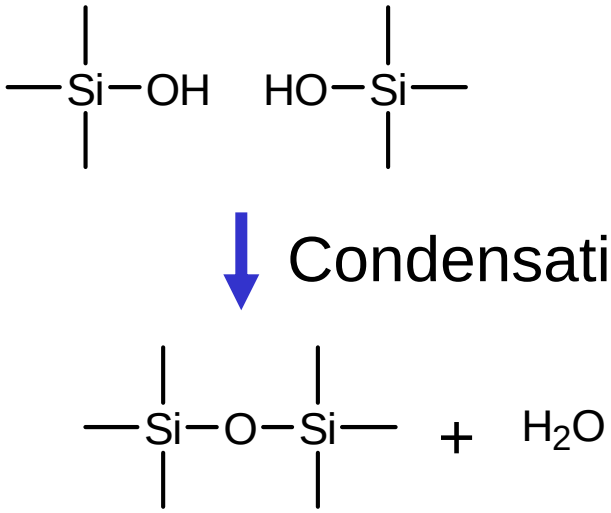


STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Simulations Reproduce Local Chemical Structure

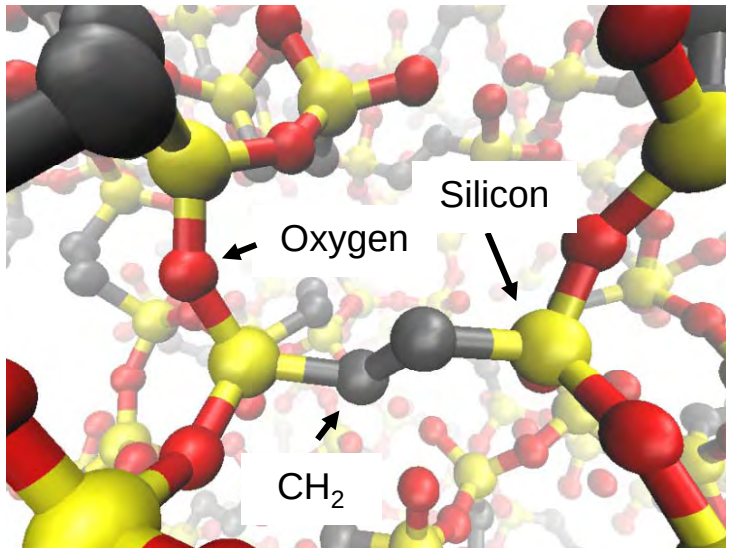
Characteristics of simulation with 750 OCS molecules and 2800 O atoms
Variable condensation

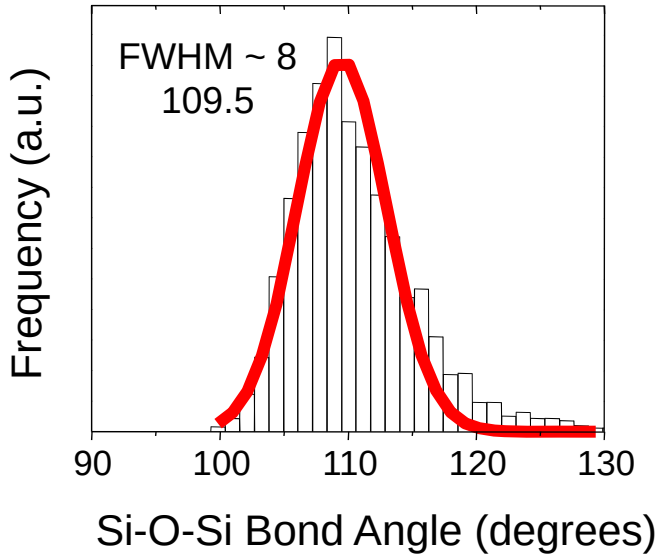
Condensation and network connectivity



Condensation degree, q

- fraction of Si-O-Si bonds formed
- typical values: 0.7 to 0.9





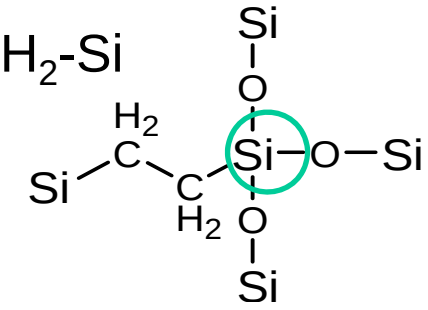
STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Si-X-Si Network Connectivity

Si-X-Si connectivity, p = fraction of bridging Si-X-Si bonds present

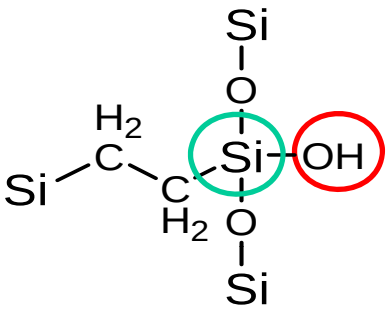
Bridging Si-X-Si bonds

- Si-O-Si
- Si-CH_2–CH_2-Si

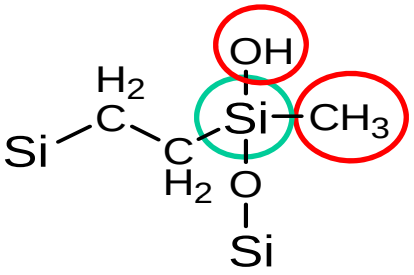


p = 4/4 =1.0

Terminal bonds

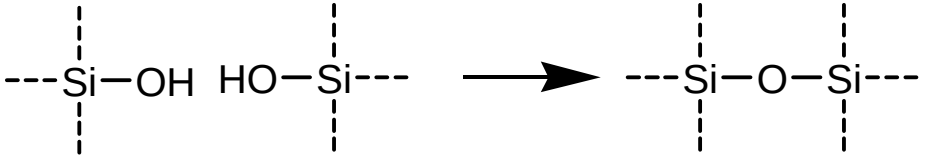


p = 3/4 = 0.75

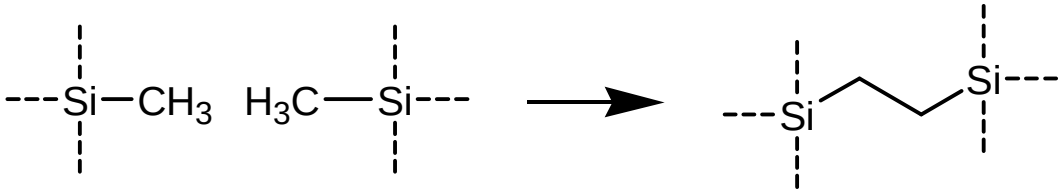


p = 2/4 = 0.50

Cure to increase condensation (UV, thermal, e-beam)



Use bridged precursors

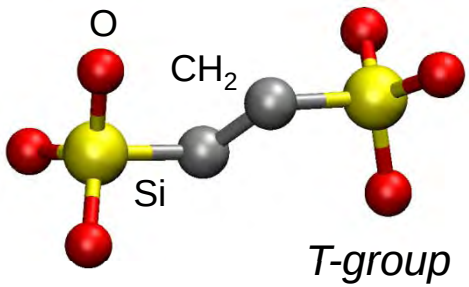


STANFORD ENGINEERING

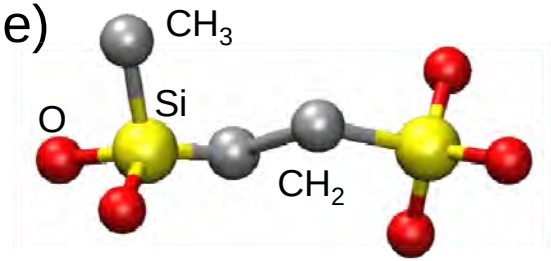
Oliver, Dubois, Sherwood, Gage, Dauskardt, Adv. Funct. Matls, 2010. In press.

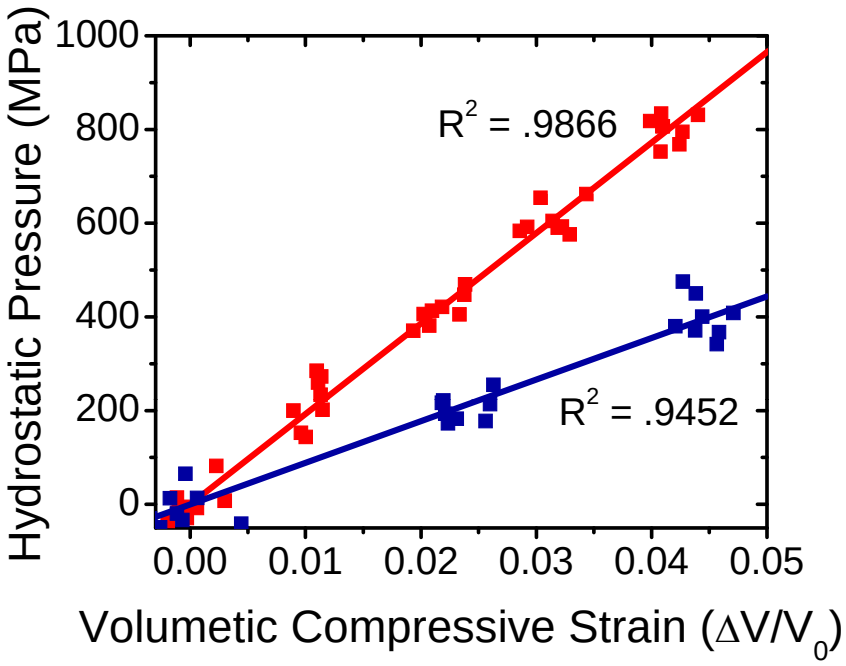
Simulating Bulk Modulus

Et-OCS

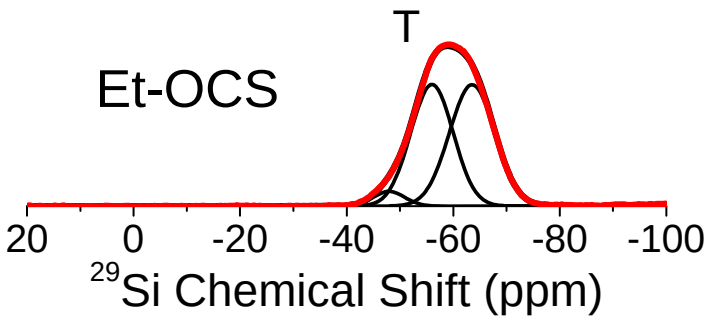


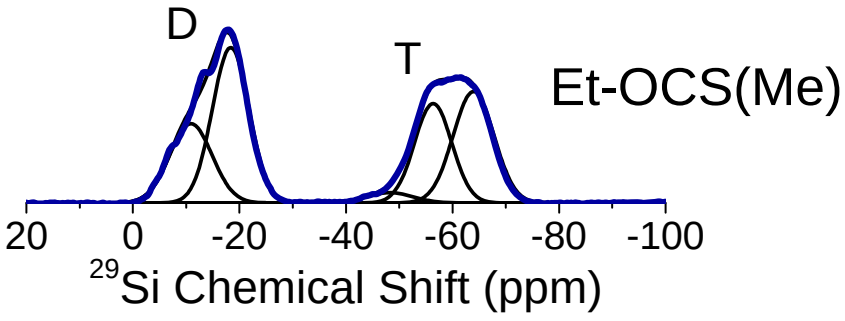
Et-OCS(Me)





