



# Molecular Modeling and Design of Hybrid Glasses

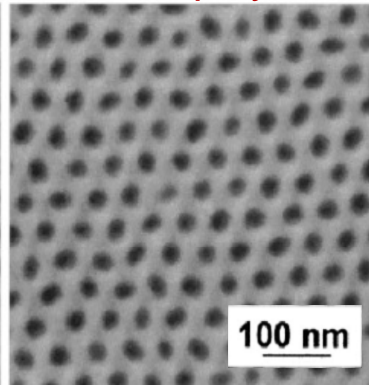
Mark Oliver, Yusuke Matsuda and Reinhold Dauskardt  
Materials Science and Engineering, Stanford University

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.

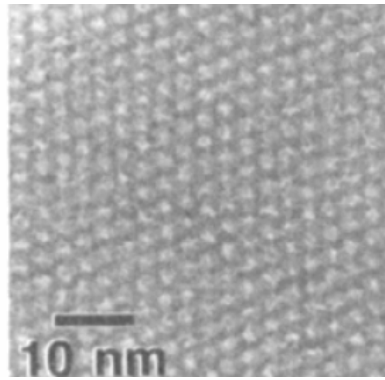
# Nanoporous Hybrid Glass Films...

Block Copolymers



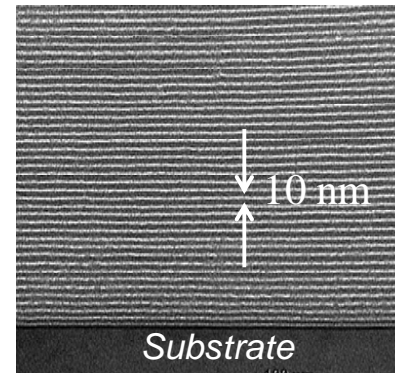
Guarini, et al. *J. Vac. Sci. Technol. B*, 2002.

Silica-Surfactant Structures



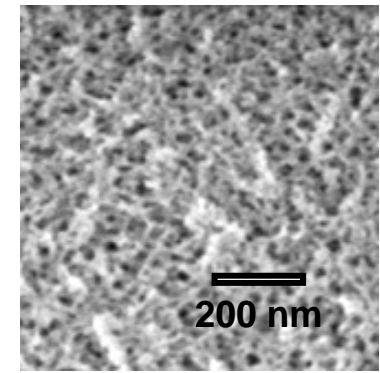
Beck, et al. *Journal Am. Chem. Soc.*, 1992.

Nano-Laminates



Dubois, et al., 2008.

MSSQ Hybrids



Maidenberg and Dauskardt, *Nature Materials*, 2002.

## Nanoscience Applications



microelectronic  
devices



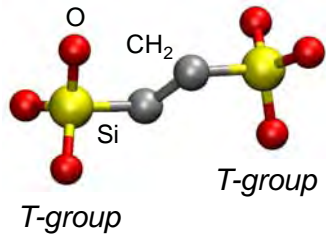
photovoltaics

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

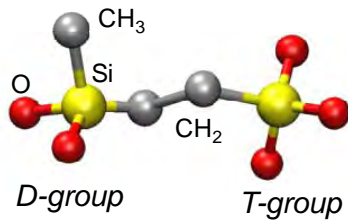
*...but hybrid glasses are mechanical fragile!*

# Molecular Modeling of Hybrid Glasses

Organosilane Precursors



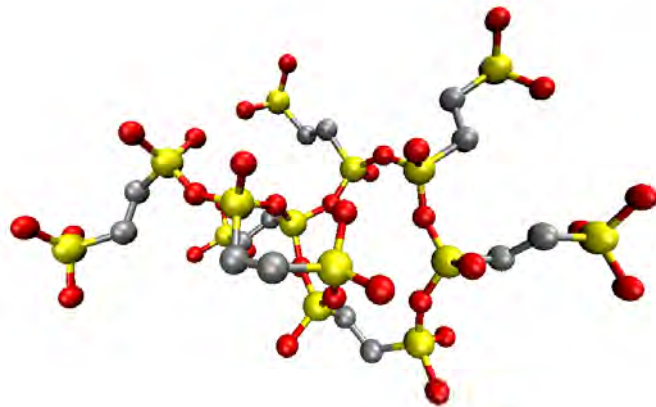
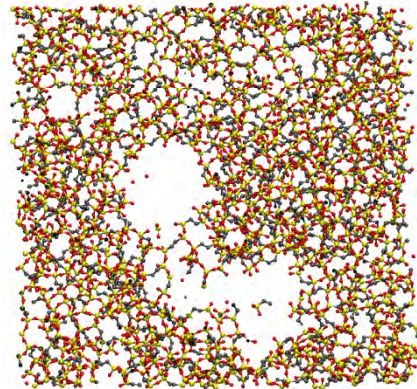
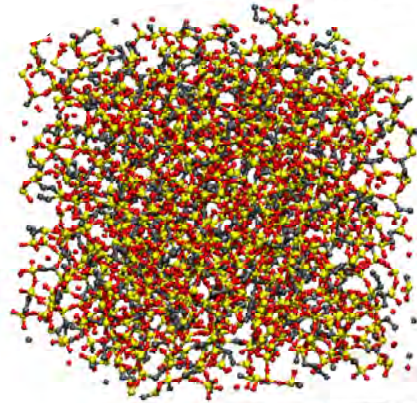
Et-OCS



Et-OCS(Me)

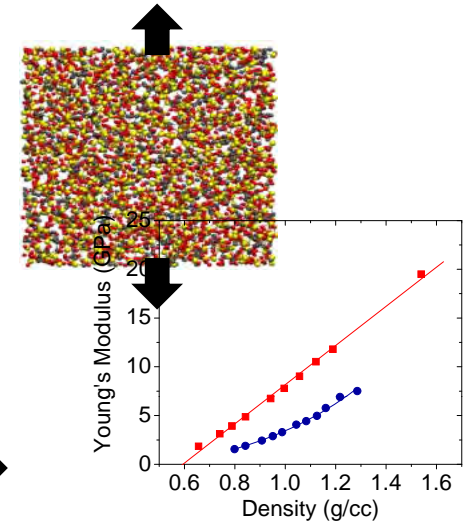
T-group

3-D glass Model

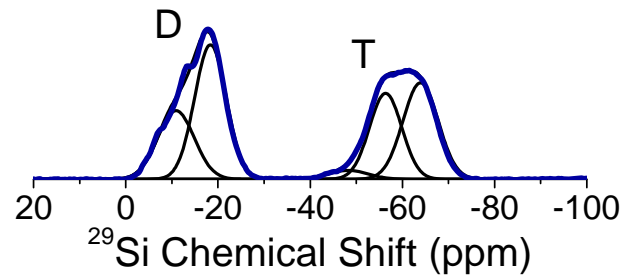
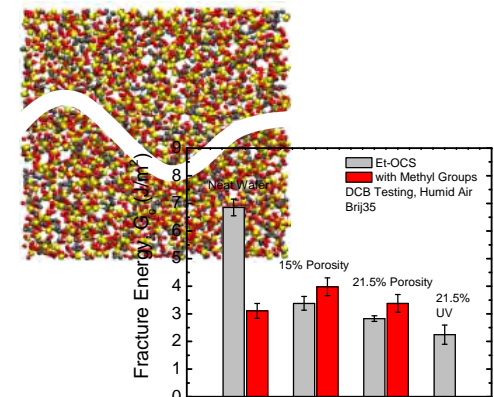


simulated anneal to create distortion free glass

Elastic Properties



Fracture Properties



# Outline

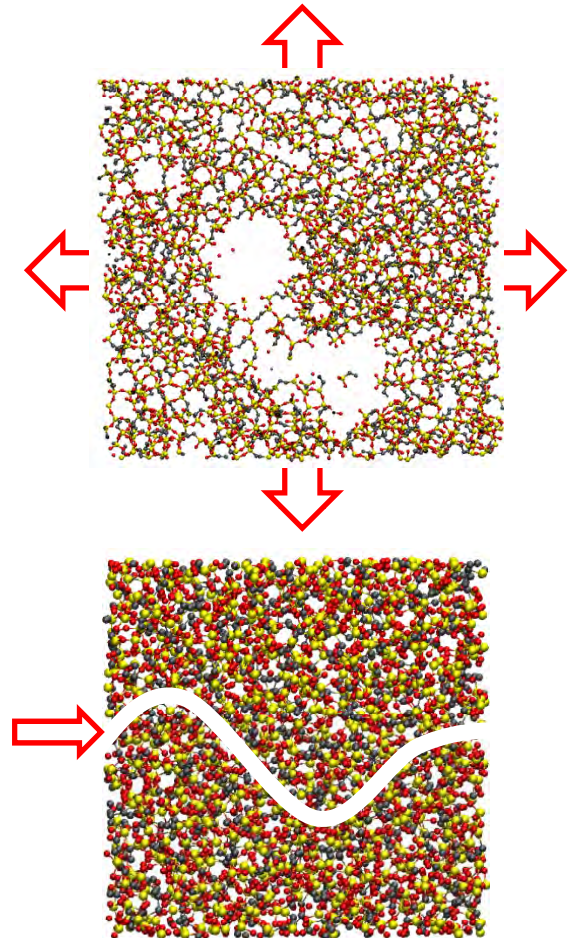
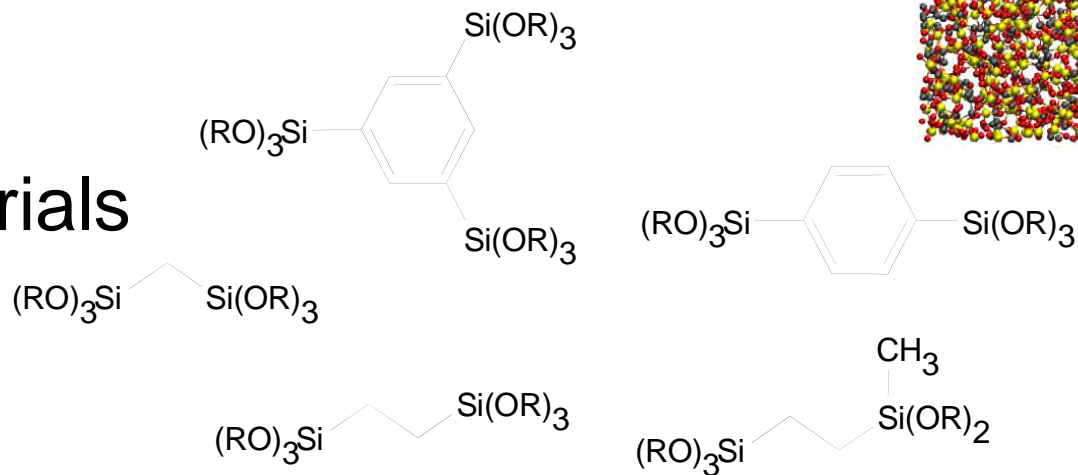
## Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

## Fracture Energy

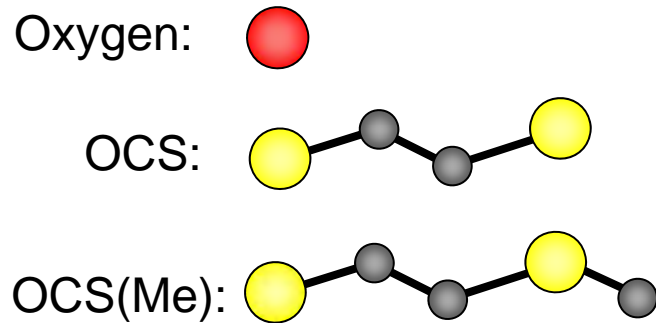
- network connectivity
- scaling relations

## New Materials



# MD Modeling of OCS/OCS(Me)

## Simulation Elements



H atoms are modeled implicitly  
(united atom approach)

## Bonded Interactions

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

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

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

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

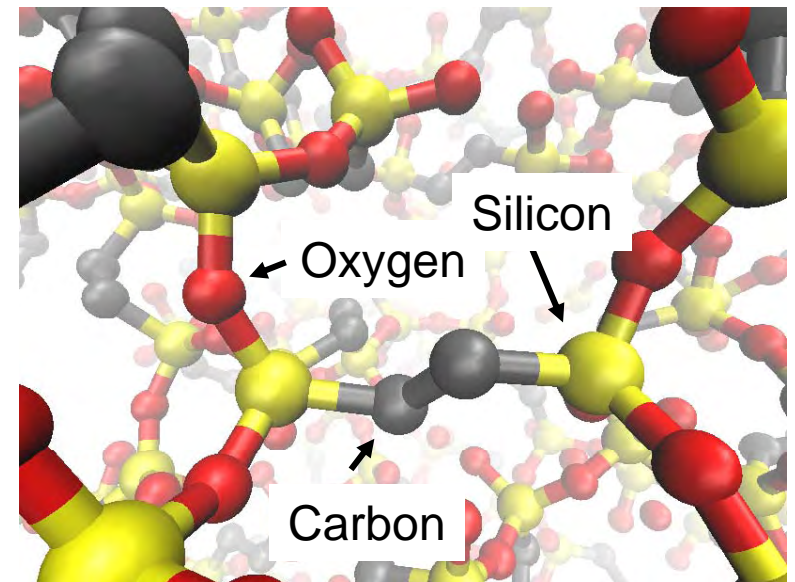
enforce all bond lengths, angles and dihedral angles

