Structure and mechanical properties of nanoporous silica and organosilicate glasses

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Meiji University, 7/21/2015

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- Established in 1890
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Largest in the world	Play Therapy Training Facility
1st in U.S.	Jazz Studies
2nd in U.S.	Health Librarianship
9th in U.S.	Information Systems
9th in U.S., 1st in Texas	Master's in Public Administration
13th in U.S.	MA/PhD in Art History
First Tier Regional Program	BBA in Management
Top 8 Undergraduate Programs	Radio, Television, Film
Top 10 Graduate Programs	Radio, Television, Film
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- Innovative **Research Clusters** working across disciplines and linking faculty, students, and research in new ways.

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- Established in 2003
- Six departments
  - o 12 BS degrees
  - o 6 MS degrees
  - o 5 PhD degrees
- 75 T/TT Faculty
- 12 Lecturers
- 2,637 students

(*2013 data)

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- BS Computer Science
- BS Computer Engineering
- BS Electrical Engineering
- BS Mechanical and Energy Engineering
- BS Materials Science and Engineering
- BS in Engineering Technology in
  - Construction
  - Electrical
  - Nuclear
  - Mechanical
- BS Biomedical Engineering

- MS Computer Science
- MS Computer Engineering
- MS Electrical Engineering
- MS Mechanical and Energy Engineering
- MS Materials Science and Engineering
- MS Engineering Systems
- MS Biomedical Engineering

- PhD Computer Science and Engineering
- PhD Materials Science and Engineering
- PhD Mechanical and Energy Engineering
- PhD Electrical Engineering

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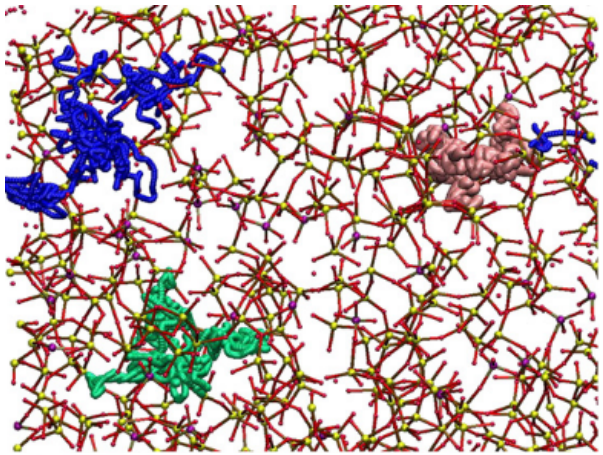
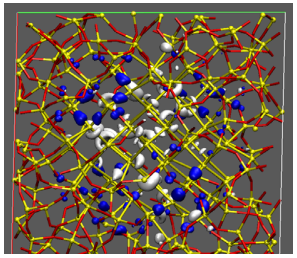
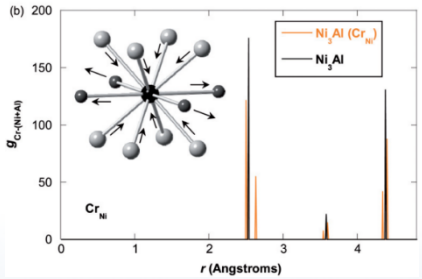
Functional Glasses and Materials Modeling Group

Jincheng Du, Depart. Material Sci. & Eng., Univ. North Texas

Focus on atomistic and *ab initio* computer simulation methods to understand the structure and structural origin of material properties of glass/ceramics, nano- and complex-structured materials for biomedical, microelectronic, energy and environmental applications.







Current projects:

- Atomic structure – property correlations of multicomponent oxide glasses (NSF,)
- Chemical durability and dissolution of bioactive and nuclear waste glasses (DOE)
- Defects and mechanical behaviors of complex oxide ceramics (NSF, *coll. T. Scharf*)
- Bulk and surface electronic properties of ZnO based ceramics (NSF, *coll. N. Shepherd*)
- Lithium ion solid state electrolytes: ceramics and glass-ceramics based.
- Bonding, defects and properties of Ni-based super alloys (ISES, *coll. R. Banerjee*)
- Plasma interaction and radiation effects in dielectric materials (SRC, *coll. J. Kelber*)

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NSF

SRC Semiconductor Research Corporation

rial and ring

Outline

- Background and motivations
- Simulation methodologies
- Atomic and micro-structures of nanoporous silica
- Mechanical properties of nanorpous silica
- Organosilicate glass structures using ReaxFF
- AIMD simulations of plasma interactions
- Conclusions

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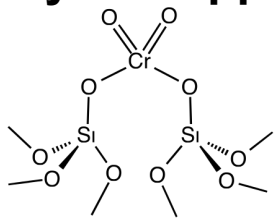
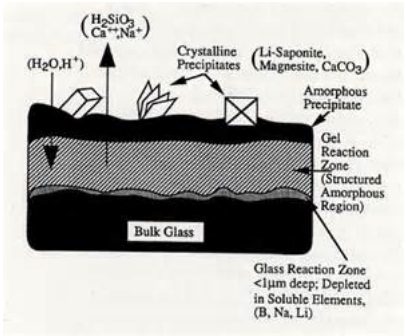
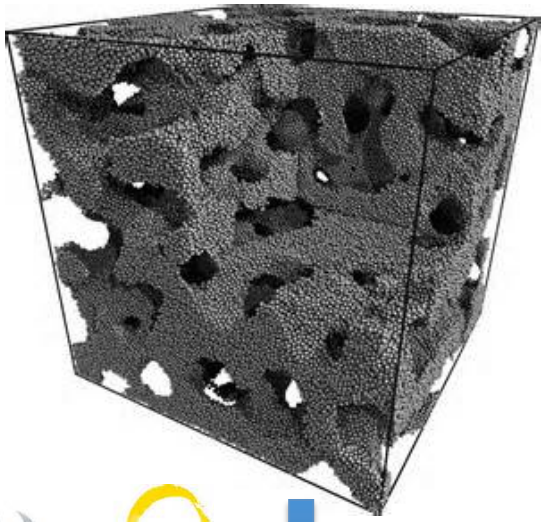
Catalysis support

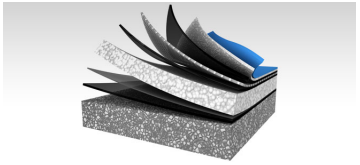




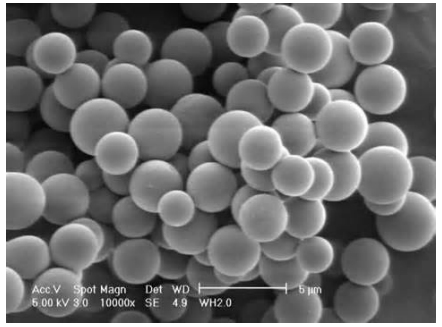
Glass corrosion

Sol-gel processing

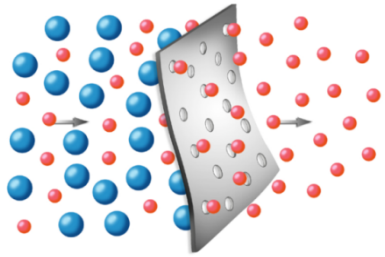




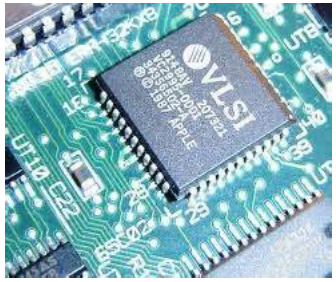
Thermal insulation



Hydrogen storage



Separation/
Molecular sieves



microelectronics

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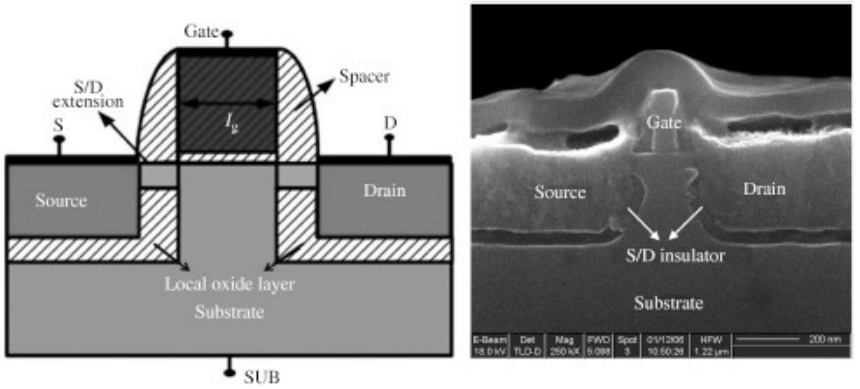
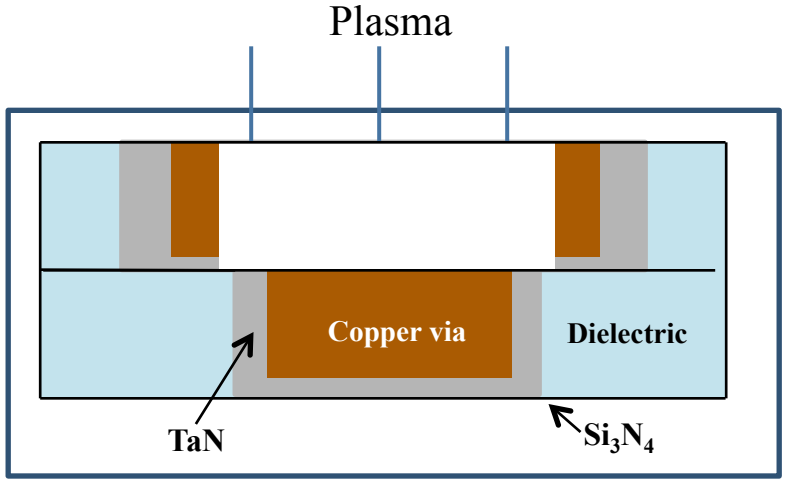
Low k dielectrics and plasma etching

- Low k dielectric material such as porous organosilicate glass (OSG) has been used in Very Large Scale Integration (VLSI) in advanced microelectronic devices.
- Decrease of k values can limit RC delay and cross talk caused by shrinking device features
- Plasma etching is commonly used in subtractive processes
  - Further deterioration of mechanical property of OSG
  - Increase of dielectric constant by preferentially removing organic component
  - Creating dangling bonds and change surface chemistry





Interconnect Structure

Figure 1: Plasma-Interconnect Structure

Case, Carlye. "Fundamentals of Low-k Chemistry". *Future Fab International.* 17 (2004)

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OSG low k materials for micro/nano-electronics

