

# Atomistic Simulation of Materials: Introduction to Molecular Dynamics Method

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Pratibha Dev, Aiichiro Nakano, Ken-ichi Nomura, Tao Wei

CACS



# Outline – Part I

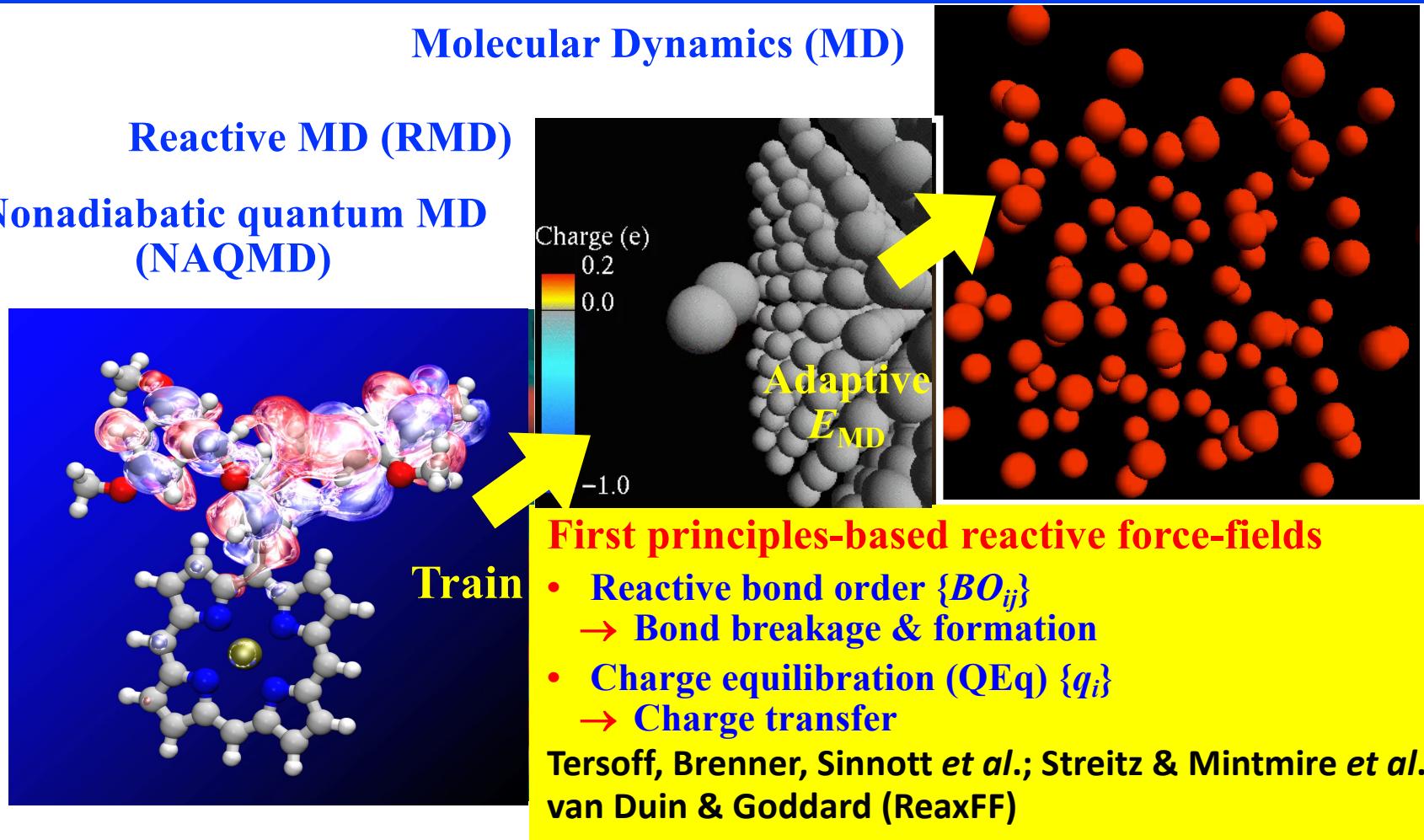
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# Introduction to Molecular Dynamics Method with Reactive Force Fields on Parallel Computers

**Collaboratory for Advanced Computing and Simulations:**  
**Faculty:** Rajiv Kalia and Aiichiro Nakano (USC),  
Fuyuki Shimojo and Postdocs and Grad Students

# Simulation Methods: NAQMD, RMD and MD



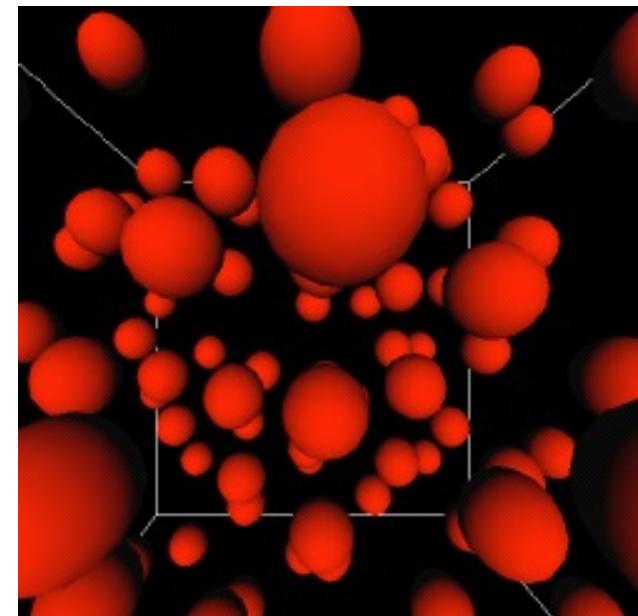
# Molecular Dynamics Method

**Newton's second law of motion:**

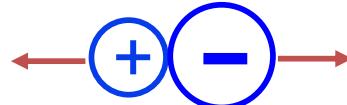
$$\{r_1(t), \dots, r_N(t)\} \quad m_i \frac{d^2 r_i(t)}{dt^2} = - \frac{\partial V}{\partial r_i}$$

**Interatomic potential for  $\text{SiO}_2$  &  $\text{Si}_3\text{N}_4$ :**

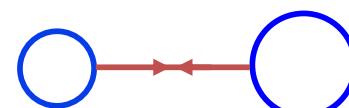
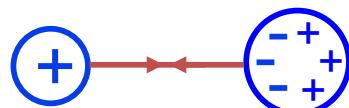
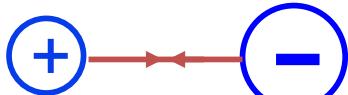
$$V = \sum_{i < j} V_{ij}^{(2)}(r_{ij}) + \sum_{i,j < k} V_{ijk}^{(3)}(r_{ij}, r_{ik})$$



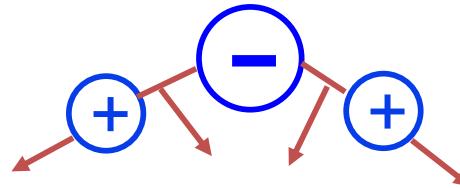
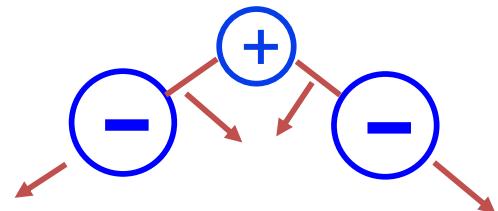
> Two-body: (1) steric repulsion



(2) Coulomb ; (3) charge-dipole ; (4) induced dipole-dipole



> Three-body: covalent bond bending & stretching

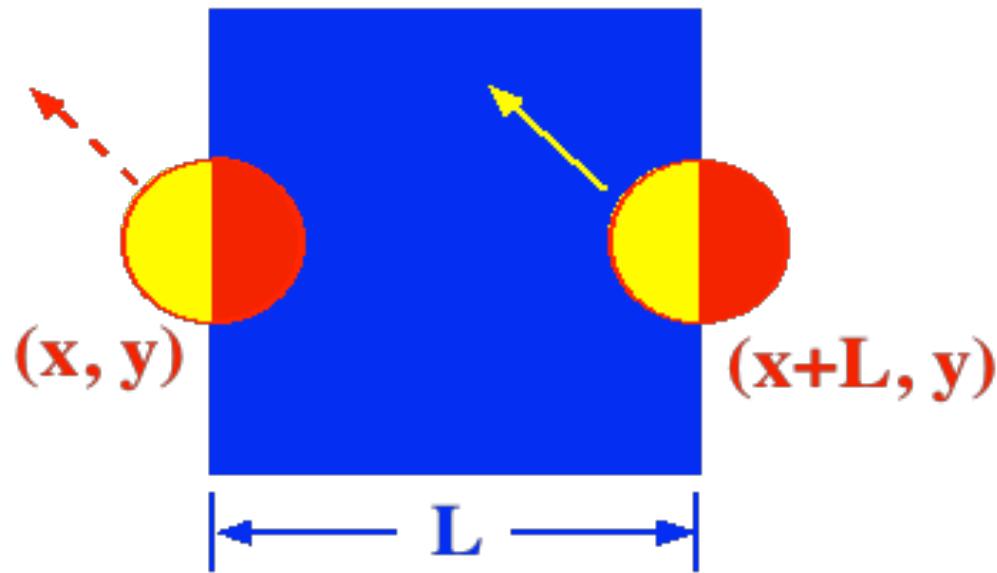


# MD Simulation: Numerical Algorithm

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- Equations of motion: 2nd order, non-linear, coupled ODE → Finite-difference equations:  
 $[\vec{r}_i(t), \vec{p}_i(t)] \longrightarrow [\vec{r}_i(t+\Delta t), \vec{p}_i(t+\Delta t)]$
- Initial conditions:  
lattice positions, random velocities
- Boundary conditions:  
periodic boundary conditions (PBC)
- Integration algorithms:  
Gear, Beeman, Verlet, Velocity-Verlet , etc,

# Periodic Boundary Conditions (PBC)



- Simulation box is taken as basic unit
- The whole space is filled by periodically repeating the basic unit

leaving particle is replaced by its image  
entering from the opposite side  
short-range interactions are between  
minimum images

# Velocity-Verlet Algorithm

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Stage 1  $\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \Delta t \vec{v}_i(t) + \frac{1}{2} \Delta t^2 \vec{a}_i(t)$

$$\vec{v}_i(t+\frac{1}{2}\Delta t) = \vec{v}_i(t) + \frac{1}{2}\Delta t \vec{a}_i(t)$$

Stage 2      <<< Force evaluation >>>

Stage 3  $\vec{v}_i(t + \Delta t) = \vec{v}_i(t + \frac{1}{2}\Delta t) + \frac{1}{2}\Delta t \vec{a}_i(t + \Delta t)$

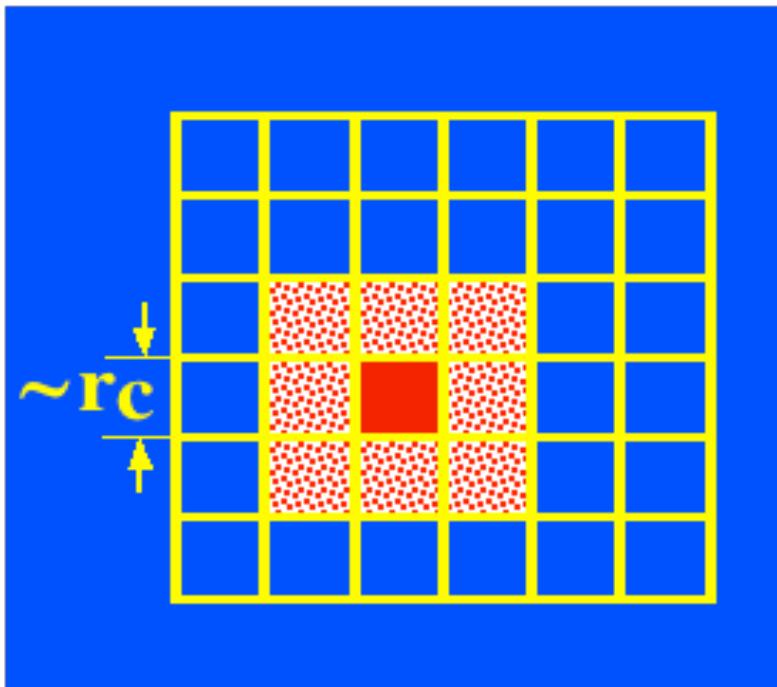
Time reversible - stability in long time simulations

# Link-Cell-List Scheme:

$$O(N^2) \rightarrow O(N)$$

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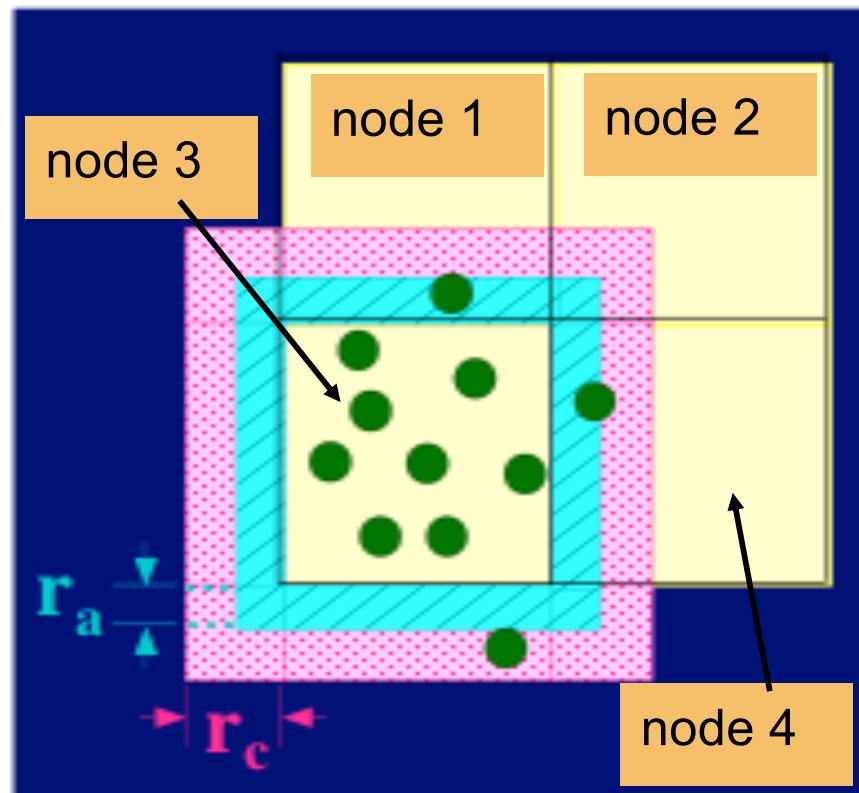
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- Particles are divided into **cells** of size  $r_c$
- Particles are linked in each cell into **link-lists**
- Particles in neighbor cells are grouped into **neighbor-lists**

Interactions are evaluated within neighbor lists:  $O(NN_b)$

# Domain Decomposition Scheme



- System is divided into subsystems
- Subsystems are geometrically matched onto nodes
- Interaction between neighbor nodes are calculated through message-passing