## Non-Bonded Interactions: Stillinger-Weber Type Potential

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

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

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



# 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

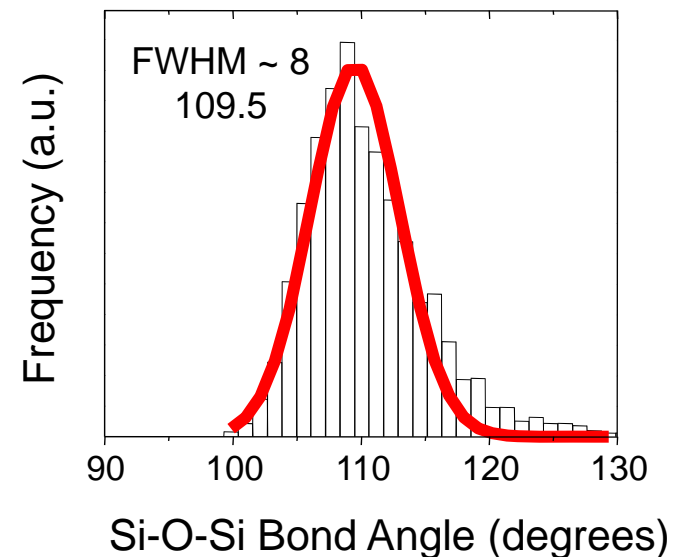
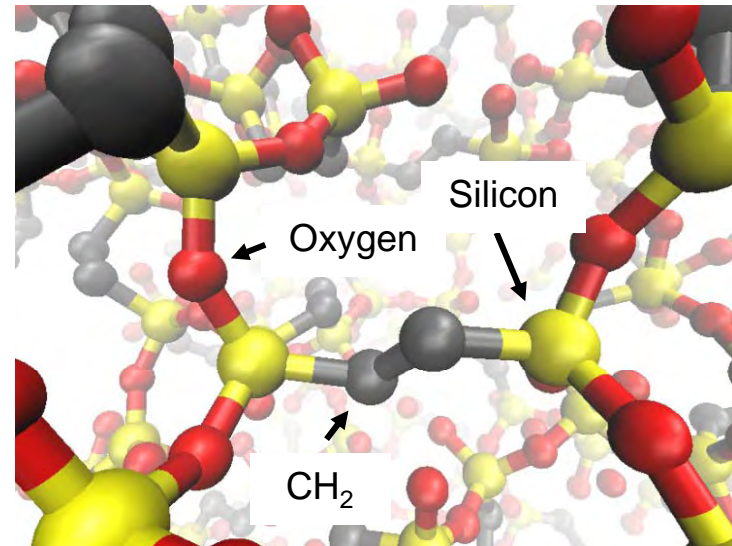
- only 1% O atoms are unbound

## Correct density

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

## Correct Si-O-Si bond angle distribution

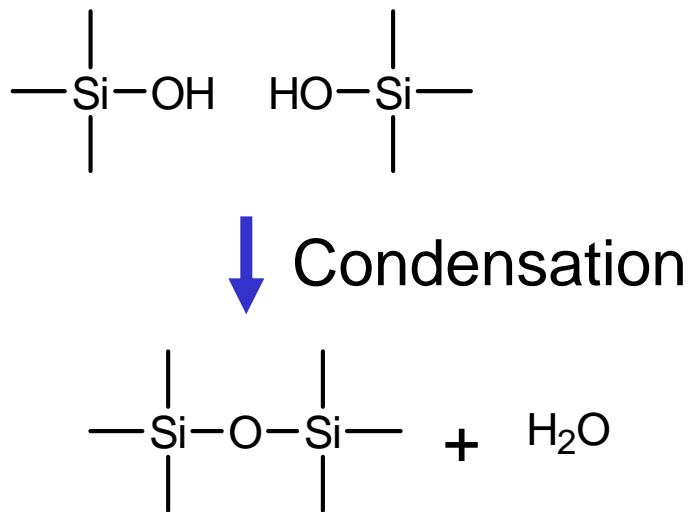
FWHM of ~ 8 degrees consistent with 7 degree FWHM reported for silica  
[Feuston and Garofalini *J. Phys. Chem.* 1988]



# Simulations Reproduce Local Chemical Structure

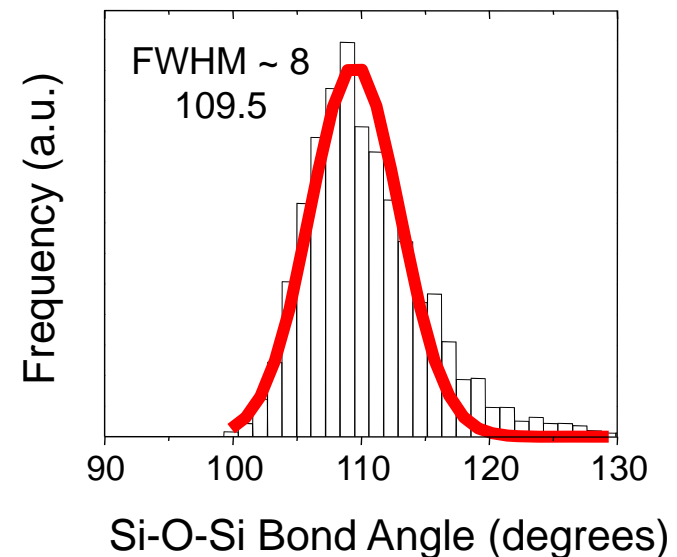
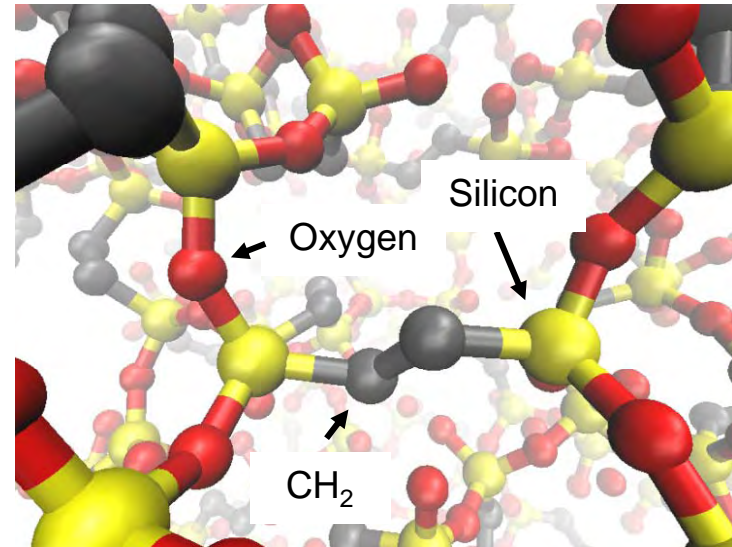
Characteristics of simulation with 750 OCS molecules and 2800 O atoms  
Variable condensation

## Condensation and network connectivity



## Condensation degree, $q$

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

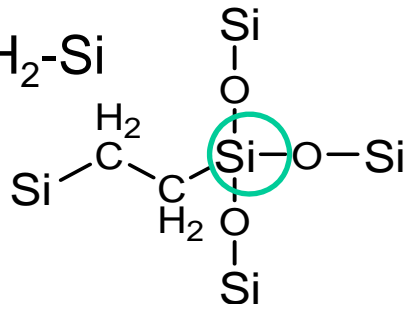


# Si-X-Si Network Connectivity

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

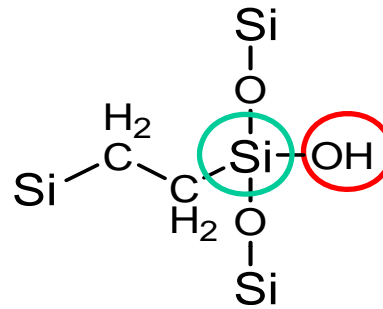
## Bridging Si-X-Si bonds

- Si-O-Si
- Si-CH<sub>2</sub>-CH<sub>2</sub>-Si

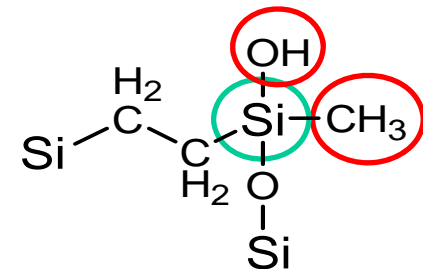


$$p = 4/4 = 1.0$$

## Terminal bonds

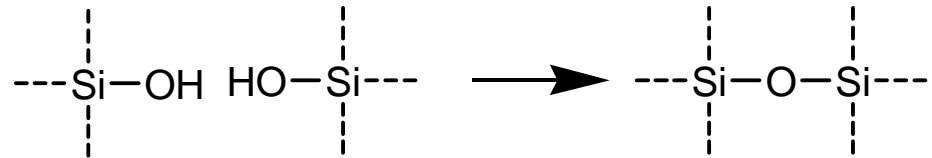


$$p = 3/4 = 0.75$$

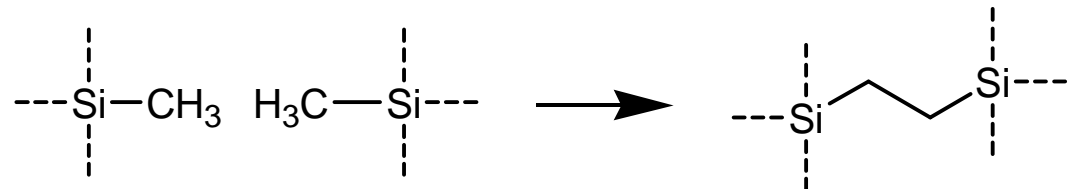


$$p = 2/4 = 0.50$$

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

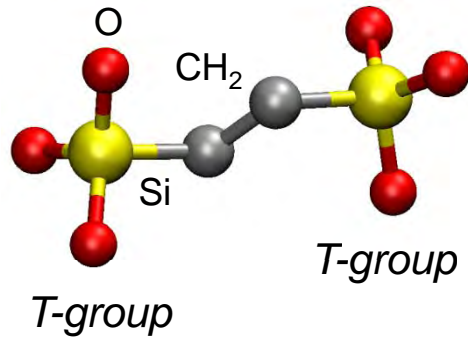


Use bridged precursors

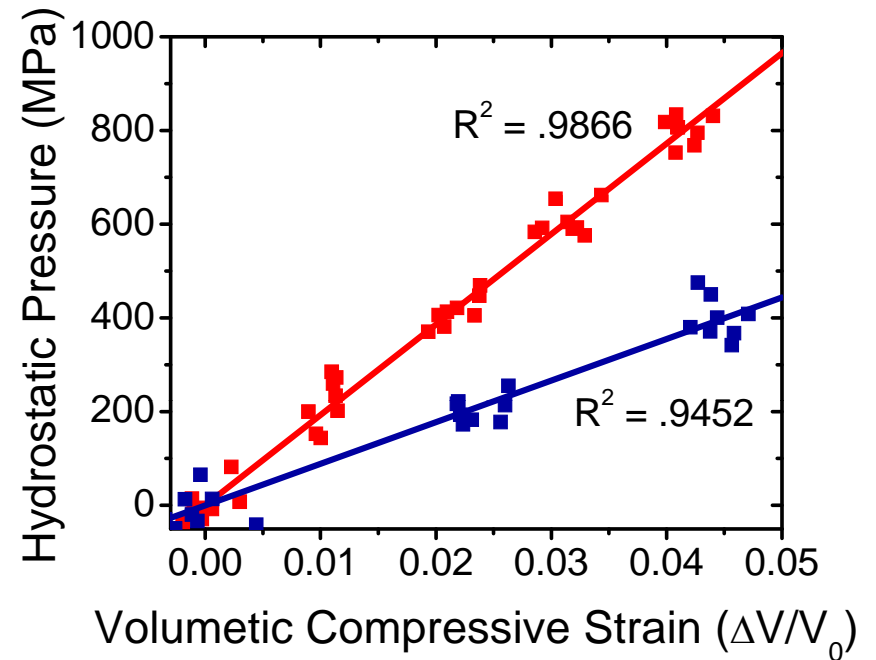
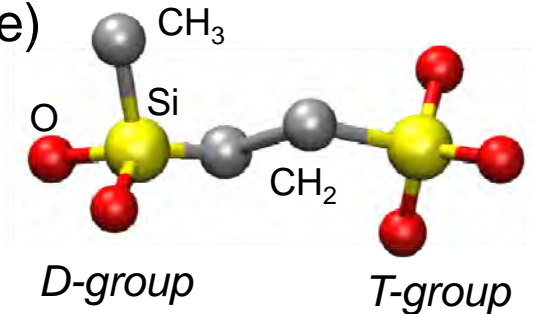


