SAND2016-9264PE

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Sandia National Laboratories

# Predictive Atomistic Simulations of Materials Using LAMMPS

**Aidan P. Thompson**

Center for Computing Research

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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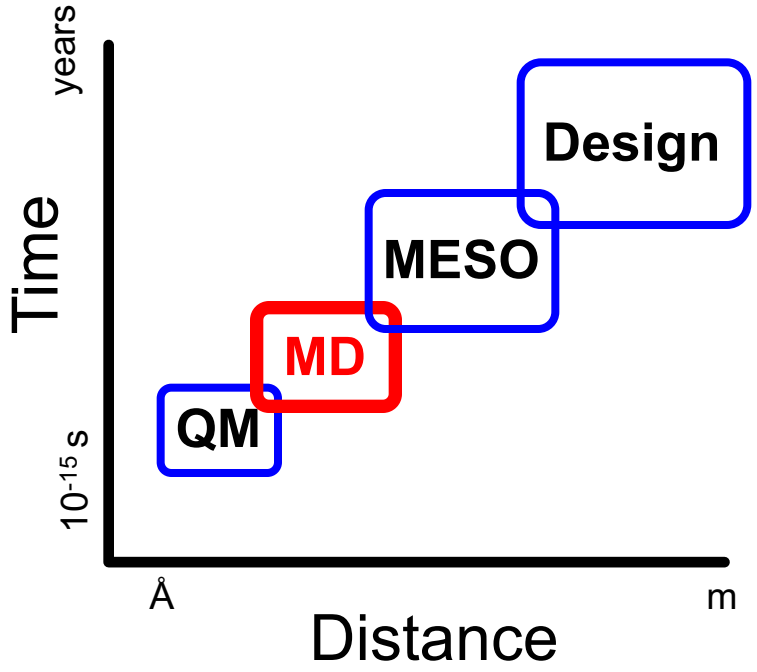
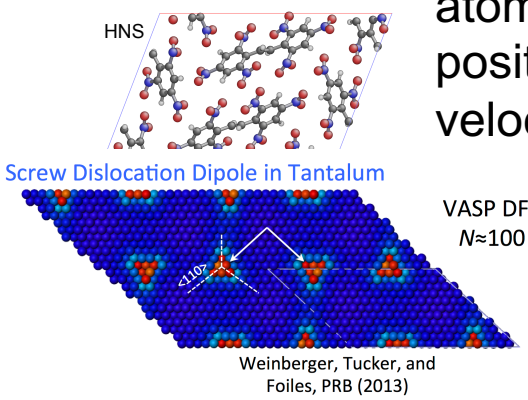
# Talk Outline

- **Molecular Dynamics**
- Interatomic Potentials
- ReaxFF
- SNAP
- Outlook

# What is Molecular Dynamics Simulation?

- Continuum models require underlying models of the materials behavior
- Quantum methods can provide very complete description for 100s of atoms
- Molecular Dynamics acts as the “missing link”
  - Bridges between quantum and continuum models
  - Moreover, extends quantum accuracy to continuum length scales; retaining atomistic information

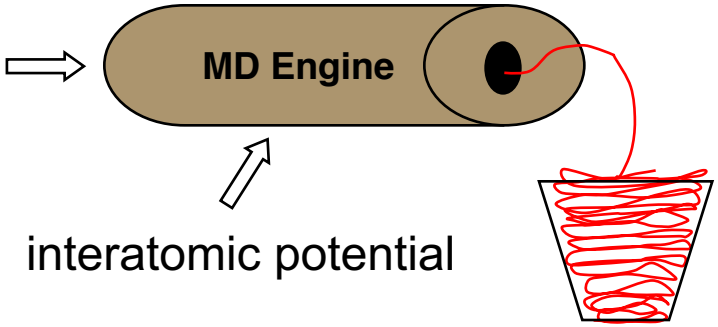



Weinberger, Tucker, and Foiles, PRB (2013)