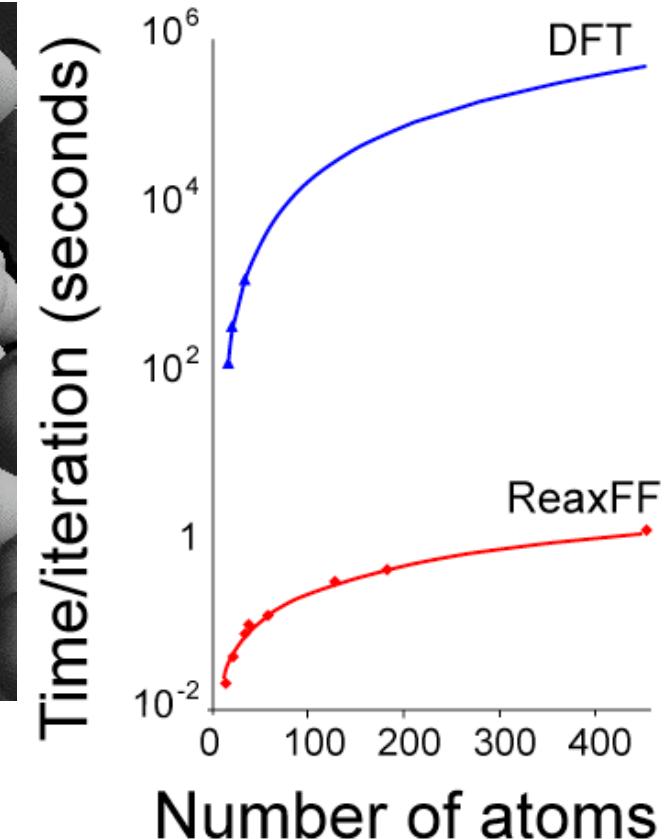
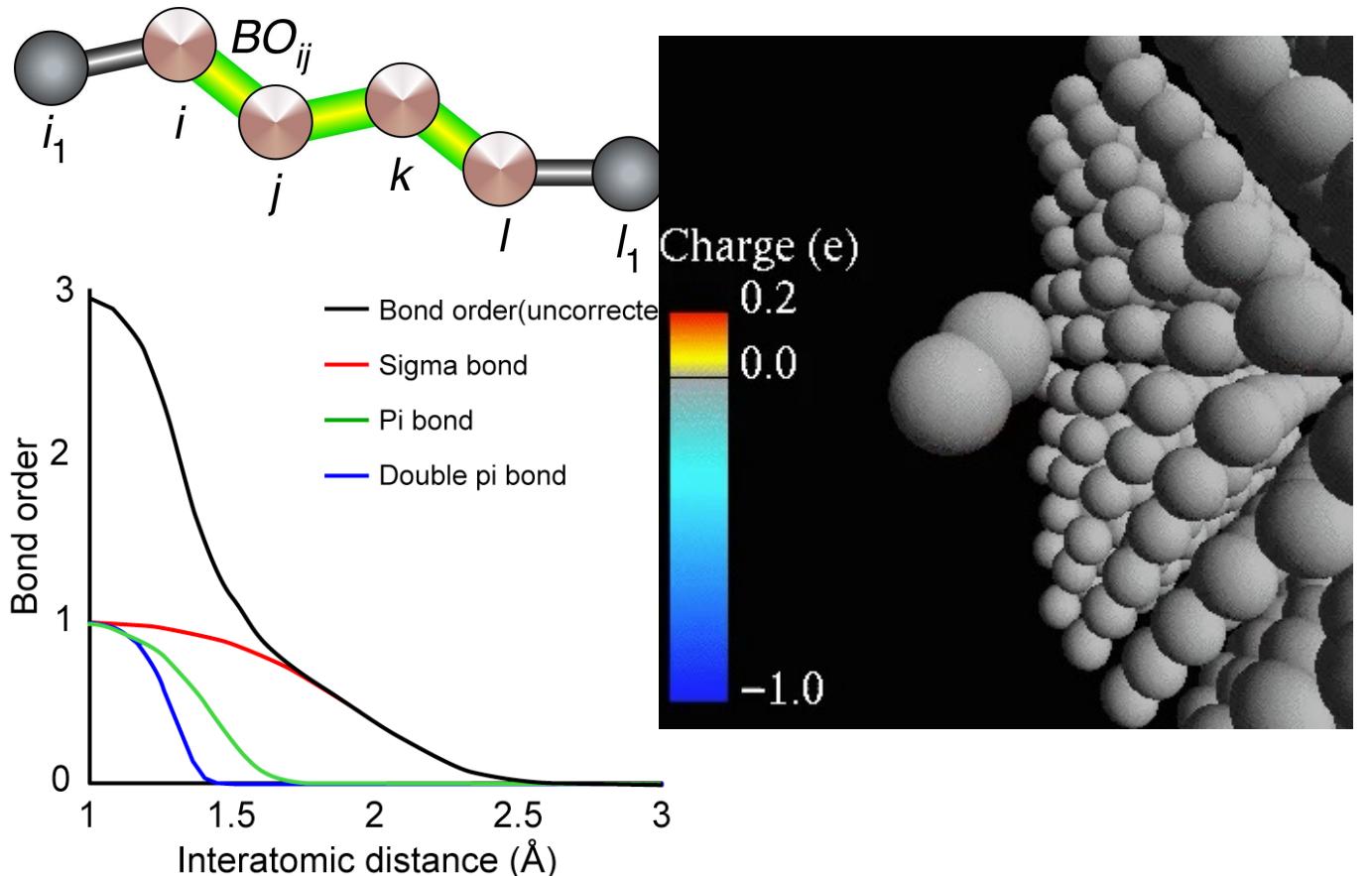
**Multiple Time Step:** Primary surface is copied every  $\Delta t$   
secondary surface is copied every  $n\Delta t$

# Reactive Force Field (ReaxFF) MD

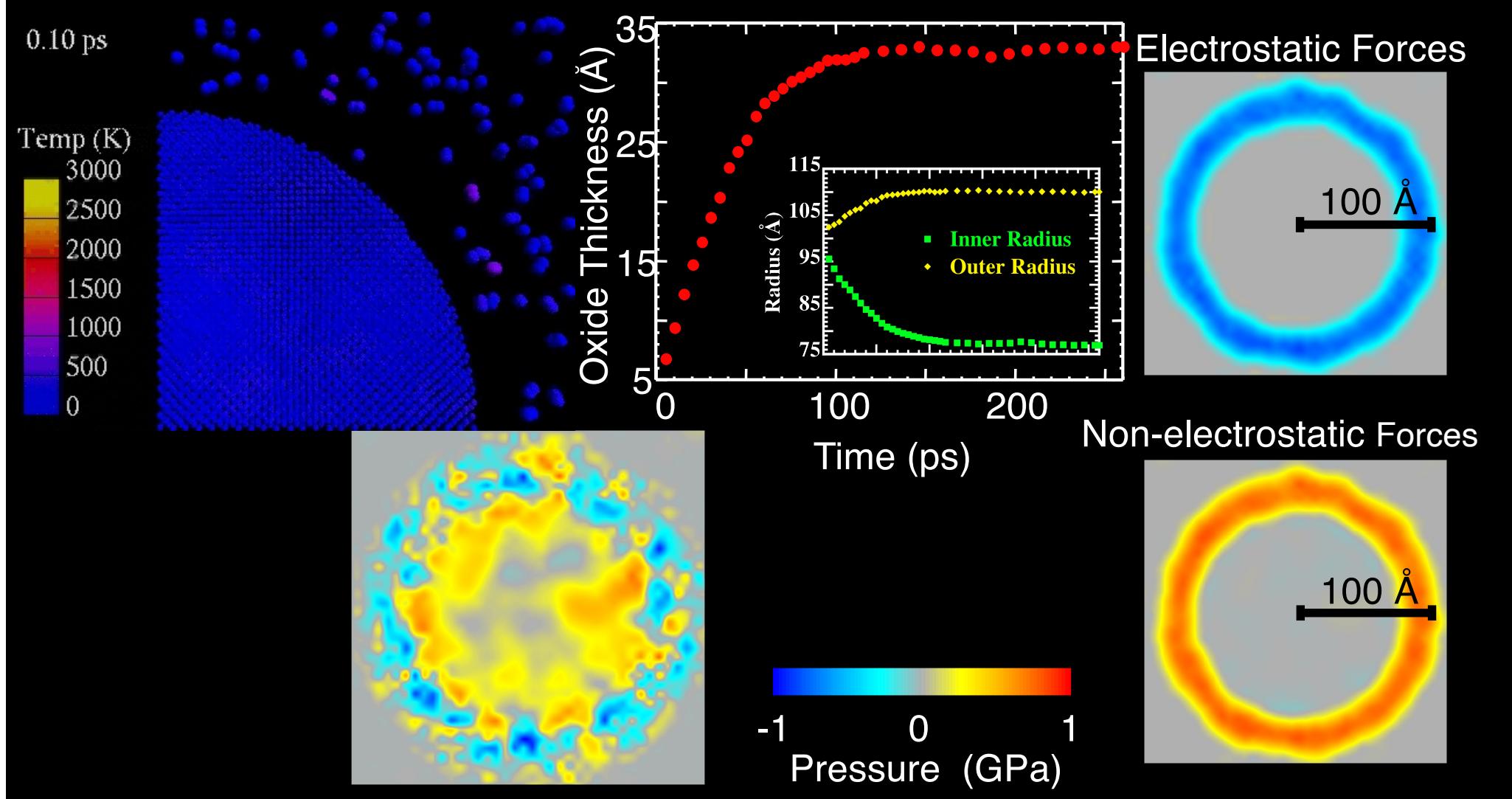
First principles-based reactive force-field [van Duin, Goddard, Caltech]

- Reactive bond order:  $E_{\text{BO}}((\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l), \{\text{BO}_{ij}\})$   
→ Bond breakage & formation [Tersoff, '85; Brenner, '90]
- Charge equilibration (QE<sub>q</sub>):  $\{\mathbf{q}_i^*\} = \text{argmin } E_{\text{ES}}(\{\mathbf{r}_i\}, \{\mathbf{q}_i\})$   
→ Charge transfer [Goddard & Rappe, '91; Streitz & Mintmire, '94]

Significantly less computing time than the density functional theory (DFT)

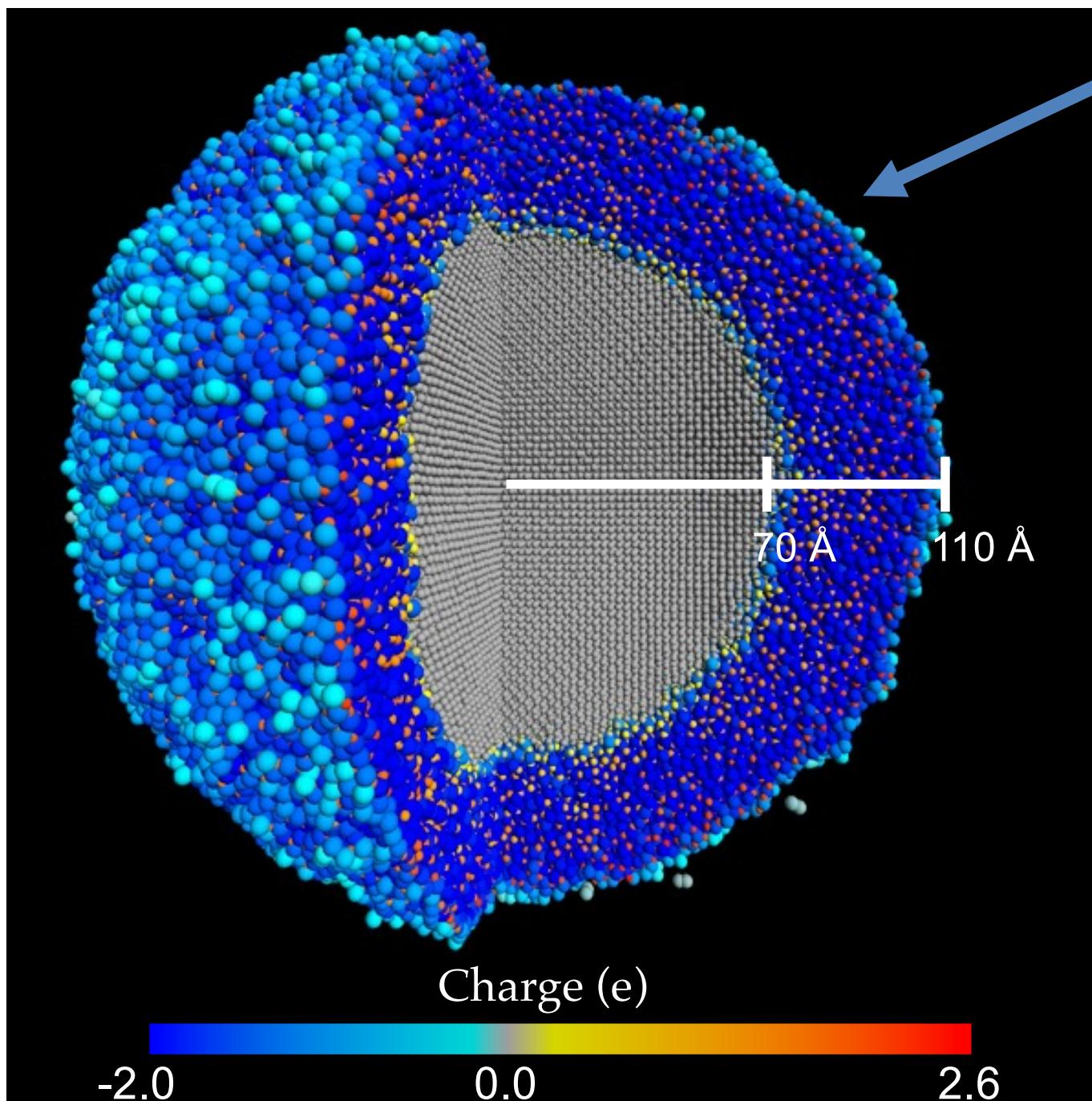


# Oxidation of an Al Nanoparticle (n-Al)



- Oxide thickness saturates at 40 Å after 0.5 ns, in agreement with experiments
- Oxide region/metal core is under negative/positive pressure
- Attractive Al-O Coulomb forces contribute large negative pressure in the oxide

# Structure of Oxide Scale



Snapshot at 466 ps

Oxide scale is amorphous

Oxide thickness is 40 Å,  
in agreement with experiment

Average density of oxide  
is 2.9 g/cm<sup>3</sup>;  
75% of alumina

## Developing a Materials Innovation Infrastructure

EXECUTIVE OFFICE OF THE PRESIDENT  
NATIONAL SCIENCE AND TECHNOLOGY COUNCIL  
WASHINGTON, D.C. 20502

June 24, 2011

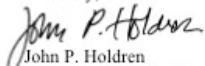
Dear Colleague:

In much the same way that silicon in the 1970s led to the modern information technology industry, the development of advanced materials will fuel many of the emerging industries that will address challenges in energy, national security, healthcare, and other areas. Yet the time it takes to move a newly discovered advanced material from the laboratory to the commercial market place remains far too long. Accelerating this process could significantly improve U.S. global competitiveness and ensure that the Nation remains at the forefront of the advanced materials marketplace. This *Materials Genome Initiative for Global Competitiveness* aims to reduce development time by providing the infrastructure and training that American innovators need to discover, develop, manufacture, and deploy advanced materials in a more expeditious and economical way.

Prepared by an *ad hoc* group of the National Science and Technology Council, this initiative proposes a new national infrastructure for data sharing and analysis that will provide a greatly enhanced knowledgebase to scientists and engineers designing new materials. This effort will foster enhanced computational capabilities, data management, and an integrated engineering approach for materials deployment to better leverage and complement existing Federal investments.

The success of this initiative will require a sustained effort from the private sector, universities, and the Federal Government. I look forward to working with you to make this vision a reality.

Sincerely,



John P. Holdren

Assistant to the President for Science and Technology  
Director, Office of Science and Technology Policy

### Computational Tools

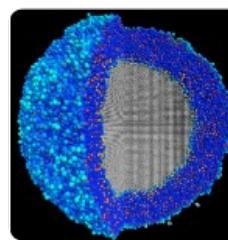
Major advances in modeling and predicting materials behavior have led to a remarkable opportunity for the use of simulation software in solving materials challenges. New computational tools have the potential to accelerate materials development at all stages of the continuum. For example, software could guide the experimental discovery of new materials by screening a large set of compounds and isolating those with desired properties. Further downstream, virtual testing via computer-aided analysis could replace some of the expensive and time-consuming physical tests currently required for validation and certification of new materials.

These computational tools are still not widely used due to industry's limited confidence in accepting non-empirically-based conclusions. Materials scientists have developed powerful computational tools to predict materials behavior, but these tools have fundamental deficiencies that limit their usefulness. The primary problem is that current predictive algorithms do not have the ability to model behavior and properties across multiple spatial and temporal scales; for example, researchers can measure the atomic vibrations of a material in picoseconds, but from that information they cannot predict how the material will wear down over the course of years. In addition, software tools that utilize the algorithms are typically written by academics for academic purposes in separate universities, and therefore lack user-friendly interfaces, documentation, robustness, and the capacity to scale to industrial-sized problems. These deficiencies inhibit efficient software maintenance and can result in software failures. Significant improvements in software and the accuracy of materials behavior models are needed.

Open innovation will play a key role in accelerating the development of advanced computational tools. A system that allows researchers to share their algorithms and collaborate on creating new tools will rapidly increase the pace of innovation, which currently occurs in isolated academic settings. An existing system that is a good example of a first step toward open innovation is the nanoHUB, a National Science Foundation program run through the Network for Computational Nanotechnology.<sup>6</sup> By providing modeling and simulation applications that researchers can download and use on

their data, nanoHUB.org supports the use of computational tools in nanotechnology research. Researchers can access state-of-the-art modeling algorithms and collaborate with colleagues via the website. To rapidly increase knowledge of first principles and advance modeling algorithms, it is essential for the materials industry to accept open innovation and design these tools on an open platform.

The ultimate goal is to generate computational tools that enable real-world materials development, that optimize or minimize traditional experimental testing, and that predict materials performance under diverse product conditions. An early benchmark will be the ability to incorporate improved predictive modeling algorithms of materials behavior into existing product design tools. For example, the crystal structure and physical properties of the materials in a product may change during the product's processing, due to varying conditions. It could be disastrous to the performance of a product if, for instance, the tensile strength of its bolts changed during manufacture. The ability to model these morphology and property changes will enable faster and better design.



Achieving these objectives will require a focus in three necessary areas: (1) creating accurate models of materials performance and validating model predictions from theories and empirical data; (2) implementing an open-platform framework to ensure that all code is easily used and maintained by all those involved in materials innovation and deployment, from academia to industry; and (3) creating software that is modular and user-friendly in order to extend the benefits to broad user communities.