Experimental Glasses: surface acoustic wave (SAW's) modulus

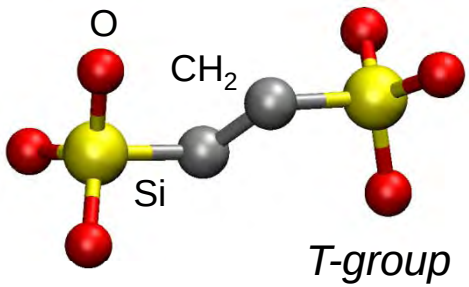




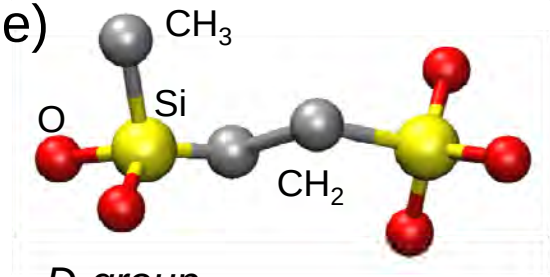
STANFORD MATERIALS SCIENCE AND ENGINEERING

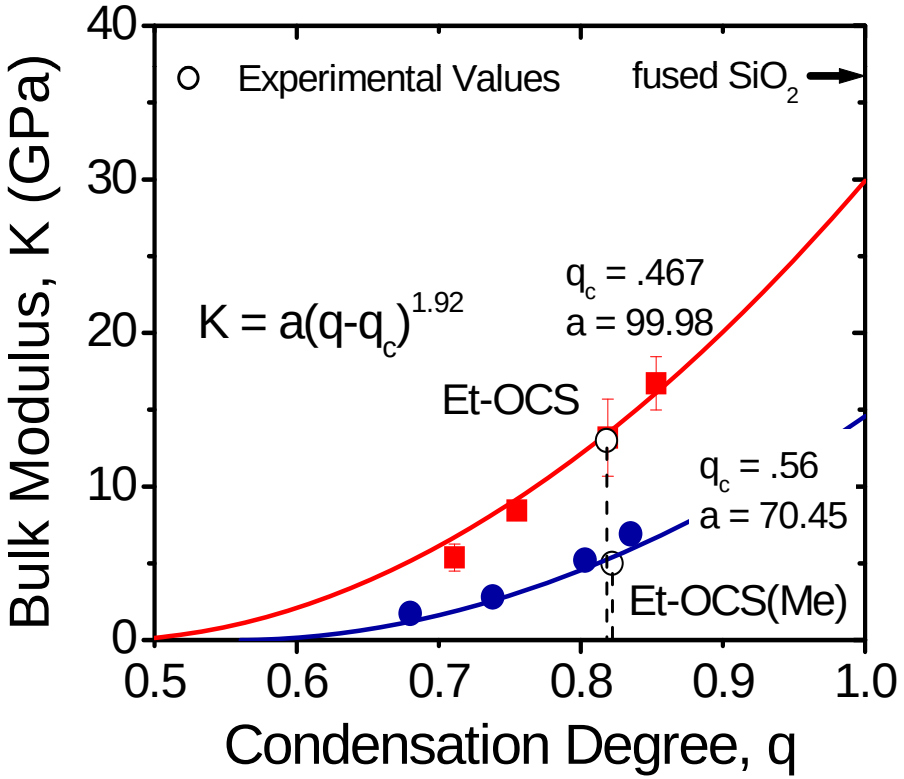
Simulating Bulk Modulus

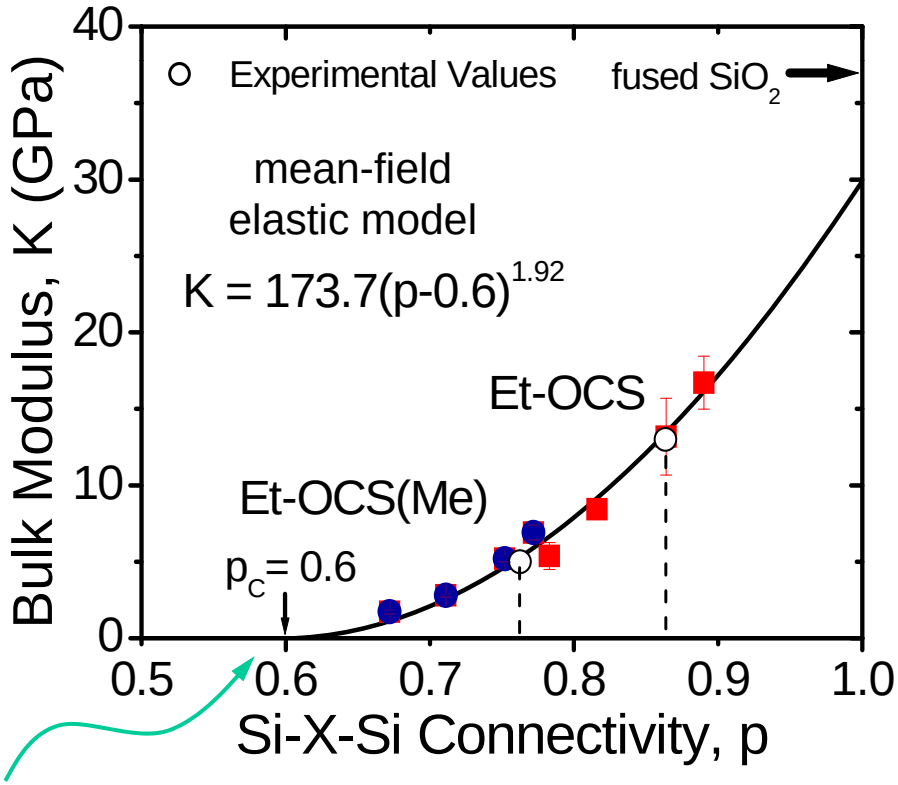
Et-OCS



Et-OCS(Me)







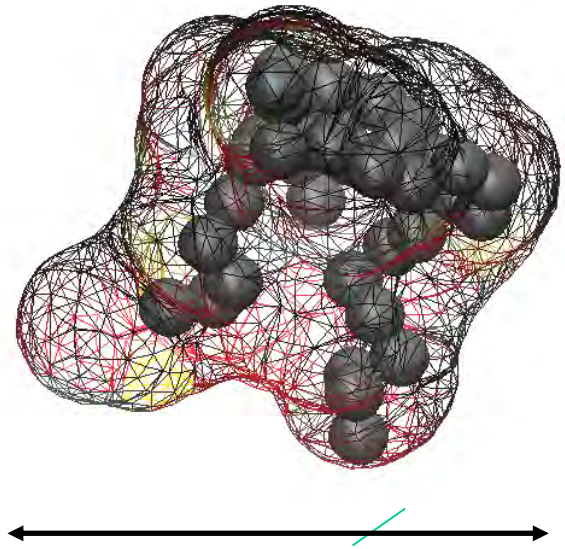
rigidity percolation

Oliver, Dubois, Sherwood, Gage, Dauskardt, Adv. Funct. Matls, 2010. In press.

Model Nanoporous Glasses

Sample Pore:

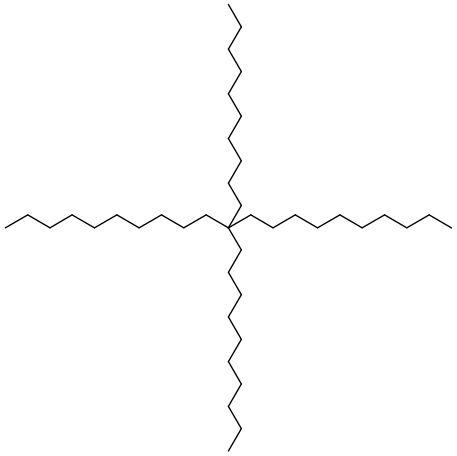
atoms of porogen shown
mesh grid shows pore surface



~1.2 nm

Model Porogen:

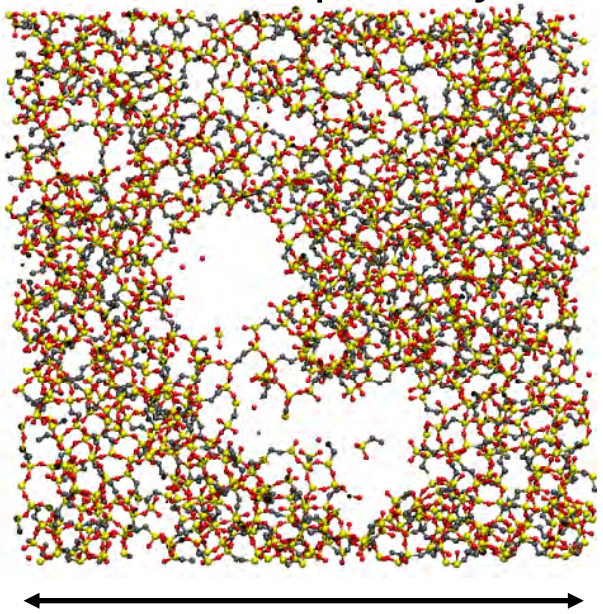
4 C_{10} arms



$R_{gyration}$ = 0.6 nm

Porous Glass Model:

25 vol% porosity



7.6 nm

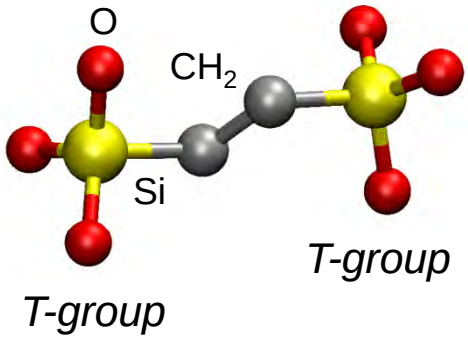
STANFORD ENGINEERING

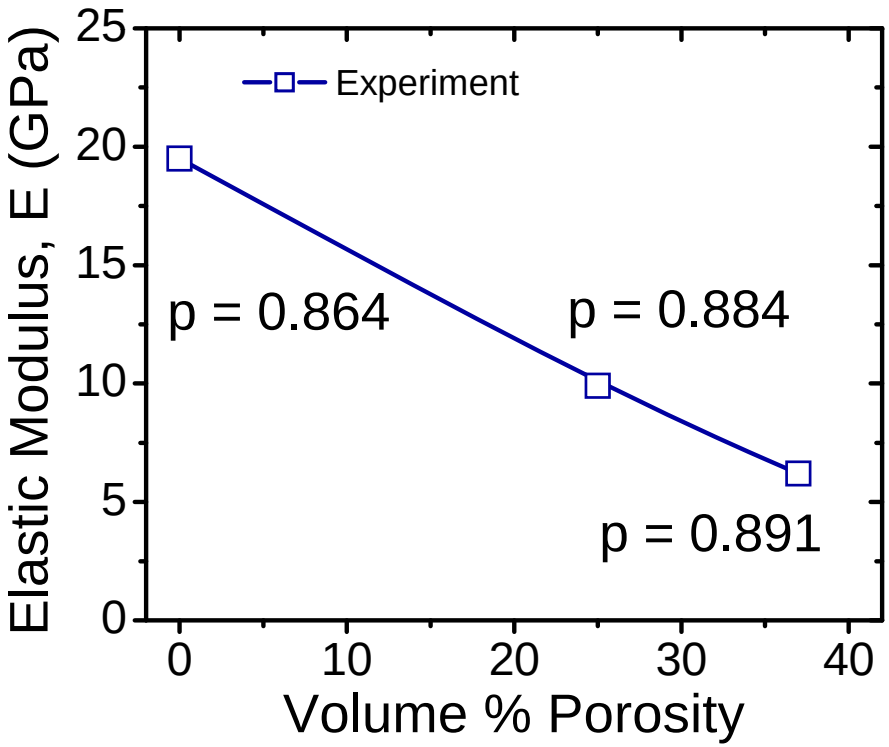
Effect of Porosity on Elastic Stiffness

Experimental data

vol% porosity (porosimetry)	p (NMR)	E (GPa)
0	.864	19.5
25	.884	9.9
37	.891	6.15

Et-OCS





STANFORD
MATERIALS SCIENCE
AND ENGINEERING

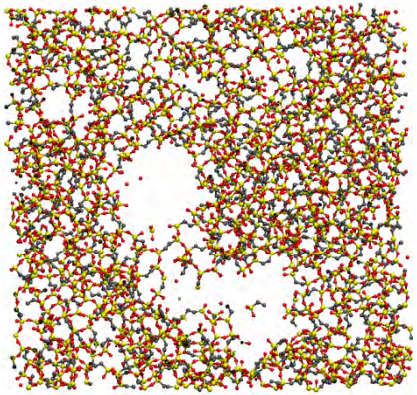
Effect of Porosity on Elastic Stiffness

Experimental data

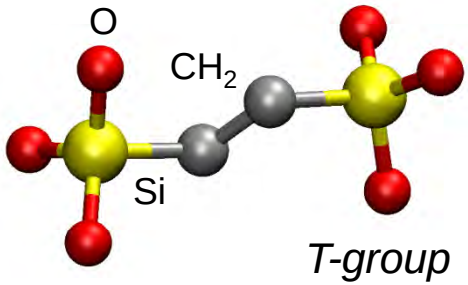
vol% porosity (porosimetry)	p (NMR)	E (GPa)
0	.864	19.5
25	.884	9.9
37	.891	6.15

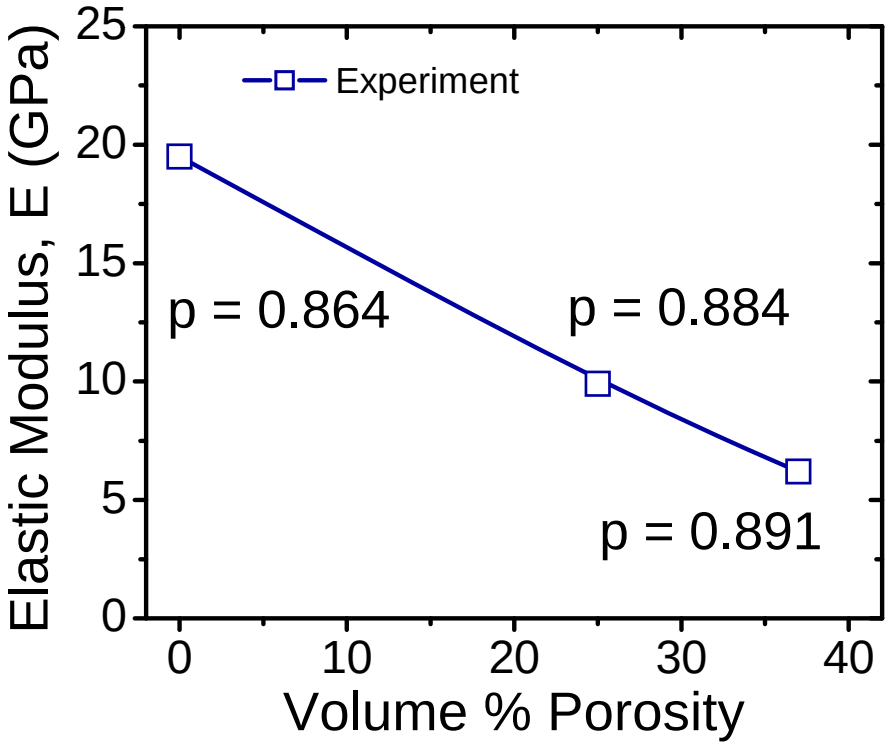
Model inputs: vol% pore, p

accurate models of real glasses



Et-OCS





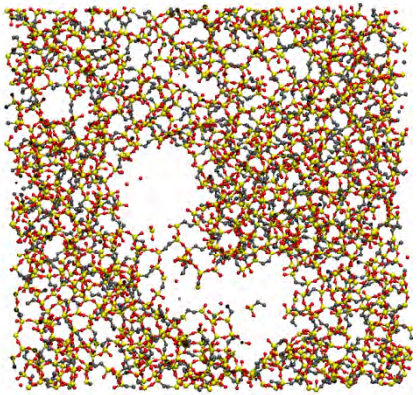
Effect of Porosity on Elastic Stiffness

Experimental data

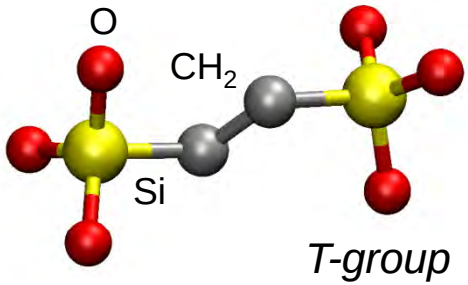
vol% porosity (porosimetry)	p (NMR)	E (GPa)
0	.864	19.5
25	.884	9.9
37	.891	6.15

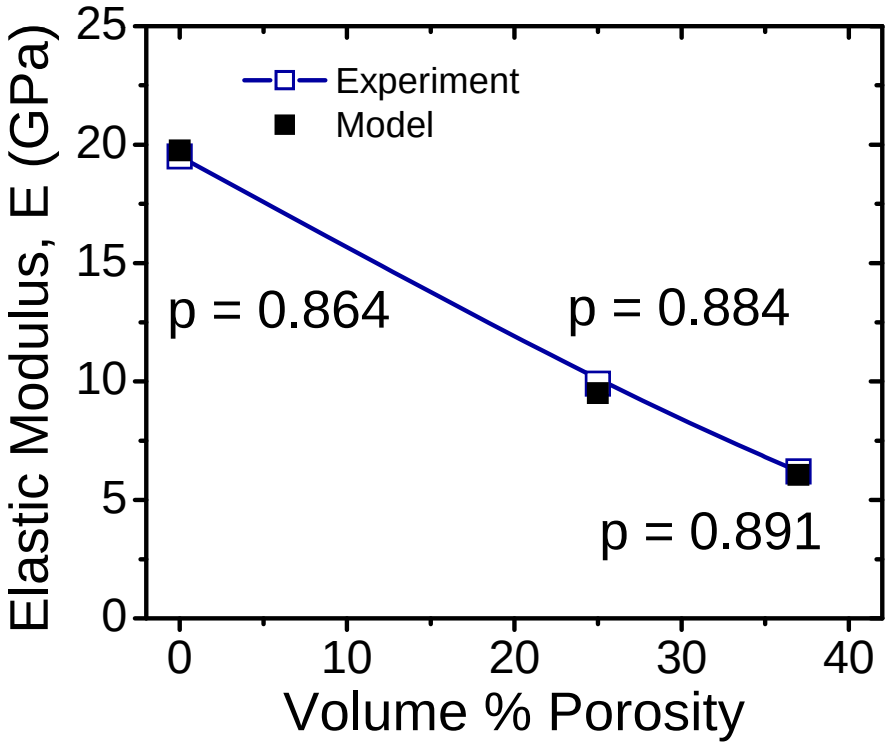
Model inputs: vol% pore, p

accurate models of real glasses



Et-OCS

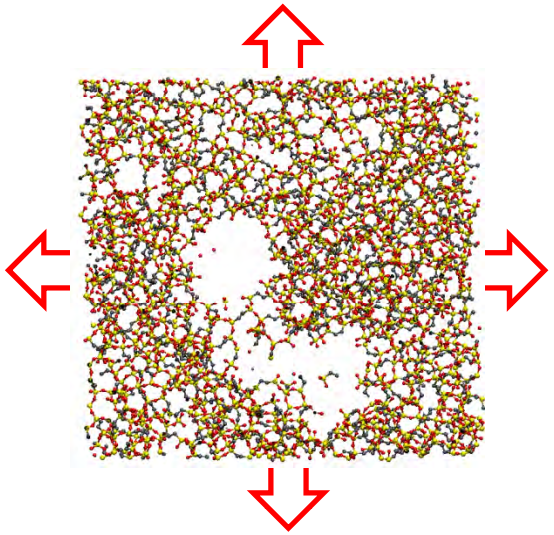




Outline

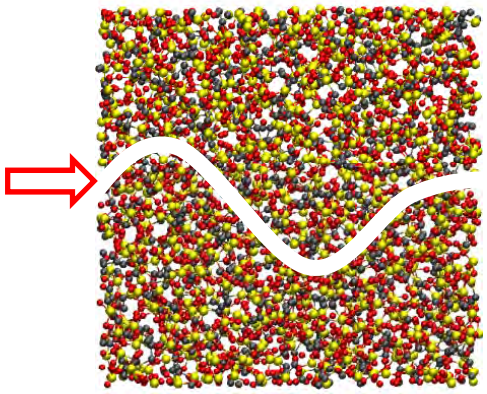
Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