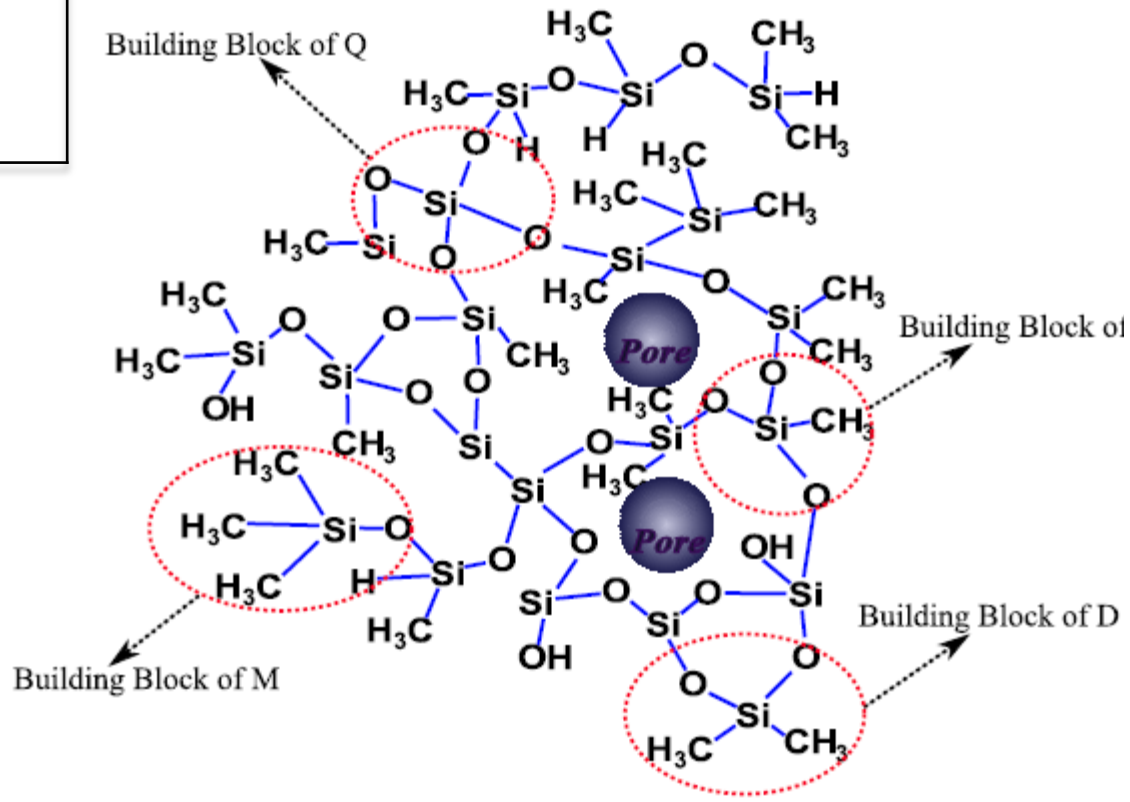
Dense SiO_2	**3.9-4.2**
F-Doped SiO_2	**3.7**
Low k dielectrics	**2-3**
Vacuum	**1**

Organosilicate Glass (OSG) is a type of low-K dielectric material to replace silica (SiO_2) to continue the scaling of microelectronic devices (Moore's law).

Two mechanisms to decrease the dielectric constant: organic groups and porosity.

Key issues:

- Decrease of mechanical properties
- Porosity leads to water diffusion and deterioation of properties



Yuan et al, Microelectr. Reliab. 2008,

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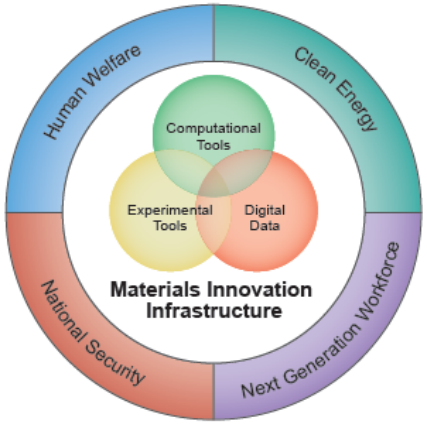
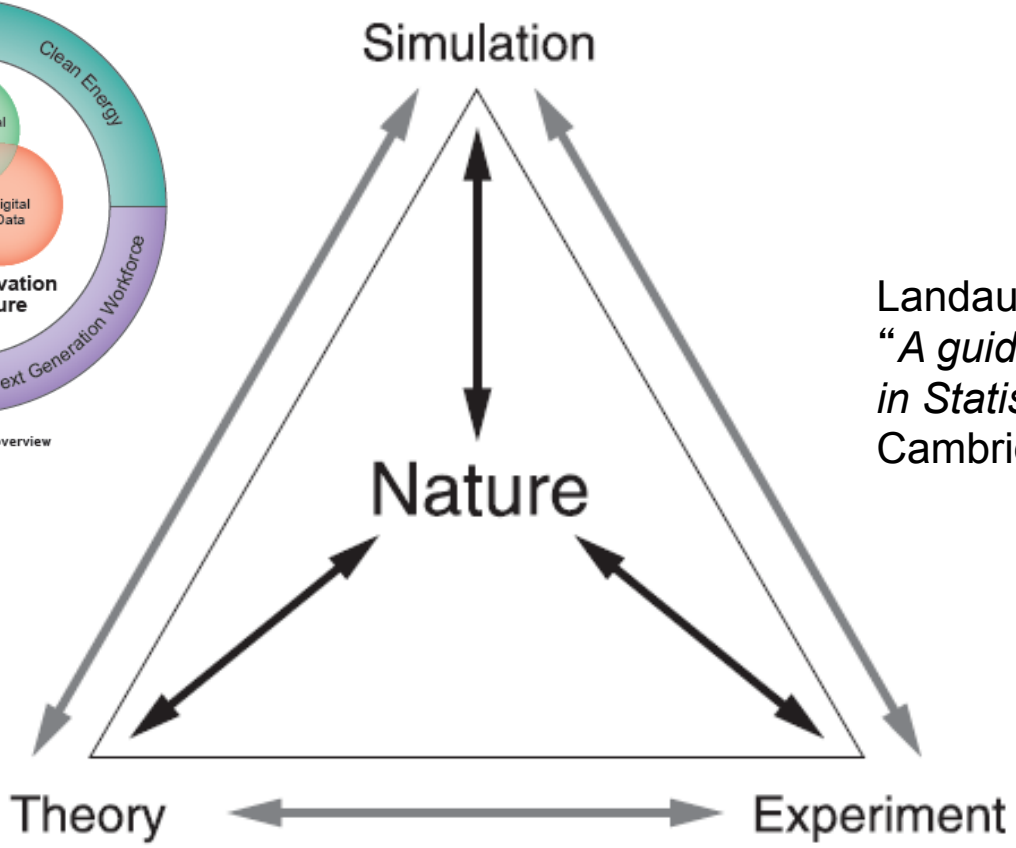


Figure 3: Initiative overview



Landau and Binder
"*A guide to Monte Carlo Simulations in Statistical Physics*"
Cambridge University Press

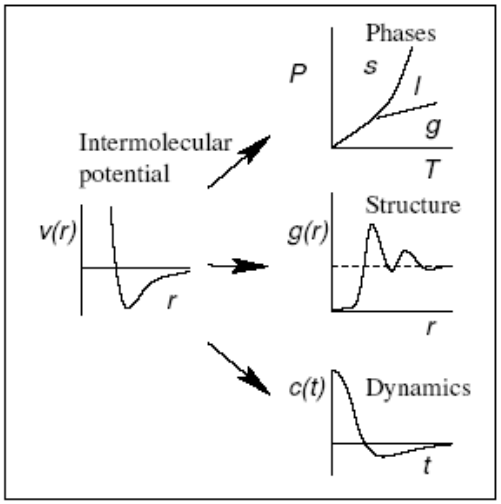
* … each is distinct but each is strongly connected to the other two
* The goal (of simulation) is to create an understanding of physical properties or processes as complete as possible, making use of perfect "experimental" conditions in the "computer experiment"…

Molecular Dynamics (MD) simulations

MD is an atomistic computer simulation method.

MD relies on solution of equation of motion of Newton's classical mechanics.

$$m_i \ddot{r}_i = f_i \qquad f_i = -\frac{\partial}{\partial r_i} u$$



Classical MD:
based on empirical potential

$$u(r^N) = \sum_i \sum_{j>i} v(r_i, r_j) + \sum_i \sum_i \sum_k w(r_i, r_j, r_k) + \ldots$$

Fitting experimental crystal structure, physical properties
Fitting potential energy surface from *ab initio* calculations

***ab initio* MD:**
Hellmann-Feynman theorem
Quantum mechanically obtained force:
HF, DFT, MP2 etc

Born-Oppenheimer MD (BOMD)
Car-Parrinello MD (CPMD)

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Simulation methodologies

- **Classical MD** with partial charge pairwise potential (Teter parameters): DLPOLY

$$V(r_{ij}) = \frac{q_i q_j e^2}{4\pi\varepsilon r_{ij}} + A\exp(-r_{ij}/\rho) - C/r_{ij}^{6}$$

Du and Cormack, J. Am. Ceram. Soc. 2005

- **Classical MD** with Reactive Force Field (**ReaxFF**): LAMMPS

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + \underbrace{E_{\text{lone pair}} + E_{\text{conjugation}}} + E_{\text{H-bond}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

*Fogarty et al, J. Chem. Phys. **132**, 174704 (2010)*

- ***ab initio* MD** based on DFT. GGA-PBE functional: CP2k

  Born Oppenheimer dynamics

  Double zeta Gaussian basis set

  Variable time step setup for cascade simulations

VandeVondele, J, et al. Comput. Phys. Comm. 167 (2005) 103

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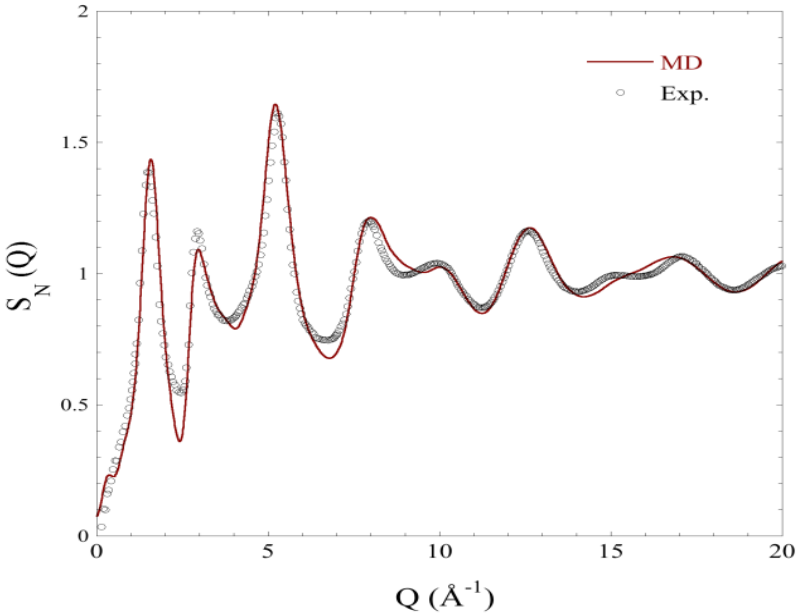
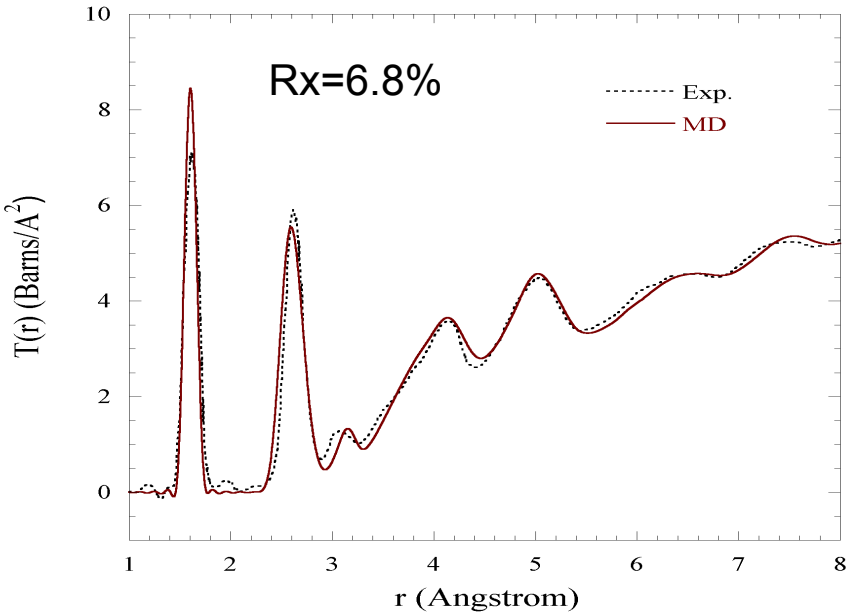
Validation of structure model: silica glass