### Experimental Tools

The emphasis of the Initiative is on developing and improving computational capabilities, but it is essential to ensure that these new tools both complement and fully leverage existing experimental research on advanced materials. Effective models of materials behavior can only be developed from accurate and extensive sets of data on materials properties. Experimental data is required to create models as well as to validate their key results. Where computations based on theoretical frameworks fall short, empirical testing will fill in the

Laser Heating

48 nm

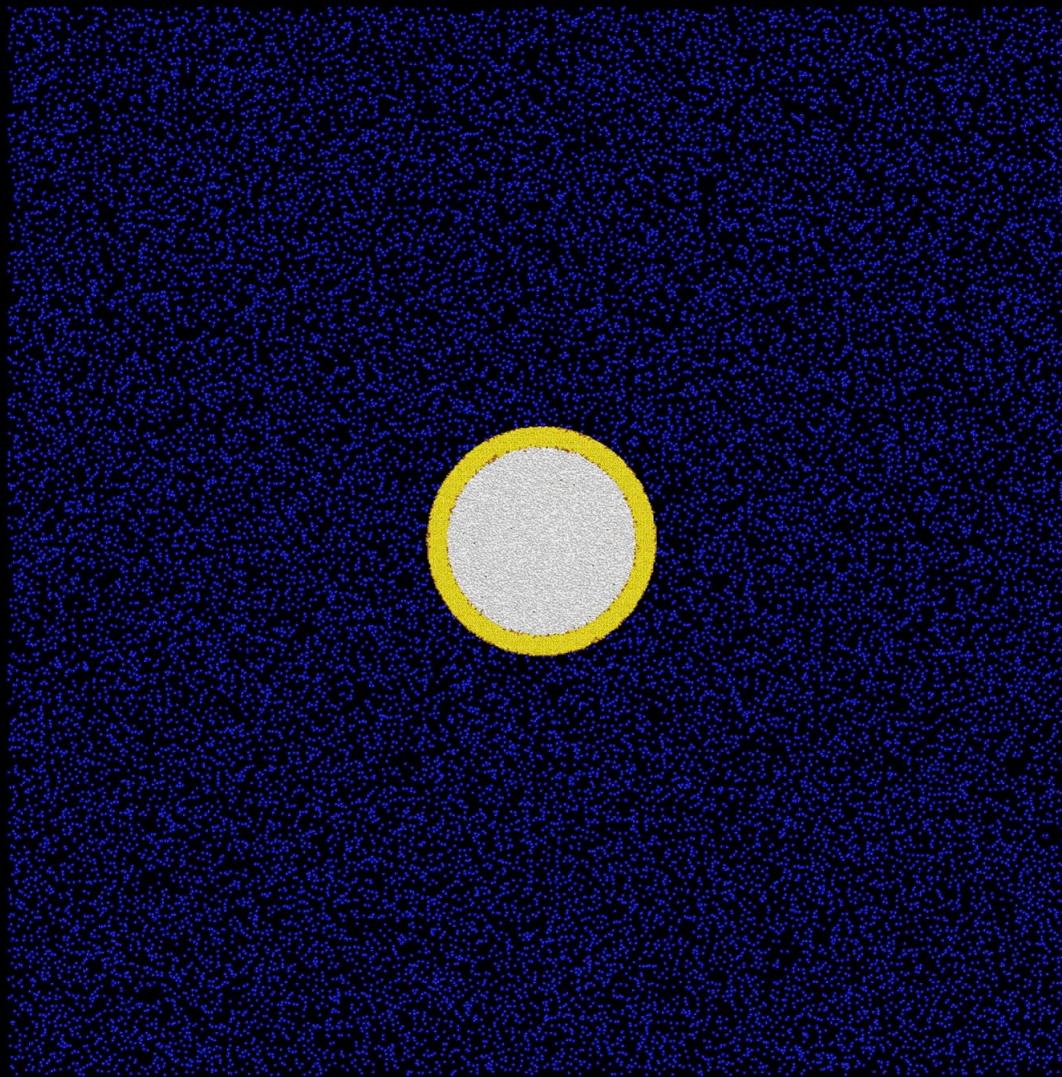
Nanoparticle with

4 nm

Alumina Nanoshell

# Nanoparticle Explosion

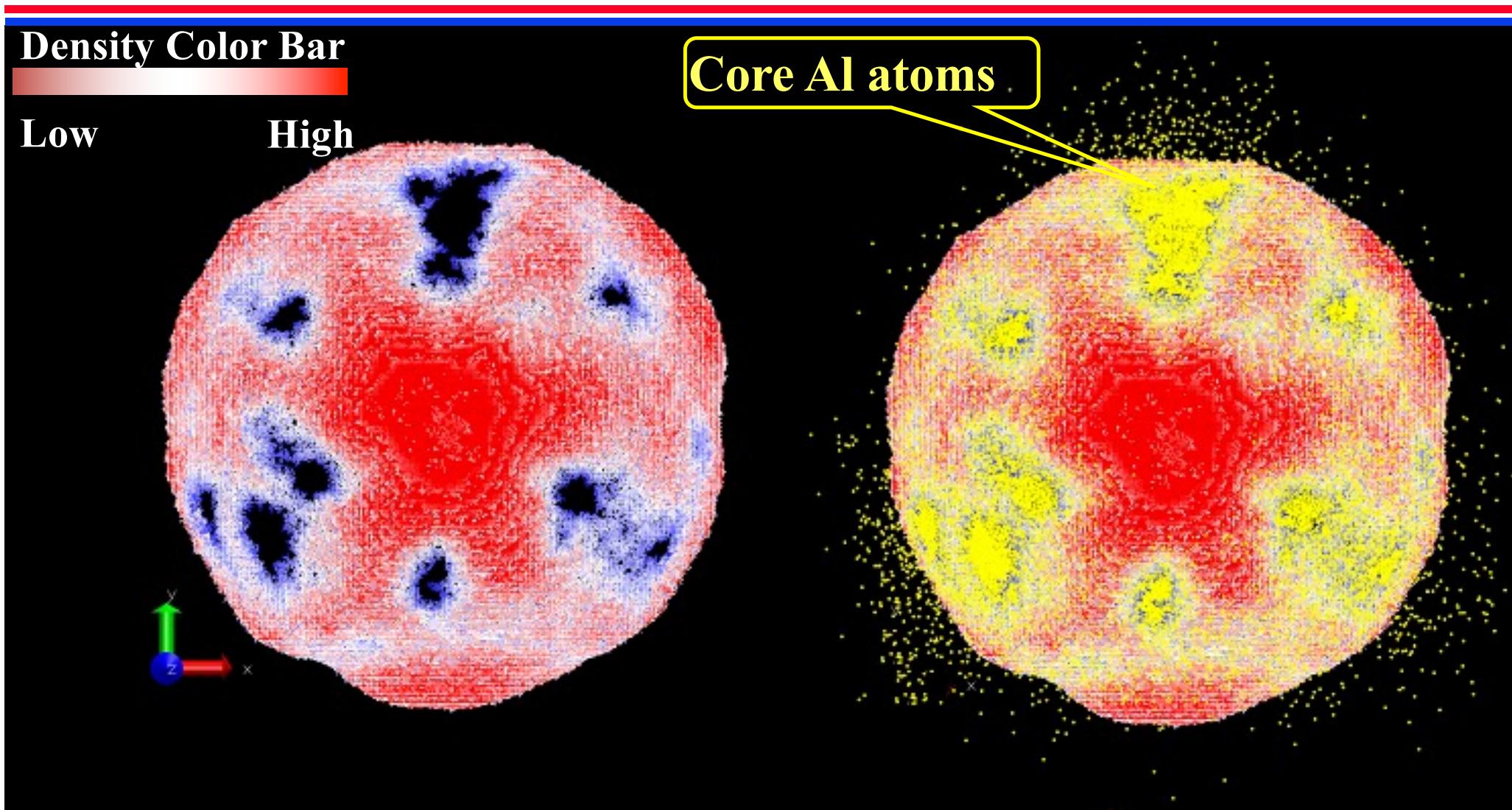
Tcore = 9000K, D= 48nm, S = 4nm



Expansion → Shell Broken → Oxidation Reaction

# Jetting out of Al Core Atoms

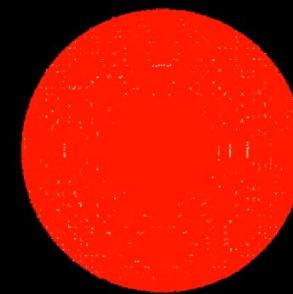
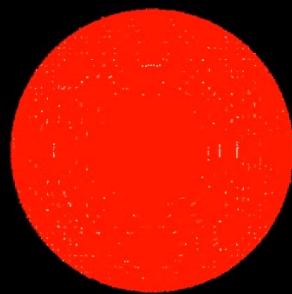
$T_{core} = 9000K, t = 72ps$



- More Al core atoms jet out from the weak areas of the shell

# Jetting out of Al Core Atoms

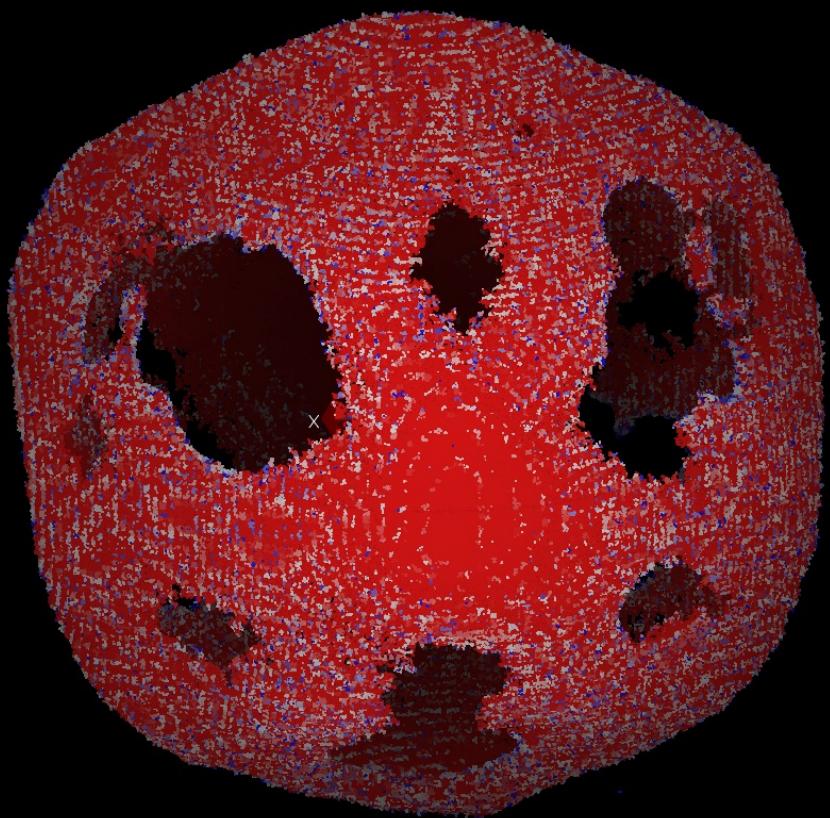
Tcore = 9000K, 4 nm Shell



- More Al core atoms jet out from the **weak areas of the shell**

# Structural Characterization of Nanoshell

$S = 4\text{nm}$ ,  $T_{\text{core}} = 9000\text{K}$



300            800

-10            +10

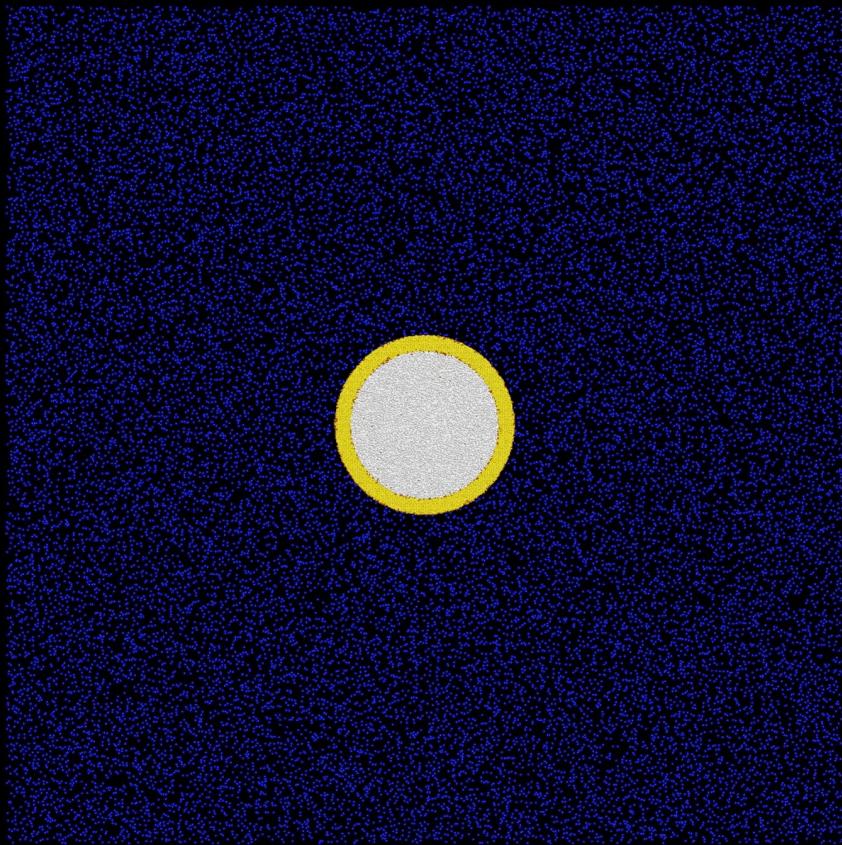
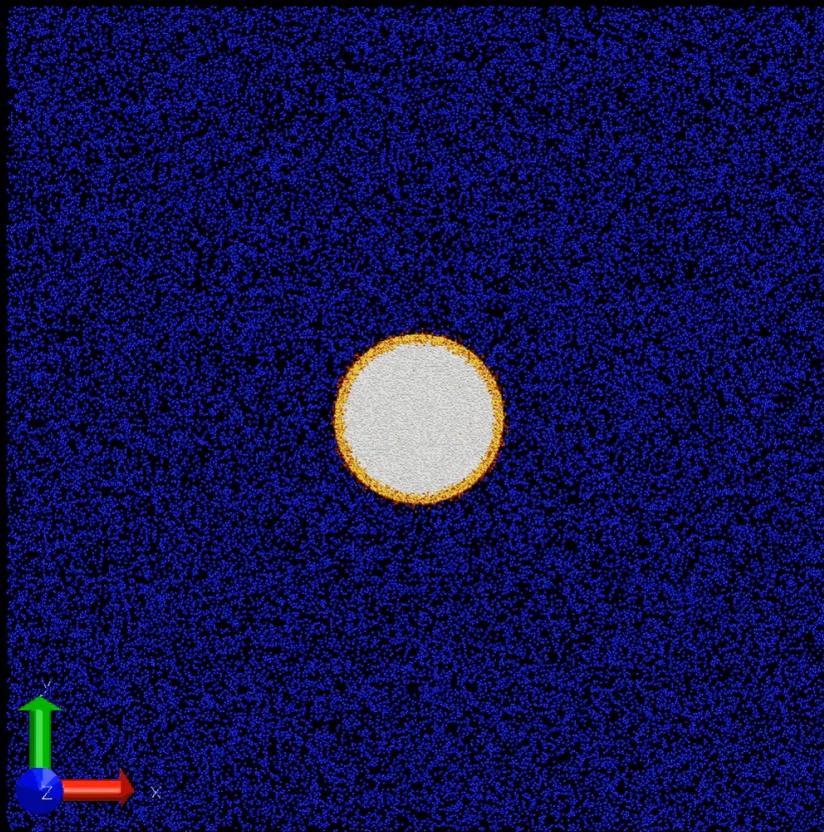
- Density: # of atoms /  $\text{nm}^3$