VASP DFT
$N \approx 100$

atoms, positions, velocities




Positions, velocities and forces at many later times

# Example: Plasticity in BCC Metals

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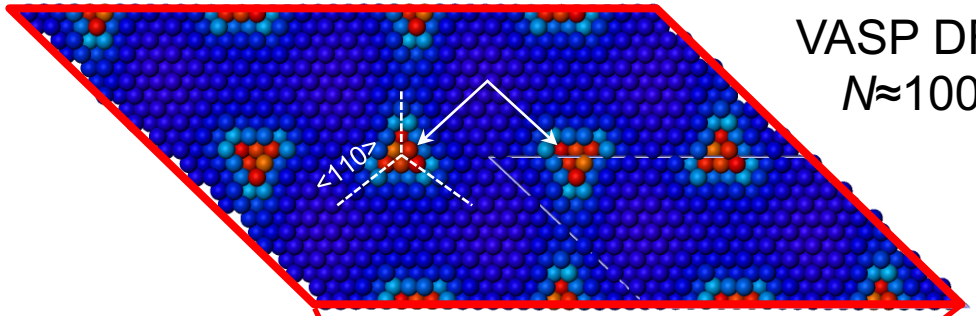
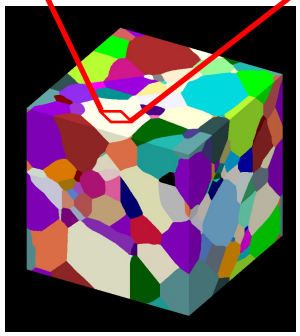
Screw Dislocation Motion in BCC Tantalum




VASP DFT
$N \approx 100$

Weinberger, Tucker, and Foiles, PRB (2013)

Polycrystalline Tantalum Sample



LAMMPS MD
$N \approx 10^8$

# What is LAMMPS?

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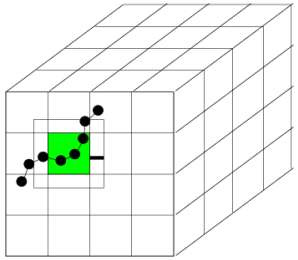
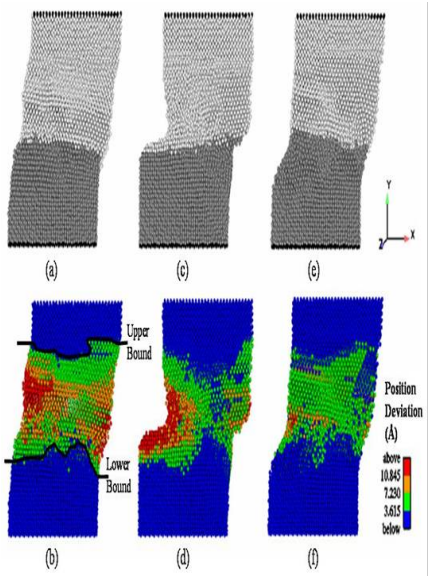
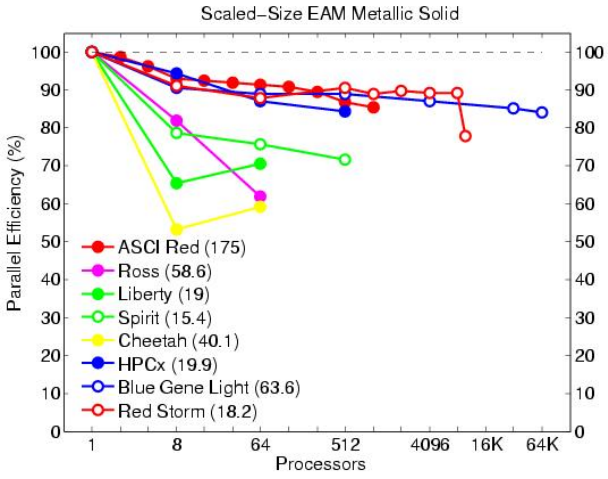
(Large-scale Atomic/Molecular Massively Parallel Simulator)

