Thermomechanical Behavior & MaterialsDamage: Multimillion-Billion Atom

Reactive Molecular Dynamics Simulations

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Outline – Part I

Very Brief Introduction to Molecular Dynamics Method with Reactive Force Fields Collaboratory for Advanced Computing and Simulations: Faculty: Rajiv Kalia and Aiichiro Nakano (USC) and

Postdocs and Grad Students:

Hierarchy of Atomistic Simulation Methods



MD Simulation: Numerical Algorithm

- 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

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



- 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

MultiplePrimary surface is copied every Δt Time Step:secondary surface is copied every $n\Delta t$

Divide-&-Conquer Algorithms



- *N*-body problem: $O(N^2) \rightarrow O(N)$
 - > Space-time multiresolution molecular dynamics (MRMD): Fast multipole method & symplectic multiple time stepping
- Variable *N*-charge problem: O(N³) → O(N)
 > Fast reactive force-field (F-ReaxFF) MD: Multilevel preconditioning
- Quantum N-body problem: O(C^N) → O(N)
 > D&C density functional theory (DC-DFT) [W. Yang, '91]: Adaptive multigrids
- Multiscale QM (DC-DFT)/MD simulation [K. Morokuma et al., '96]

Divide-&-Conquer Density Functional Theory



Scalable Simulation Algorithm Suite



4.9 trillion-atom space-time multiresolution MD (MRMD) of SiO₂
8.5 billion-atom fast reactive force-field (F-ReaxFF) RMD of RDX
4.5 trillion grid points (50.3 million-atom) DC-DFT QMD of SiC Parallel efficiency over 0.9 on 786,432 BlueGene/Q cores

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 AI-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/cm³; 75% of alumina

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. Holder John P. Holdren

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

Developing a Materials Innovation Infrastructure

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 timeconsuming 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 nonempirically-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.⁸ 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 openplatform 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 userfriendly 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

Materials Genome Initiative for Global Competitiveness

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Sulfur Segregation-Induced Embrittlement of Nickel

• Experiments at Argonne discovered a relation between S segregation-induced embrittlement & amorphization of Ni



 48 million-atom reactive moleculardynamic simulation (the largest ever) on 65,536 IBM BlueGene/P processors (50 million cpu-hours) at Argonne reveals an atomistic mechanism that links amorphization & embrittlement

USC-Purdue-CSUN-Harvard-LANL-LLNL OASCR-BES-NNSA SciDAC on Stress Corrosion Cracking



Ductile tearing in nanocrystalline Ni



Brittle cleavage with S segregation

Quantum MD of Al/Fe₂O₃ Thermite Reaction



 $2AI + Fe_2O_3 \rightarrow AI_2O_3 + 2Fe$

Nanoindentation on RDX Crystal





 $\begin{array}{c} \text{RDX molecule} \\ \text{C}_{3}\text{N}_{6}\text{O}_{6}\text{H}_{6} \end{array}$

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

Dynamics: RDX Molecules Walking



 $\begin{array}{c} \text{RDX molecule} \\ \text{C}_3\text{N}_6\text{O}_6\text{H}_6 \end{array}$

- Directed self-assembly of molecules
- Active sensing of explosives?

Maximum speed of RDX Molecules ~ 373 Meters/second

Design of Self-Healing Materials

Self-healing Ceramics

Al₂O₃ reinforced by SiC whiskers containing surface cracks and pre-healed at elevated temperature shows crack healing phenomena under three point bend test

Fracture of an Alumina Crystal Embedded with Silicon Carbide Nanoparticles (SiC-NPs)

System dimensions: 320x100x30 nm³ Total number of atoms: 112,377,540

NP radius: 5nm Number of NPs: 328 NP-Alumina volume ratio: 0.18

Temperature: 300K Strain Rate: 10⁹ sec⁻¹

NPs are randomly distributed in the alumina matrix

Interfacial Bond Purification by Annealing

K. Shimamura et al., Phys. Rev. Lett. 111, 066103 ('13)

SiC-NP Oxidation Simulation: 1000K

SiC-NP Oxidation Simulation: 1800K

SiC-NP Oxidation: Results

1000K O Si C 1800K

At 1000K, minor reaction on NP surface is observed. At 1800K, the formation of oxide layer and the large amount of CO₂ release are observed.