- Stress: GPa

**Nanoparticles with  
4 nm (Crystalline) and  
3 nm (Amorphous)  
Alumina Shell**

# Amorphous and Crystalline Shells

## Explosion: Tcore = 9000K



**46 nm**

**Nanoparticle with**

**3 nm**

**Amorphous  
Alumina Shell**

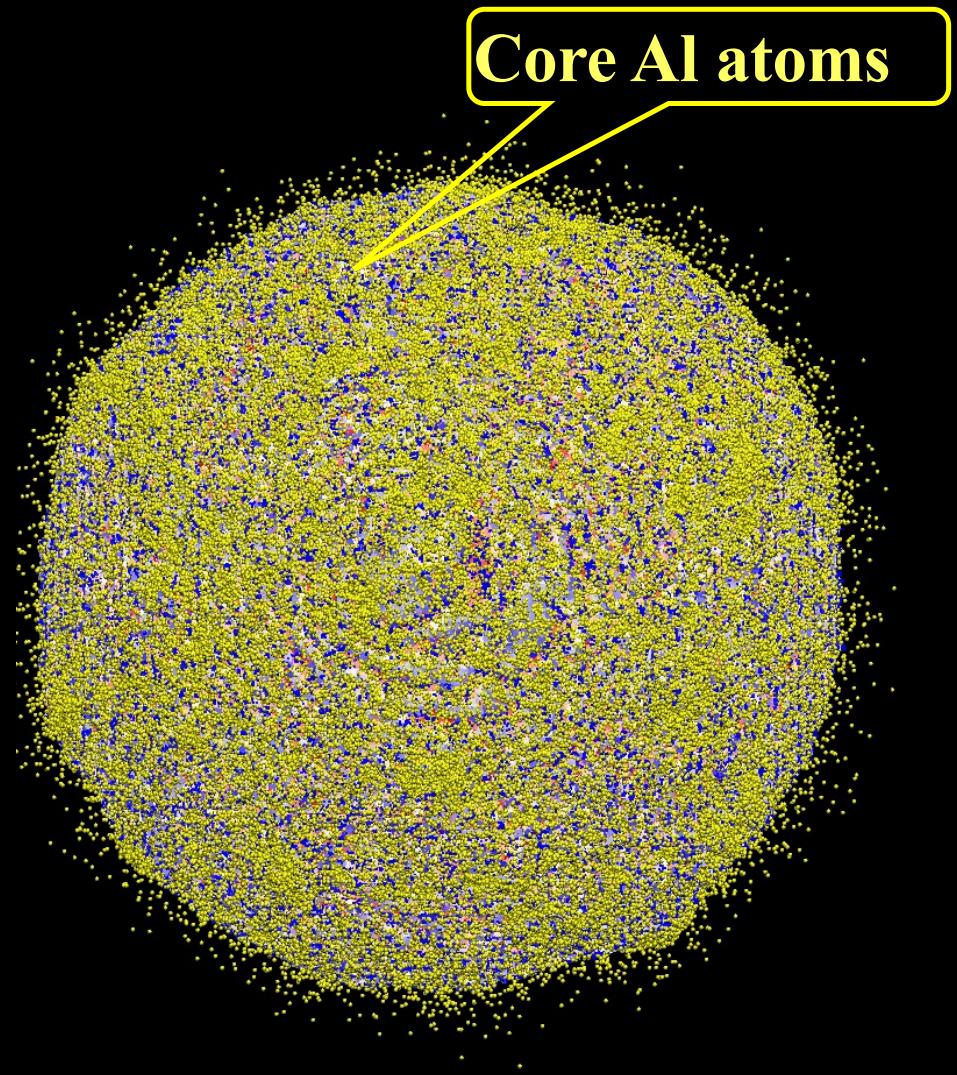
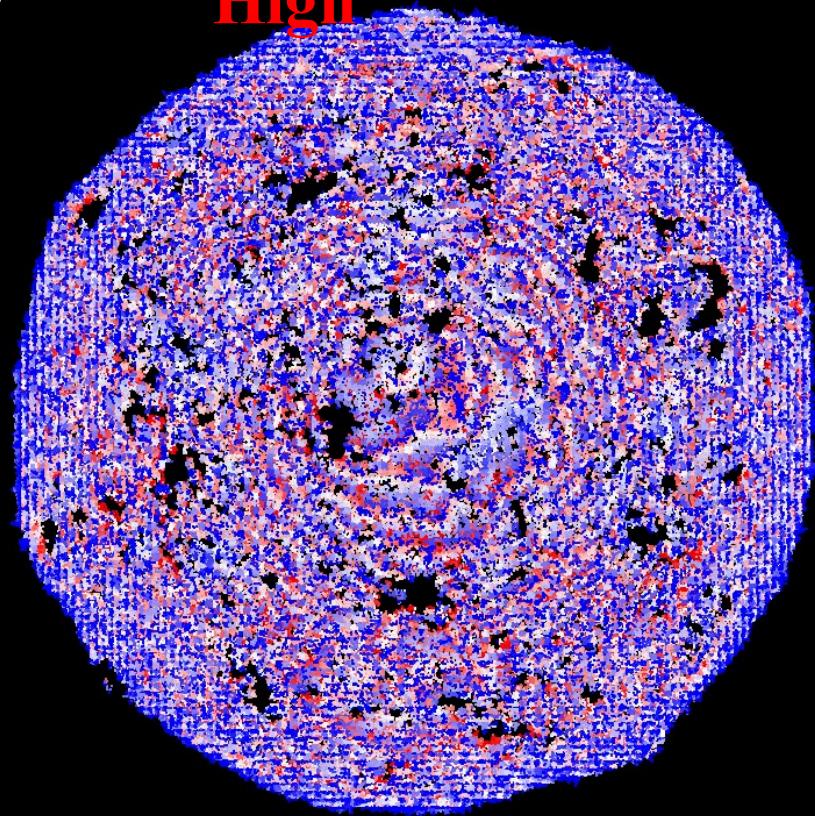
# Jetting out of Al Core Atoms

$T_{core} = 9000K, t = 60ps, \text{Amorphous Shell}$

Density Color Bar

Low

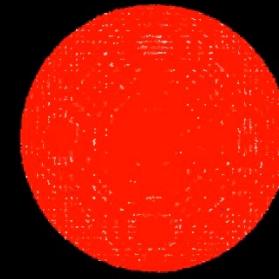
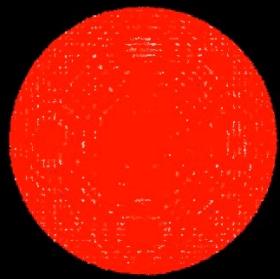
High