# Simulating Bulk Modulus

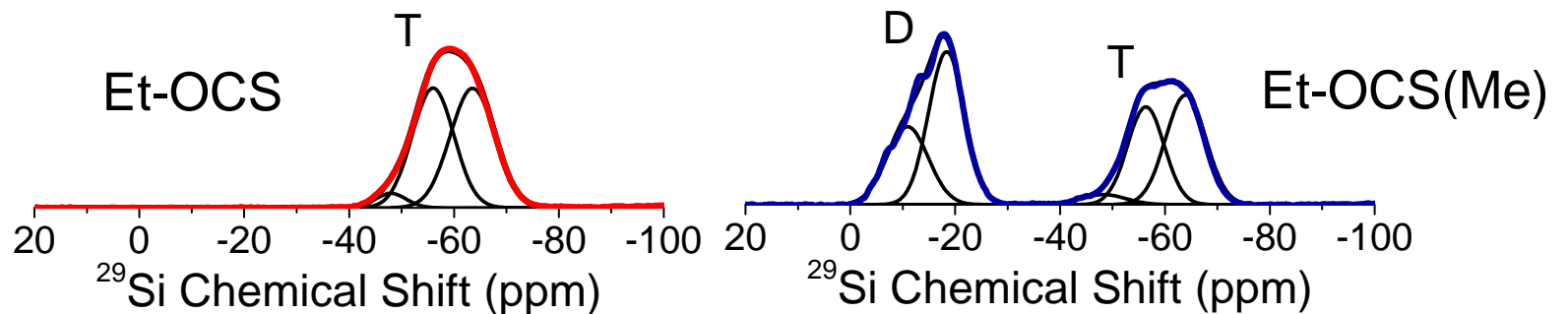
Et-OCS



Et-OCS(Me)

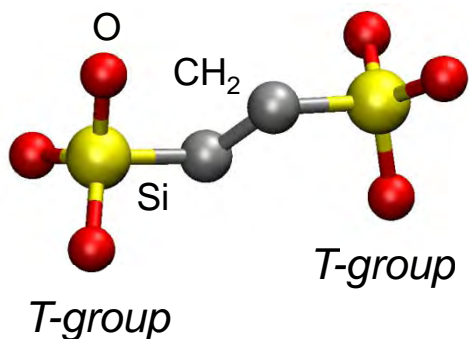


Experimental Glasses: surface acoustic wave (SAW's) modulus

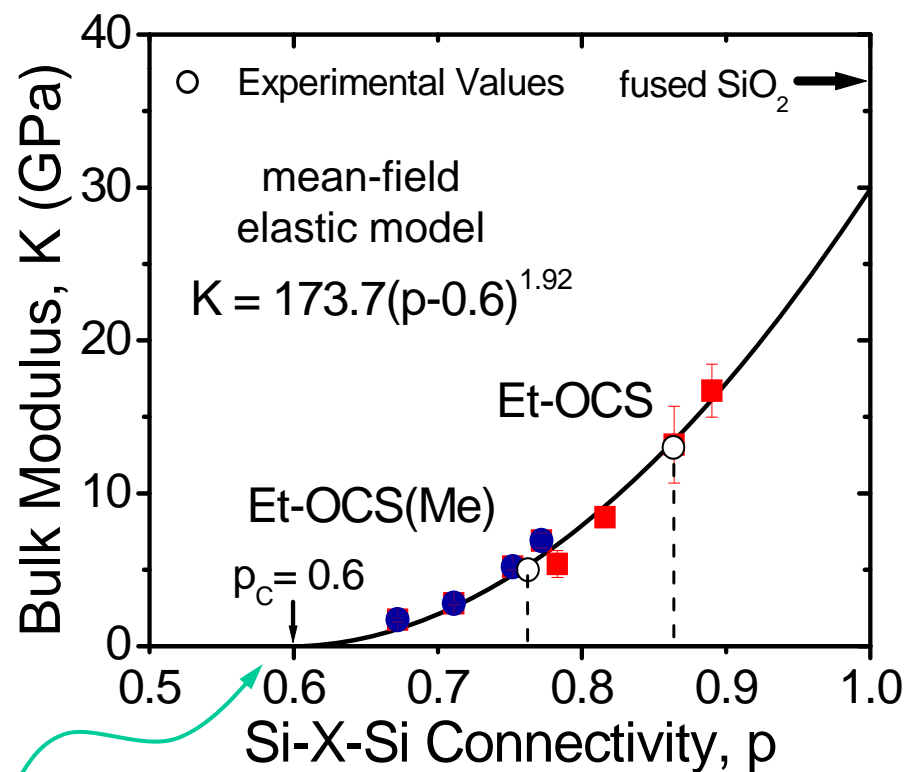
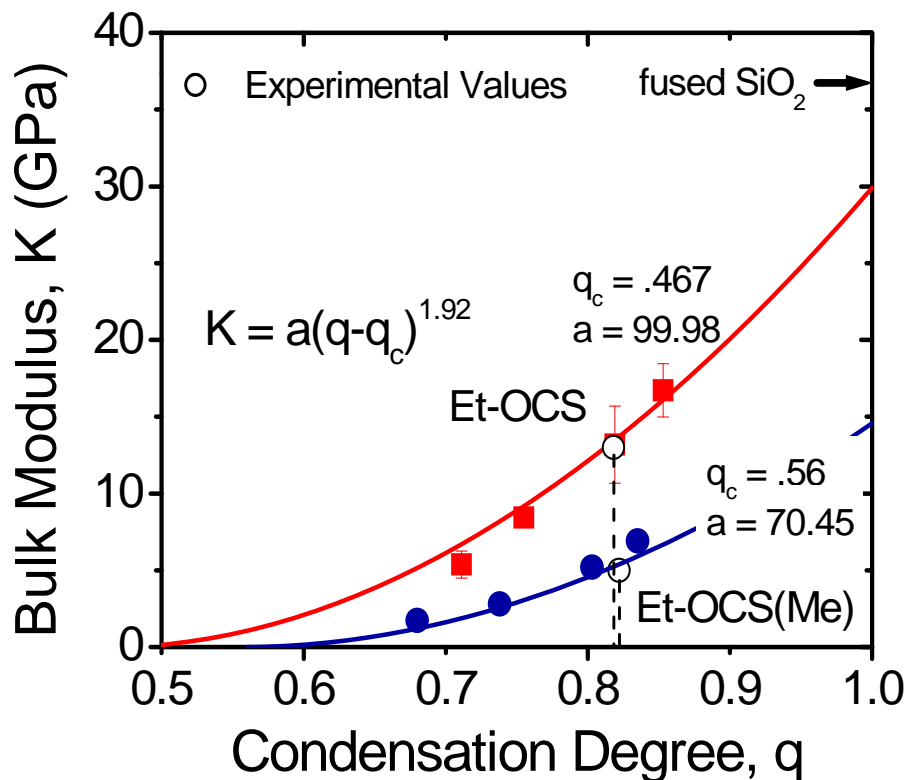
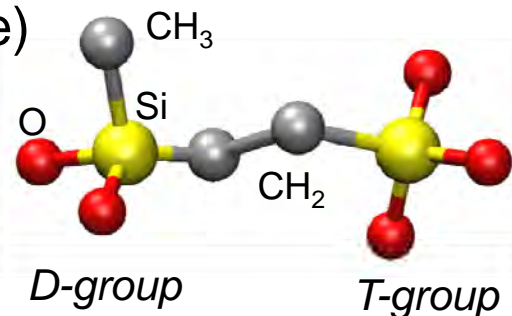


# Simulating Bulk Modulus

Et-OCS



Et-OCS(Me)

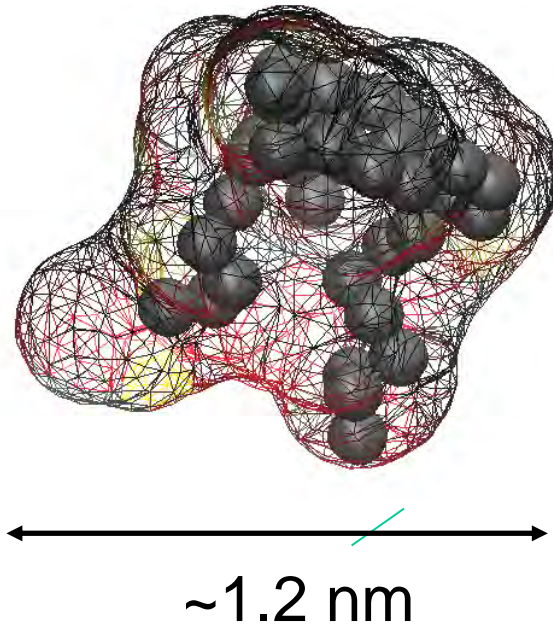
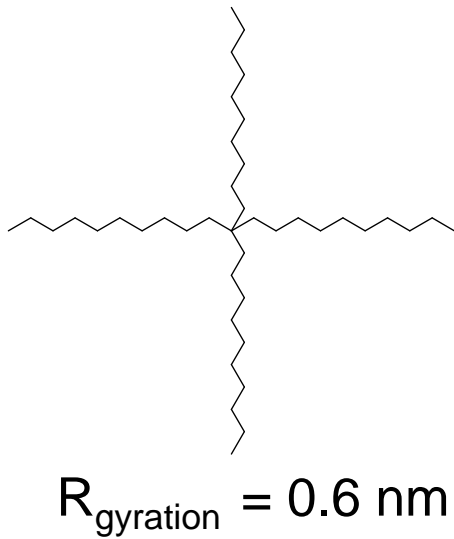