Neutron structure factor



Total correlation function



- Partial charge pairwise potential with Teter parameters (*Du and Cormack, J. Am. Ceram. Soc. 2005*)
- Comparison with neutron structure factor and total correlation function of silica glass from MD simulations. (*Du and Cormack, J. Non-Cryst. Solids, 2004).*

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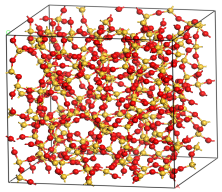
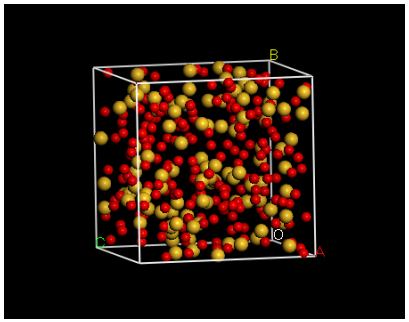
Routes for nanoporous silica generations

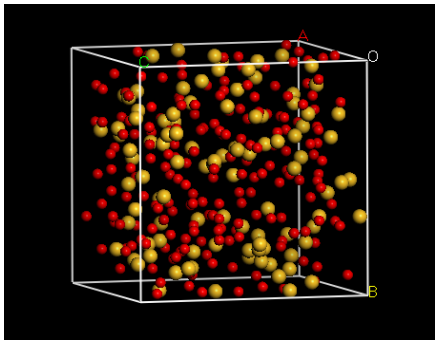
Volume scaling method:

Dense silica glass from MD simulations





Nano Porous Silica

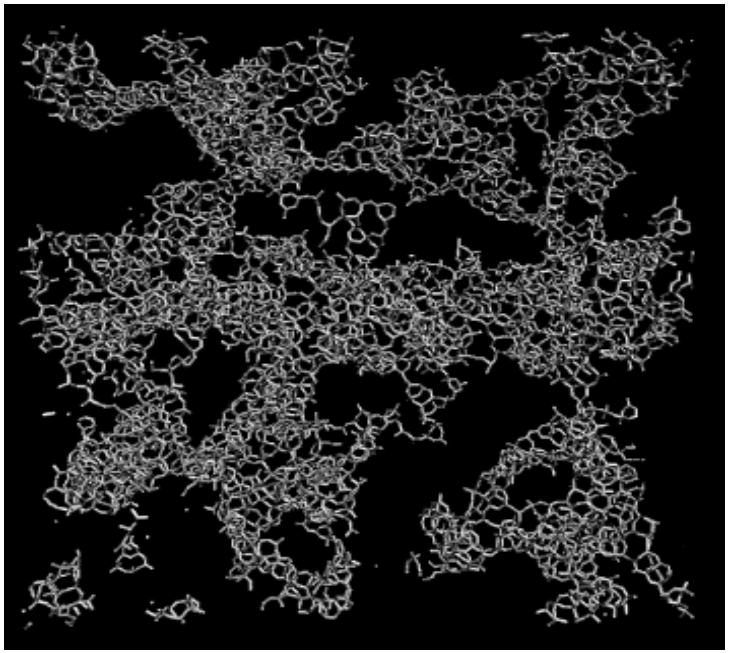


Linear scaling followed annealing at 1500K under NVT. Further relaxation under NVT and NPT at 300 K. *Nakona et al, PRB 491(1994).*

Charge scaling method:

- ***Start from low density homogeneous silica by applying low charges (20%)***
- ***The charges are gradually increased charge to facilitate aggregation and solidfication.***
- ***Thermalization run under NPT to stablize the structure under ambient pressure.***

Beckers, de Leeuw, J. Non-Cryst. Solids 261 (2001).



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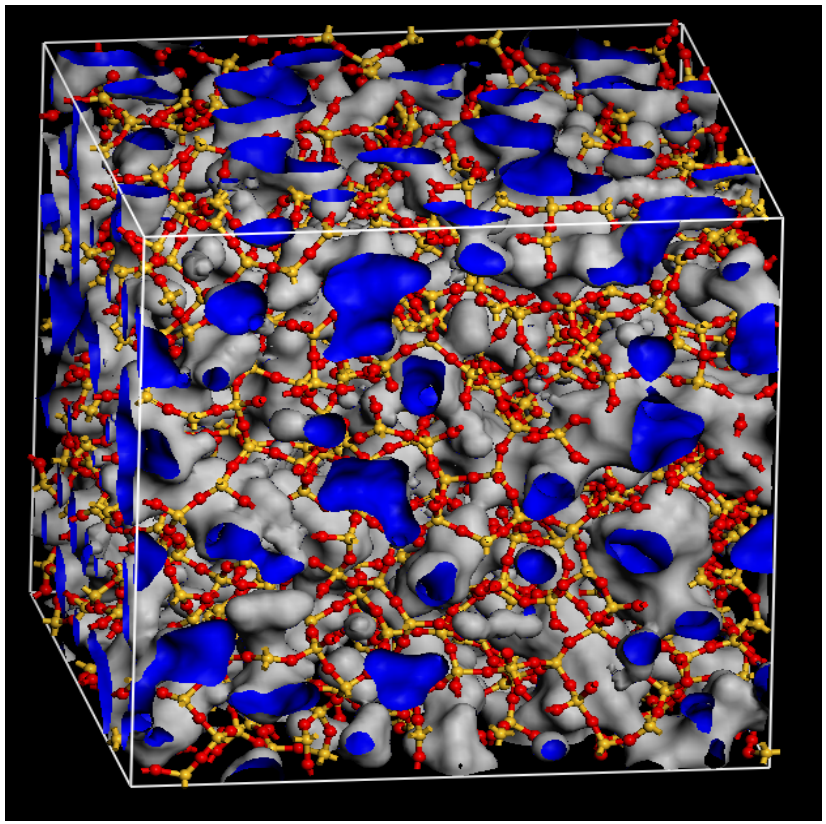
Structure Comparison

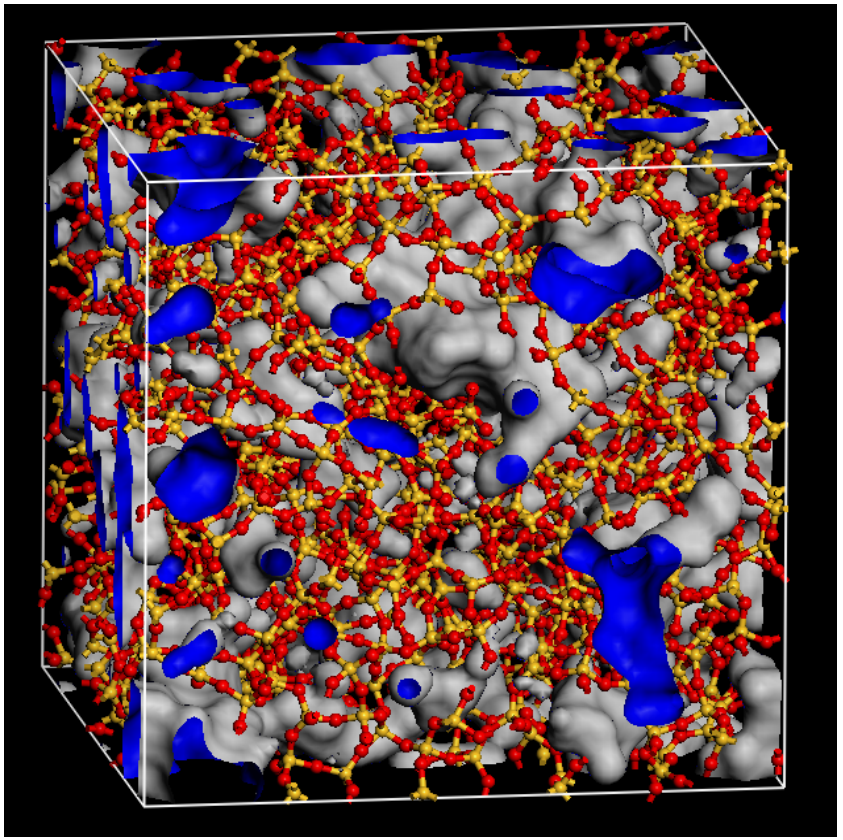
Volume scaling method



38 A

Final Porosities: 22.9%
Final Densities: 1.83 g/ml
Surface Area/Occupied Volume: 0.56

Charge Scaling method



36 A

Final Porosities: 17.2%
Final Densities: 2.16 g/ml
Surface Area/Occupied Volume: 0.26

Red: Oxygen **Yellow: Silicon**

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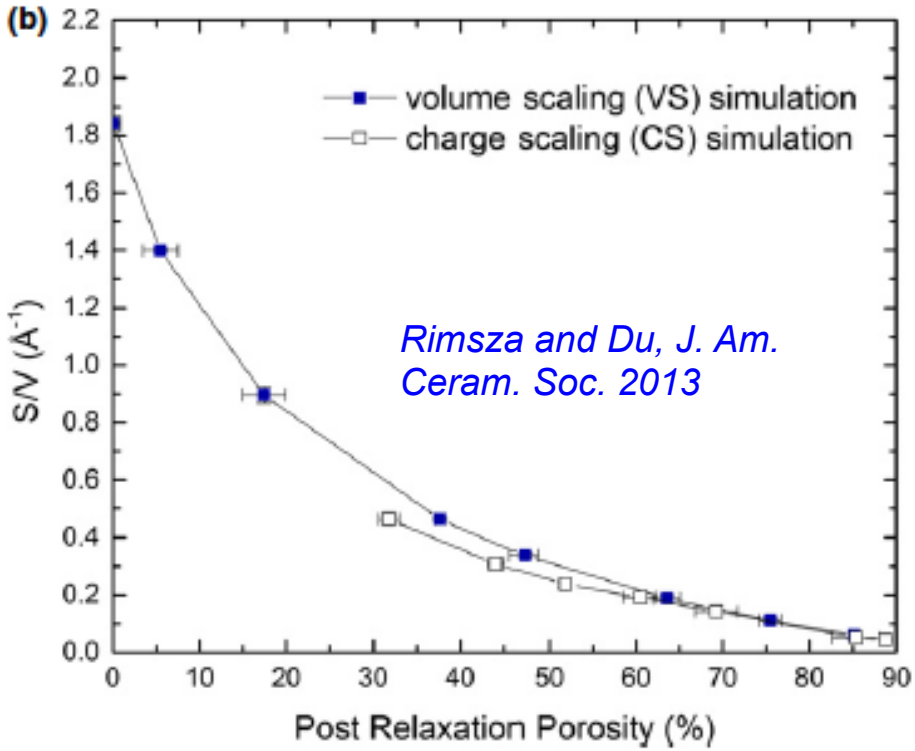
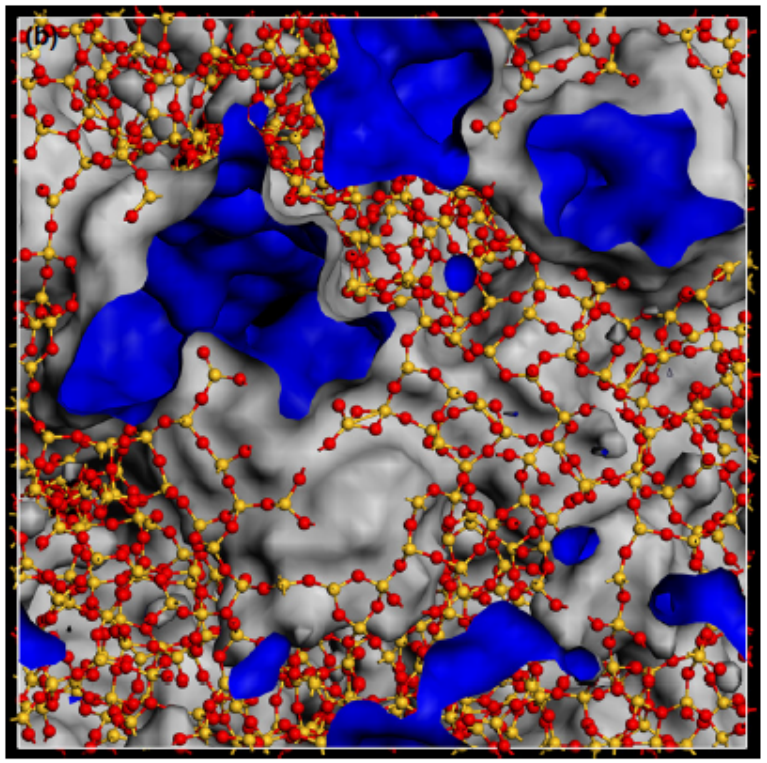
Microstucture characterization