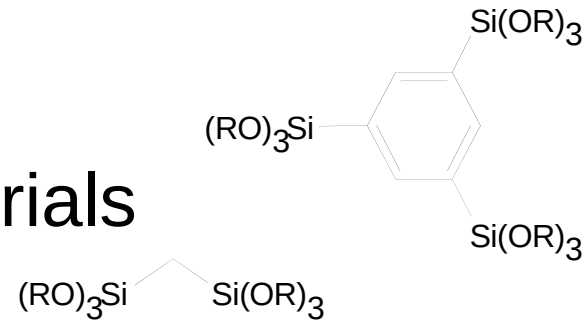


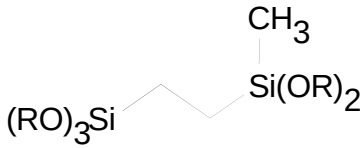
Fracture Energy

- network connectivity
- scaling relations



New Materials

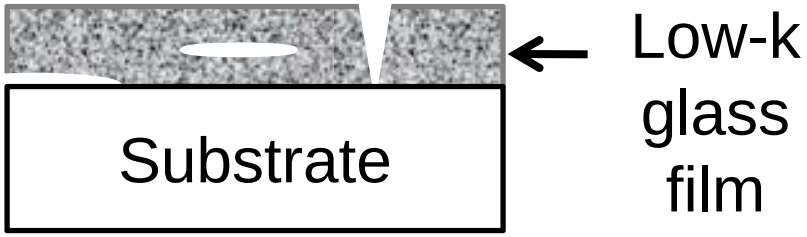


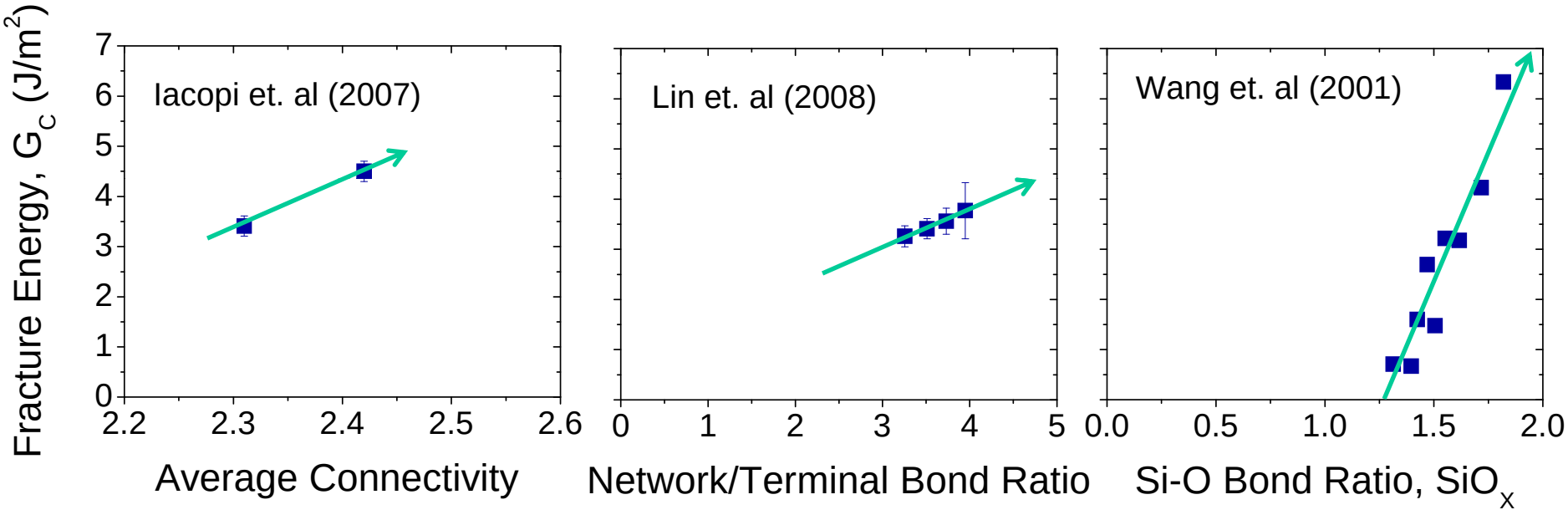


STANFORD ENGINEERING

Effect of Connectivity on Fracture Energy, G_C

Adhesive and cohesive fracture concern for reliable integration





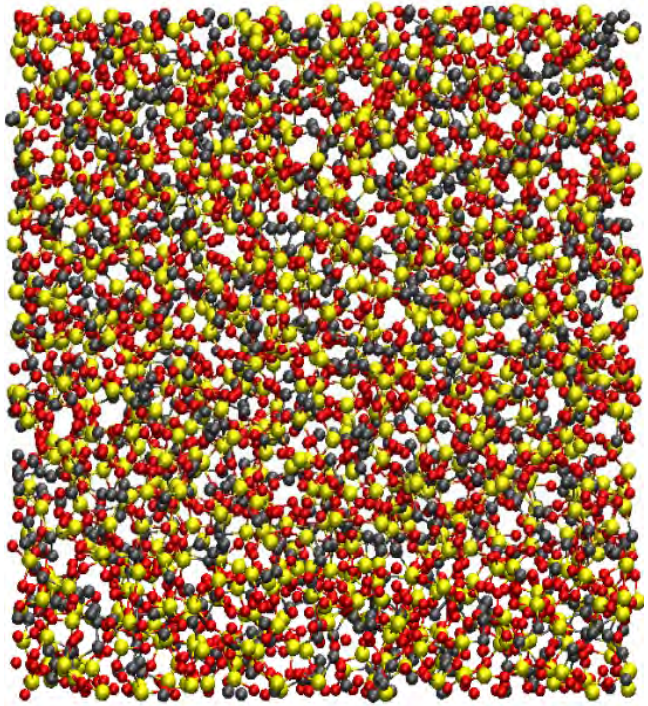
Increased connectivity → more bonds to break → higher G_C

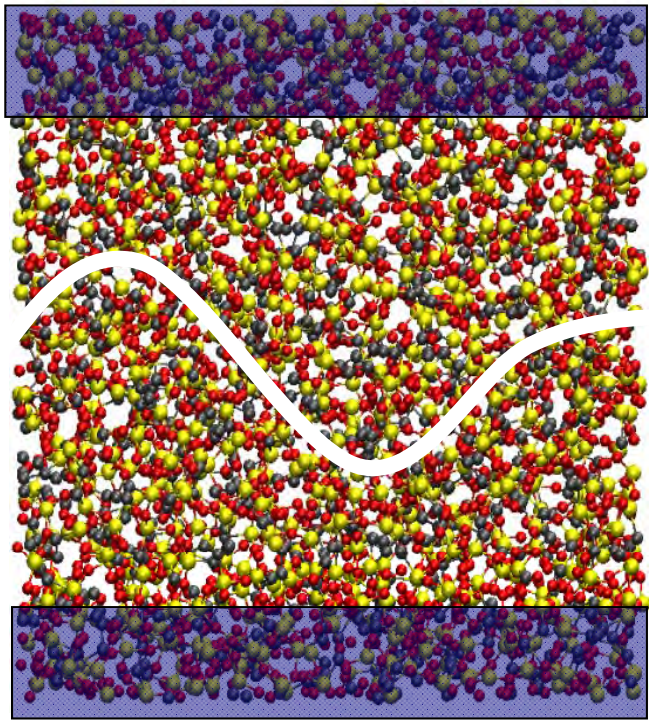
Is there a fundamental scaling law?

STANFORD ENGINEERING

Simulating Cohesive Fracture

How many and what type of bonds must be broken to fracture the network?

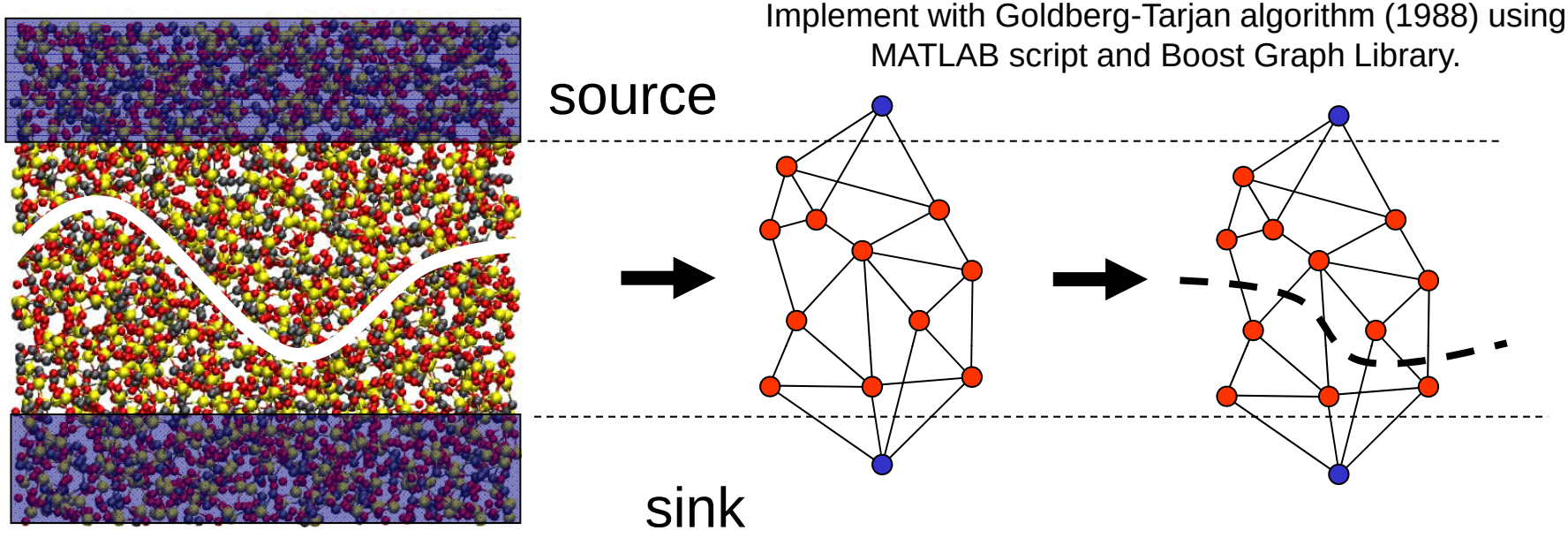




STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Applying Graph Theory to Model Networks

Ford and Fulkerson, "Maximal Flow Through a Network", Canadian J. Math. 1956.
Implement with Goldberg-Tarjan algorithm (1988) using MATLAB script and Boost Graph Library.