- Al core atoms jet out homogeneously from the shell

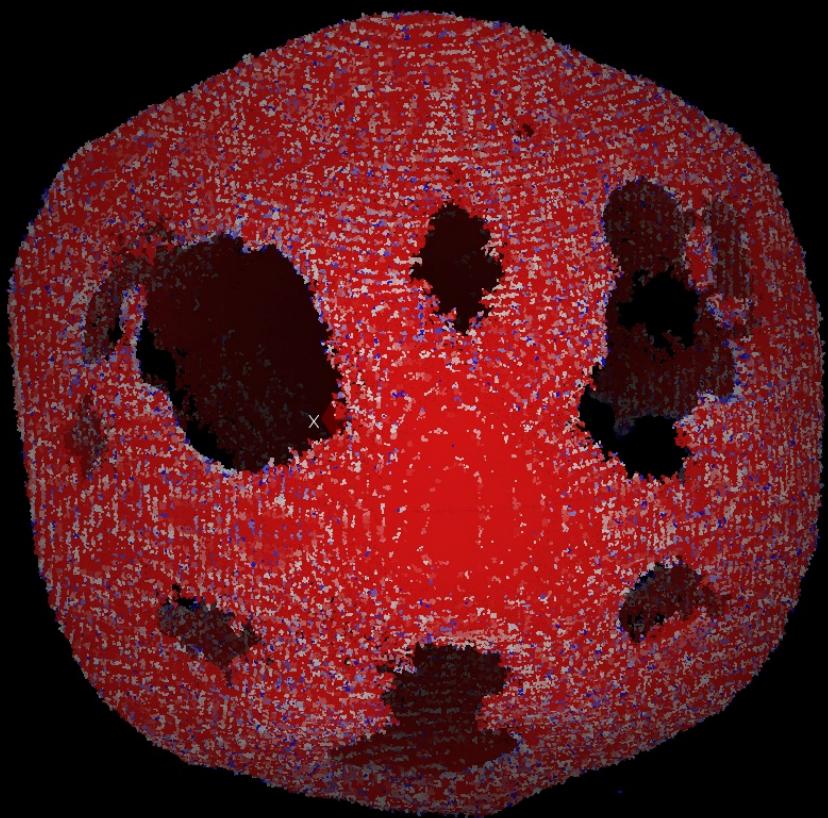
# Jetting out of Al Core Atoms

$T_{core} = 9000K$ , Amorphous Shell



- Al core atoms jet out **homogeneously from the shell**

# Structural Characterization of Nanoshell Crystalline Shell, Tcore = 9000K



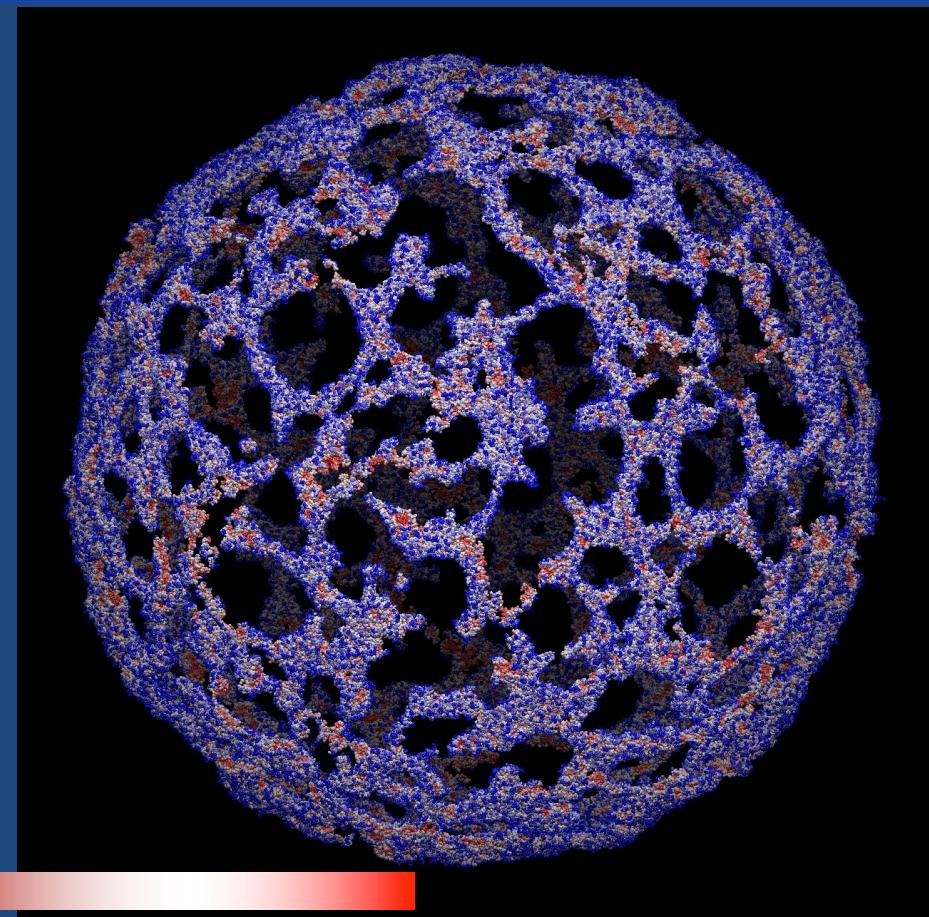
300                  800

-10                  +10

- Density: # of atoms / nm<sup>3</sup>

- Stress: GPa

# Structural Characterization of Nanoshell Amorphous Shell, Tcore = 9000K

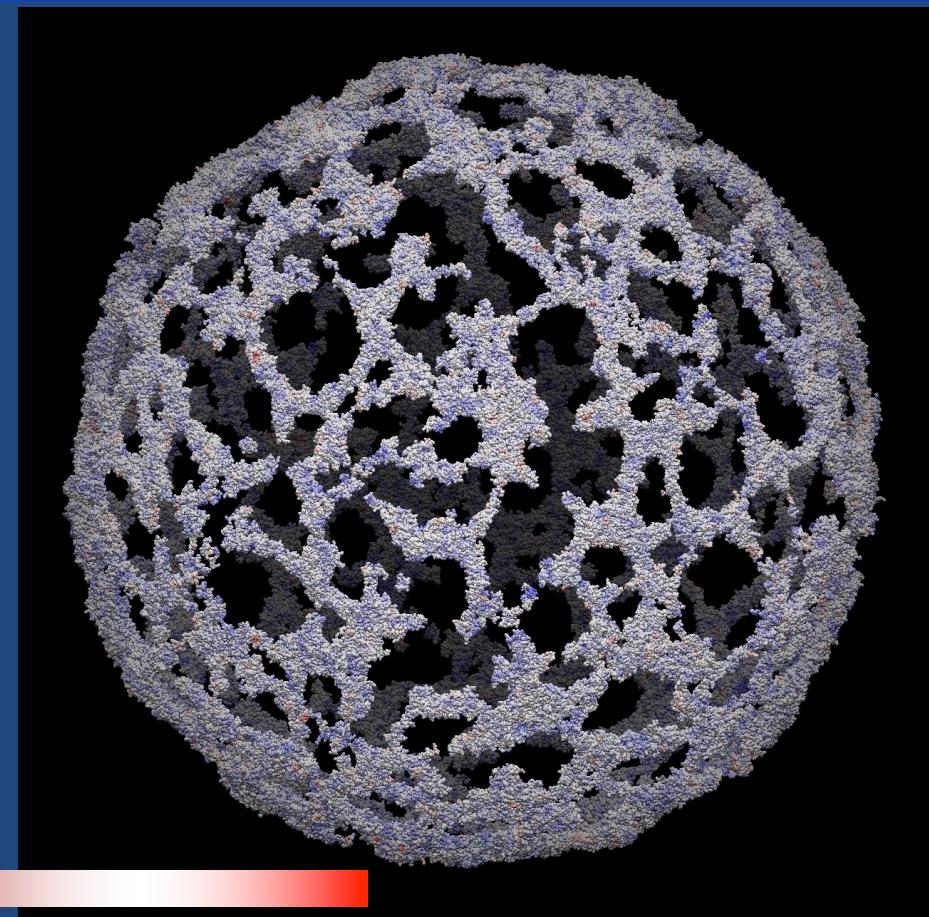


300

800

-5

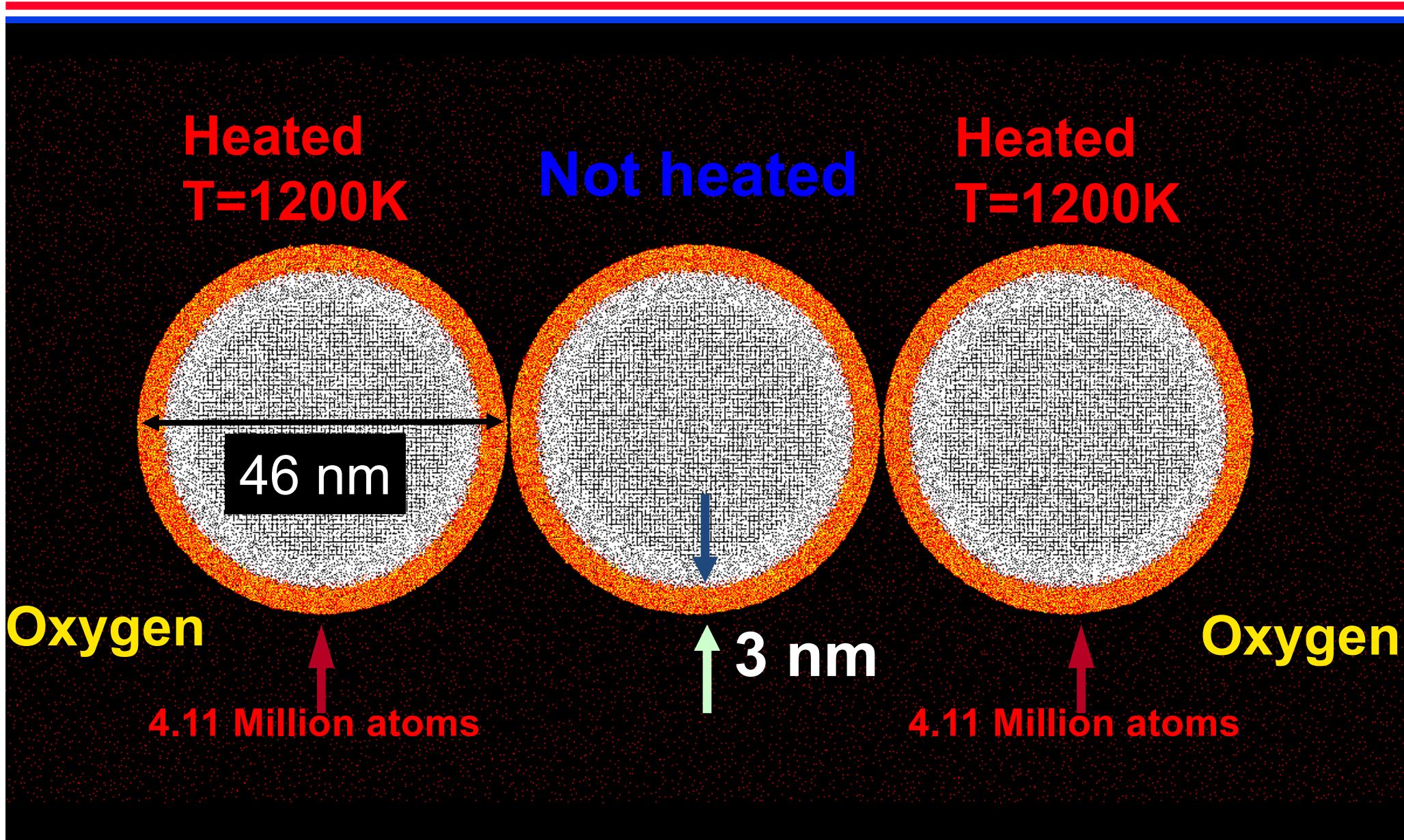
+5



- Density: # of atoms / nm<sup>3</sup>

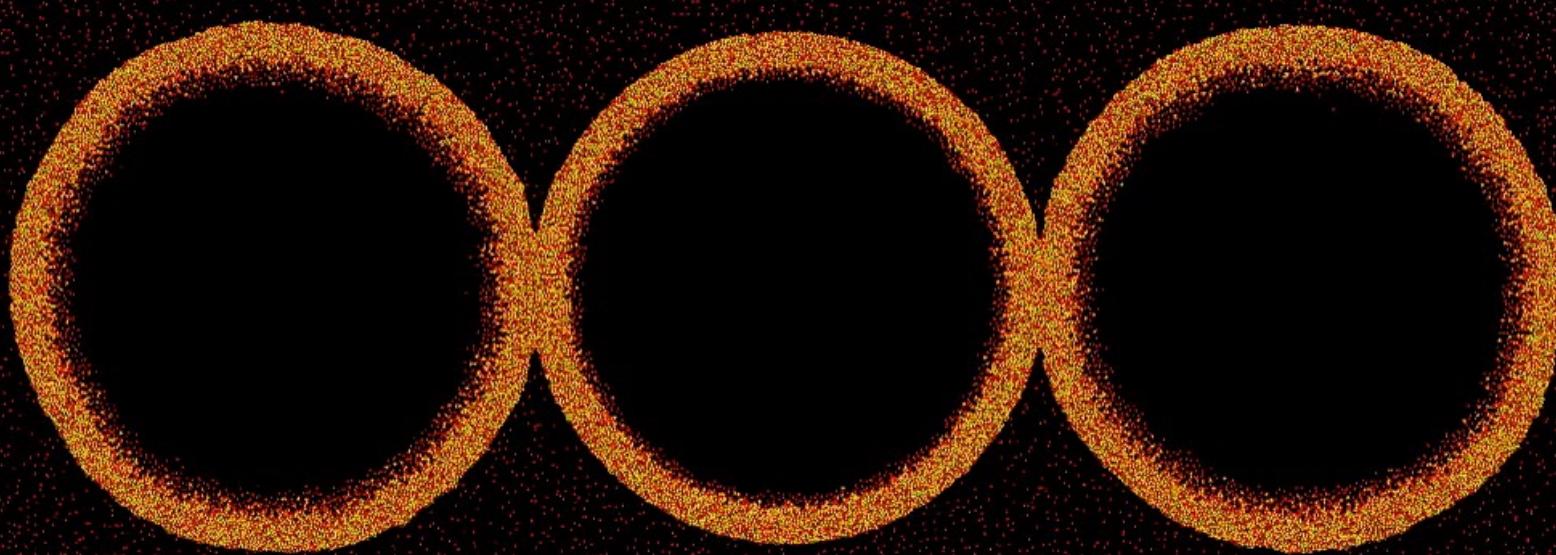
- Stress: GPa

# Three 46 nm Nanoparticles: Burning of the Center Nanoparticle



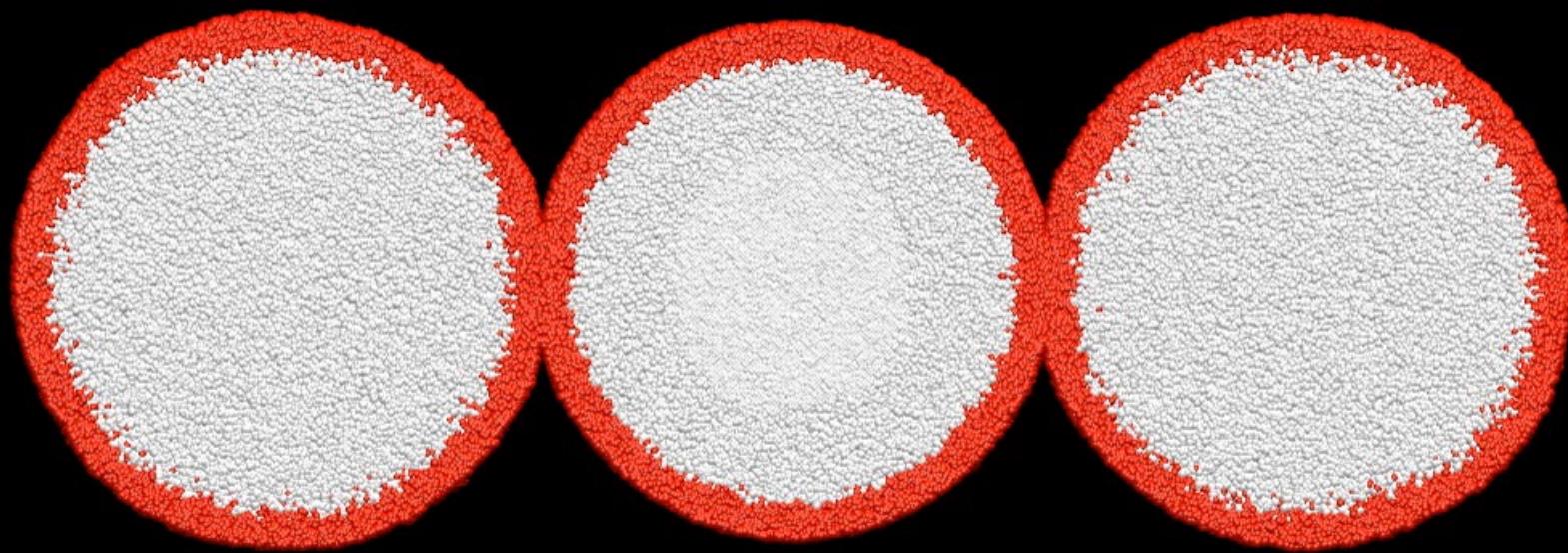
# Oxidation of the Center Nanoparticle

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**Oxidation reaction (Al core is not shown)**

# Oxidation of the Center Nanoparticle Aluminum Ejections



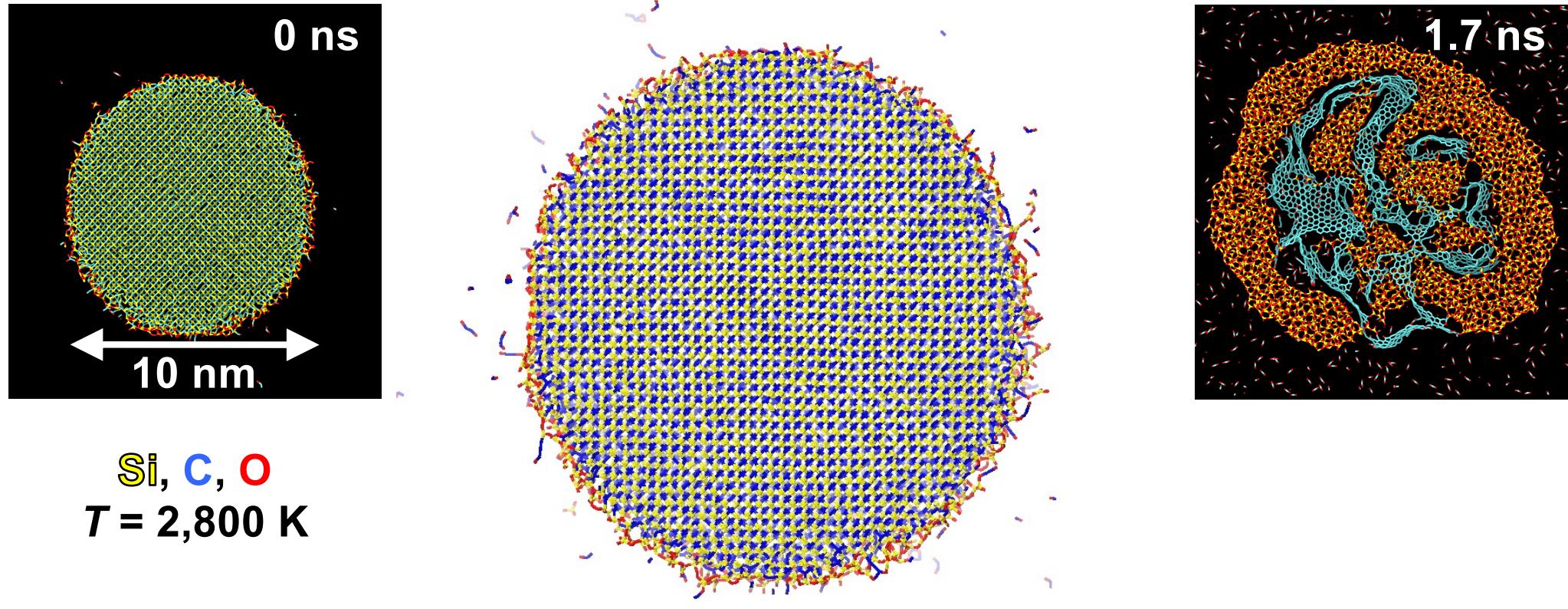
**Aluminum ejections: core (white) and shell (red)**

# Computational Synthesis

**Graphitic metamaterial from high temperature  
oxidation of silicon carbide.**

# Oxidation of SiC Nanoparticle

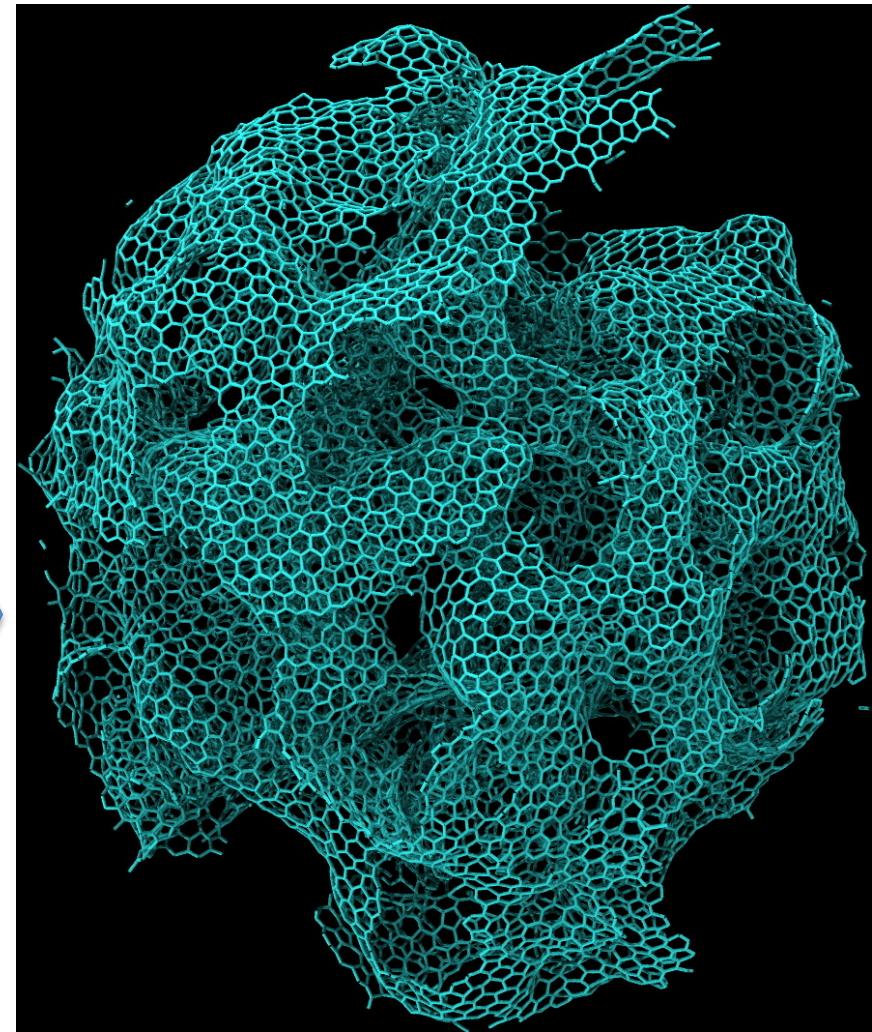
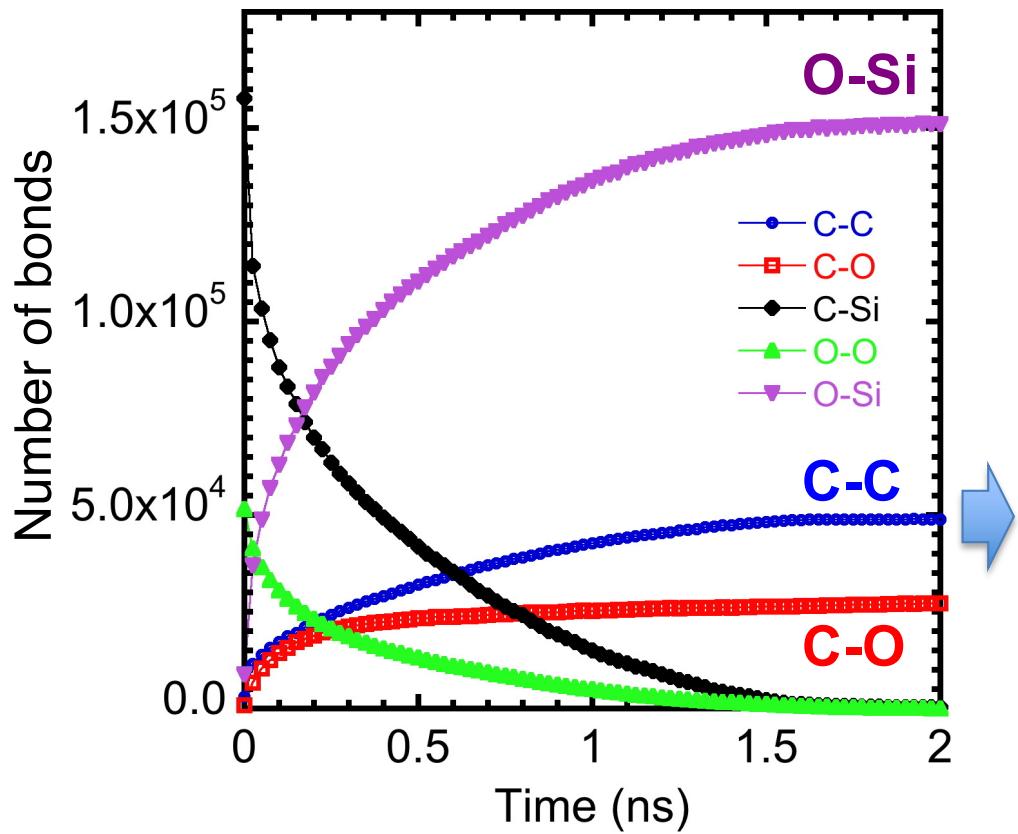
- Reactive molecular dynamics (RMD) simulations: Diameter = 10 nm (100K atoms), 46 nm (10M atoms) & 100 nm (112M atoms) on 786,432-processor IBM Blue Gene/Q



- Formation of nanocarbon, embedded within  $\text{SiO}_2$  shell

# Nanocarbon Production

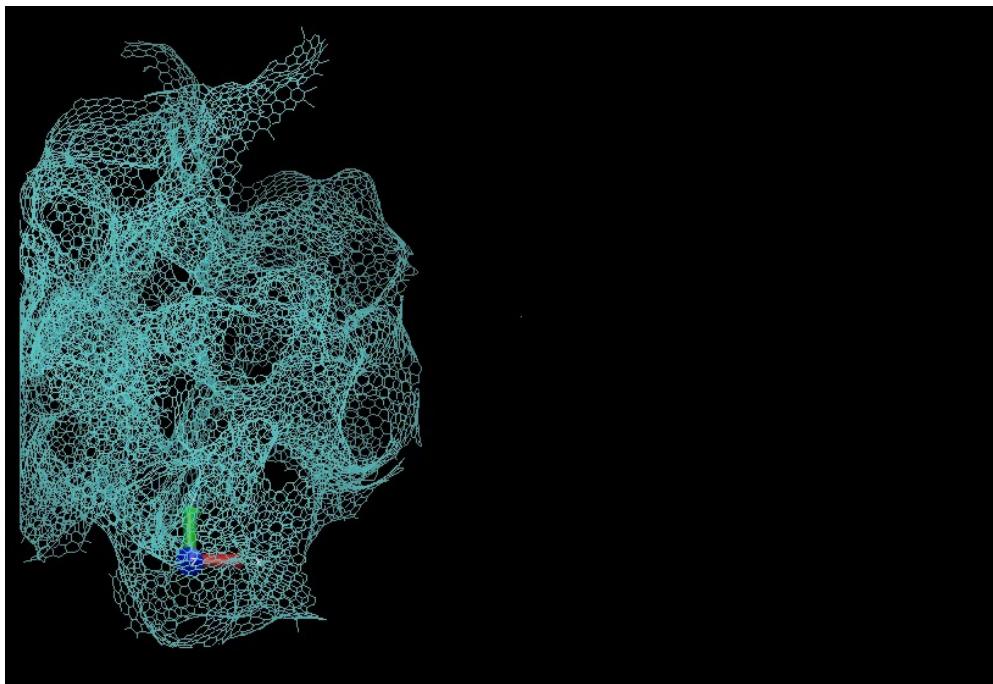
- Much more Si-O bonds are formed compared with C-O
- C-C bonds are predominantly  $sp^2$



- Silica shell acts as a *nanoreactor* by transporting O reactants & protecting C products from harsh oxidizing environment

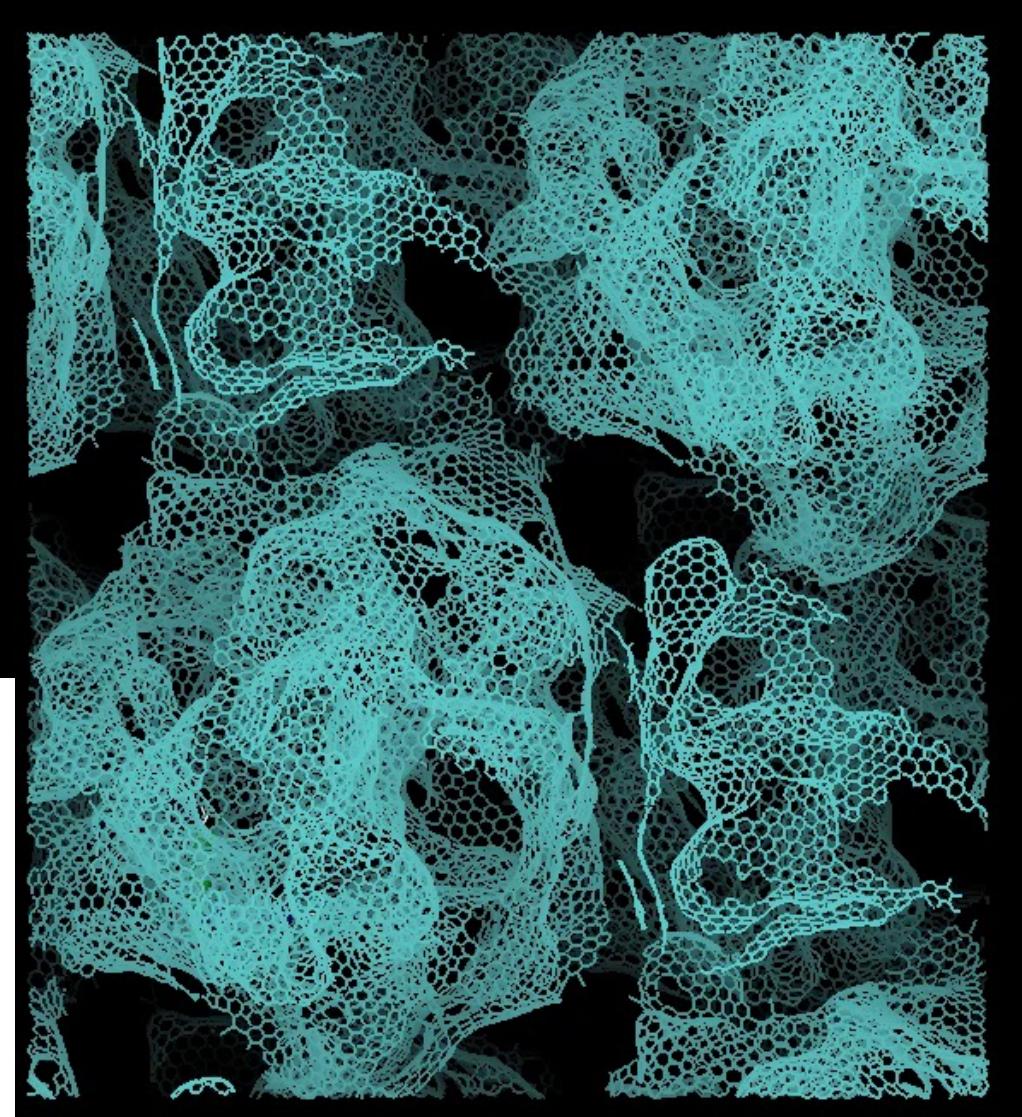
# Mechanical Metamaterial?