- Volume scaling generated nanoporous silica with wide nominal porosity (0-90%). Charge scaling generated structures with 30-95% porosity.
- Pore micro structure morphology was found to be different for the two methods. Volume scaling gave more spherical but isolated pores but charge scaling gives more open and connected pores.

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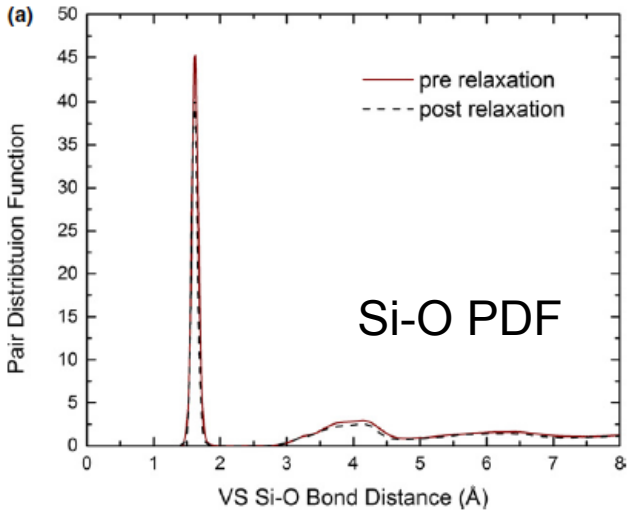
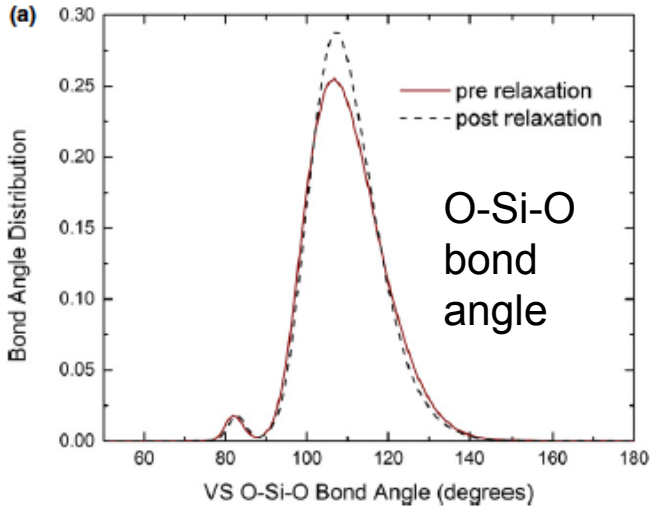
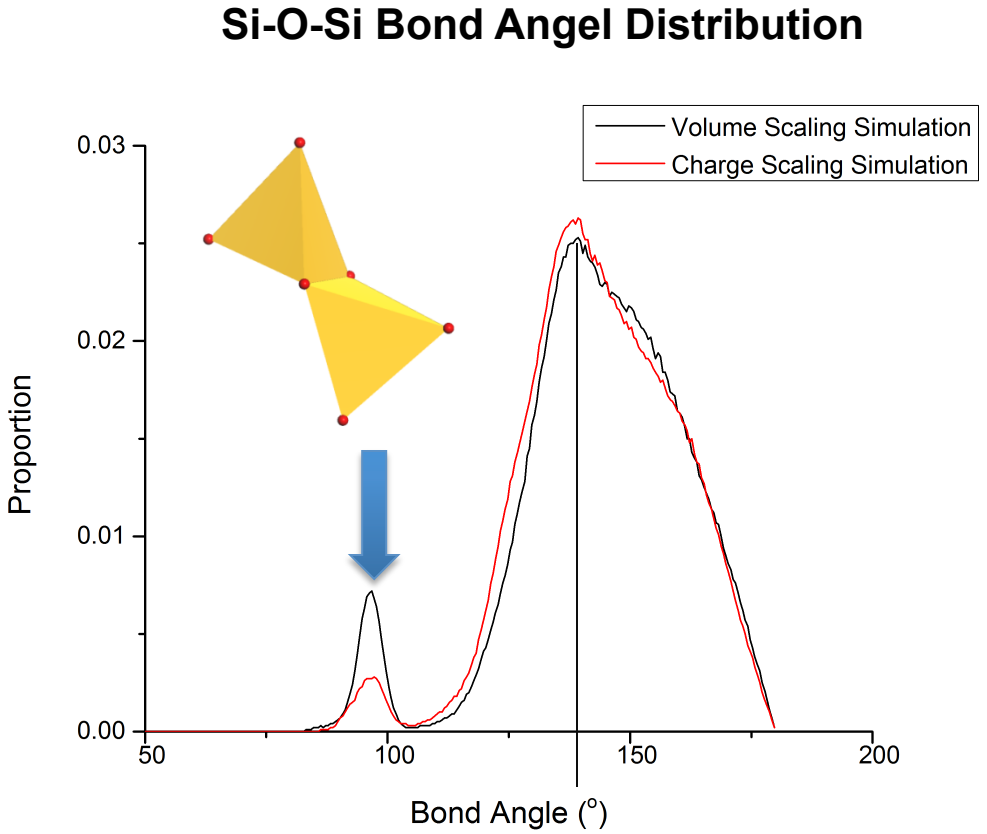
Atomic Structure Analysis







Porous silica with 40% porosity

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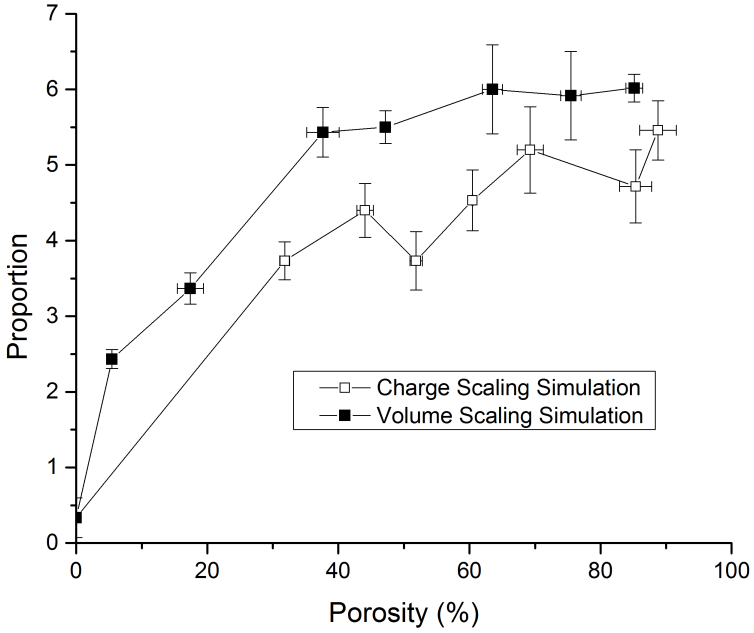
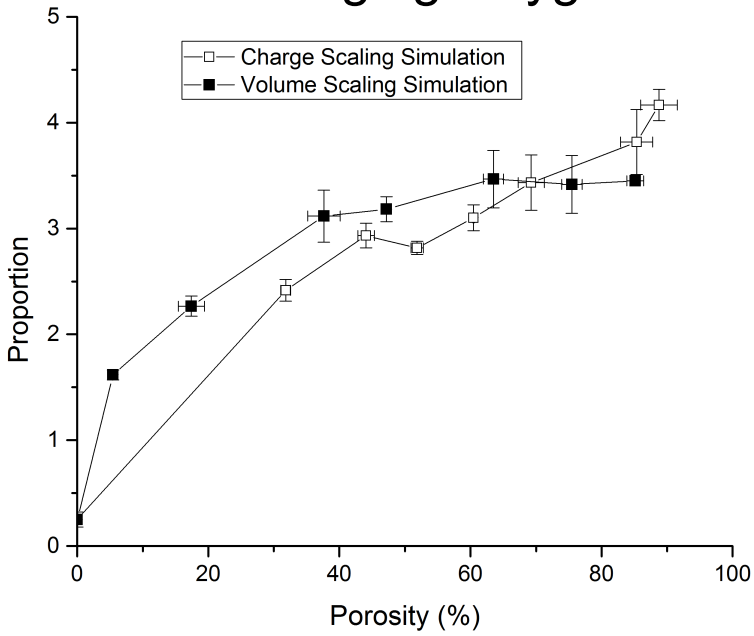
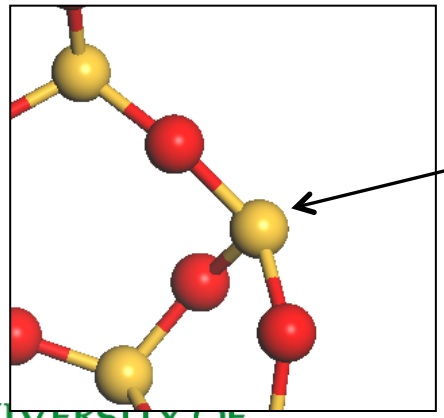
Coordination Defects