rigidity percolation

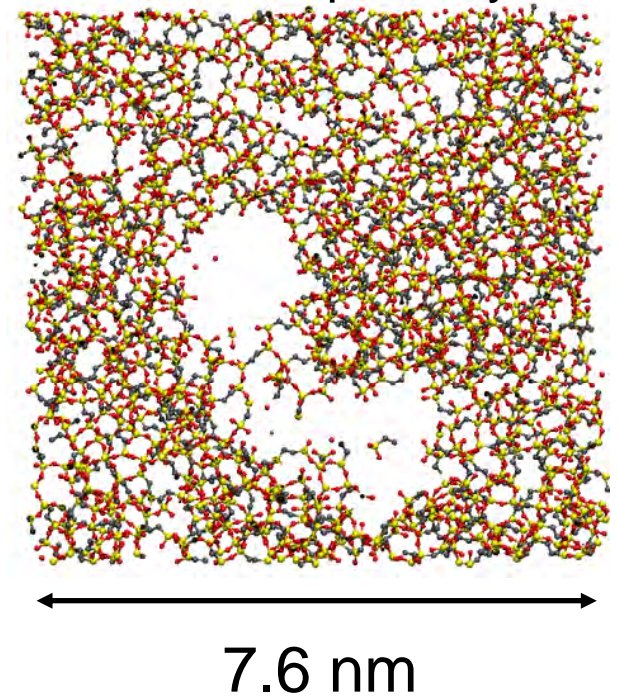
# Model Nanoporous Glasses

Sample Pore:  
atoms of porogen shown  
mesh grid shows pore surface

Model Porogen:  
4 C<sub>10</sub> arms



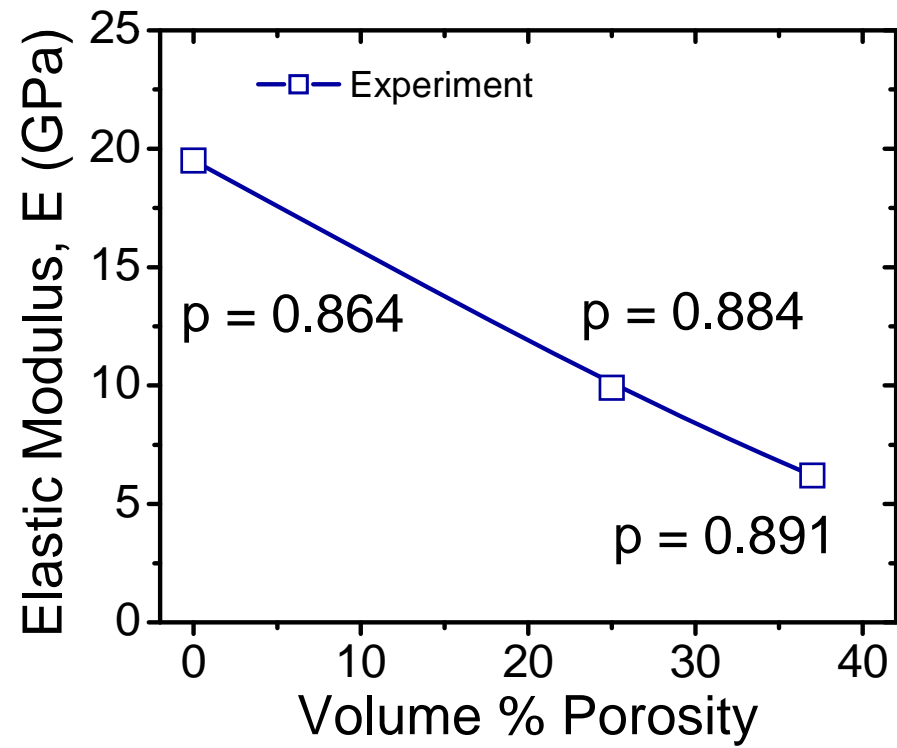
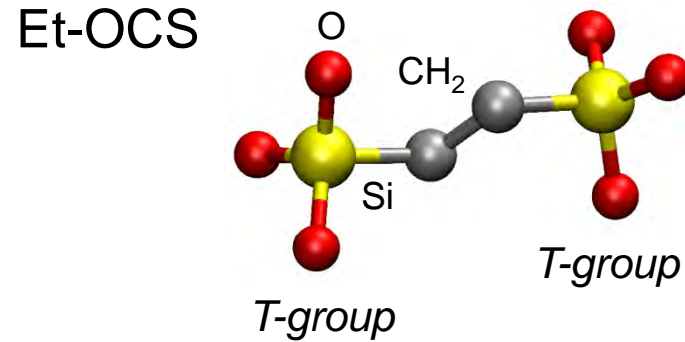
Porous Glass Model:  
25 vol% porosity



# Effect of Porosity on Elastic Stiffness

## Experimental data

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



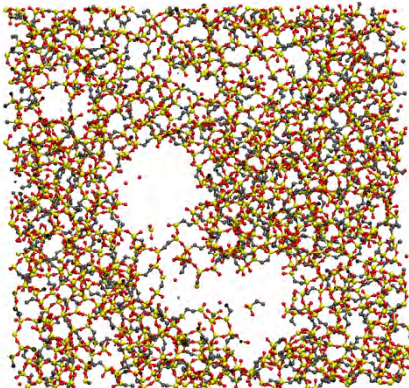
# Effect of Porosity on Elastic Stiffness

## Experimental data

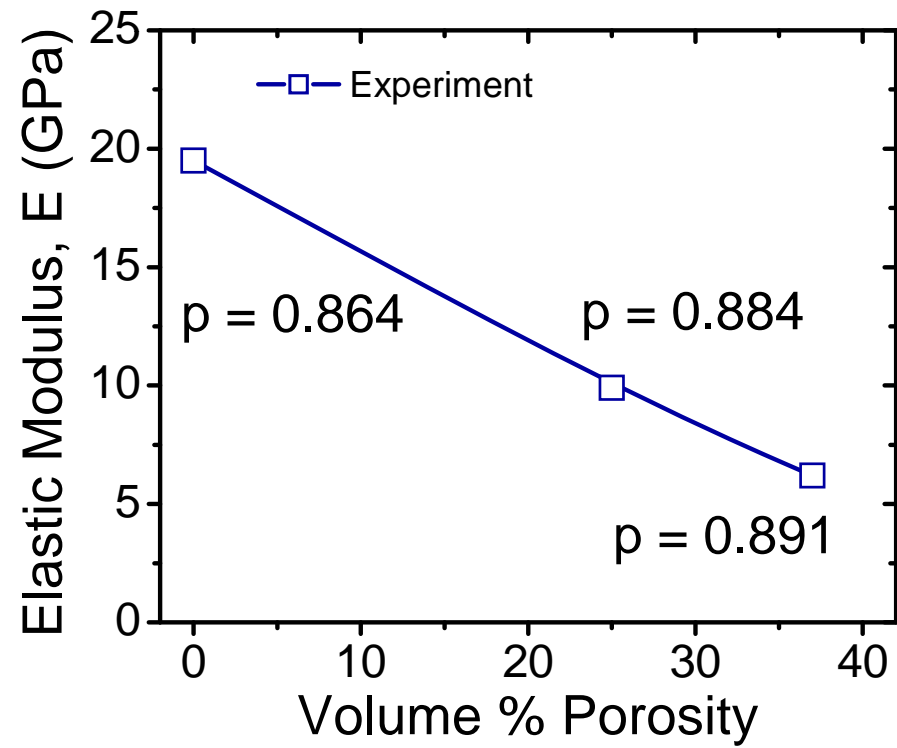
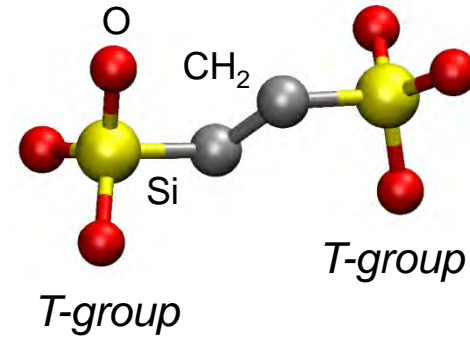
vol% porosity (porosimetry)	$\rho$ (NMR)	E (GPa)
0	.864	19.5
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37	.891	6.15

Model inputs: vol% pore,  $\rho$

accurate models of real glasses



Et-OCS



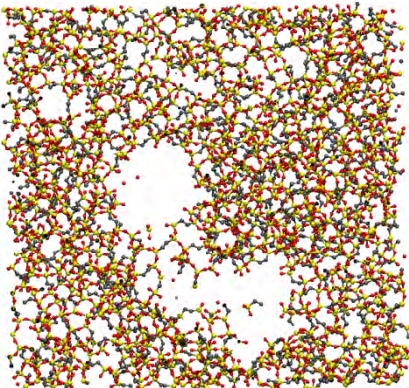
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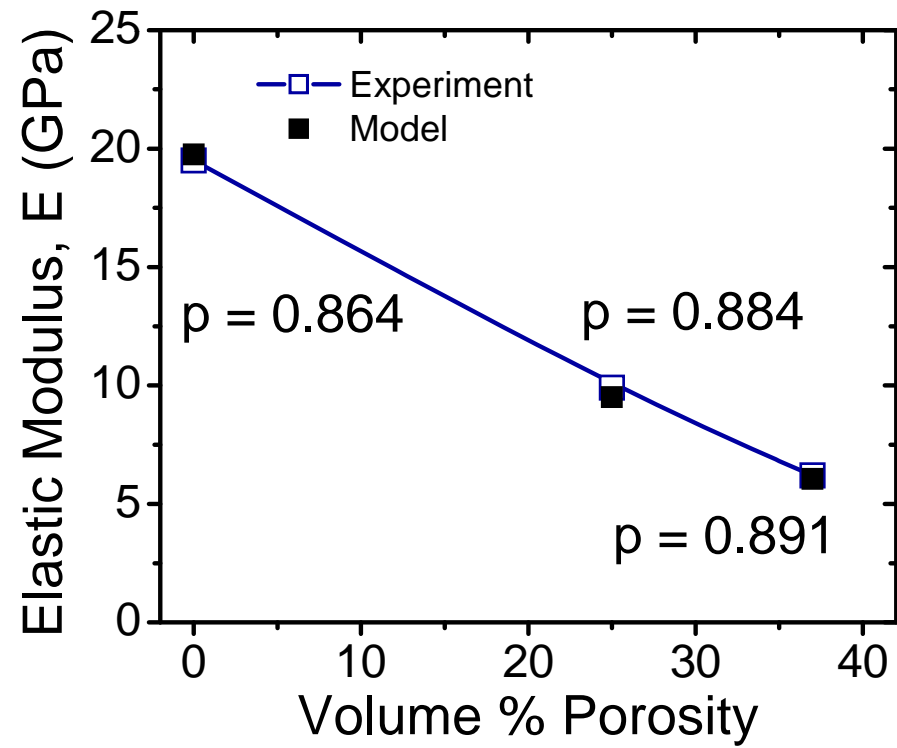
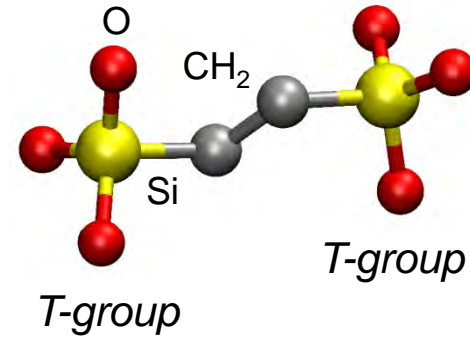
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Et-OCS



# Outline

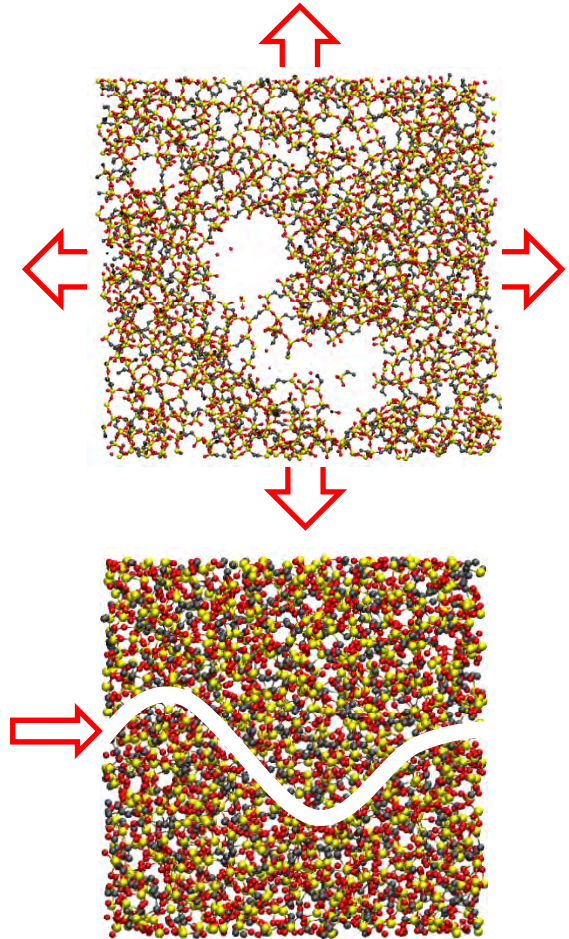
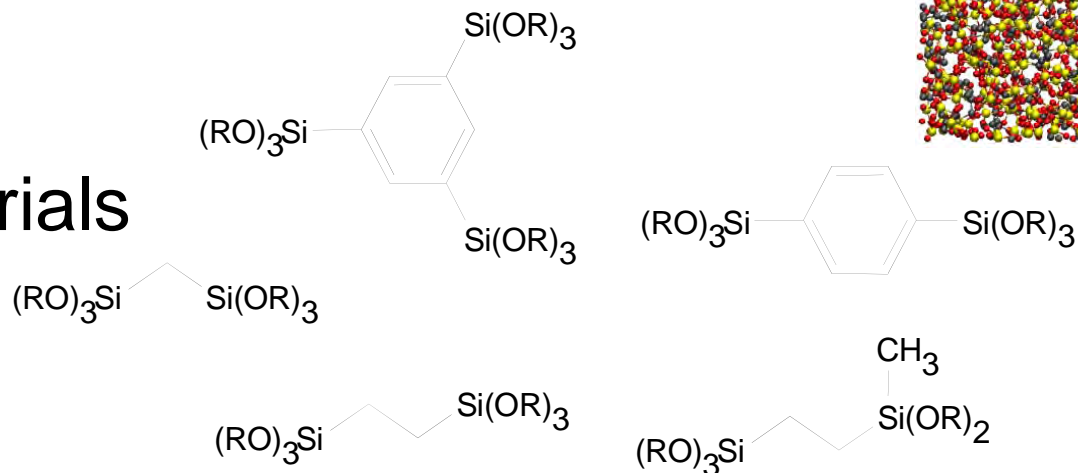
## Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