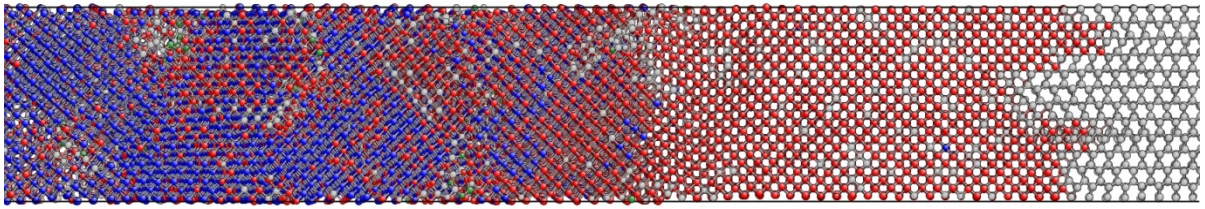
http://lammps.sandia.gov

- Classical MD code.
- Open source, highly portable C++.
- Freely available for download under GPL.
- Easy to download, install, and run.
- Well documented.
- Easy to modify or extend with new features and functionality.
- Active user's e-mail list with over 650 subscribers.
- More that 1000 citations/year
- Users' workshops: 2010, 2011, 2013, 2015
- Spatial-decomposition of simulation domain for parallelism.
- Energy minimization via conjugate-gradient relaxation.
- Atomistic, mesoscale, and coarse-grain simulations.
- Variety of potentials (including many-body and coarse-grain).
- Variety of boundary conditions, constraints, etc.





# MD is Big Consumer of Computer Time

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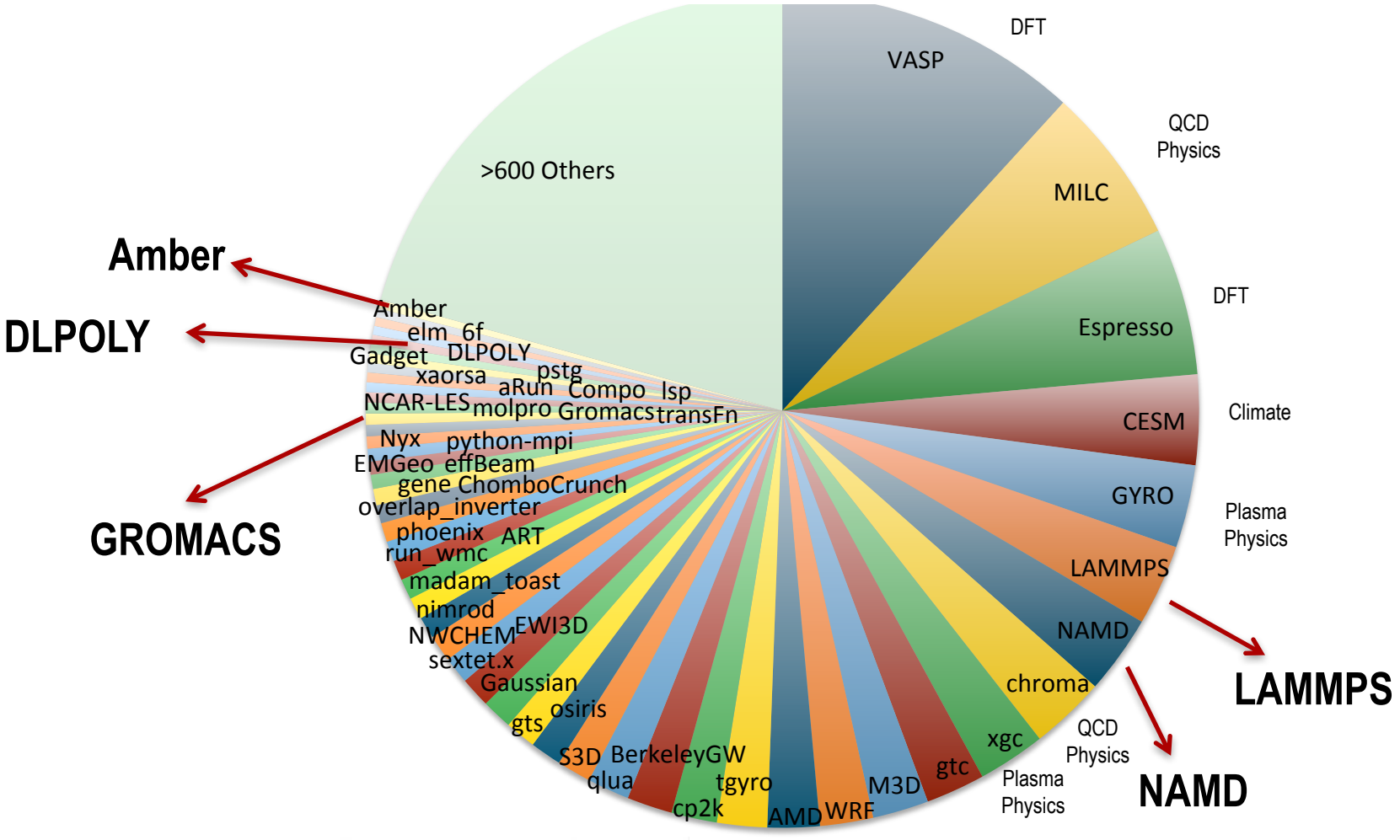