- A simple synthetic pathway to high surface-area, low-density nanocarbon with numerous energy & mechanical-metamaterial applications, including the reinforcement of self-healing composites



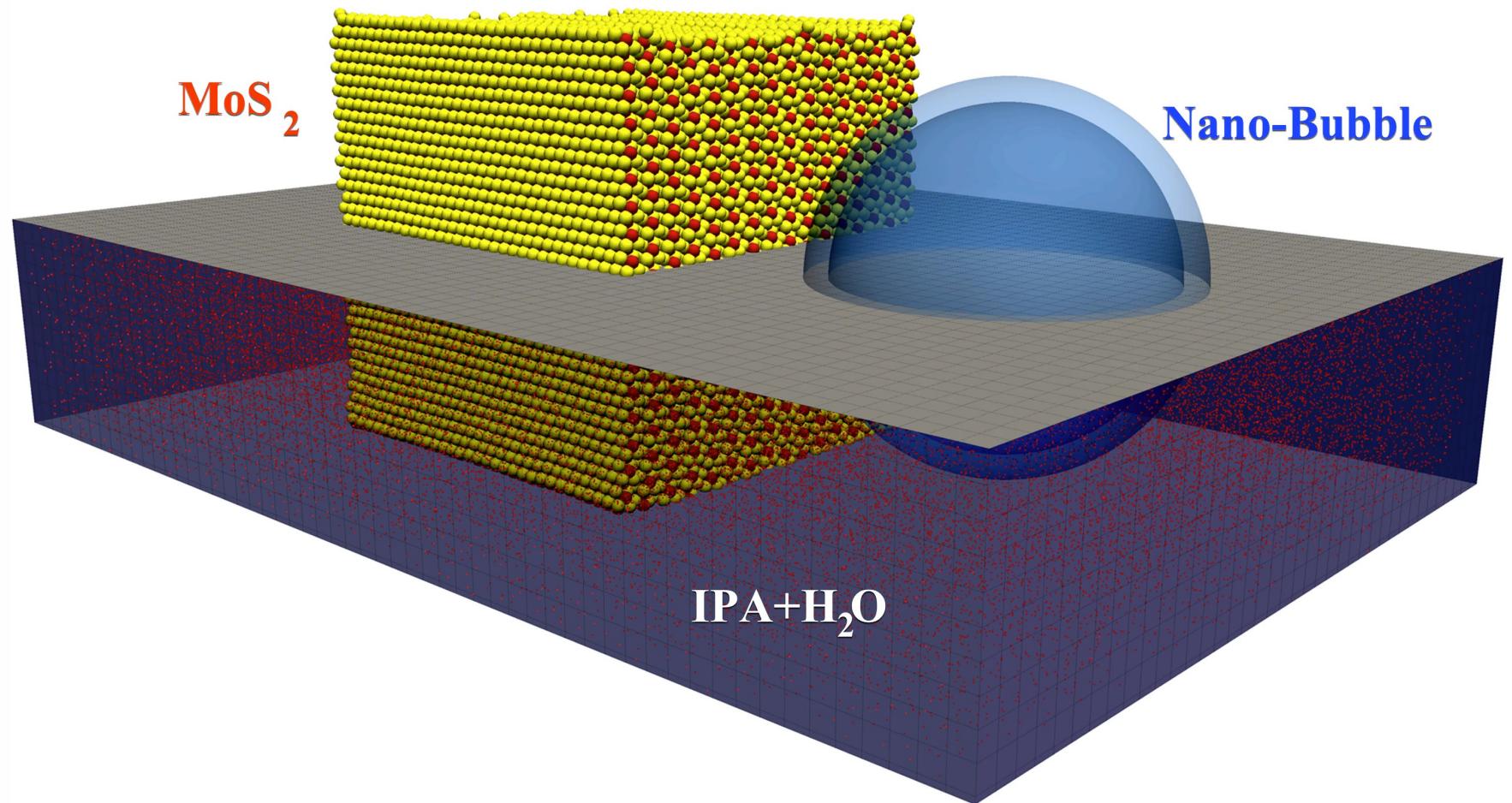
**MetaCarbon  
Under Shock Impact**

**MetaCarbon  
Under Compression**



# Molecular Mechanism of MoS<sub>2</sub> Exfoliation

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- Shear stresses on MoS<sub>2</sub> surfaces initiate exfoliation
- Shock waves reflected from MoS<sub>2</sub> surfaces enhance exfoliation

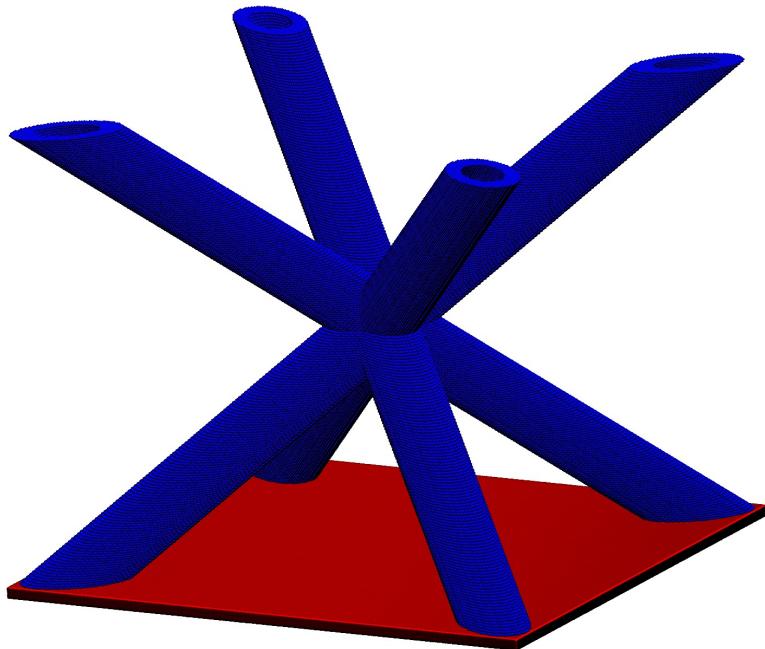
# Ultralight Mechanical Metamaterials

# Deformation of Cellular Architecture

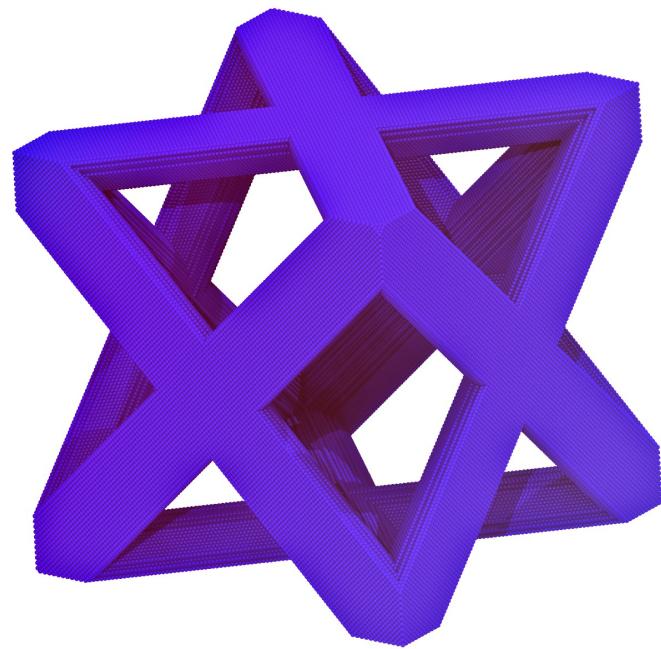
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Basic building block of cellular architecture

Kagome lattice



Octen truss

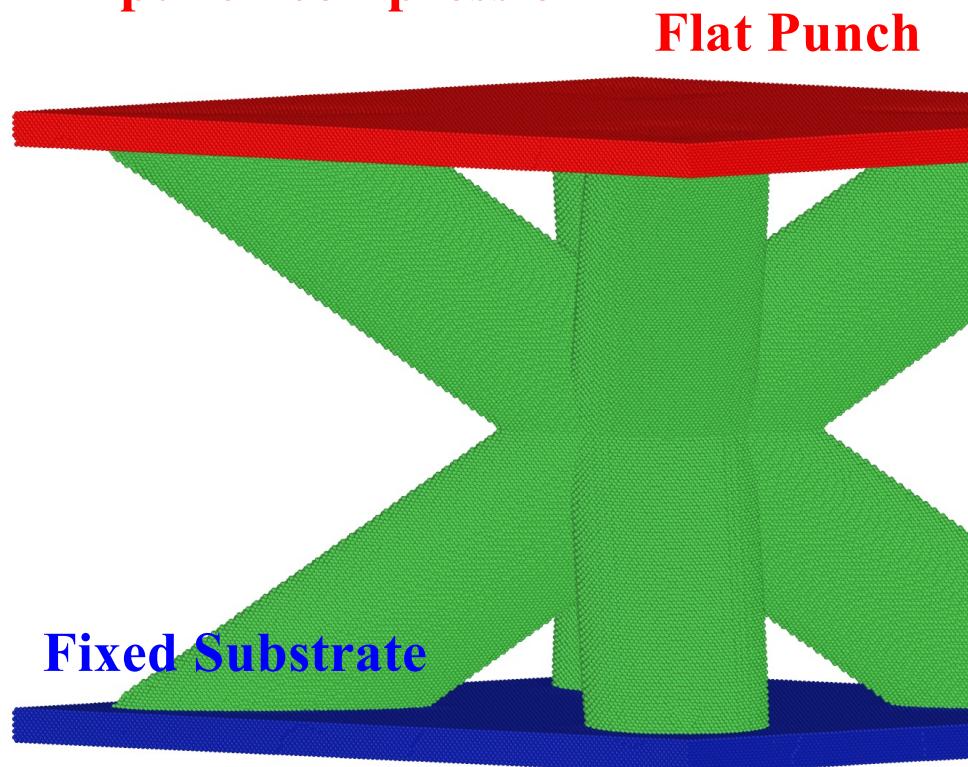


Deformation behavior of these structures at atomic level is not clear

To answer this question we have studied uniaxial compression of  
Nickel Kagome lattice using molecular dynamics simulation

# Molecular Dynamics Simulation Setup

- Uniaxial Compression of Single Kagome structure is studied using flat punch compression

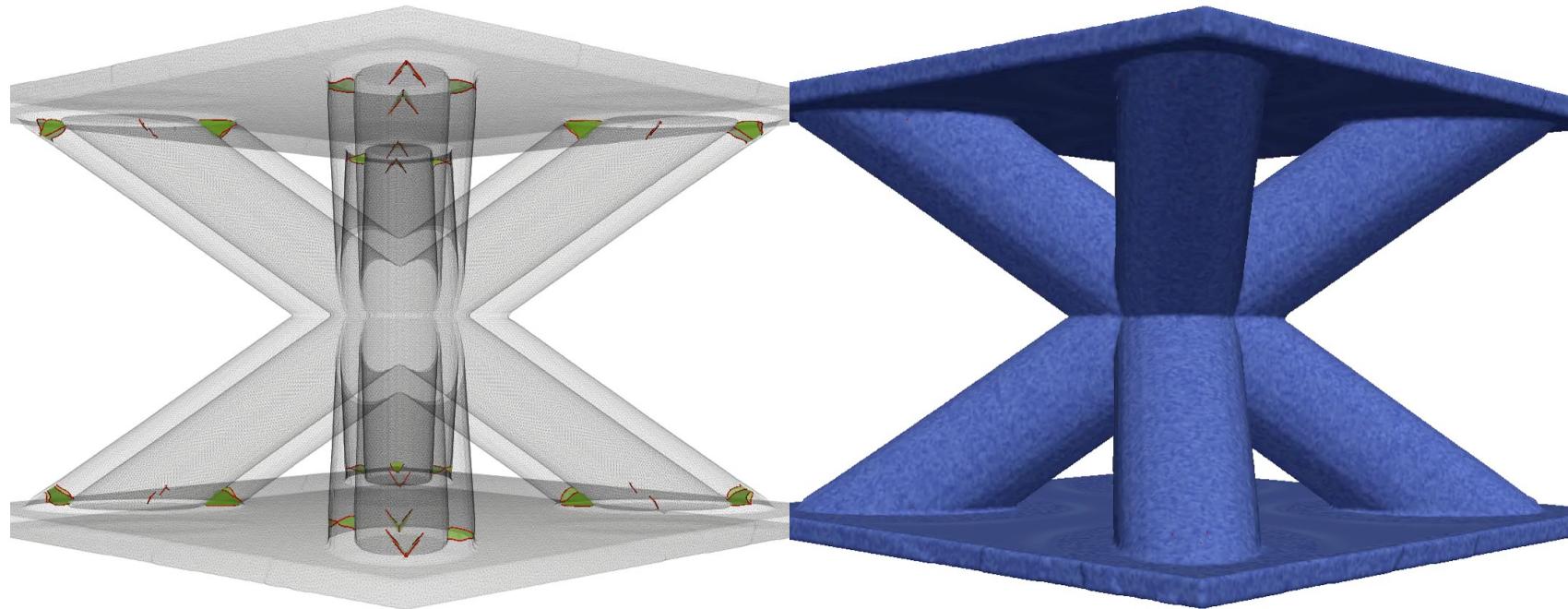


- Kagome structure made from hollow/solid Ni nanorod
- System size: 550A \* 350A \* 0A, Ni nanorod diameter 10nm & thickness 2nm
- Total number of atoms: 1 million to 2.5 million

- Flat Punch is moved at a speed of 2m/sec and after each compression of 0.5%, system is relaxed for 400ps

# Molecular Dynamics Simulation Results

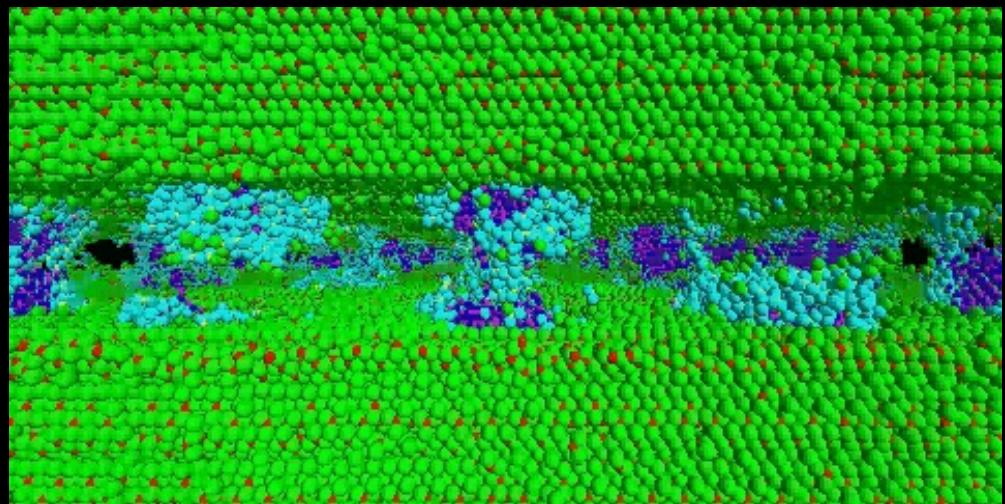
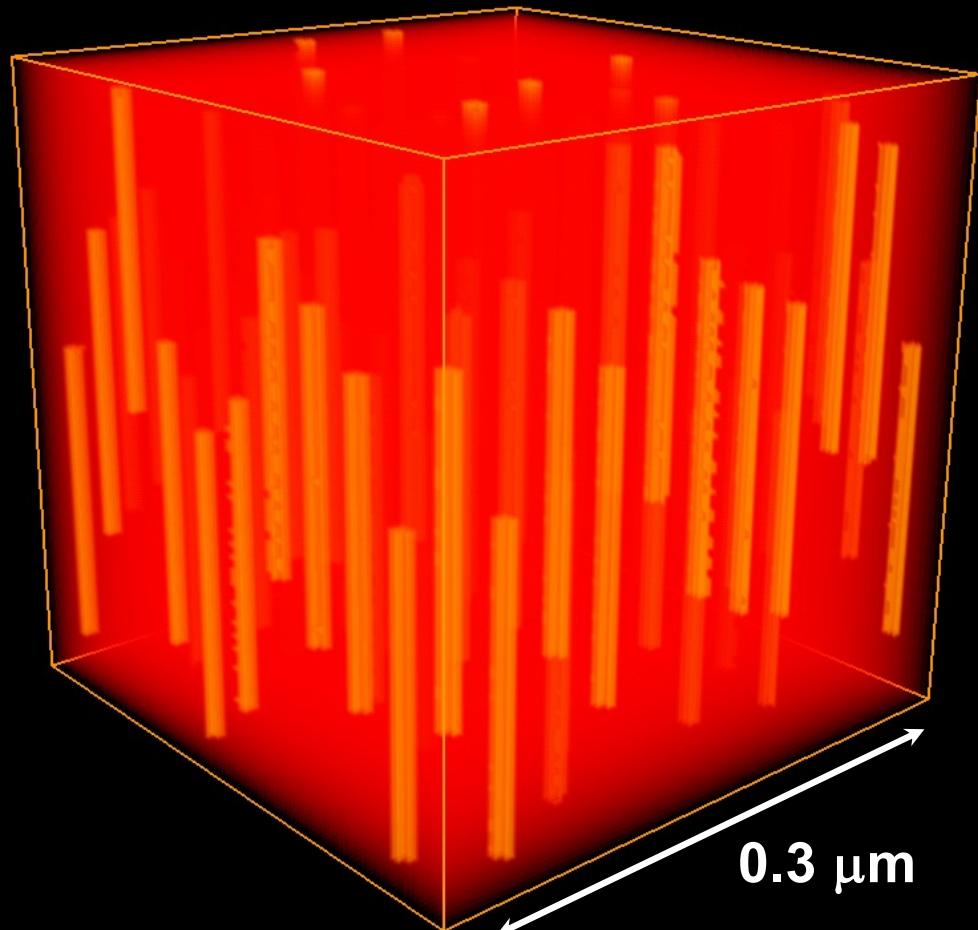
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- Mechanical Collapse of single nanorod/nanotube happens at after 3.5% strain
- Yielding in solid kagome lattice happens at 2.5% strain while for hollow lattice after 3.9% strain
- All 8 beams in solid kagome lattice shows deformation after yield point which results in the formation of several slipped and twin region in the system
- Deformation happens near the node in hollow kagome lattice up to 11% strain and after that bending of the lattice is observed