## Fracture Energy

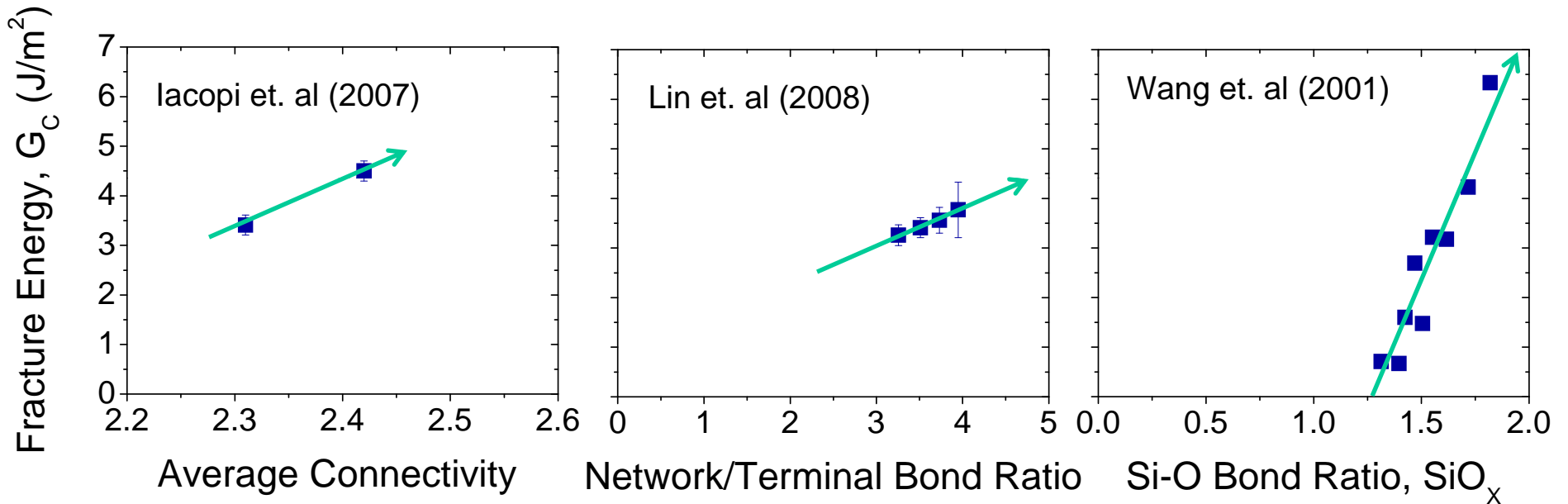
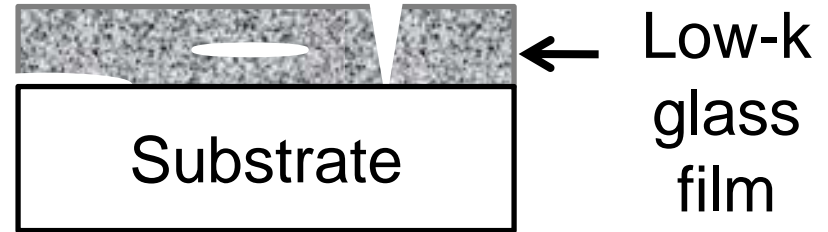
- network connectivity
- scaling relations

## New Materials



# Effect of Connectivity on Fracture Energy, $G_C$

Adhesive and cohesive fracture concern for reliable integration

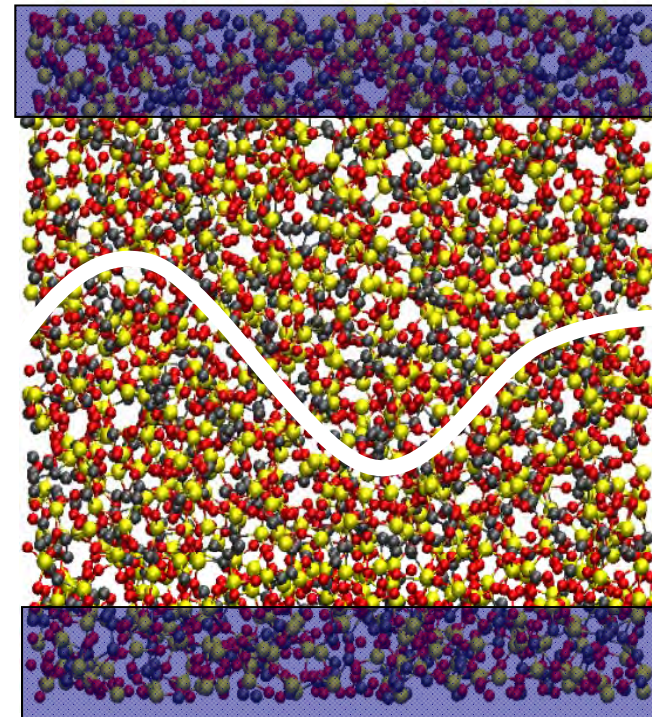
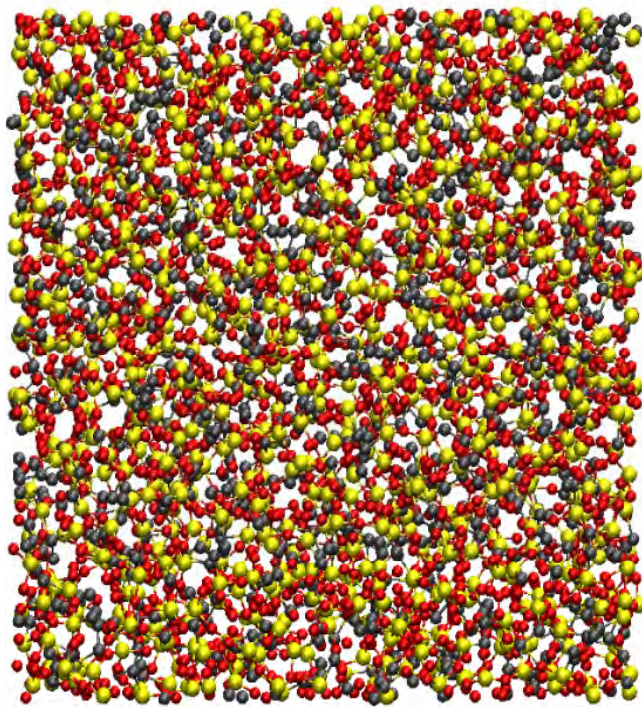


Increased connectivity  $\rightarrow$  more bonds to break  $\rightarrow$  higher  $G_C$

Is there a fundamental scaling law?

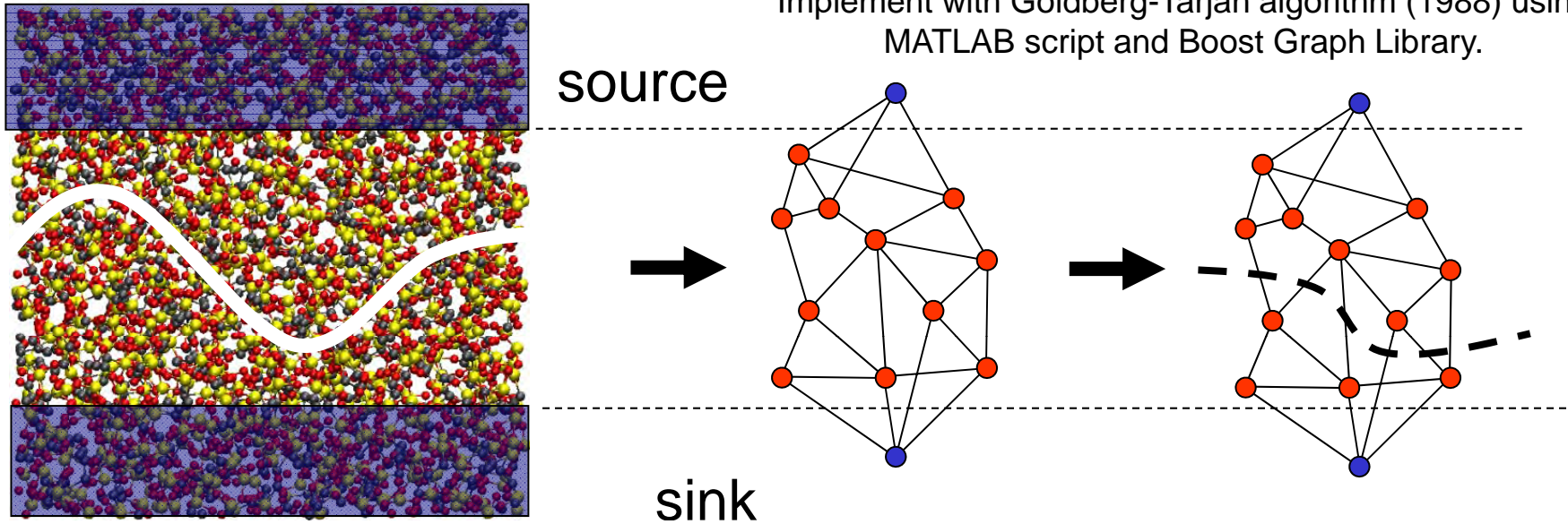
# Simulating Cohesive Fracture

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



# 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.



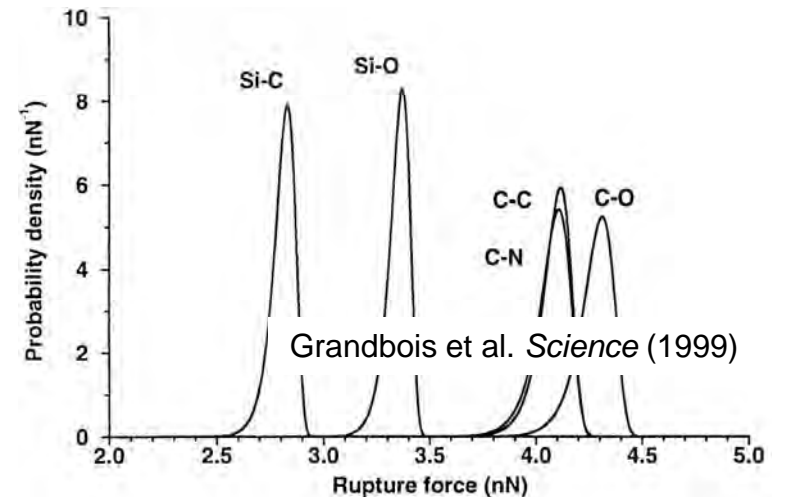
Convert to *weighted* graph and find min-cut...