**2014 Top Application Codes at NERSC (Hopper and Edison)**

# Growth in Use of MD

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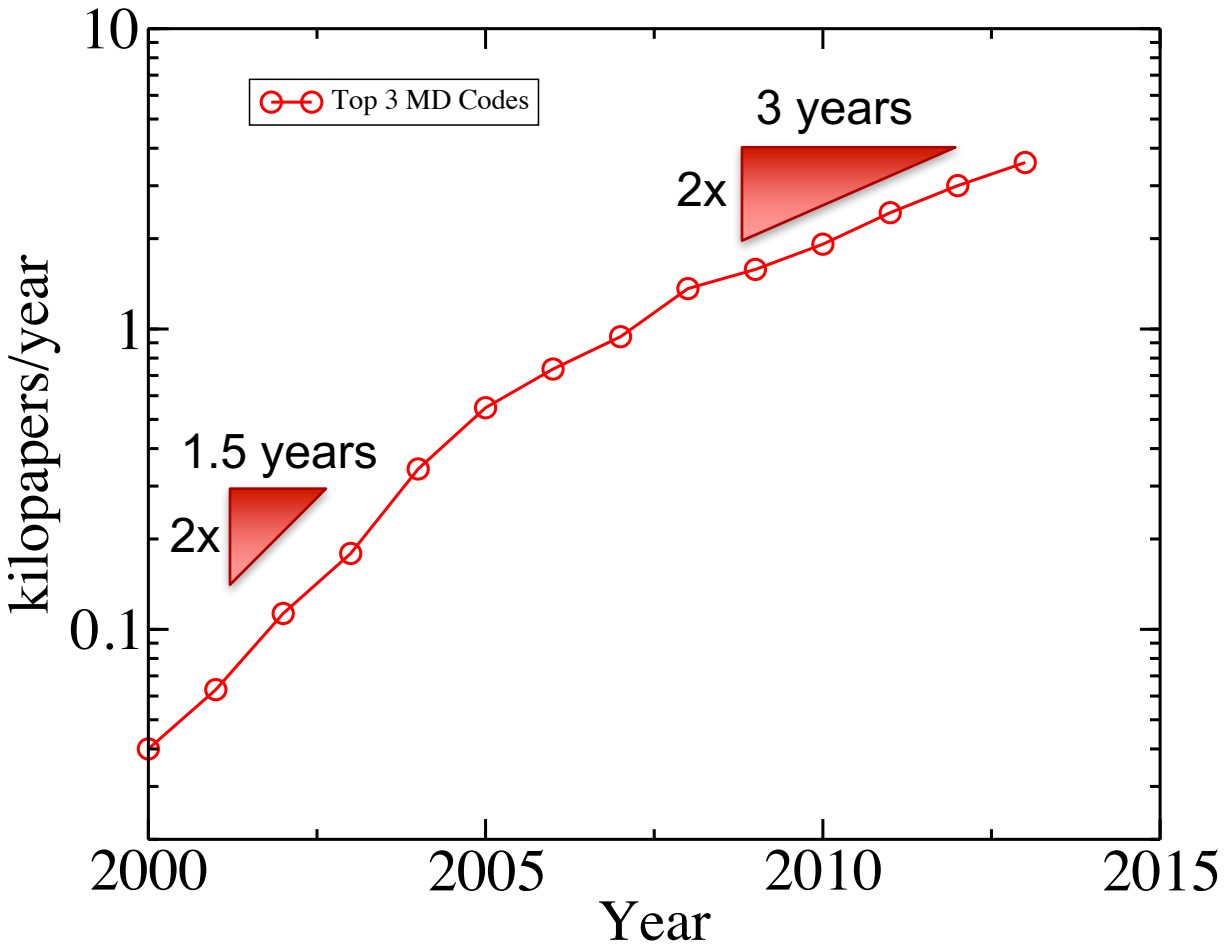
"*Global scientific output doubles every nine years or 8-9% per year*"
Nature, May 2014