3 Coordinated Silicon



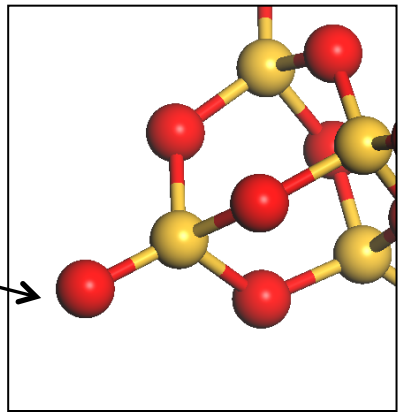
Non-Bridging Oxygen





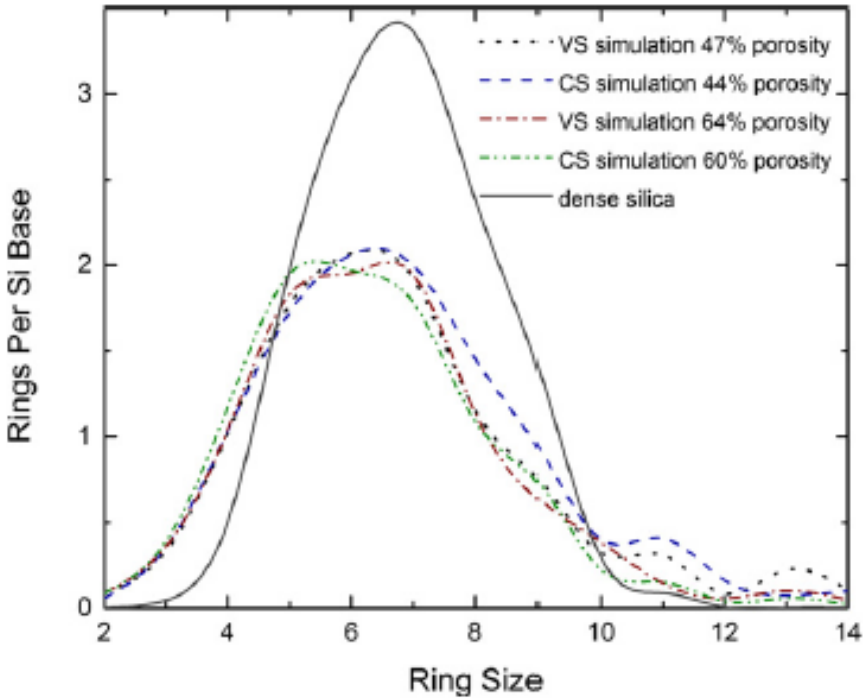
3 Coordinated Silicon

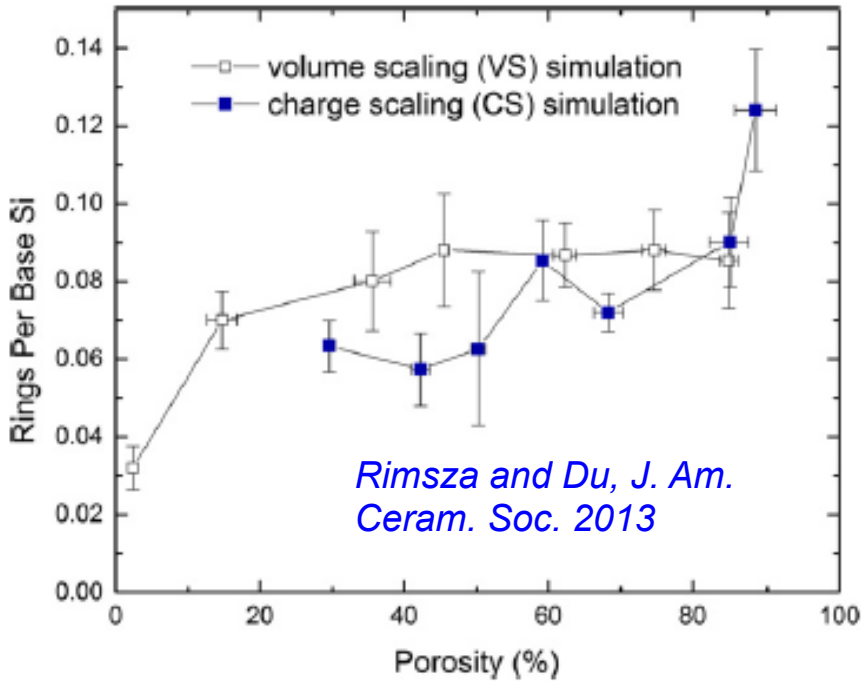
Non-Bridging Oxygen



Oxygen Silicon

Ring statistics





- Primitive ring statistics showing higher number of smaller and larger rings as compared to dense silica glass.
- The percentage of two membered rings increase with porosity but saturate at around 30% porosity for the volume scaling method.

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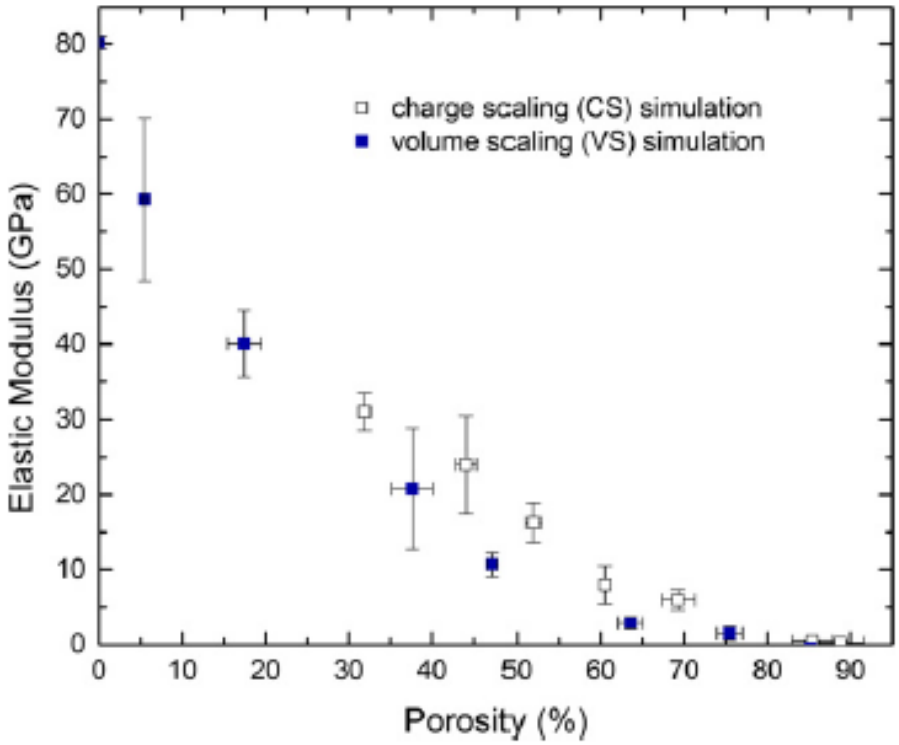
Mechanical properties

Author	Porosity (%)	Density (g/cm^3)	E (GPa)
This work – CS simulation†	50.0	1.1	14.2
This work – VS simulation†	50.0	1.1	5.5
Adachi and Sakka‖	48.5	1.13	21.3
Miyoshi *et al.*‡	52	–	5–16.5
Baskaran *et al.*§	55	–	14–17
Takada *et al.*§	56	–	2.0–3.5
Murray *et al.*§	54	–	2.0
Herrmann *et al.*§	51.4	0.78	1.28
Xiao *et al.*¶	–	1.15	1.2
Murray *et al.*¶	54	–	1.0
This work†	0	2.27	80.3
ASM Handbook	0	2.2	73

$$C_{ij} = \frac{1}{V}\left(\frac{\delta V}{\delta\varepsilon_i \delta\varepsilon_j}\right)$$



Rimsza and Du, J. Am. Ceram. Soc. 2013

- Elastic constants of porous silica with 50% porosity differs significantly by the two formation methods.
- Both are in the range of available experimental values.

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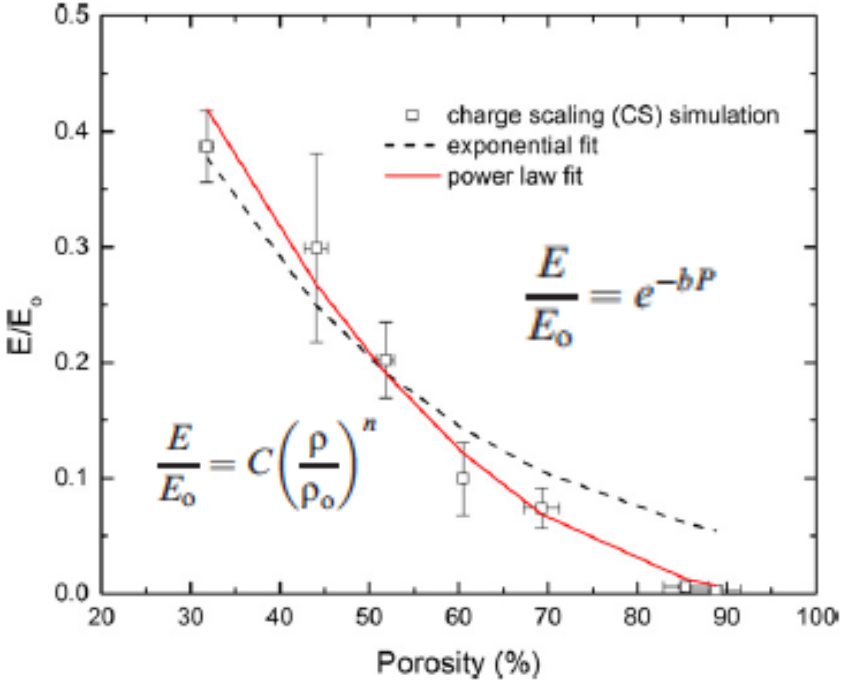
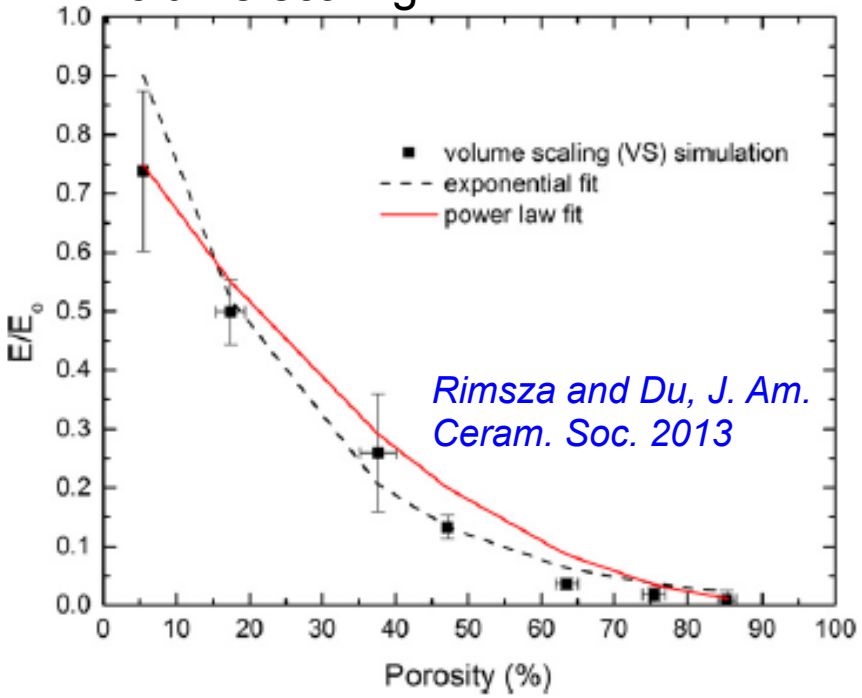
Mechanical properties vs. porosity