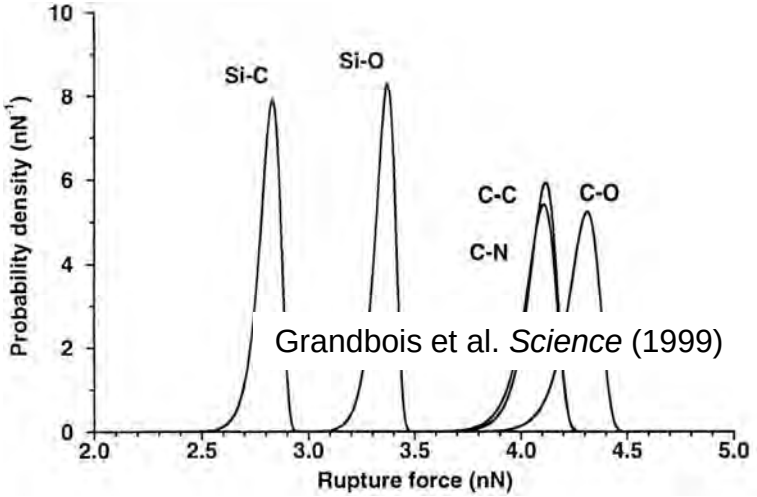
Convert to *weighted* graph and find min-cut…

atoms = vertices, bonds = edges

bond strength/energy = edge weight

collapse source/sink into single vertices

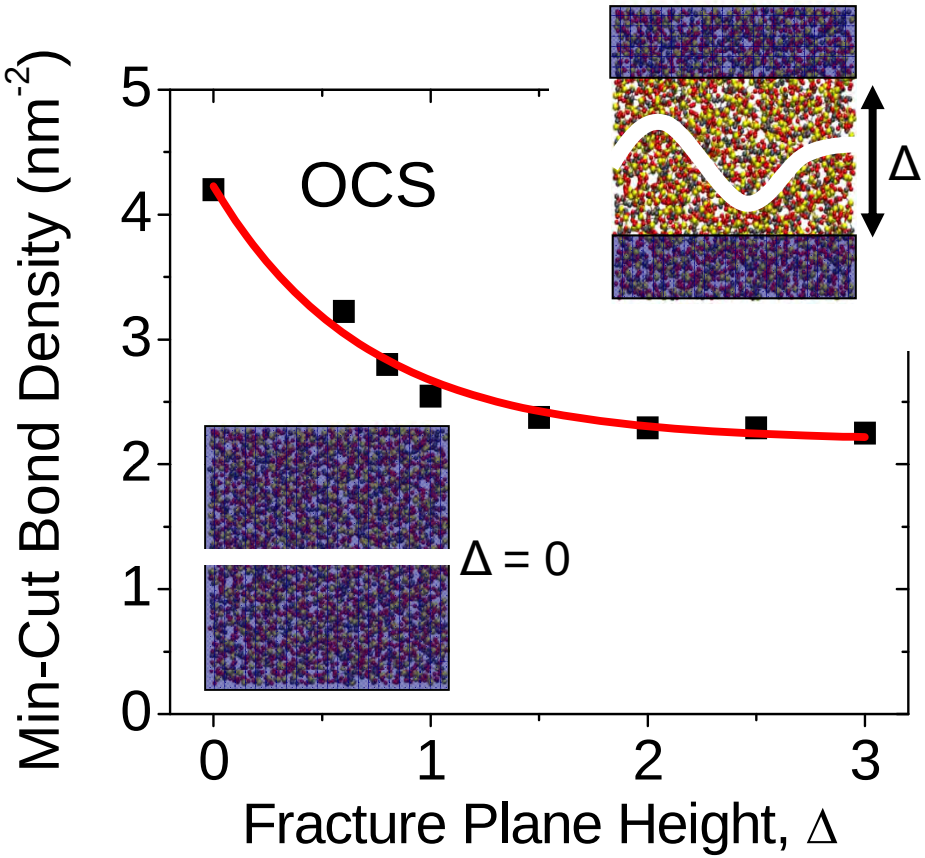
Weight edges by strength



Grandbois et al. *Science* (1999)

STANFORD
MATERIALS SCIENCE AND ENGINEERING

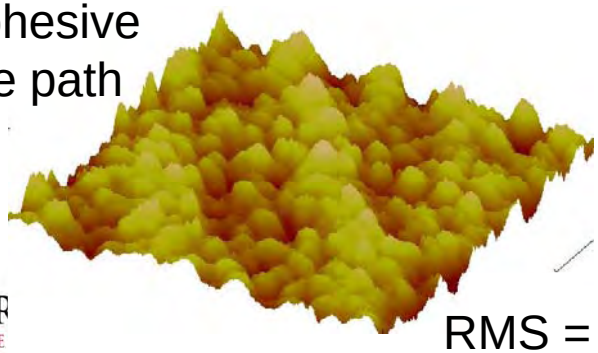
3-D Complex Fracture Path Selection



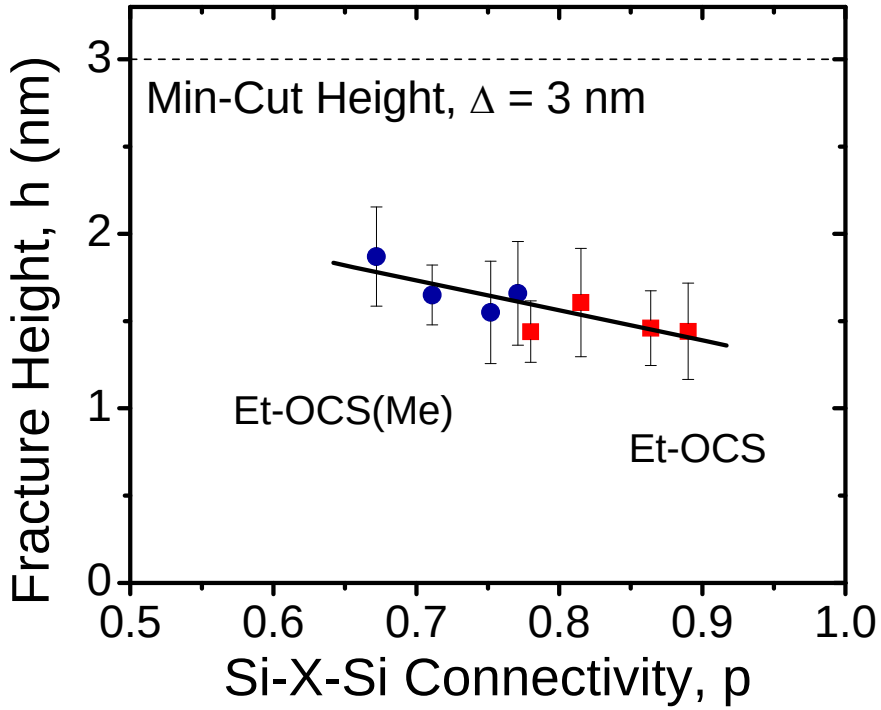
Crack path seeks out lowest energy path through network