Papers citing LAMMPS, NAMD, GROMACS
Measured using Web of Science citation reports



# Talk Outline

- Molecular Dynamics
- **Interatomic Potentials**
- ReaxFF
- SNAP
- Outlook

# Historical Development for Potentials

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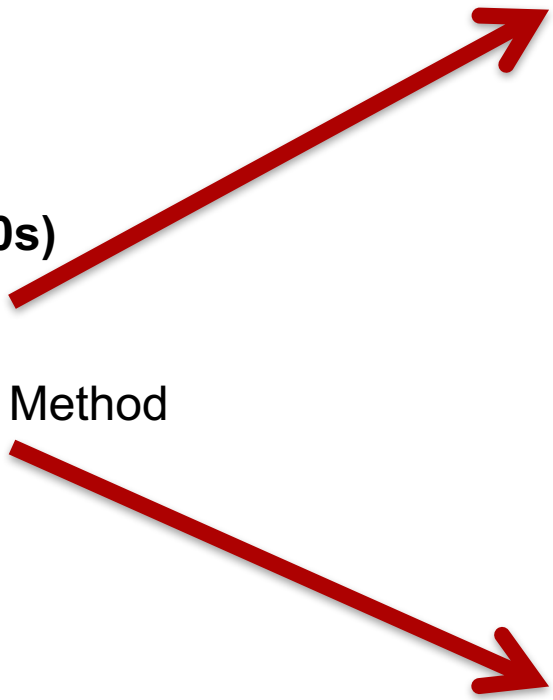
**Twobody (B.C.)**
Lennard-Jones
Hard Sphere
Coulomb
Bonded

**Manybody (1980s)**
Stillinger-Weber
Tersoff
Embedded Atom Method



**Threebody Potentials for Covalent Solids**
Diamond and other low symmetry crystals unstable for pure twobody potentials.
**Solution**: Add threebody angle terms
Tersoff
Stillinger-Weber

**Manybody Potentials for Metals**
Pure twobody potentials satisfy certain constraints:
$C_{12} = C_{14}$; $E_v = E_{coh}$
For FCC metals:
$C_{12}/C_{14} \approx 2$; $E_v/E_{coh} \approx 0.35$
**Solution**: Add manybody "embedding" energy
Embedded Atom Method
Finnis-Sinclair

# Historical Development for Potentials

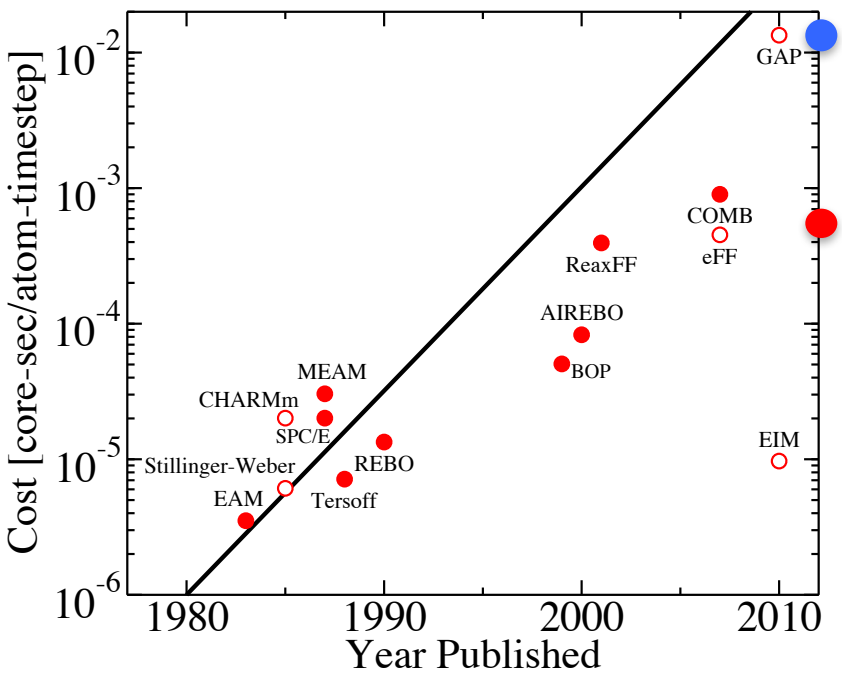
**Twobody (B.C.)**
Lennard-Jones
Hard Sphere
Coulomb
Bonded