Charge scaling



Volume scaling



Rimsza and Du, J. Am. Ceram. Soc. 2013

- Power and exponential forms were used to fit the elastic constant data.
- Exponential fits resulted poorer fit with 3–4 times higher R values than the power functions.
- Fitting in power form give parameters similar to experimental sol-gel generated silica glass in different solvent. (*Jain et al, Thin Solid Film 2001*)

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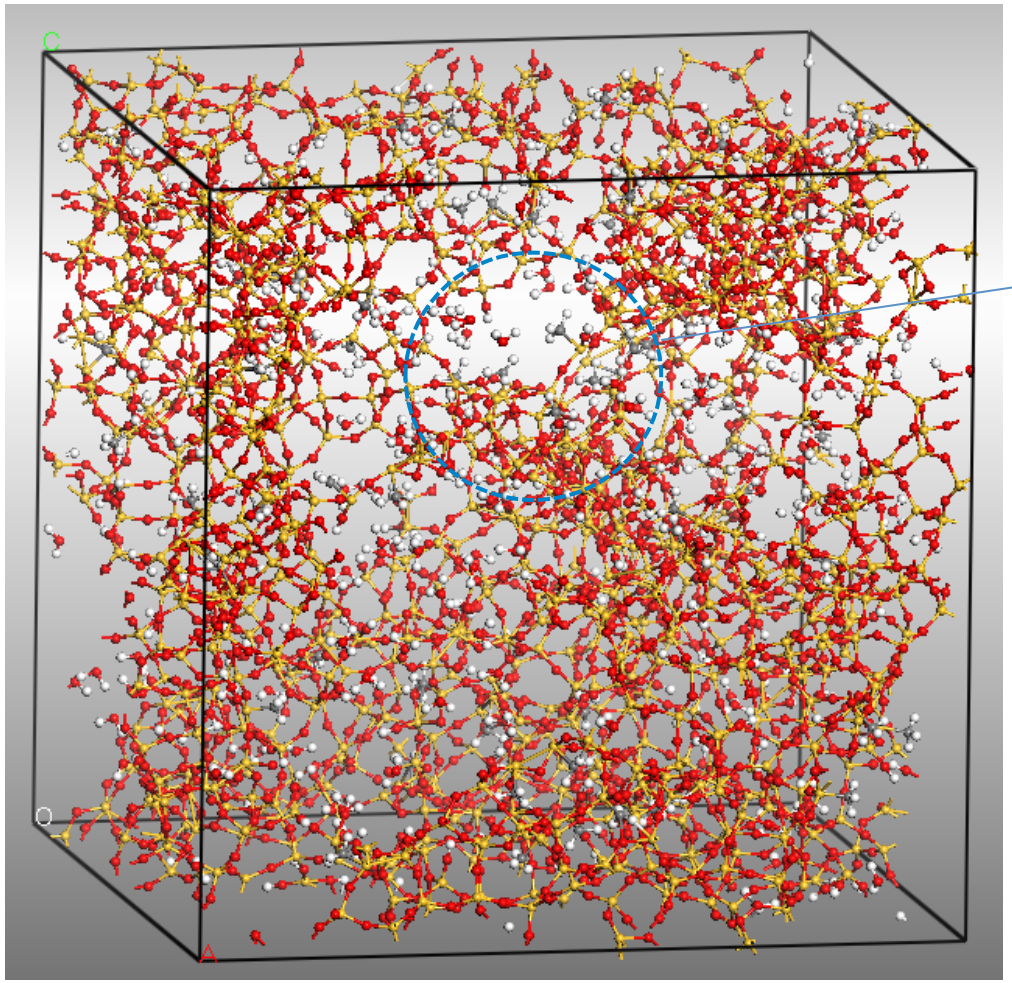
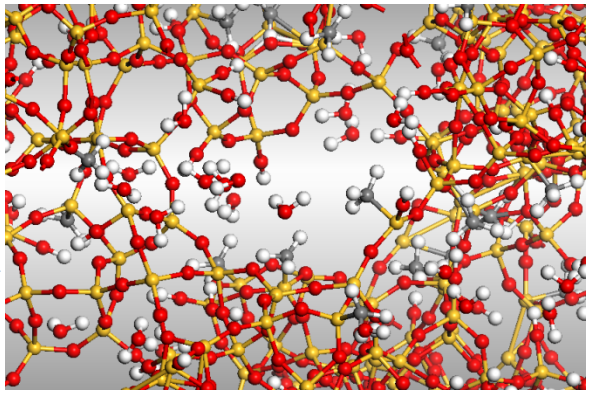
Organosilicate glass (OSG) structure

Structure models of OSG





- Generated based on nanoporous silica.
- Hydroxylation and addition of organic groups on internal surfaces
- Interaction with water and water diffusion in OSG.
- Simulation using MD with ReaxFF and AIMD.

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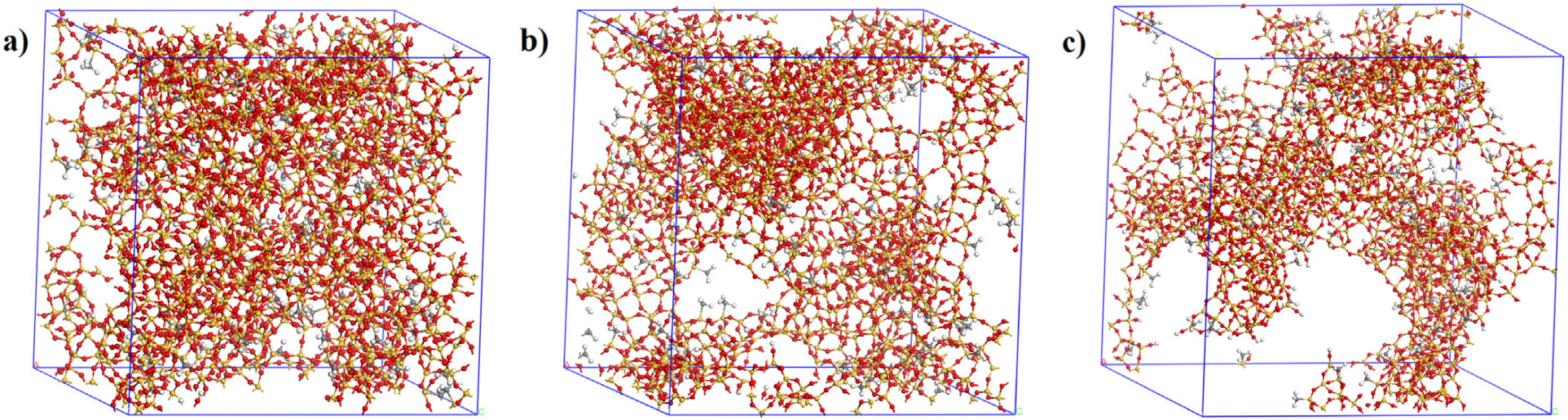
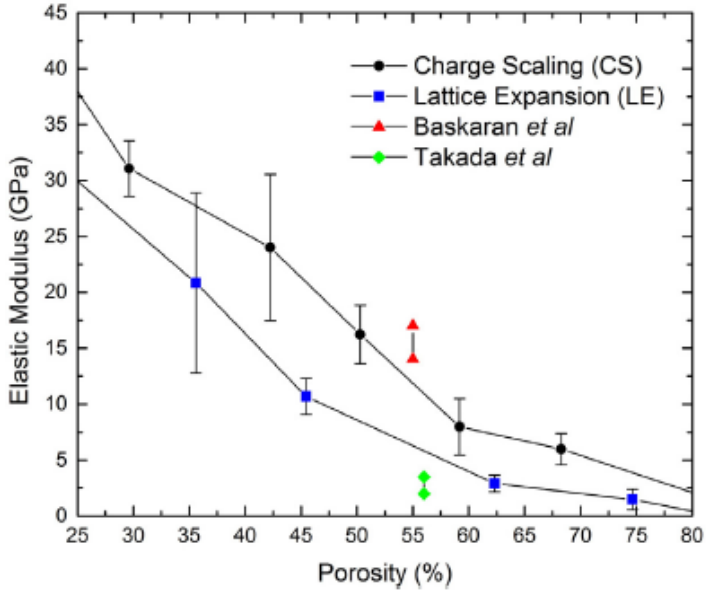
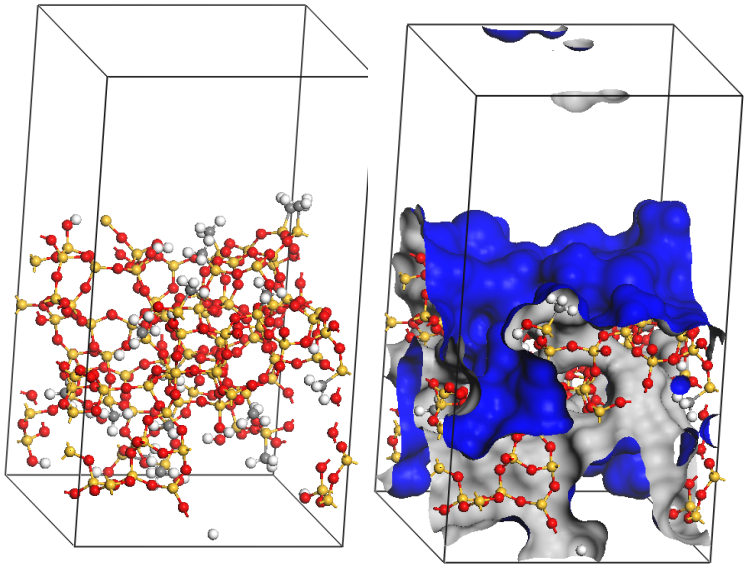
OSG structures and mechanical properties





Rimsza, Deng, Du, J. Non-Cryst. Solids, 2015



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Plasma etching simulations

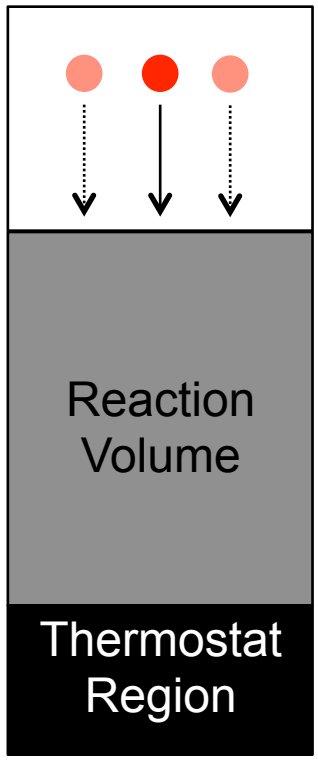
***ab initio* molecular dynamics based on DFT**

- Not limited by potential development
- Allows for unpredictable bond breakage and formation

Cascade Simulations

- Setup of variable time steps (0.05-1.0fs)
- Maximum atomic movement = 0.02Å per step
  - Maintain high resolution
- Thermostat is applied to the bottom 1/3 of the simulation
- Initial Ar-surface distance is 15Å