SiO₂ Nanoparticles embedded in Alumina Crystal

SiO₂ NPs melt at 1800K and molten silica flows into a crack tip

Hydrogen Production from Water by Superatoms

 DFT-based MD simulations show rapid H₂ production from water by aluminum superatoms (A₁₂ to A₁₈) & elucidate the mechanisms

ScienceNews, March 4, 2010 issue

H, **O**, Al

Fuyuki Shimojo, Satoshi Ohmura, Aiichiro Nakano, Rajiv K. Kalia & Priya Vashishta, Physical Review Letters <u>104</u>, 126102 (2010)

Al_n Superatoms & H₂O: Experiments and Theory

Patrick J. Roach, W. Hunter Woodward, A. W. Castleman Jr., Arthur C. Reber, Shiv N. Khanna, Science 323(2009) 492

Hydrogen Molecule (H₂) Production

• Two atoms are considered bonded when they are within a cutoff distance for a time duration of more than 12 fs

Hydrogen Production by Al₁₇ in Water

• DFT-based MD shows rapid H₂ production from water by a superatom (Al₁₇)

Rapid Hydrogen Production Mechanism

• Found a low activation-barrier H₂ production mechanism at a pair of Lewis acid & base sites on Al₁₂ surface:

$AI-OH_2 + AI'-H \rightarrow AI-OH + AI' + H_2$

 Nudged elastic-band estimation of the activation barrier ∆ = 0.1 eV
 → reaction rate at temperature 300K

$$k_{\rm H_2} = (k_{\rm B}T / h) \exp(-\Delta / k_{\rm B}T_{\rm room})$$

= 10¹¹(s⁻¹)

Low energy barrier ~0.1 eV for our hydrogen production mechanism

Proton Transport Mechanism in Water Grotthuss Mechanism Published in 1806!

- Grotthuss proposed the mechanism in 1806!!!
- "Theory of decomposition of liquids by electrical currents" by <u>Theodor Grotthuss</u> (1806)
- Proton diffuses along a chain of hydrogen bonds in water by attaching and detaching along the chain of water molecules.
- We define the chain length l is the number of oxygen atoms, e.g. l = 4.

In our Quantum Molecular Dynamics, simulations we observe H transport by Grotthuss Mechanism involved in H₂ production.

Oxidization of Al₁₈: Al-O-Al Bond Formation

 Al_{18} *at t* = 17.23 ps

...AI-O-AI...

Al oxidization observed in Al₁₈ system

Conclusions for H₂ Production

- 1) Fast hydrogen (H₂) production is observed in the reaction Al_n (n = 12, 16, 17, 18) superatoms with water. Unlike experiments there is no size selectivity of Al_n.
- 2) New mechanism (different from the one proposed in the experimental paper in Science) gives energy barriers as low as 0.02eV indicating a fast reaction rate.

School of Engineering

H₂ Production from Water Using LiAl Particles

16,661-atom QMD simulation of Li_nAl_m in water on 786,432 IBM BlueGene/Q cores

High-Yield H₂-Production Mechanism

• Low H₂-production yield using Al particles: Formation of passive oxide coating layer

Formation of a passive oxide layer on an Al nanoparticle in oxygen environment

• High yield using LiAl particles: Dissolution of Li into water produces corrosive basic solution to prevent coating formation

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

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

Conclusion

- **1.** Scalable reactive atomistic simulations based on spatiotemporal data locality principles
- 2. Broad materials & energy applications

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