**Manybody (1980s)**
Stillinger-Weber
Tersoff
Embedded Atom Method

**Advanced (90s-2000s)**
REBO
BOP
COMB
ReaxFF

**Big/Deep/Machine Data/Learning (2010s)**
GAP, SNAP, NN,…

Moore's Law for Interatomic Potentials
Plimpton and Thompson, MRS Bulletin (2012).




**Drivers**
- Increased computer resources
- Application to Real Materials
- Quantum Methods

# Two philosophical extremes in the development of interatomic potential models

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## *The Force!*

- Functional forms based on fundamental understanding of electronic origins of bonding
  - Bond Order Potentials (BOP)
  - Model Generalized Pseudopotential Theory (MGPT)
  - COMB
  - ReaxFF
  - …
- Gives confidence that it will interpolate/extrapolate reasonably

**Luke:** ***Is the dark side stronger?***
**Yoda:** ***No, no no. Quicker, easier, more seductive.***

## *The Dark Side!*

- Empirical fit of a flexible functional form
  - Gaussian Approximation Potentials (GAP)
  - Spectral Neighbor Analysis Potential (SNAP) - this work
  - …
- Replaces the need for intuition/art with extensive computation
  - Automate the fitting process?
  - Apply across multiple materials classes?

**Darth Vader:** ***You underestimate the power of the dark side!***

Borrowed from **Stephen Foiles** and Lucasfilm

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# ReaxFF Potential

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**van Duin**, Dasgupta, Lorant, and Goddard, *J. Phys. Chem. A*, **105** 9396 (2001)