- 4000 step simulations (0.5-1.2ps)
- 25 unique simulations were preformed



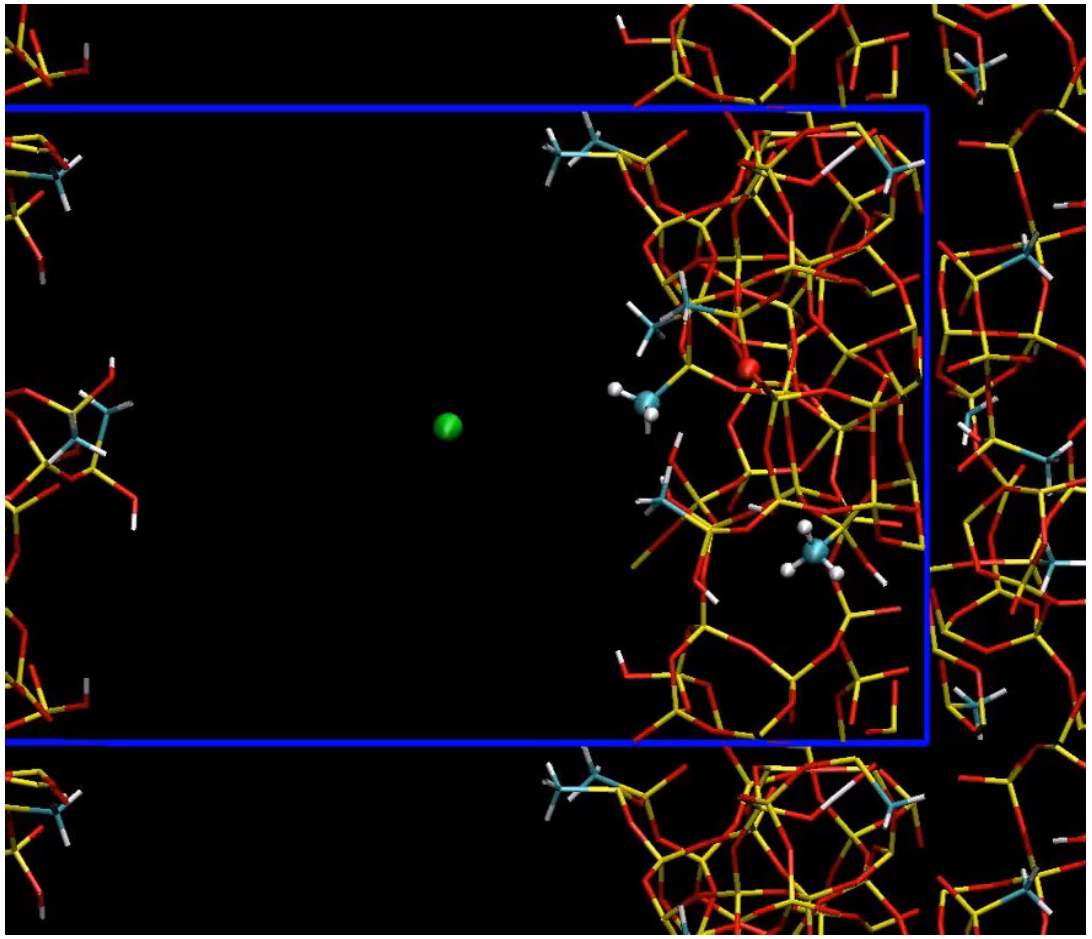
Schematic of cascade simulation setup

VandeVondele, Joost, and Juerg Hutter. *The Journal of chemical physics* 127.11 (2007): 114105.

Molecular abstraction due to Ar plasma

- Molecule were removed in 26% of the simulations
- Si is rarely removed
  - Si is pushed into the OSG structure
- H atoms are removed most often
- Carbon is removed as both CH_3 and CO molecules

Condition:
Ar atom, 100eV, normal incidence, 20Åx20Å surface
Products:
H_2, CO, and CH_3 molecules removed



Common removed molecules (percentage of total removed molecules)

Removed Molecule	H(%)	H_2(%)	H_2O(%)	CO(%)	CH_3(%)	SiO(%)	OH(%)
Percentage	22.22	11.11	11.11	11.11	22.22	11.11	11.11

H. Kazi, J. Rimsza, J. Kelber, J. Du, *Journal of Vacuum Science & Technology A* 32.5 (2014): 051301.

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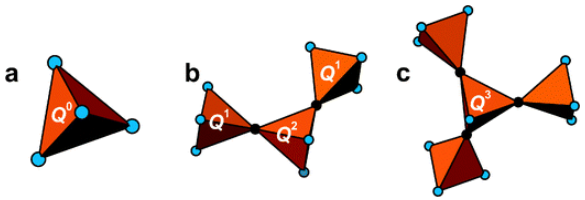
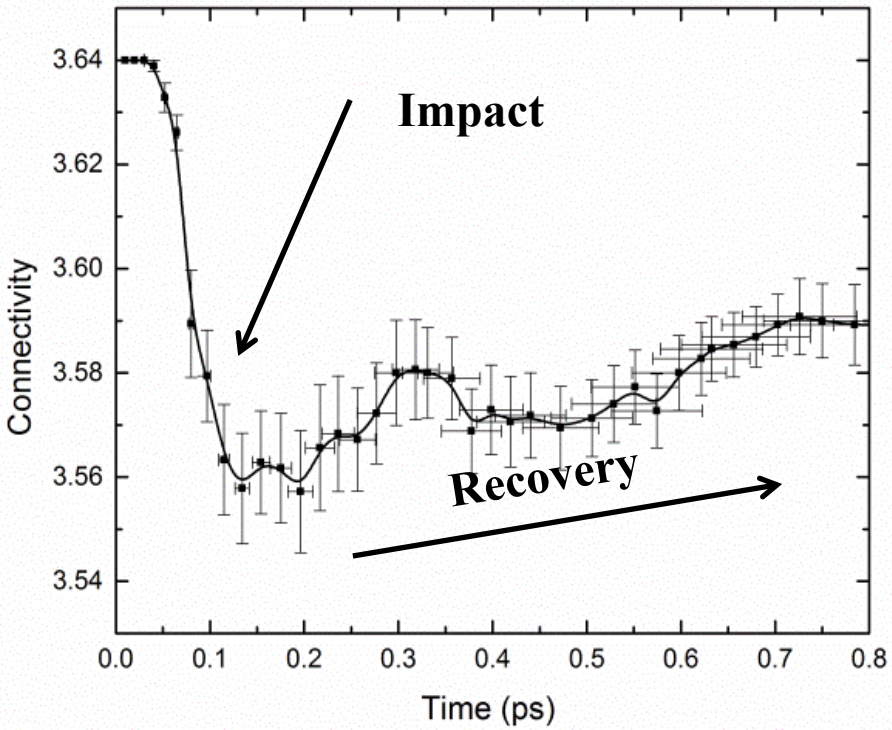
Change of network connectivity

- Network connectivity after collision cascade impact
- Perfect silica structure = 4.0 connectivity
- During plasma impact there is a connectivity loss of ~0.08
- A portion of the Si-O network reforms (connectivity increases by ~0.04)





OSG connectivity with time average over the 25 simulations. Error bars are equal to the standard error.

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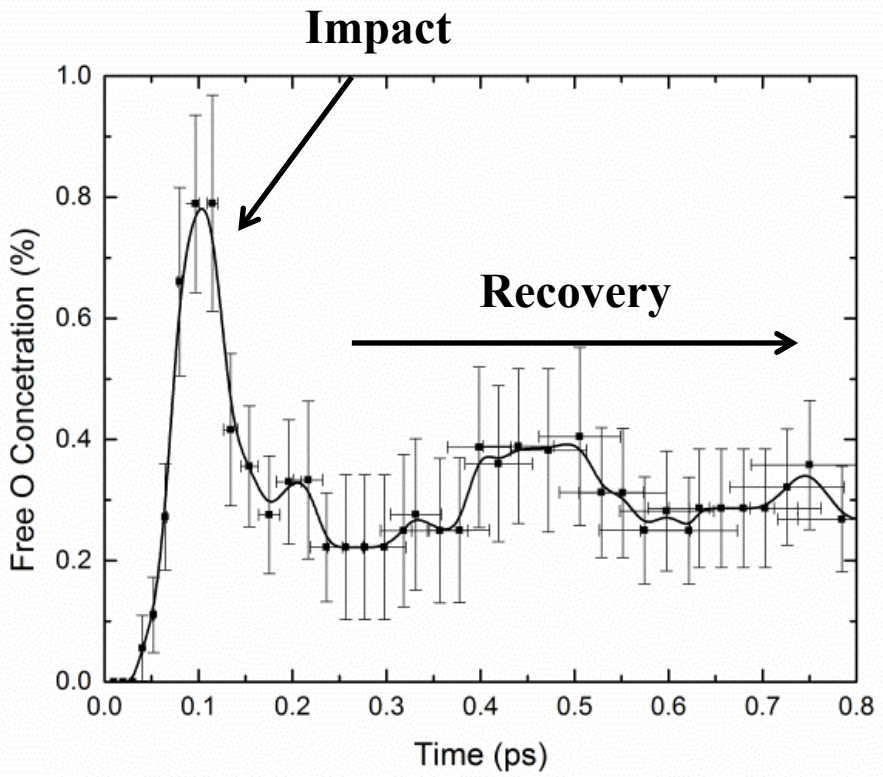
Free Oxygen Concentrations

- Atomic oxygen radicals are generated after Ar bombardment
- Spike in the free oxygen during initial impact
- Free oxygen concentrations stabilize (molecules diffuse into the vacuum)
- Free atomic oxygen energies are between (8-18eV)
- Threshold energies for CH_3 removal is as low as 0.1 eV



Free oxygen concentrations with time averaged over the 25 simulations. Error bars are equal to the standard error.

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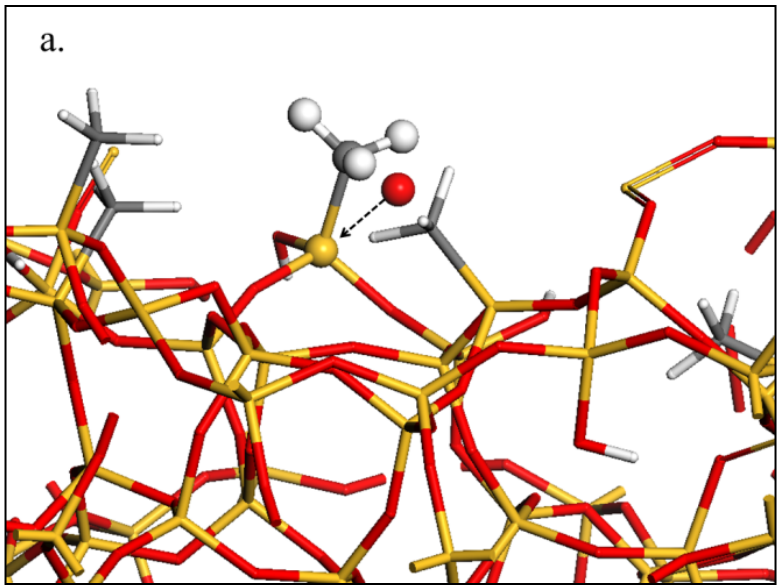
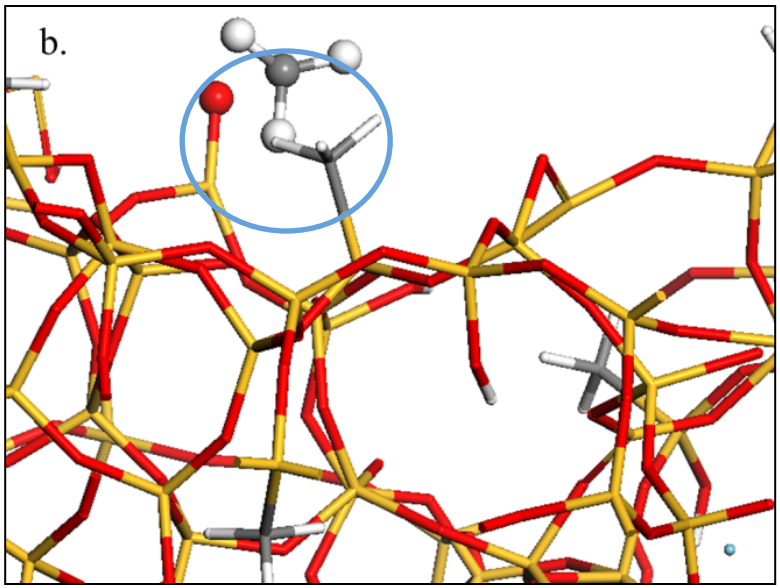
M. Chaudhari, J. Du, et al. Applied Physics Letters 94.20 (2009): 204102-204102.