Results in nanometer roughness

AFM cohesive fracture path

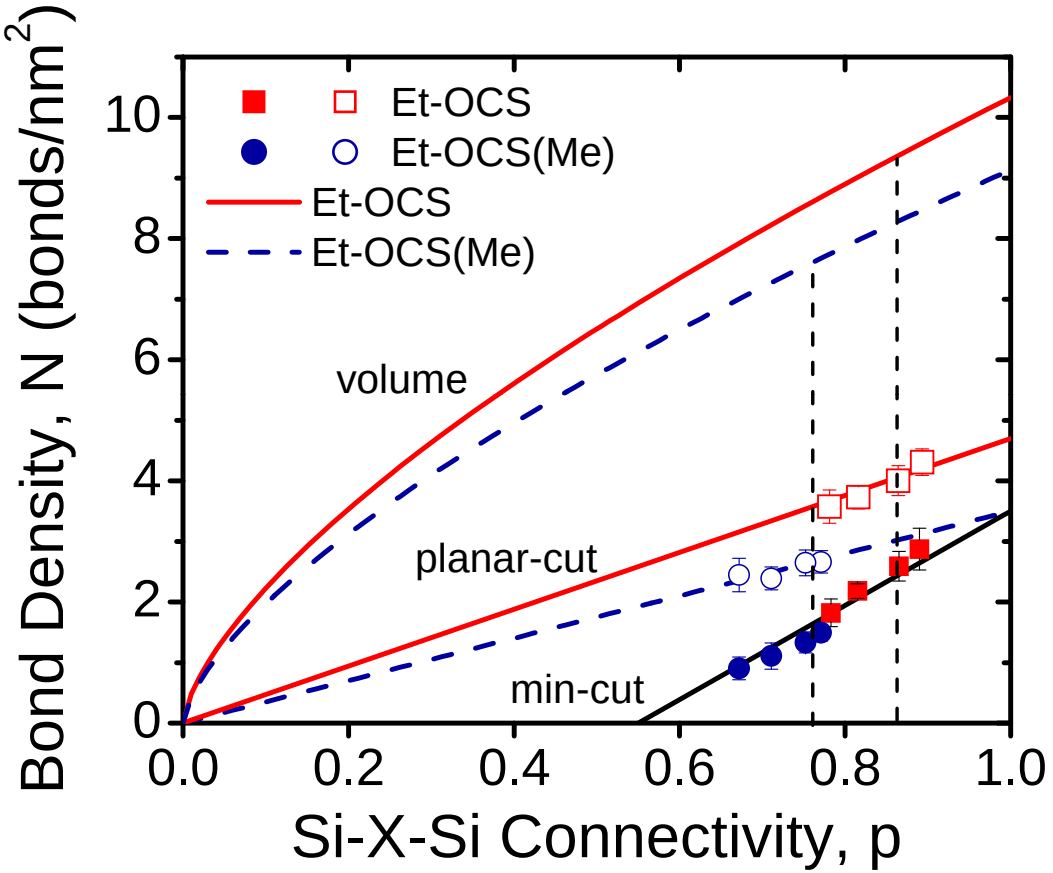


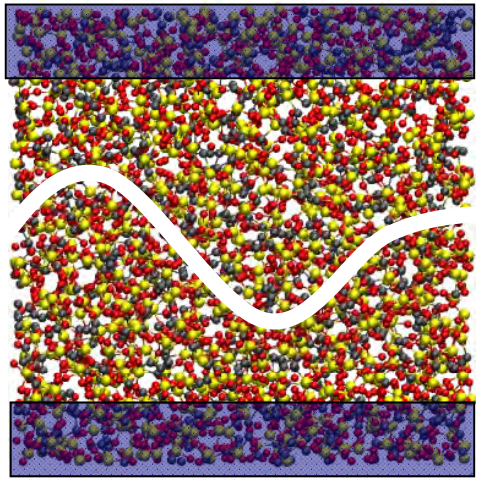
RMS = 1.2nm

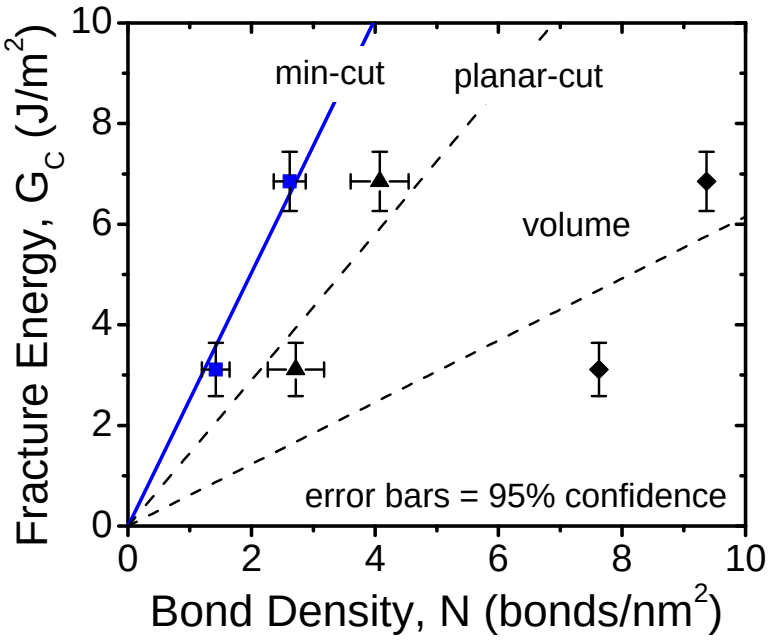


STANFOR
MATERIALS SCIE
AND ENGINEER

Effect of Connectivity on Fracture Energy, G_C



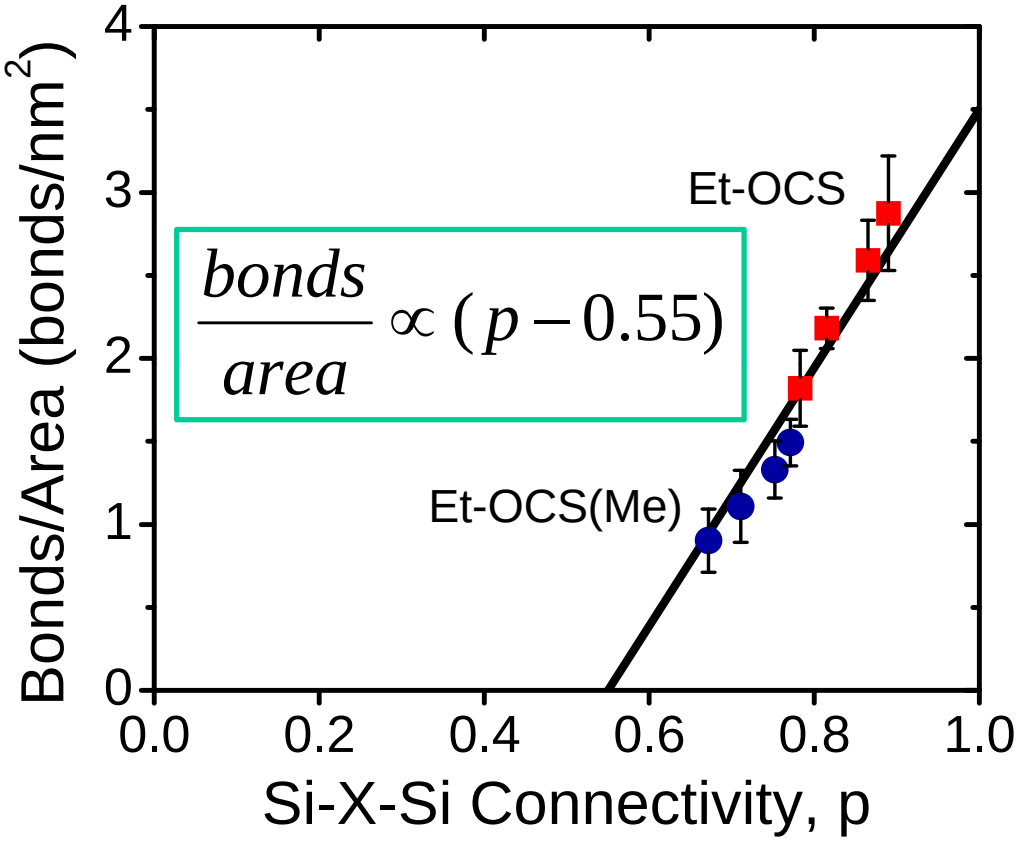




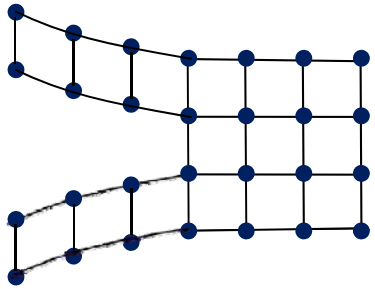
$$G_C\left[\frac{energy}{area}\right] = \frac{bonds}{area}\frac{energy}{bond}$$

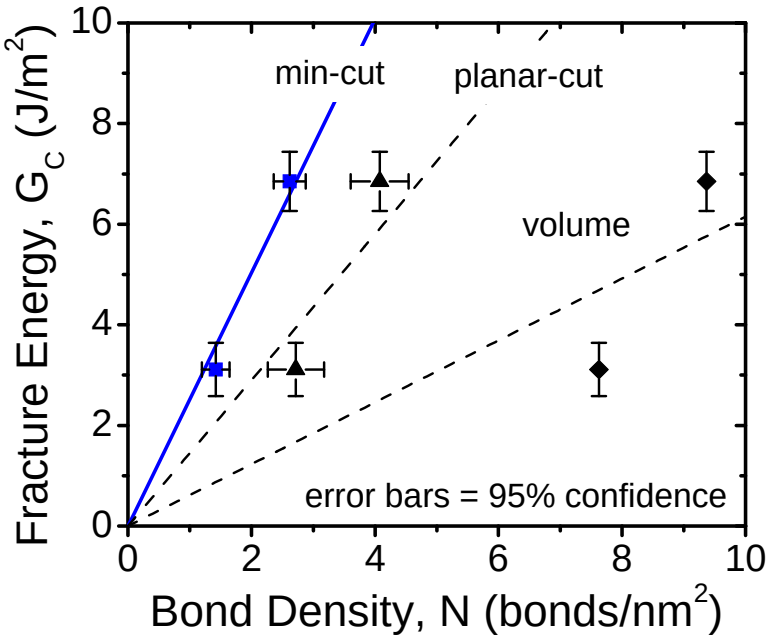
STANFORD
MATERIALS SCIENCE
AND ENGINEERING

Effect of Connectivity on Fracture Energy, G_C



assume no plastic deformation





$$G_C\left[\frac{energy}{area}\right] = \frac{bonds}{area}\frac{energy}{bond}$$

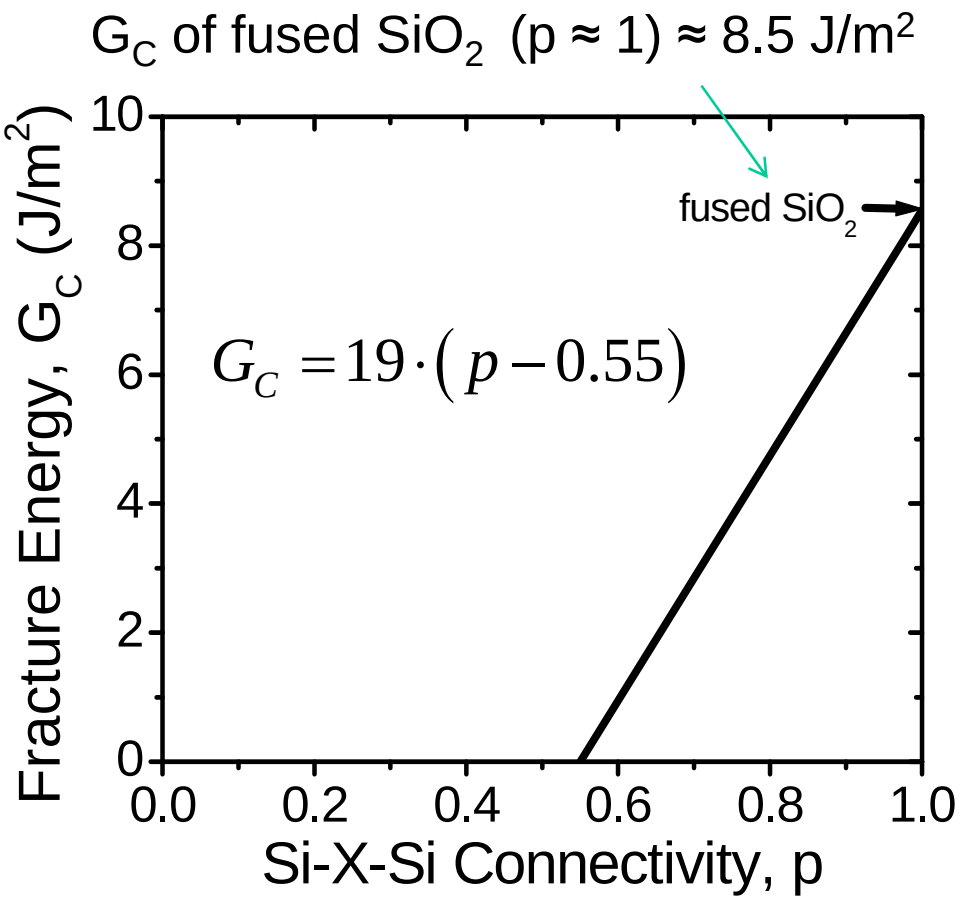
STANFORD MATERIALS SCIENCE AND ENGINEERING

Predicted Fracture Energy Scaling

$$G_C\left[\frac{energy}{area}\right] = \frac{bonds}{area}\frac{energy}{bond}$$

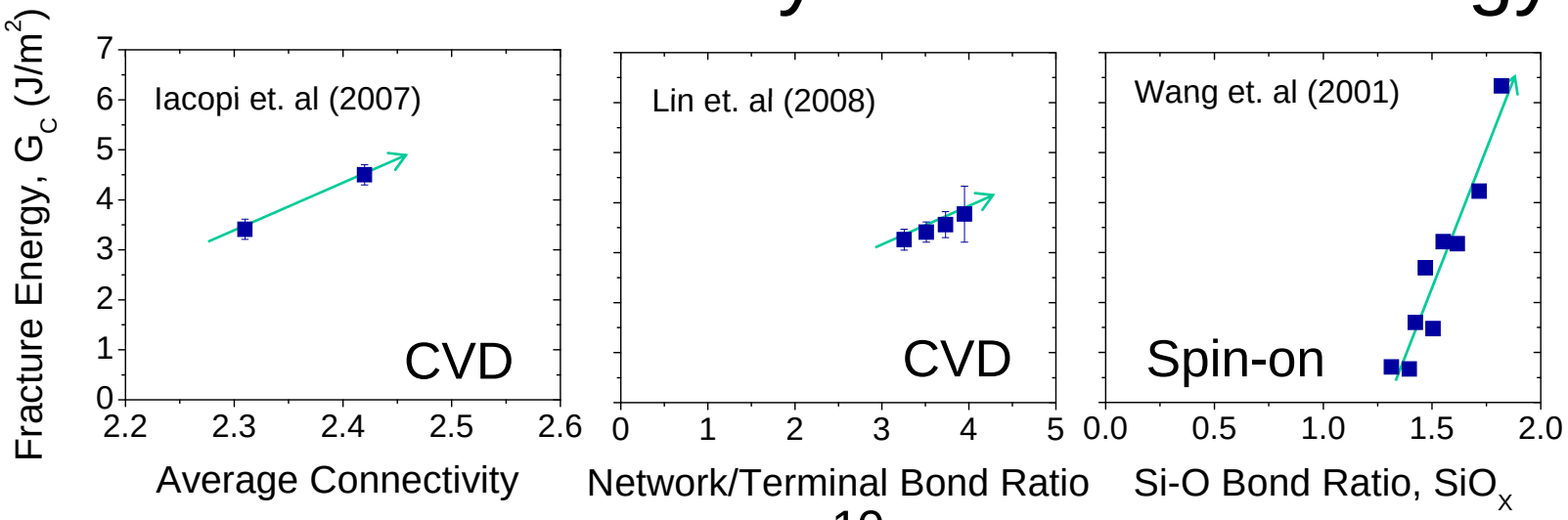
$$\frac{bonds}{area} \propto (p - 0.55)$$