$$E^{ReaxFF} = E^{vdW} + E^{Coul} + E^{polar}$$

Twobody Repulsion and Charge

$$+ E^{over} + E^{under}$$

Manybody Atom Coordination

$$+ E^{bond} + E^{angle} + E^{torsion}$$

Standard 2-, 3-, 4-Body Bonding Terms

$$+ E^{lone-pair} + E^{angle,penalty}$$

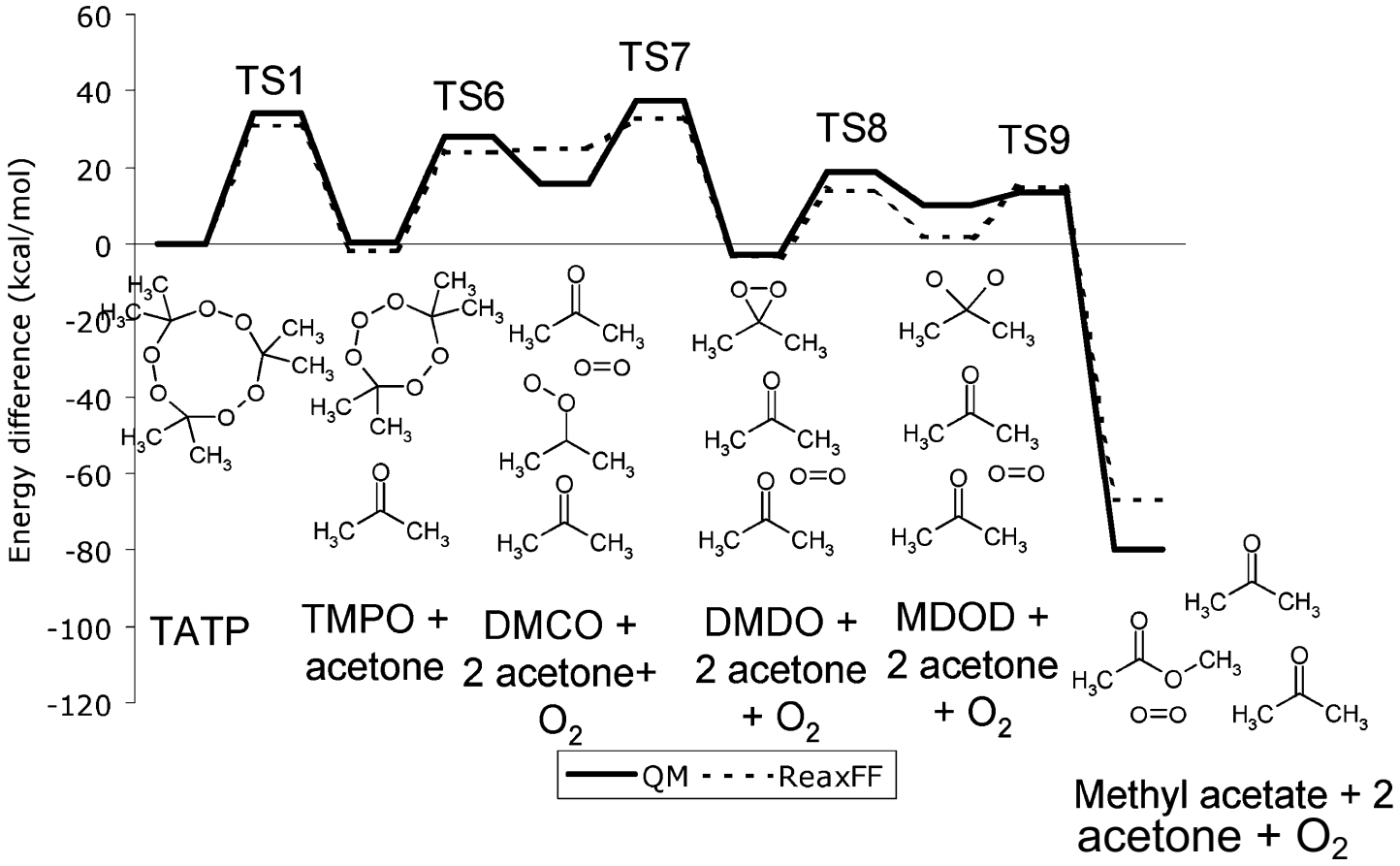
$$+ E^{conj} + E^{angle,conj} + E^{H-bond}$$

Special Chemical Bonding Terms

- Very powerful formulation
- About 100 citations/year
- Typical ReaxFF parameterization involves several hundred parameters
- Fit to large data sets of small gas phase QM calculations
- A lot of art involved in the fitting process

# ReaxFF for Decomposition of TATP

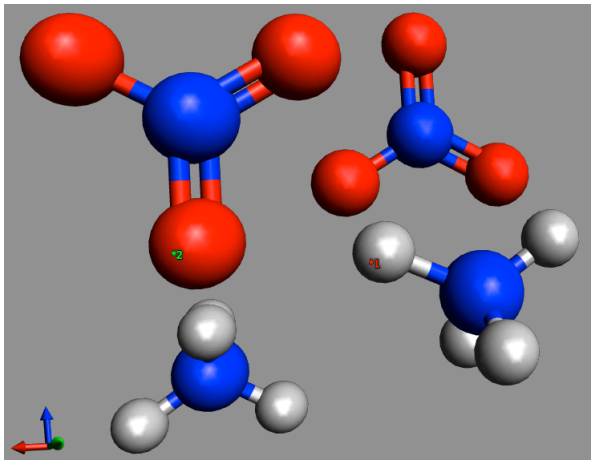
- QM and ReaxFF energies for a TATP unimolecular dissociation pathway