CH_3 Removal – Mechanism 1

- Ar impacts the OSG surface generating a free oxygen species (7.34eV)
- Free O radical reacts with a surface Si with a terminal CH_3 group
- The CH_3 is removed and an O replaces the CH_3 forming a NBO group
- Previous cluster TMCTS calculations indicated a 0.1eV threshold for Si-CH_3 breakage by O at an angled attack





(a) initial and (b) final atomic positions for CH_3 removal by reaction mechanism 1. Yellow is silicon, red is oxygen, and white is hydrogen.

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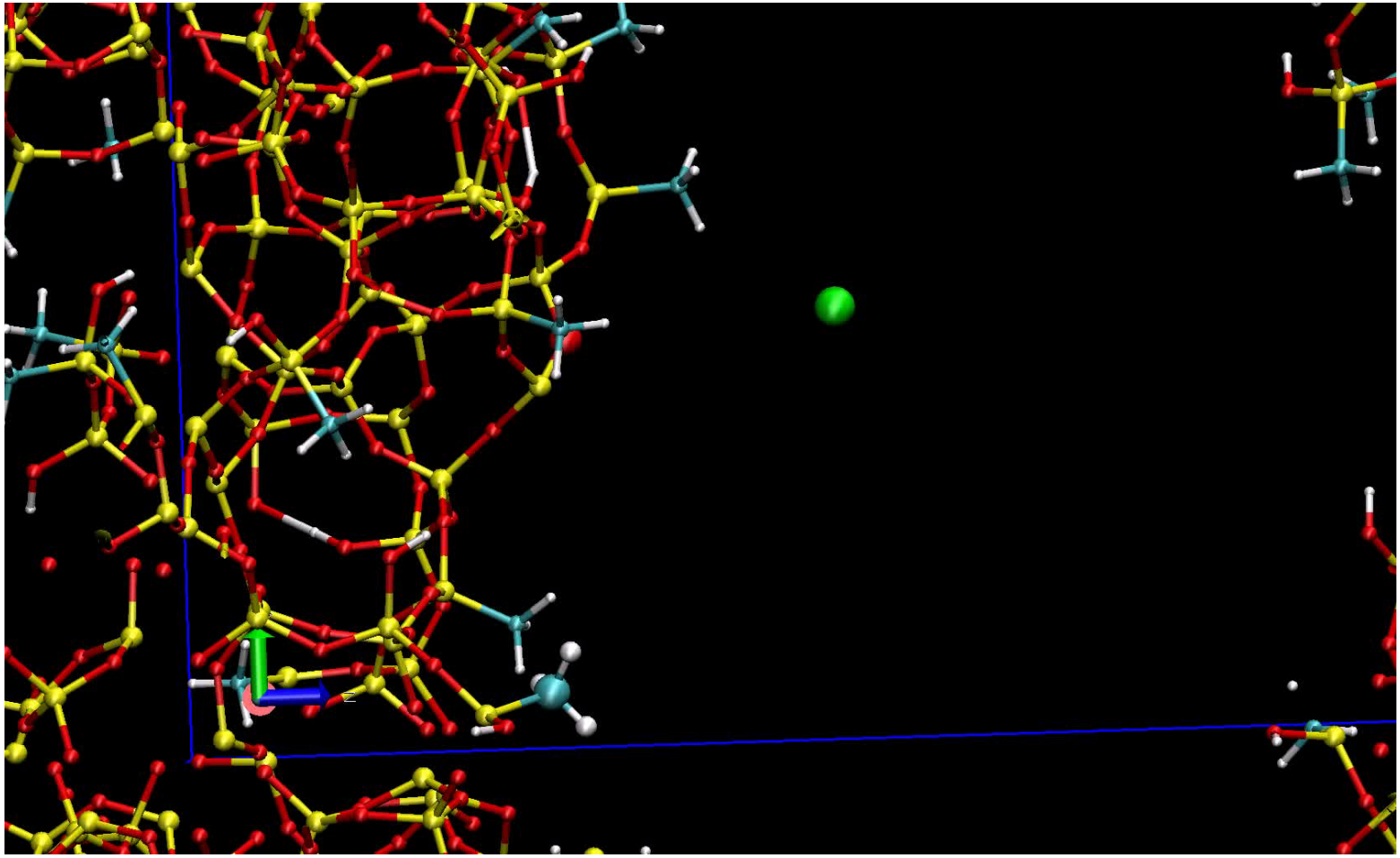
CH_3 Removal – Mechanism 1



Condition: Ar atom, 100eV, normal incidence, 20Åx20Å surface
Products: free oxygen generated (7.7eV), methyl radical formation

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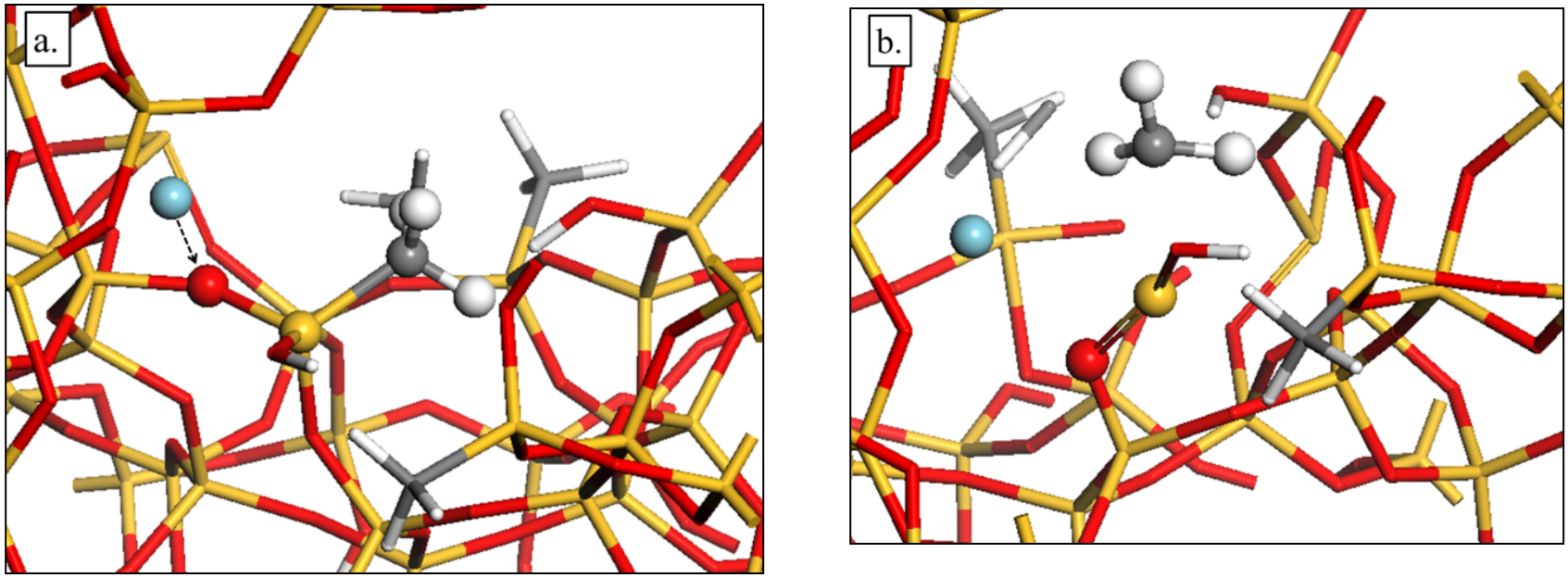
CH_3 Removal – Mechanism 2

- Ar impacts a bridging oxygen in the structure
- This forces the O into the Si which moves and breaks the Si-CH_3 bond
- The CH_3 diffuses into the vacuum and the Si^3 remains unbonded



(a) initial and (b) final atomic positions for CH_3 removal by reaction mechanism 2. Yellow is silicon, red is oxygen, white is hydrogen, and blue is argon.

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Conclusions

- Realistic structure models of nanoporous silica and porous organosilicate glass (OSG) with wide range of porosity have been generated using molecular dynamics simulations with ReaxFF.
- Mechanical properties were calculated and correlated with porosity and more morphologies. Power and exponential empirical fitting were compared.
- Ar plasma collision cascade reactions were studied using AIMD simulations and reaction mechanisms for carbon abstraction identified.
- Water confined in nanoporous silica were studied using AIMD and there are challenges to enable reactions on some highly reactive sites in MD simulations.

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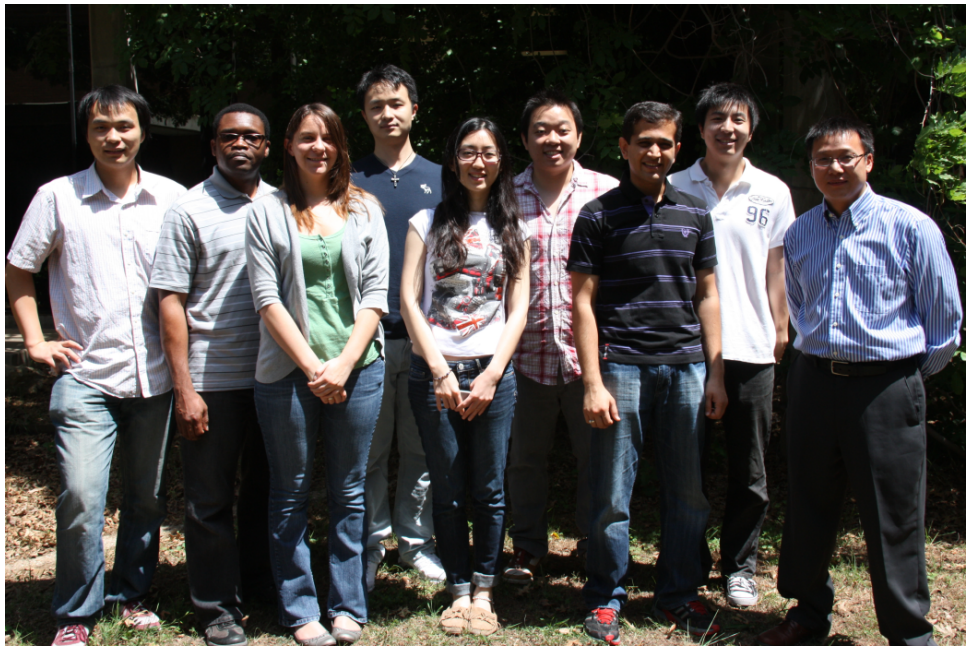
Joe Ryan (PNNL)

Graduate students:

Mrunal Chaudhari, Jessica Rimsza, Lu Deng



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