# **Si<sub>3</sub>N<sub>4</sub>-Matrix SiC-Fiber Nanocomposite**

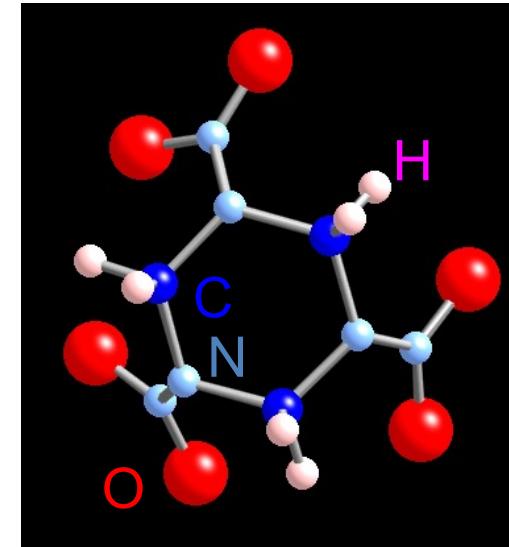
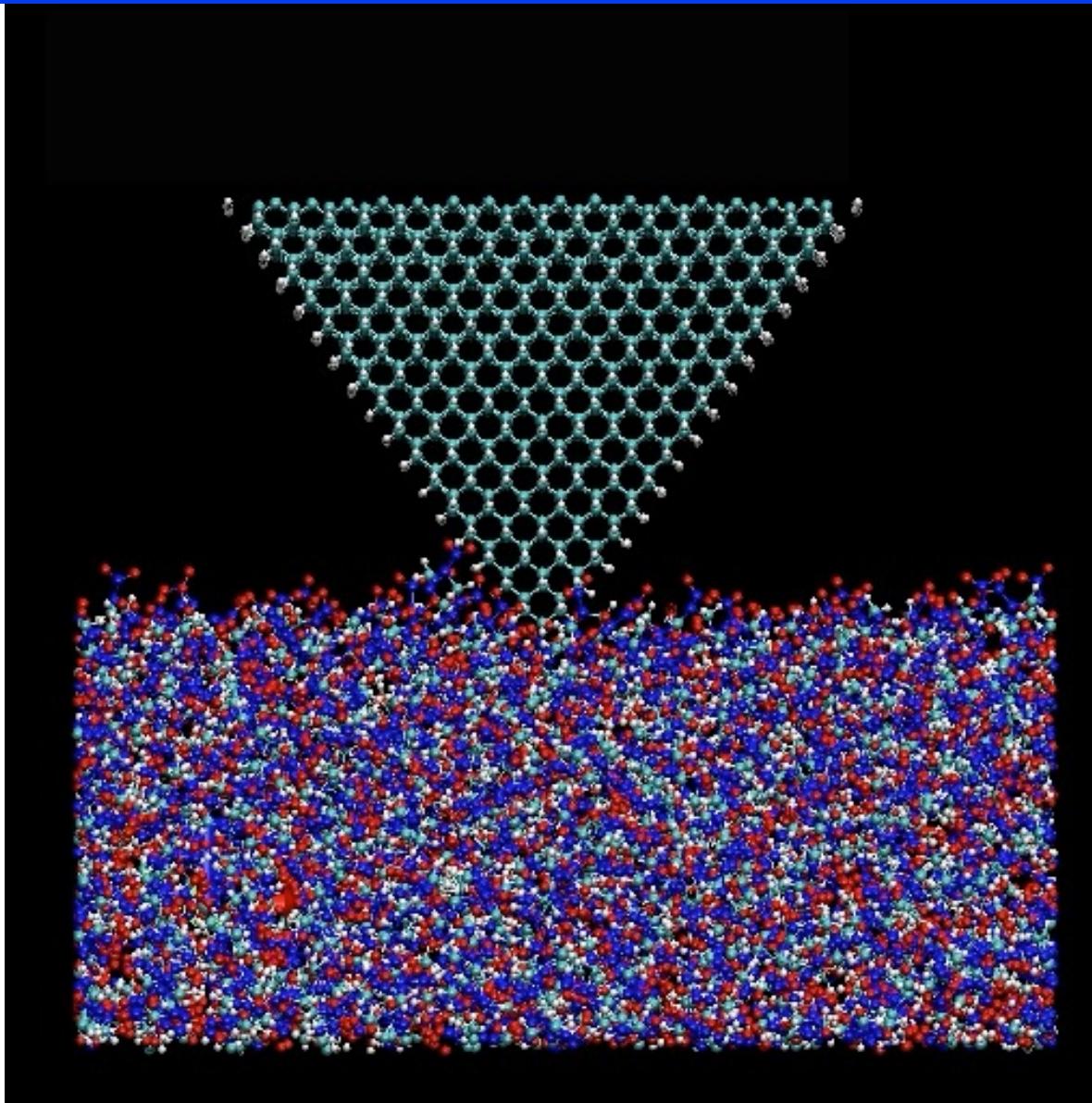
**1.5-billion-atom MD on IBM SP3**



Color code: Si<sub>3</sub>N<sub>4</sub>; SiC; SiO<sub>2</sub>

**Fracture surfaces in ceramic-fiber  
nanocomposites: Toughening mechanisms?**

# Nanoindentation on RDX Crystal



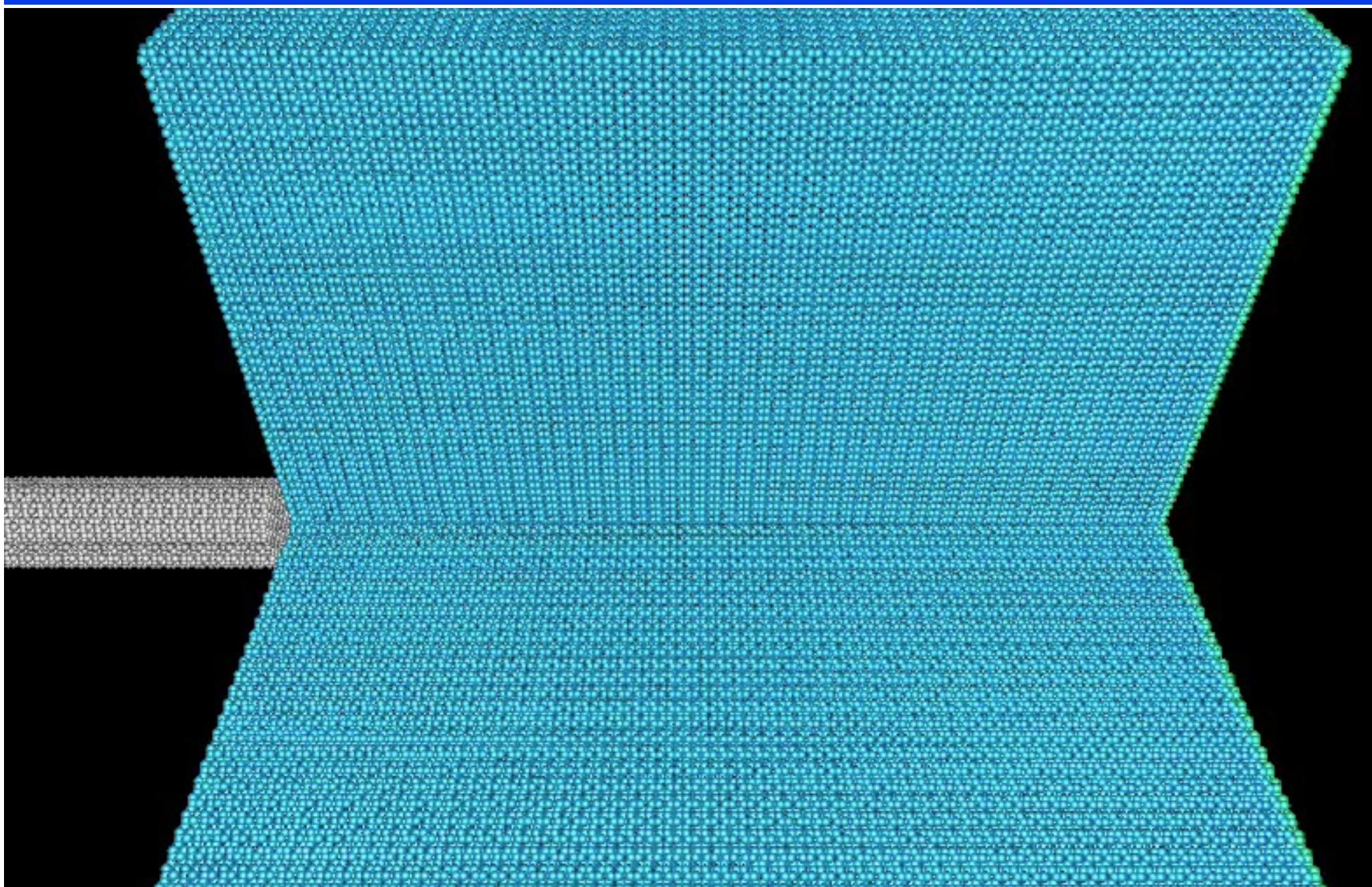
RDX molecule  
 $\text{C}_3\text{N}_6\text{O}_6\text{H}_6$

- Localized melting under a diamond AFM tip
- RDX molecules climb on the indenter surface

# Hypervelocity Impact Damage

# Damage from “Hard Impactor” in AlN Ceramic

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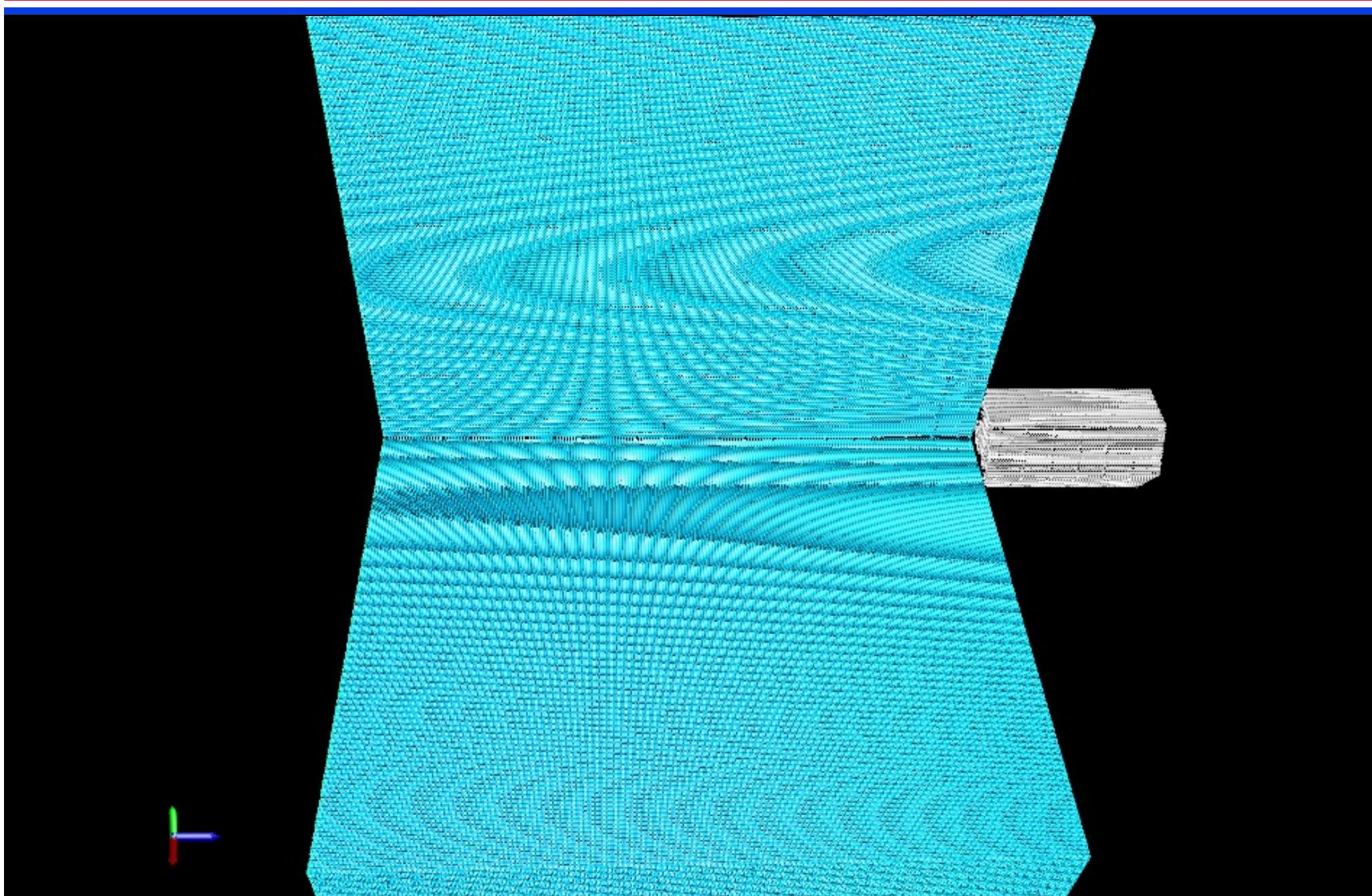
# **Damage Viewed from Behind the Impactor**

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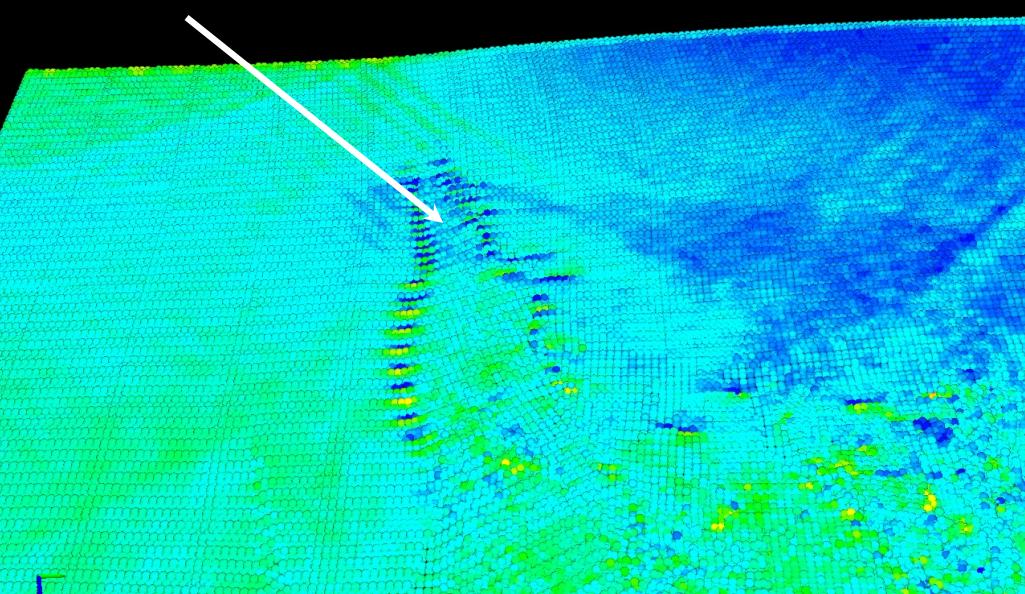
# Damage from Real Impactor in AlN Ceramic