atoms = vertices, bonds = edges

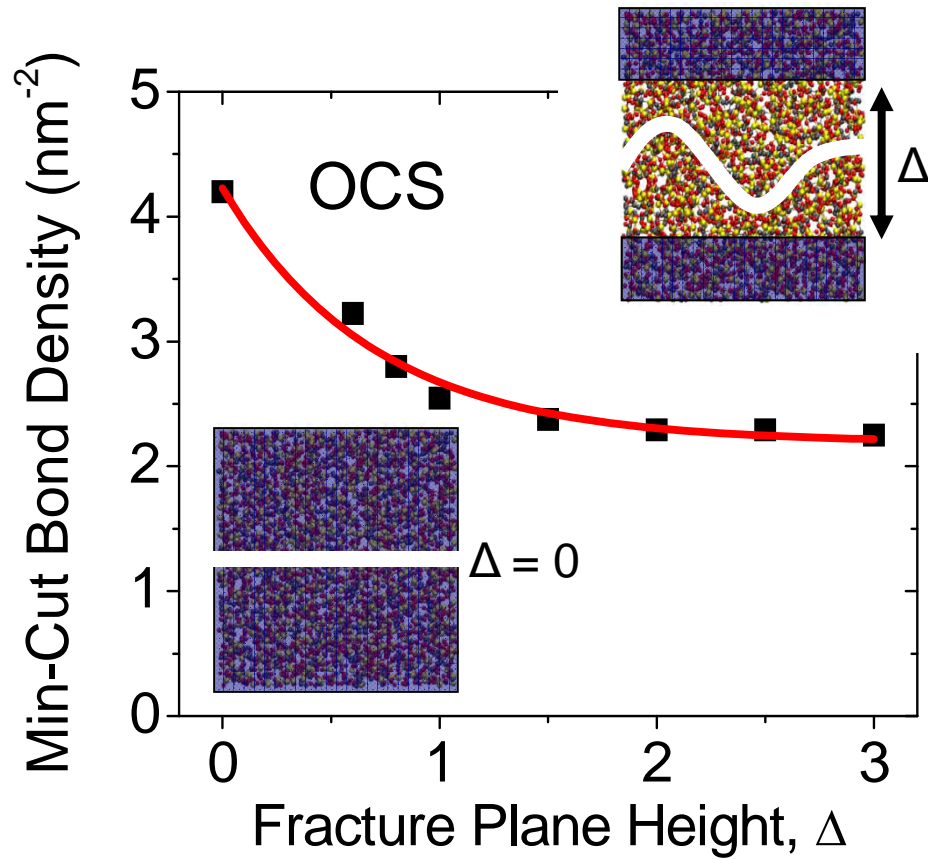
bond strength/energy = edge weight

collapse source/sink into single vertices

Weight edges by strength



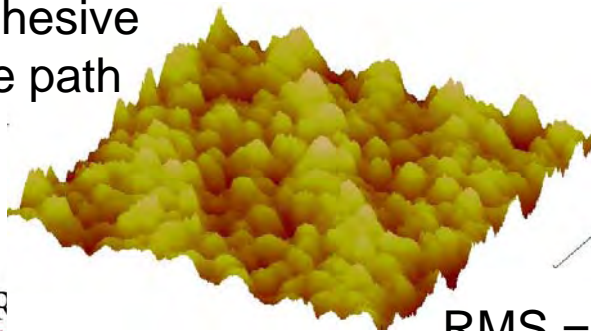
# 3-D Complex Fracture Path Selection



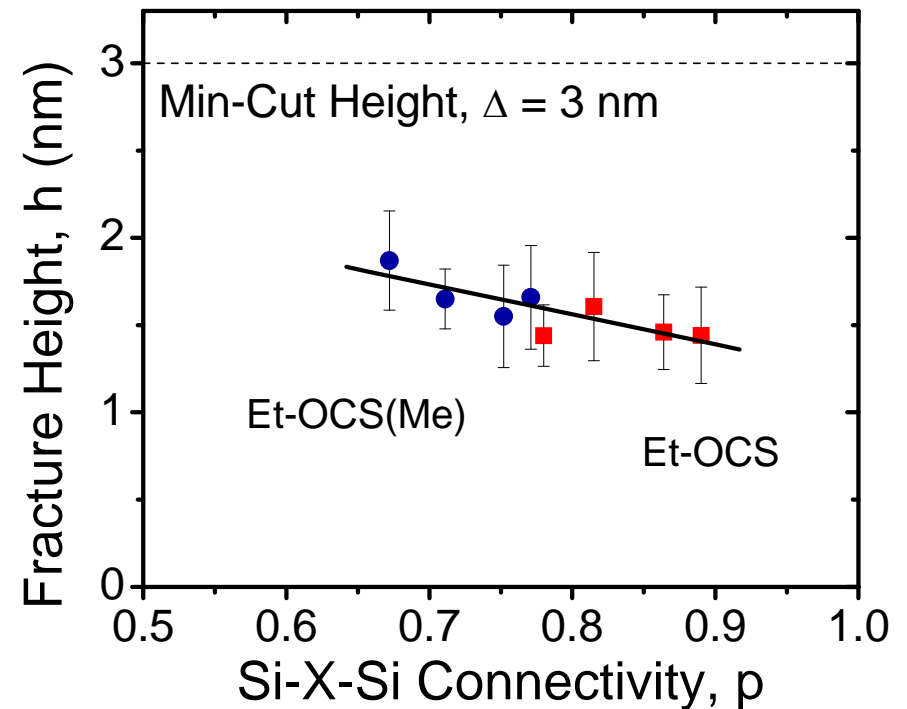
Crack path seeks out lowest energy path through network

Results in nanometer roughness

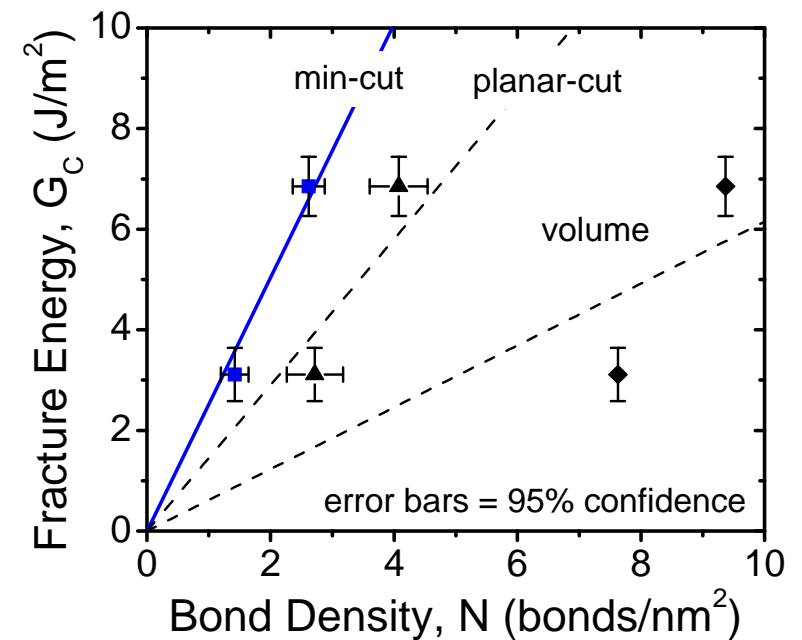
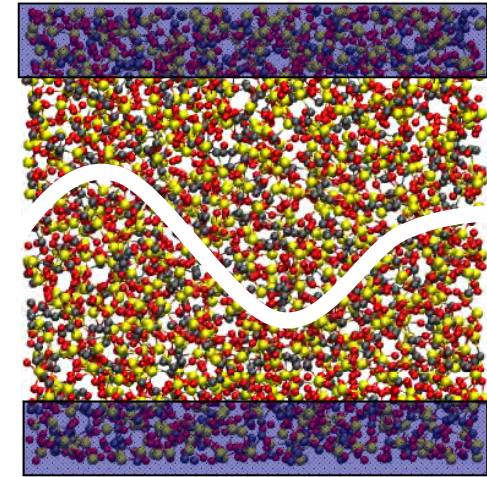
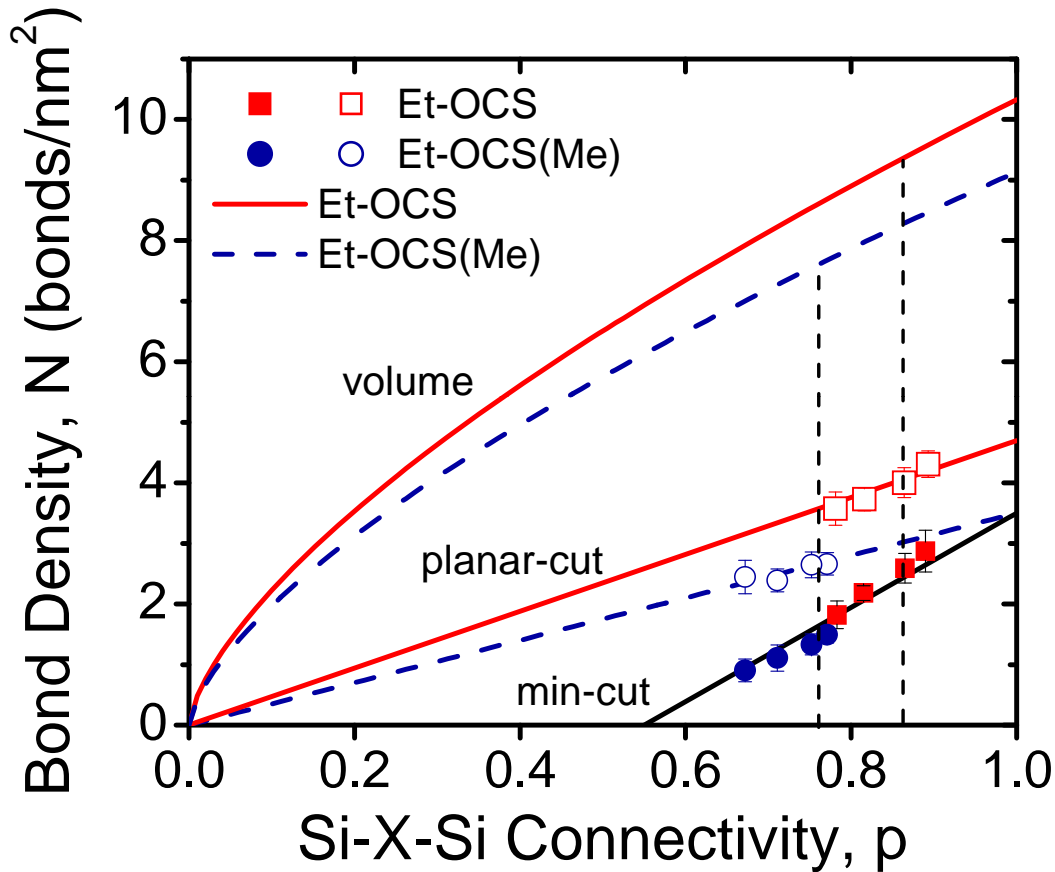
AFM cohesive fracture path



RMS = 1.2nm

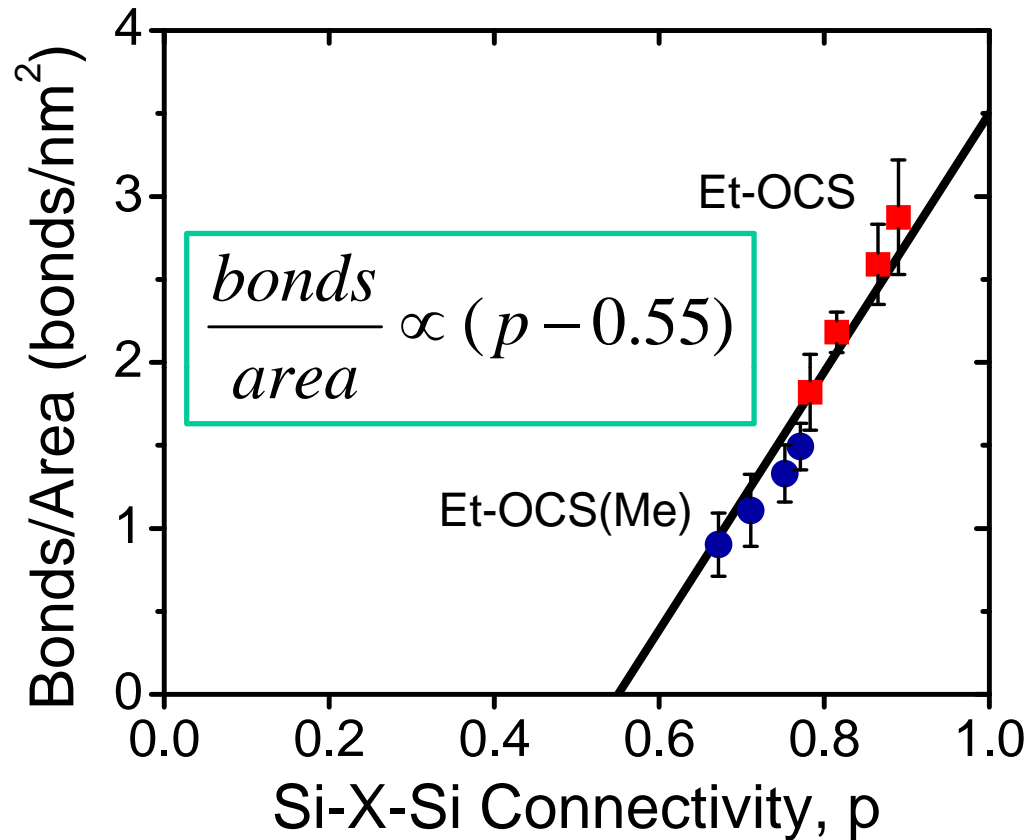


# Effect of Connectivity on Fracture Energy, $G_C$



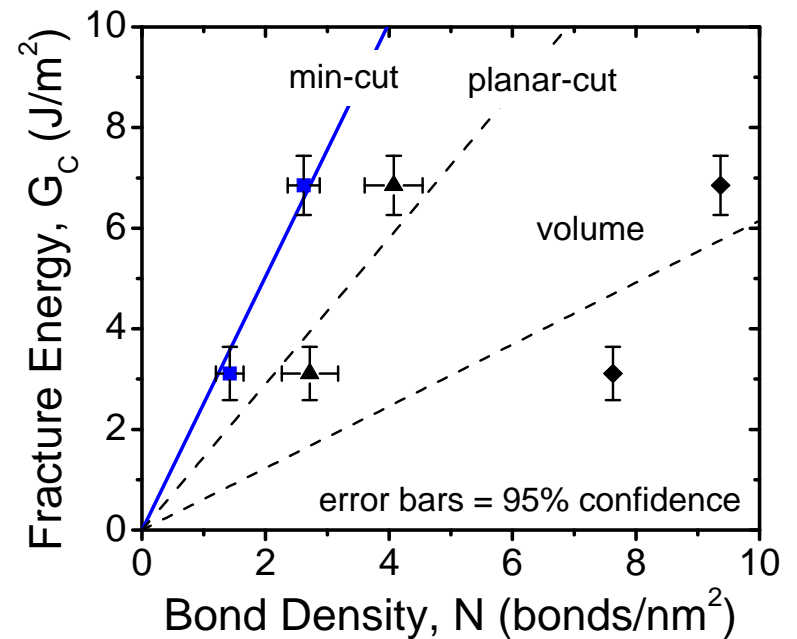
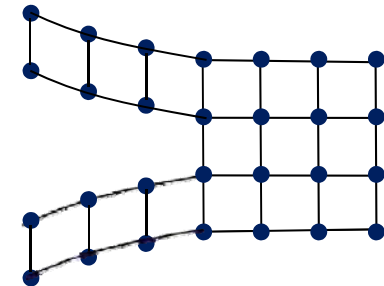
$$G_C \left[ \frac{\text{energy}}{\text{area}} \right] = \frac{\text{bonds}}{\text{area}} \frac{\text{energy}}{\text{bond}}$$