$$G_C \propto \left(p - 0.55\right)$$



STANFORD ENGINEERING

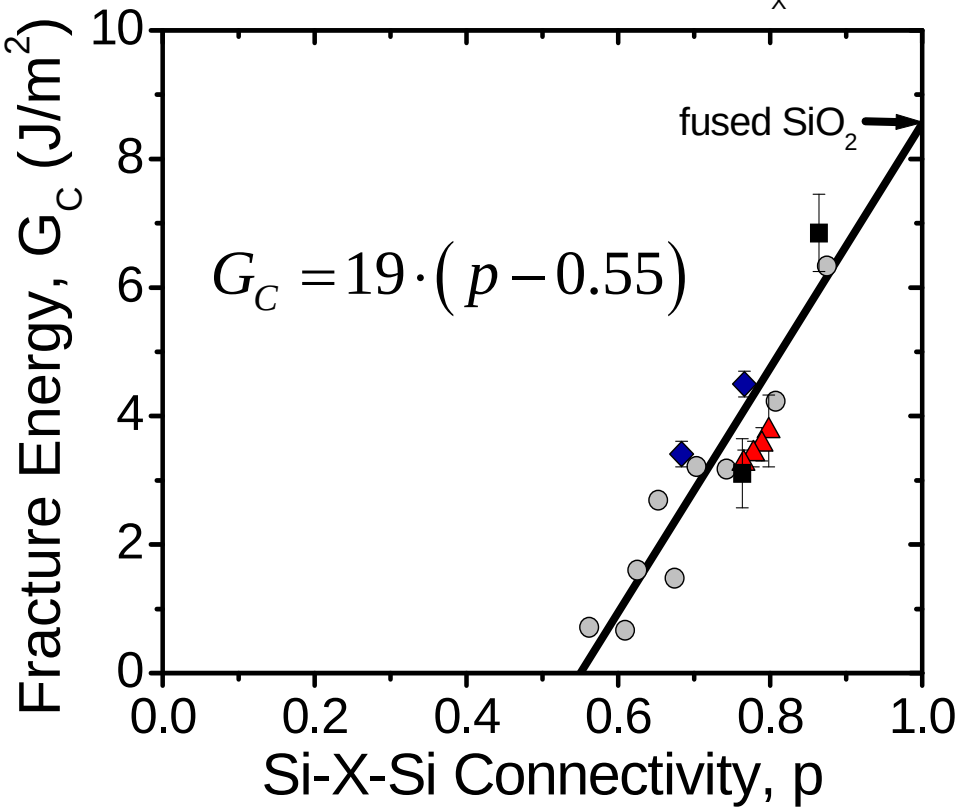
Effect of Connectivity on Fracture Energy



- universal scaling of G_C for brittle organosilicates

$$G_C \propto (p - 0.55)$$

- CVD and spin-on

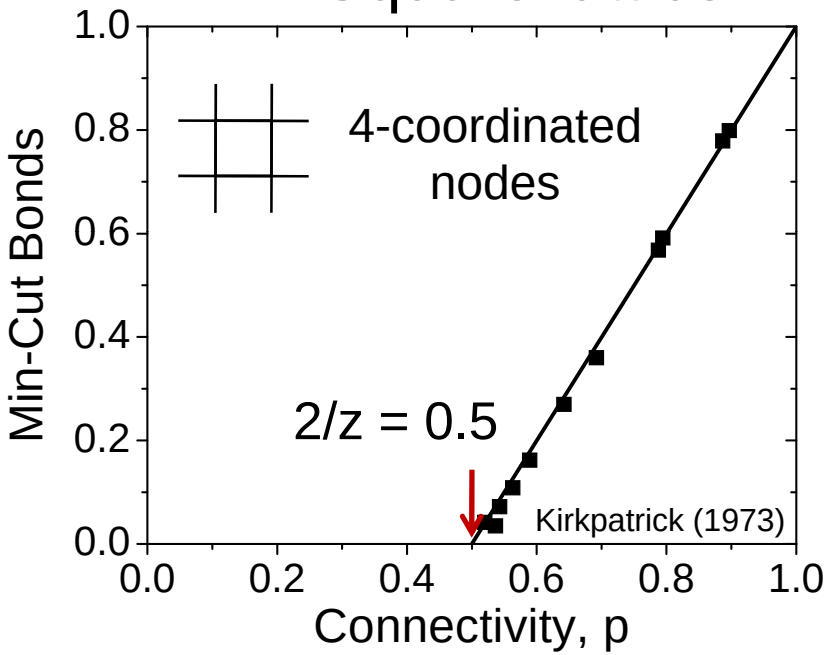


STANFORD ENGINEERING

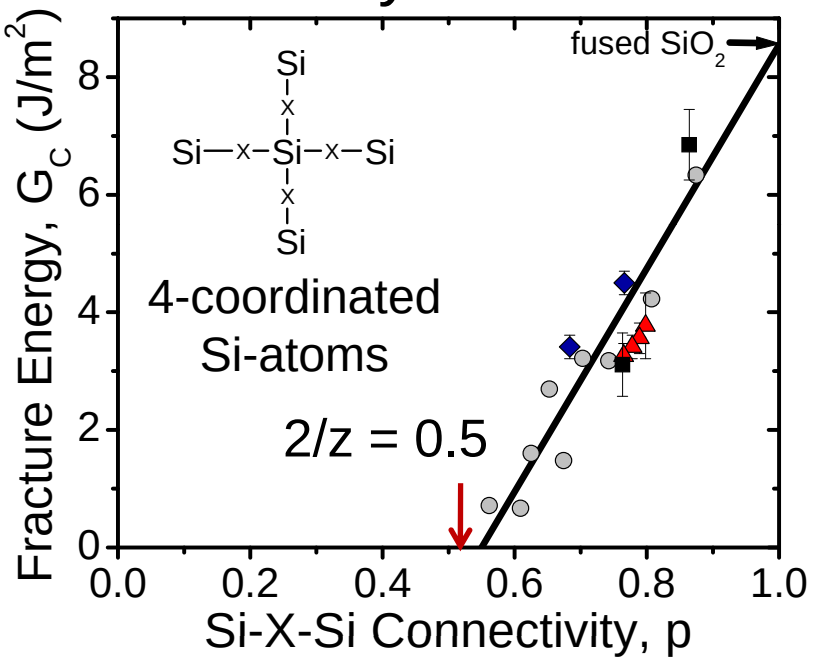
Why (p-0.55)? Bond Percolation Theory

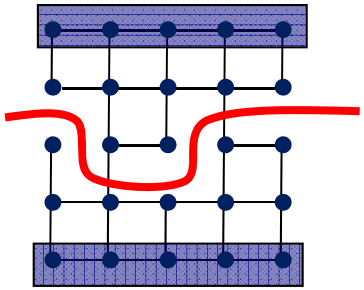
Effective Medium Approximation: percolation threshold at 2/z = 2/4
linear scaling with p

2-D Square lattice

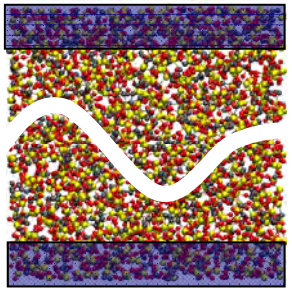


3-D Hybrid Glass





Can almost model hybrid glass as a 2-D square lattice of Si atoms!



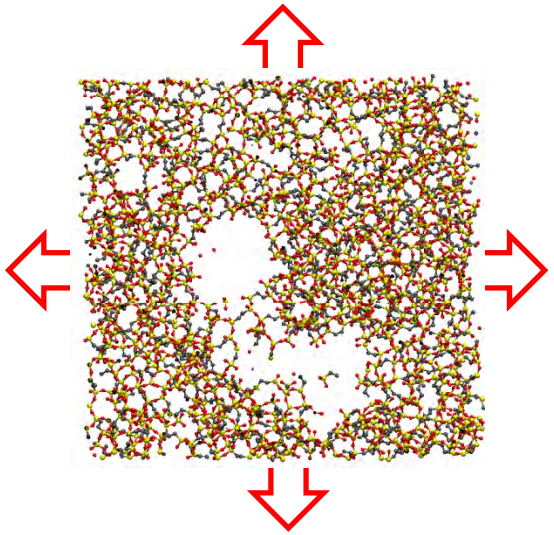
STANFORD ENGINEERING

Oliver, Dubois, Sherwood, Gage, Dauskardt, Adv. Funct. Matls, 2010. In press.