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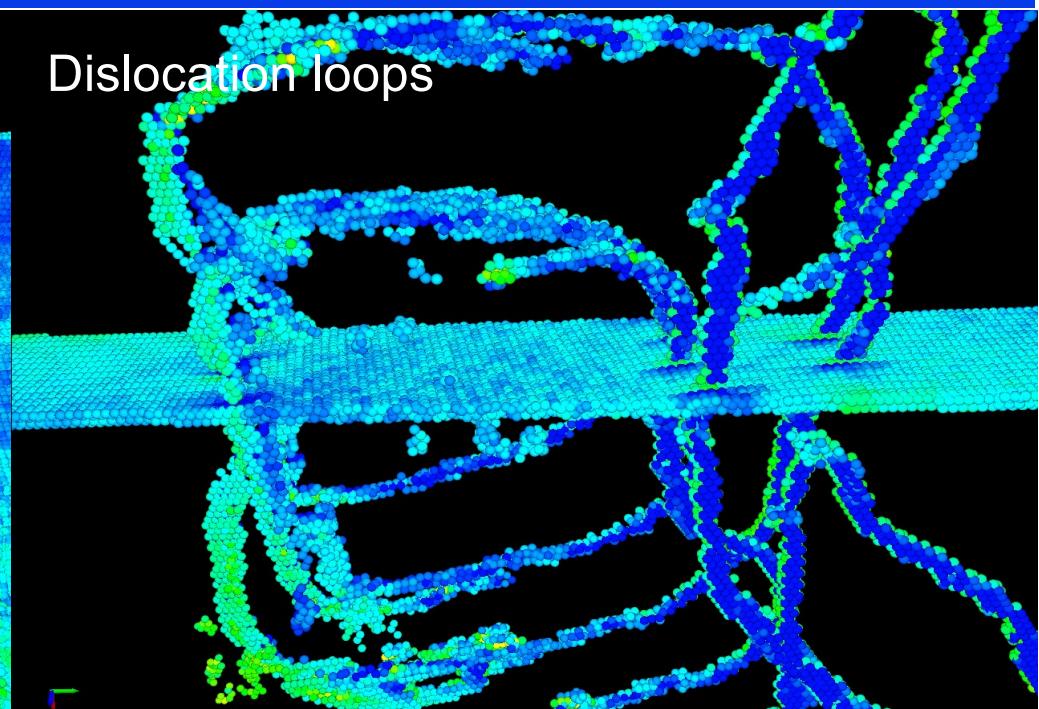


# Summary of Shock Damage in AlN

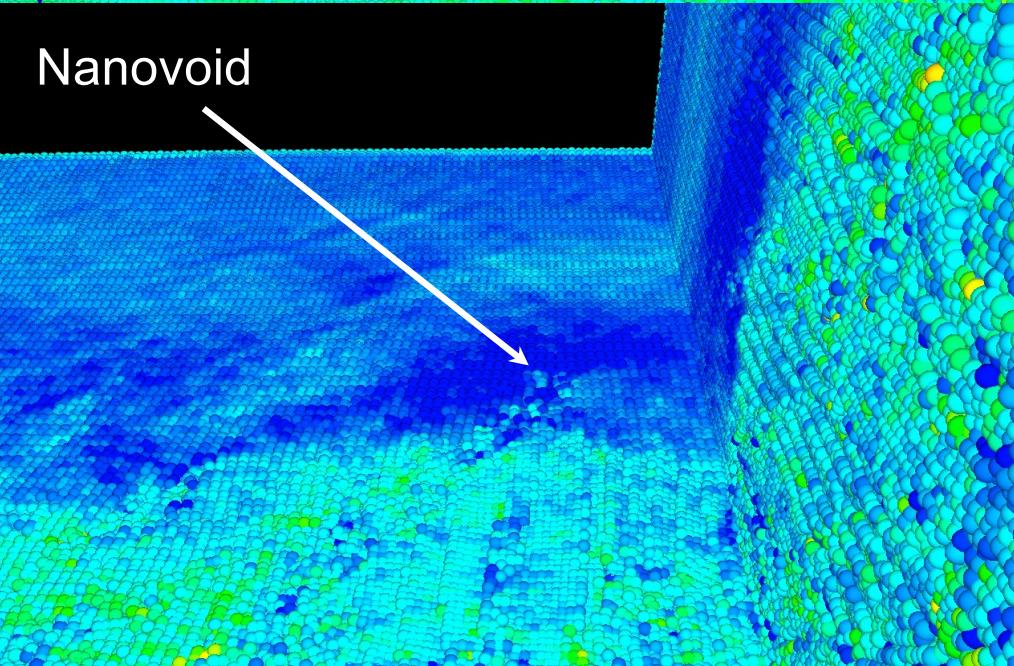
Shear band



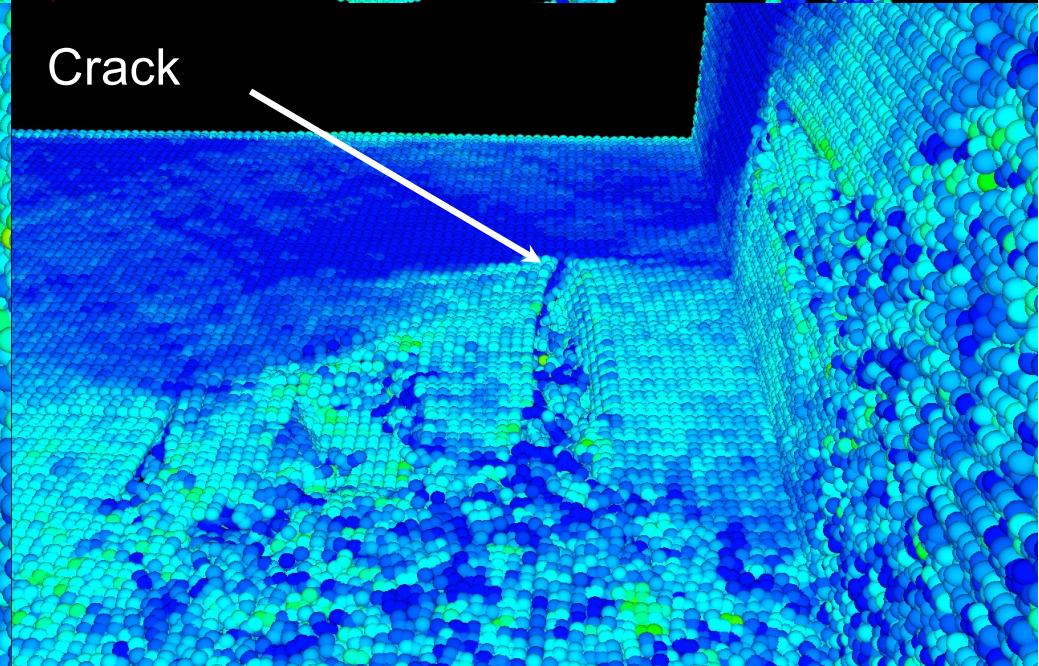
Dislocation loops



Nanovoid

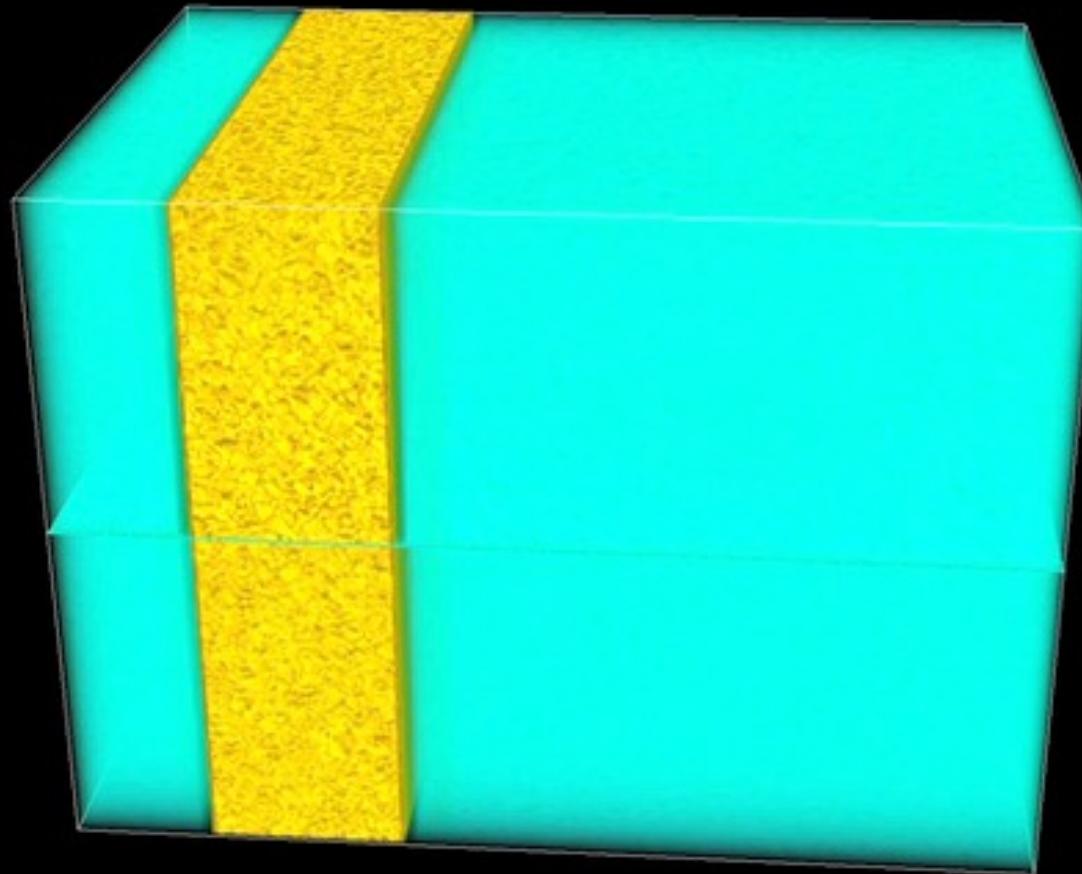


Crack

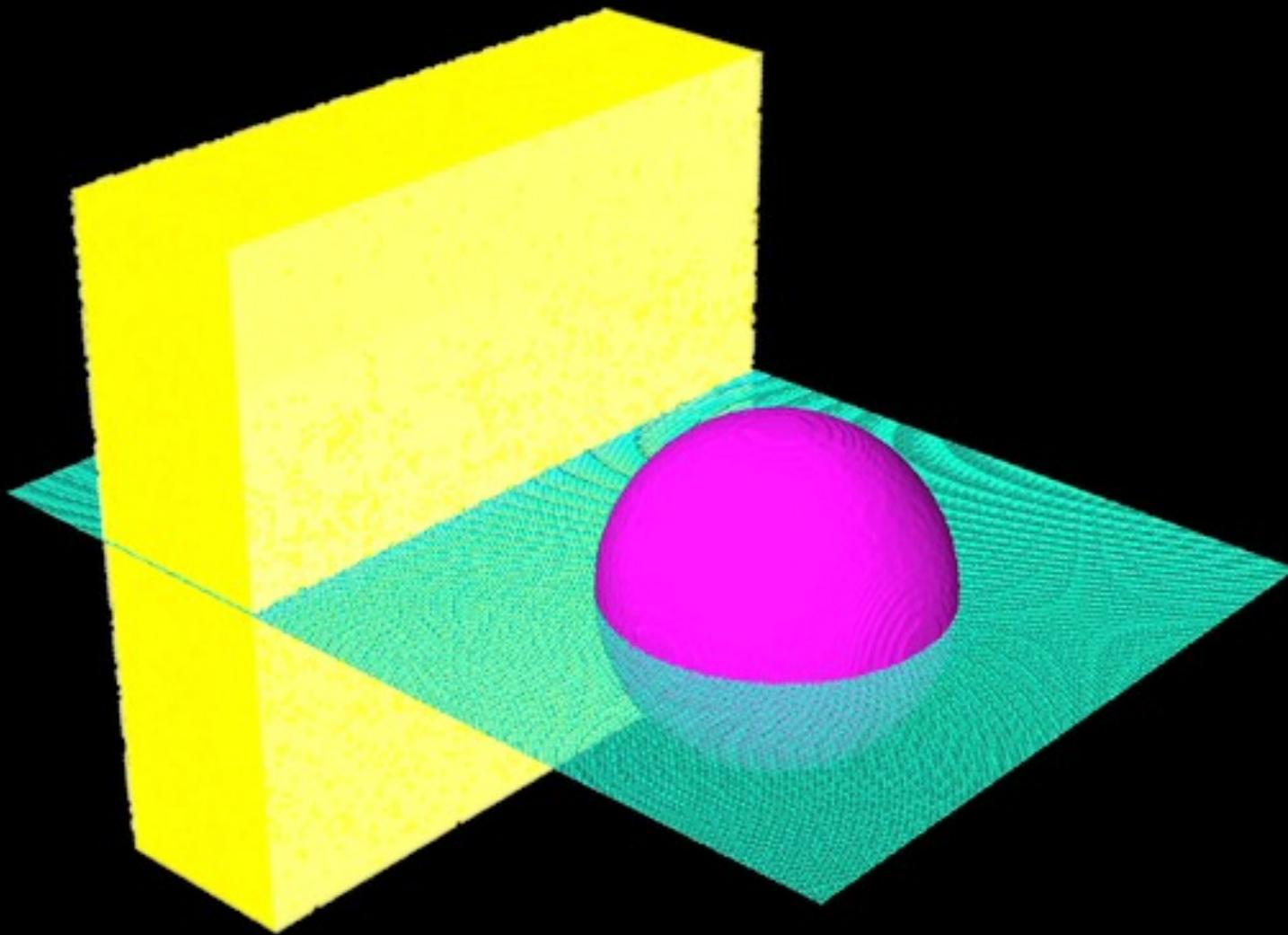


# One Billion Atom Reactive Simulation of Shock-induced Nanobubble Collapse (Empty)

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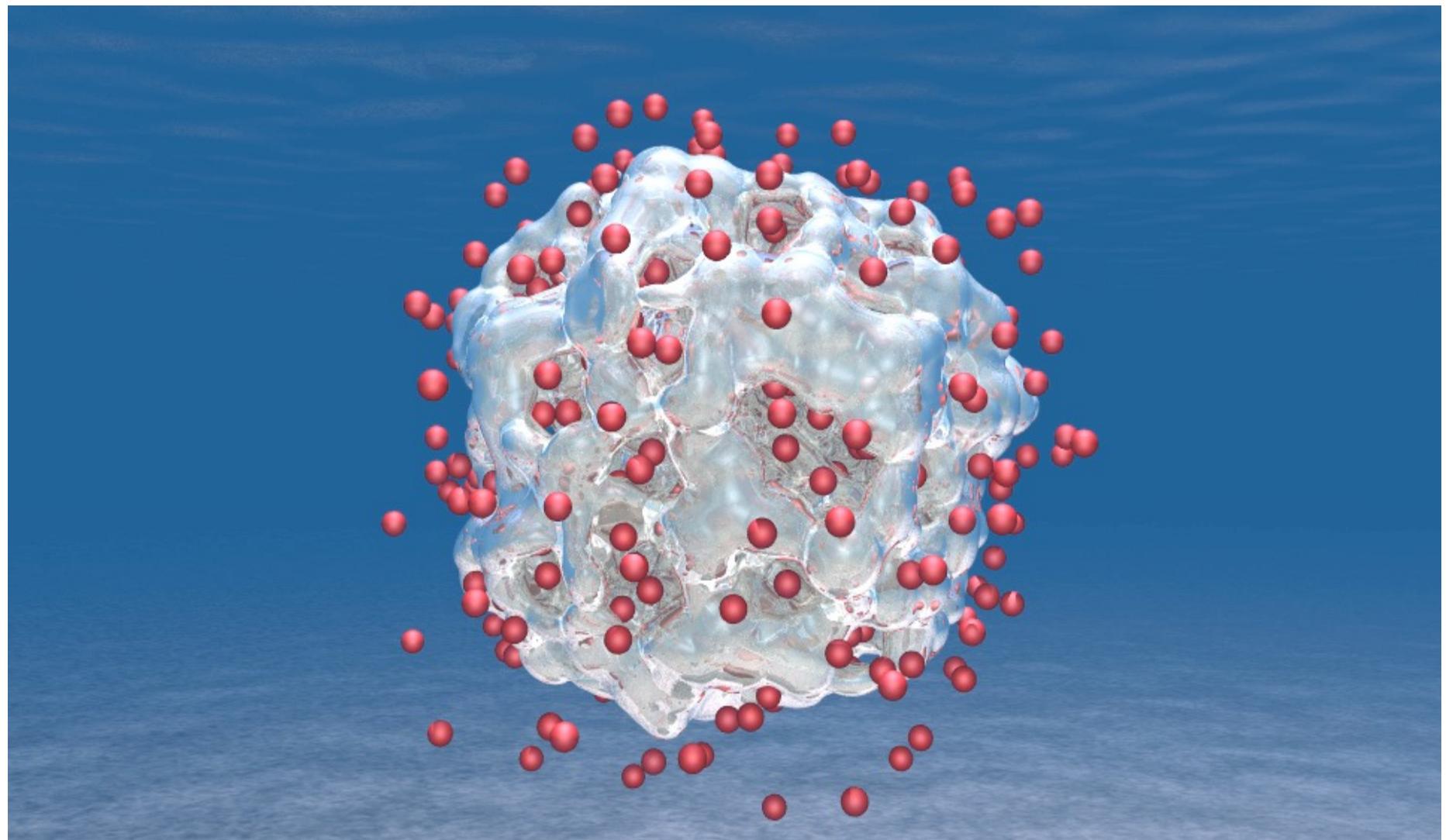


# One Billion Atom Reactive Simulation of Shock-induced Nanobubble Collapse (Gas Filled)



# H<sub>2</sub> Production from Water Using LiAl Particles

16,661-atom QMD simulation of Li<sub>441</sub>Al<sub>441</sub> in water  
on 786,432 IBM BlueGene/Q cores





**Thank you for your attention!**

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**Department of Energy**  
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