# Effect of Connectivity on Fracture Energy, $G_C$



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

assume no plastic deformation

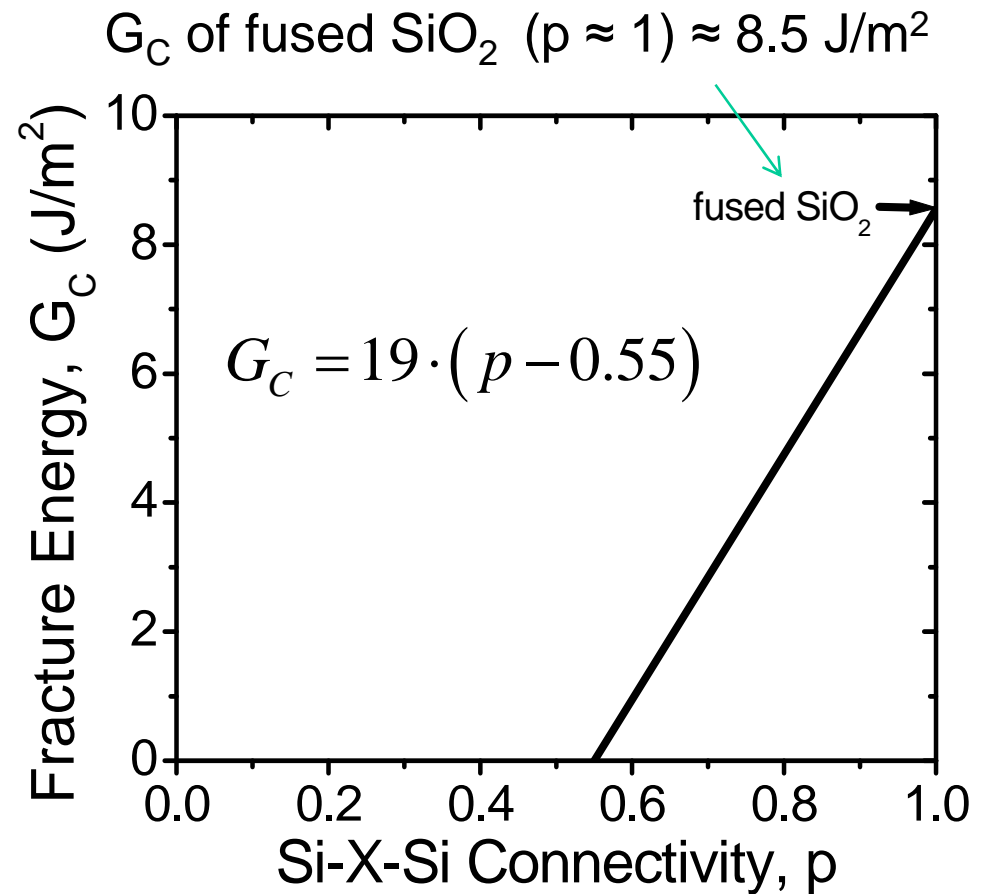


# Predicted Fracture Energy Scaling

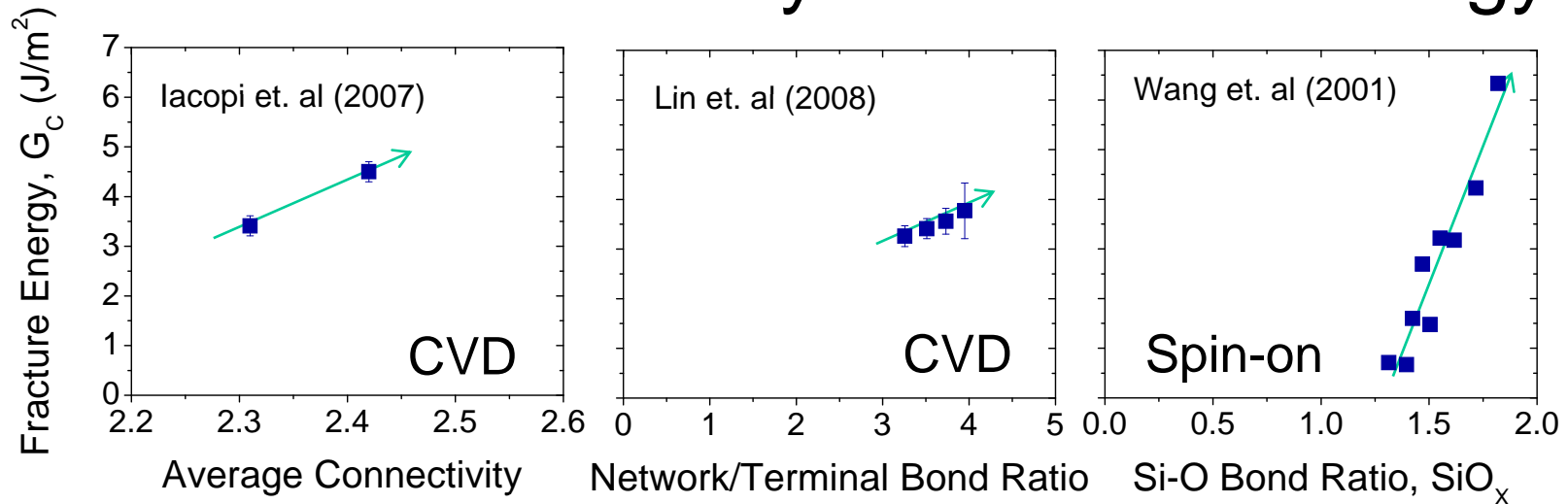
$$G_C \left[ \frac{\text{energy}}{\text{area}} \right] = \frac{\text{bonds}}{\text{area}} \frac{\text{energy}}{\text{bond}}$$

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

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



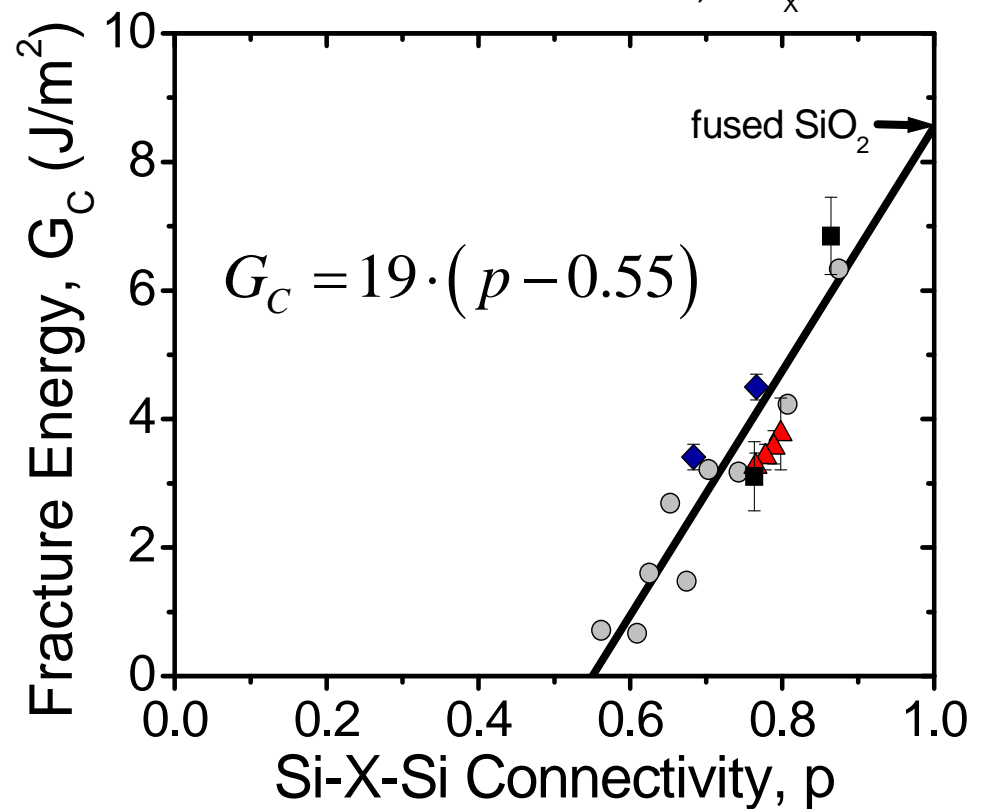
# Effect of Connectivity on Fracture Energy



- universal scaling of  $G_C$  for brittle organosilicates

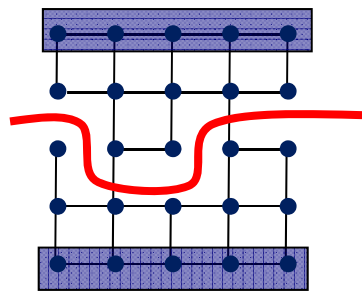
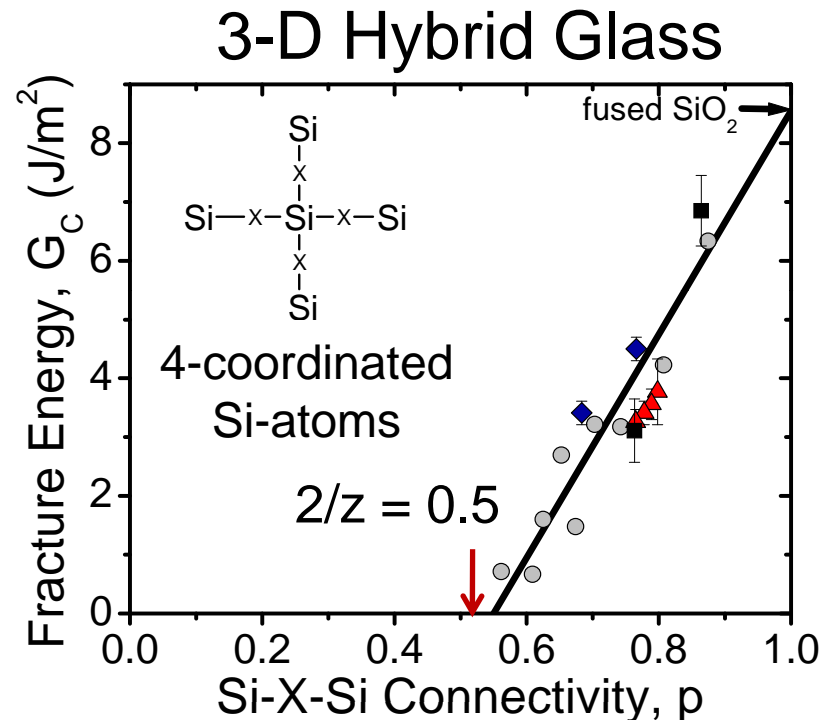
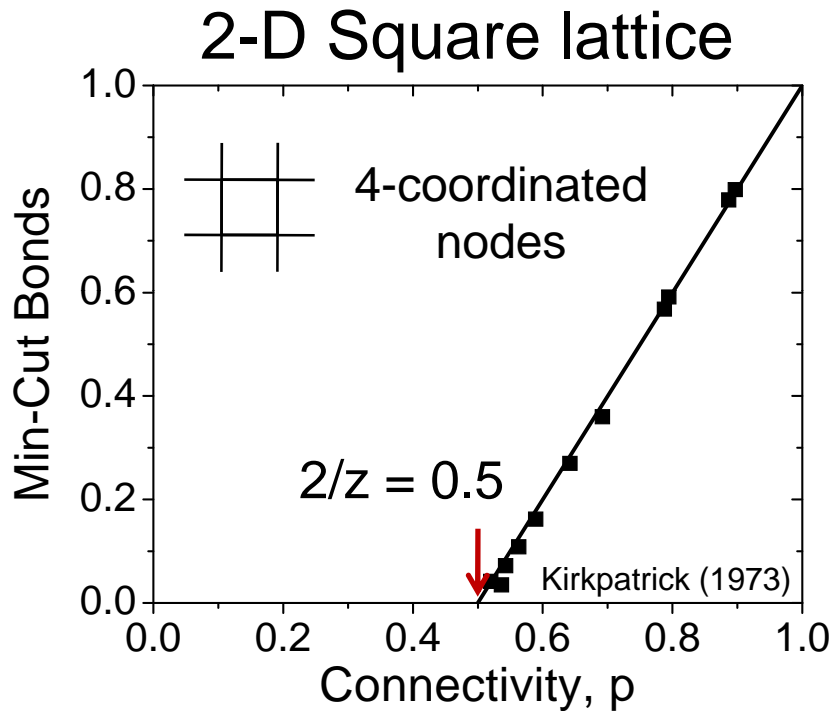
$$G_C \propto (p - 0.55)$$