Outline

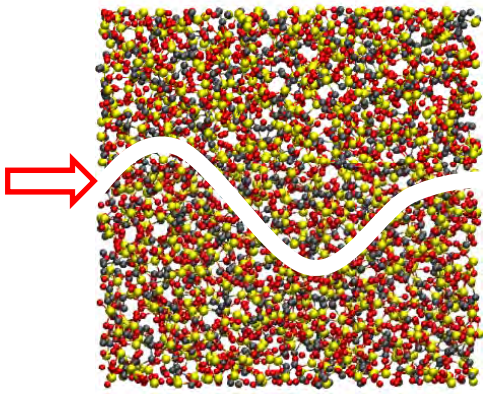
Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

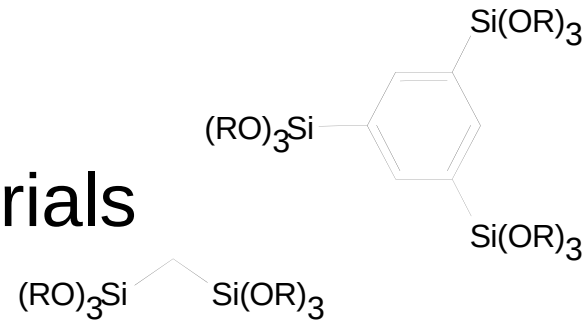


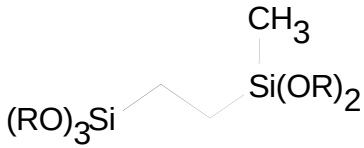
Fracture Energy

- network connectivity
- scaling relations



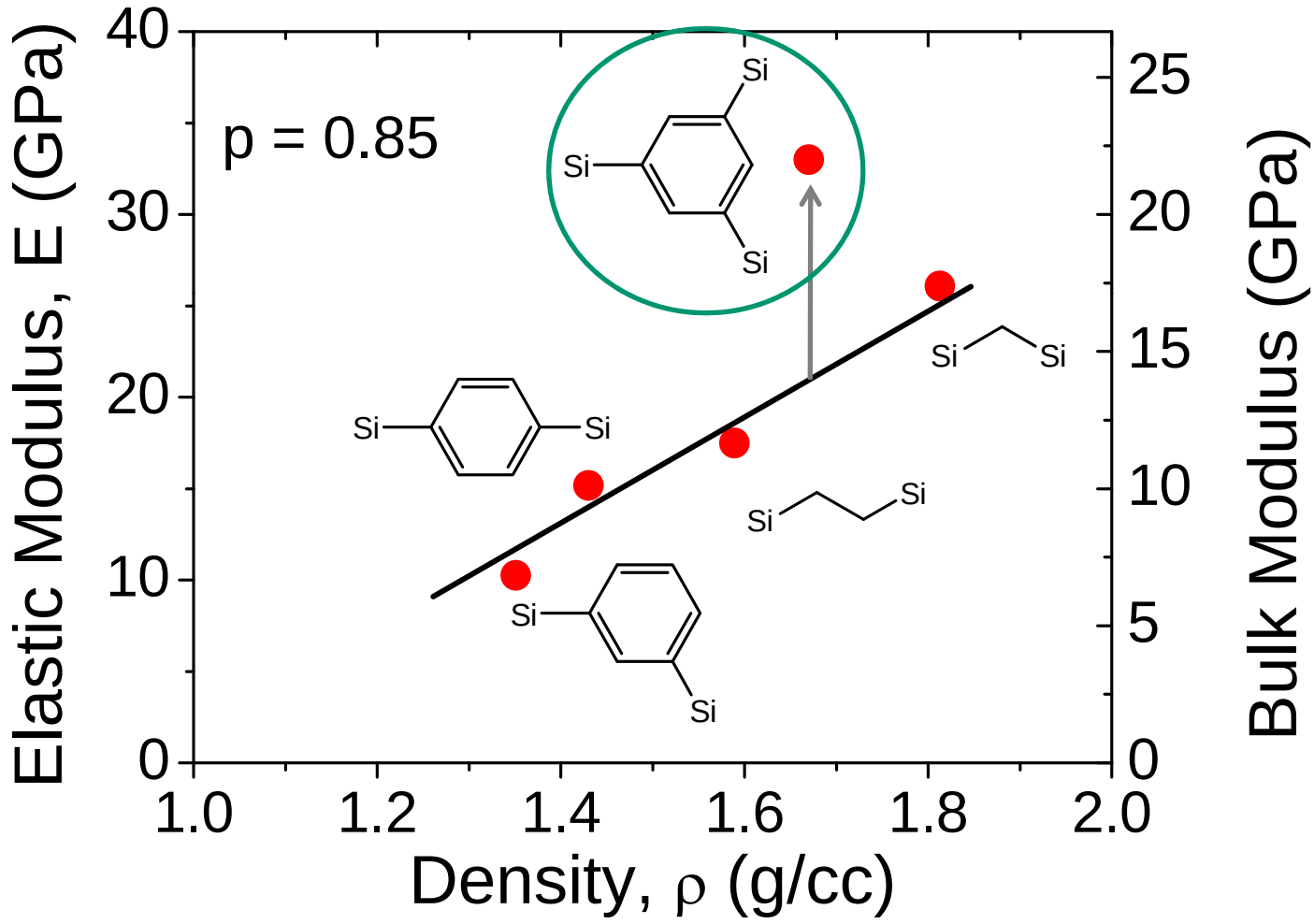
New Materials





STANFORD ENGINEERING

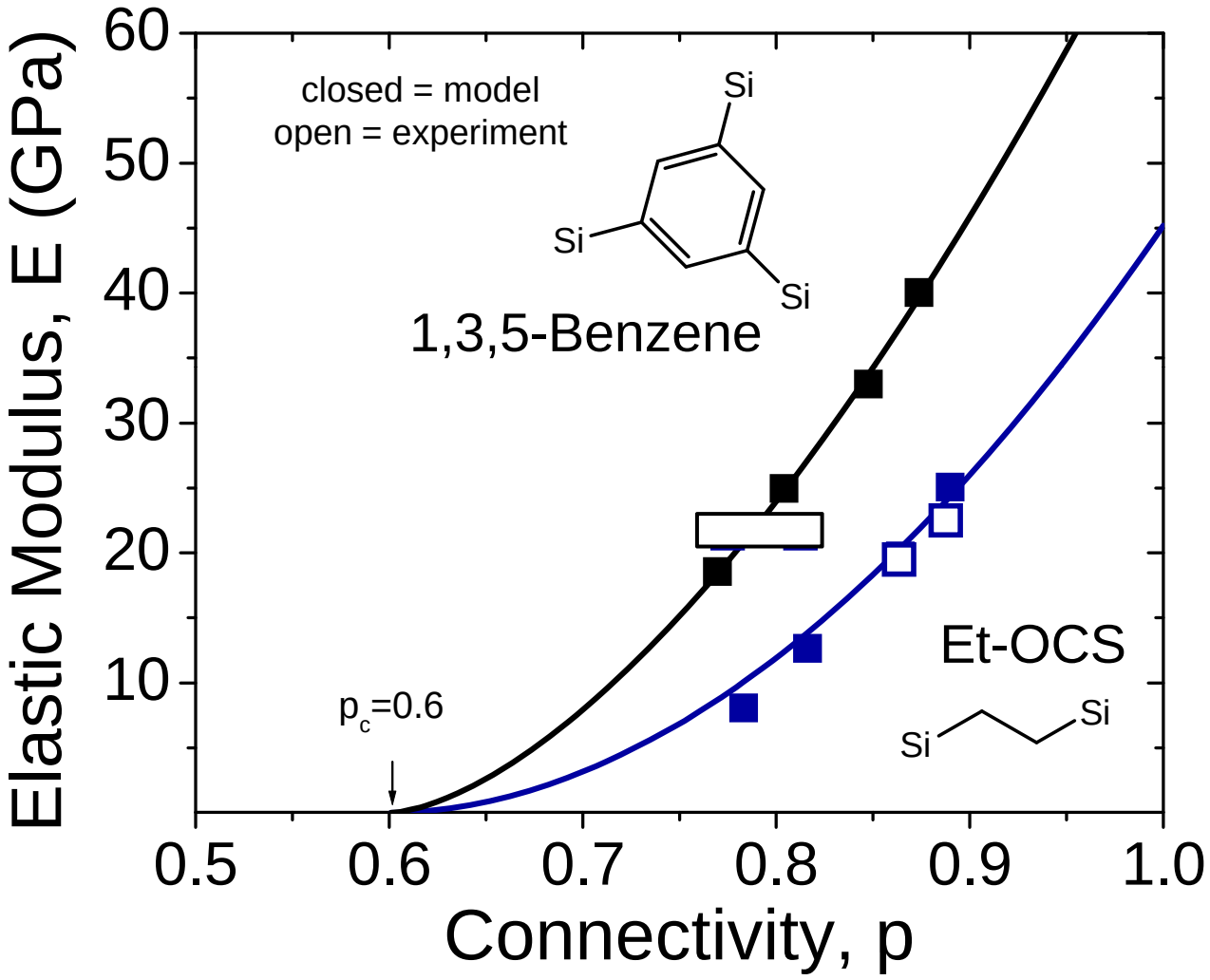
Predicting Modulus of New Glasses



STANFORD ENGINEERING

Oliver, Dubois, Sherwood, Gage, Dauskardt, Adv. Funct. Matls, 2010. In press.

High Modulus 1,3,5-Benzene Glasses

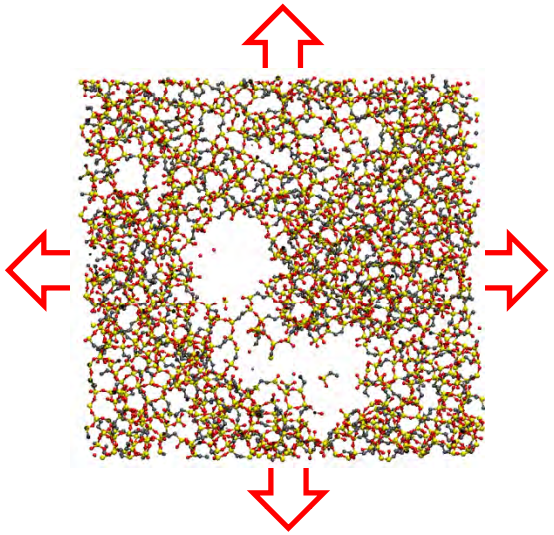


- 1,3,5-Benzene is inherently more stiff than Et-OCS, as predicted

Summary

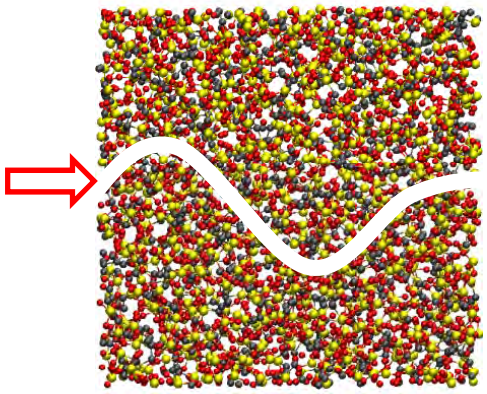
Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

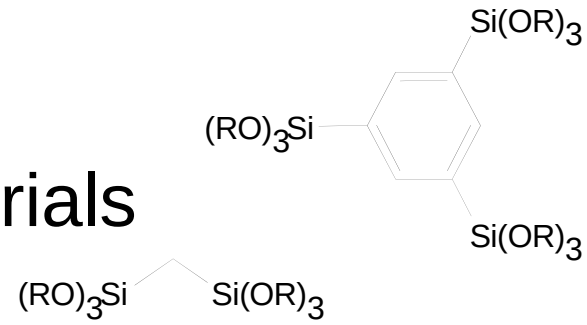


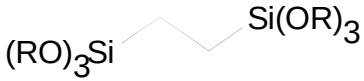
Fracture Energy

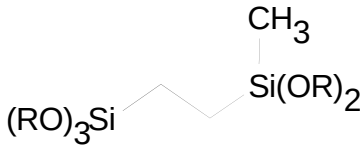
- network connectivity
- scaling relations



New Materials







STANFORD ENGINEERING