- CVD and spin-on

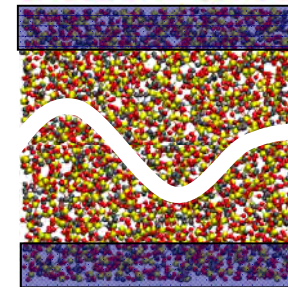


# Why (p-0.55)? Bond Percolation Theory

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



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



# Outline

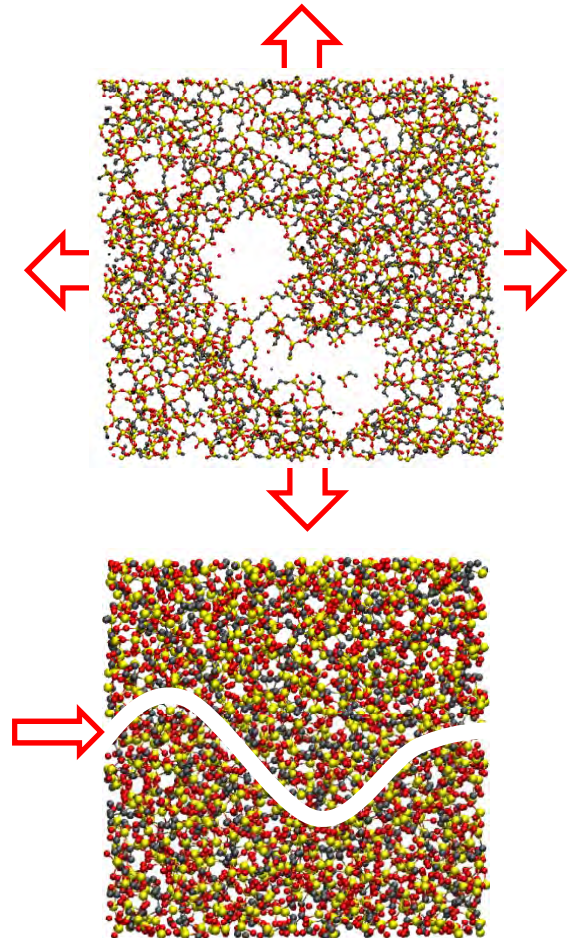
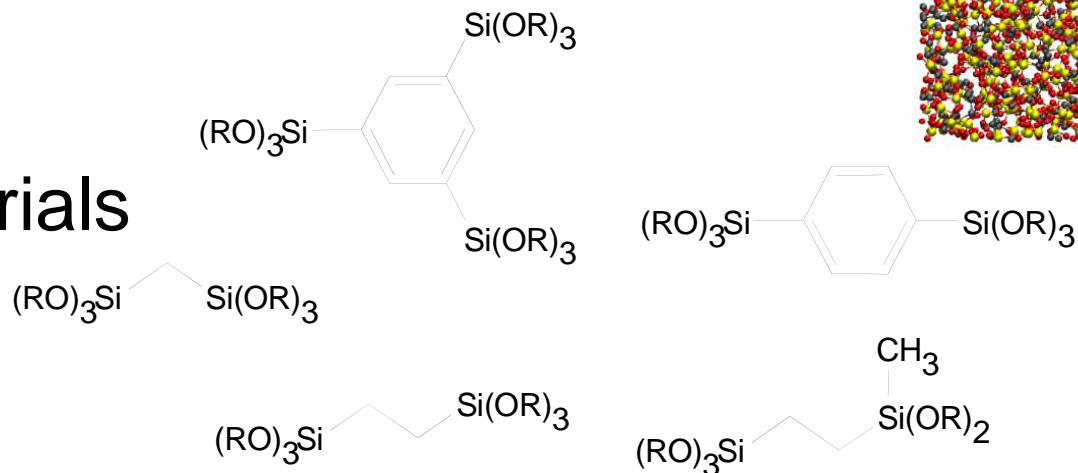
## Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

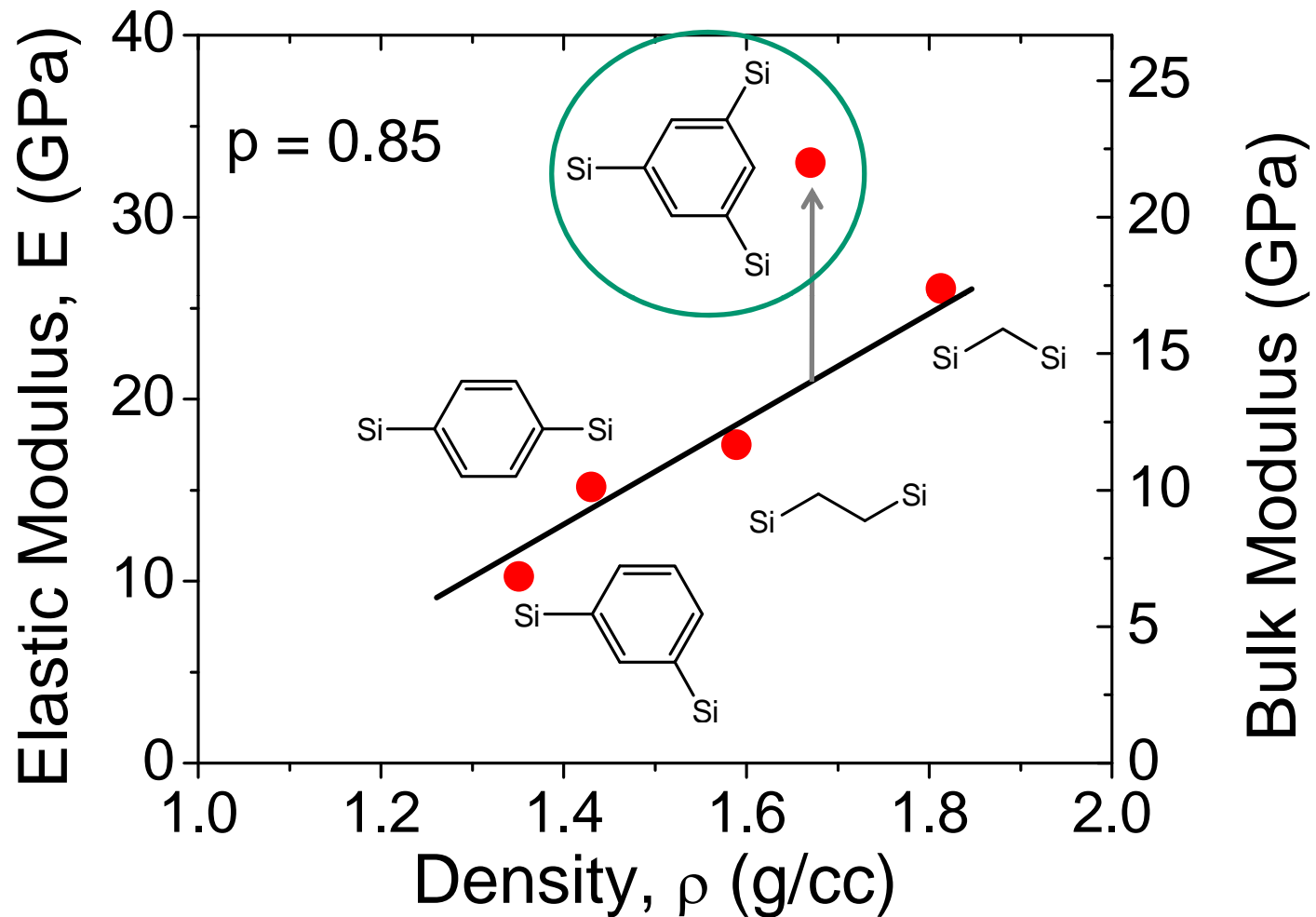
## Fracture Energy

- network connectivity
- scaling relations

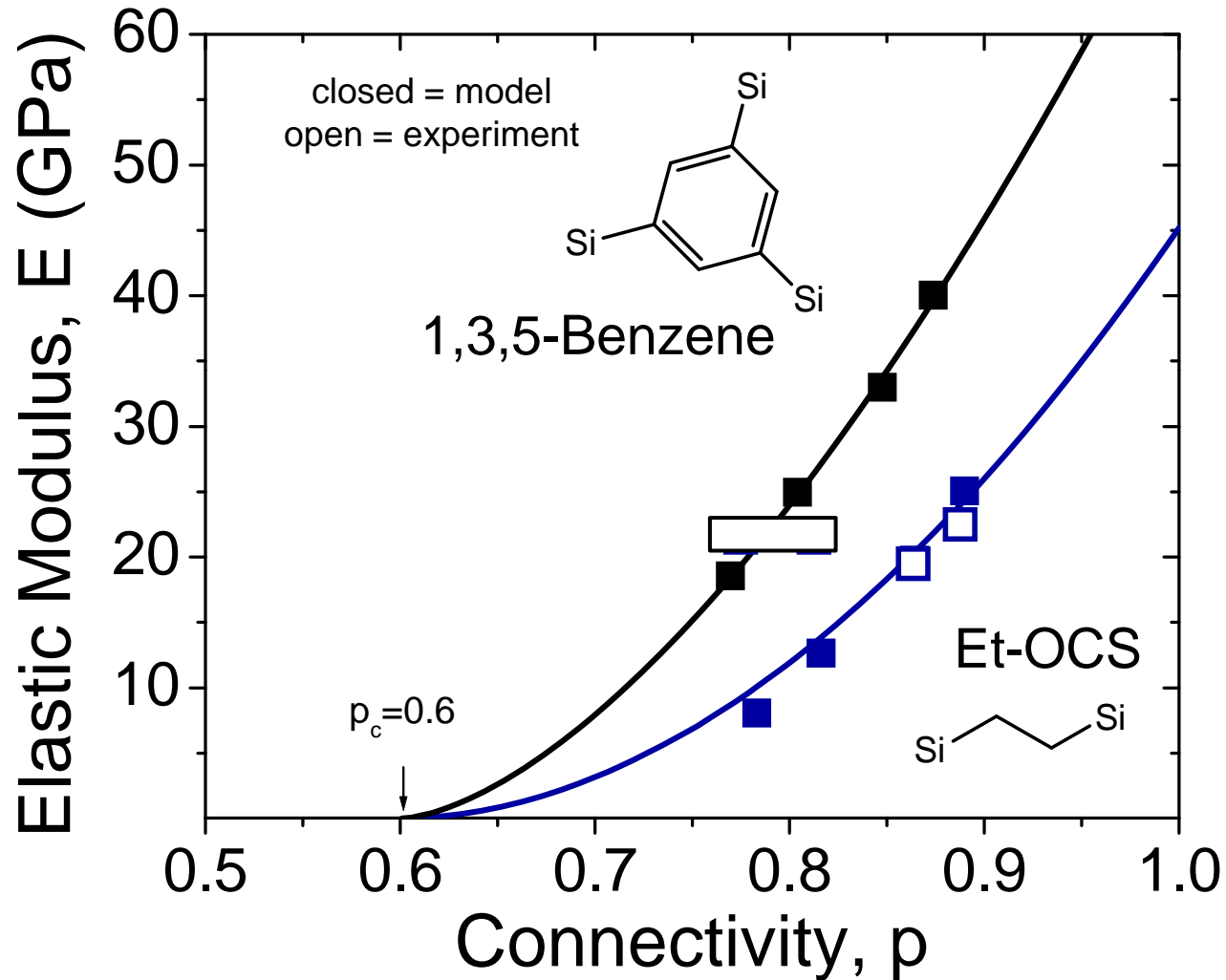
## New Materials



# Predicting Modulus of New Glasses



# High Modulus 1,3,5-Benzene Glasses



# Summary

## Elastic Modulus

- precursors and molecular structure
- effect of nanoporosity

## Fracture Energy

- network connectivity
- scaling relations

## New Materials