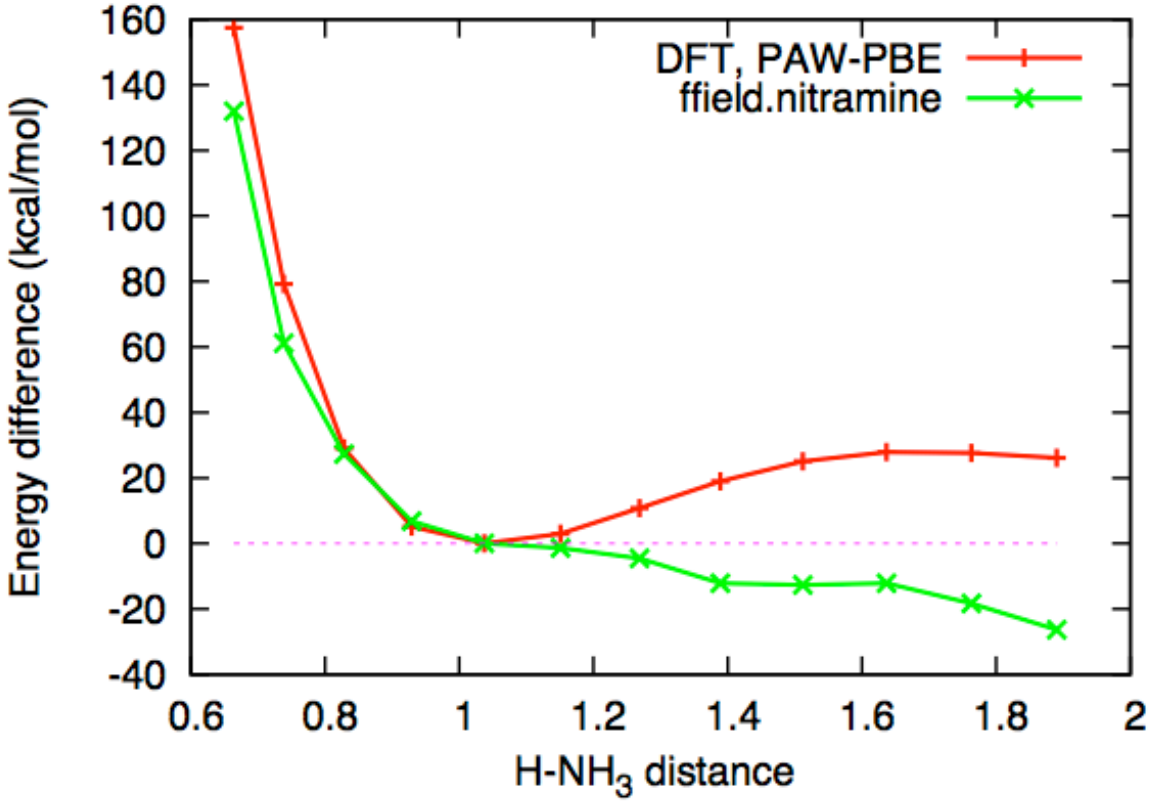



A. C. T. **van Duin**, Y. **Zeiri**, F. **Dubnikova**, R. **Kosloff**, W. A. **Goddard III**, J. Am. Chem. Soc. 127, 11053 (2005)

# ReaxFF for ANFO

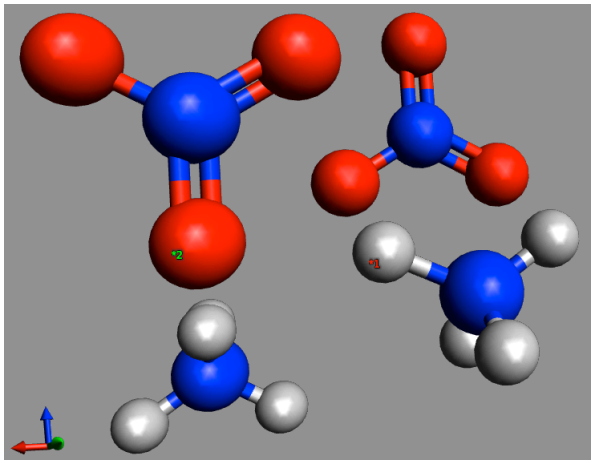


- One AN IV unitcell.
- Scanning one H moving from $NH_4$ to $NO_3$with VASP
- Ions fixed, electrons relaxed




- VASP calculations indicate stable NH4-NO3
- However more stable to decompose to NH3 + HNO3 with the general nitramine force filed

# ReaxFF for ANFO



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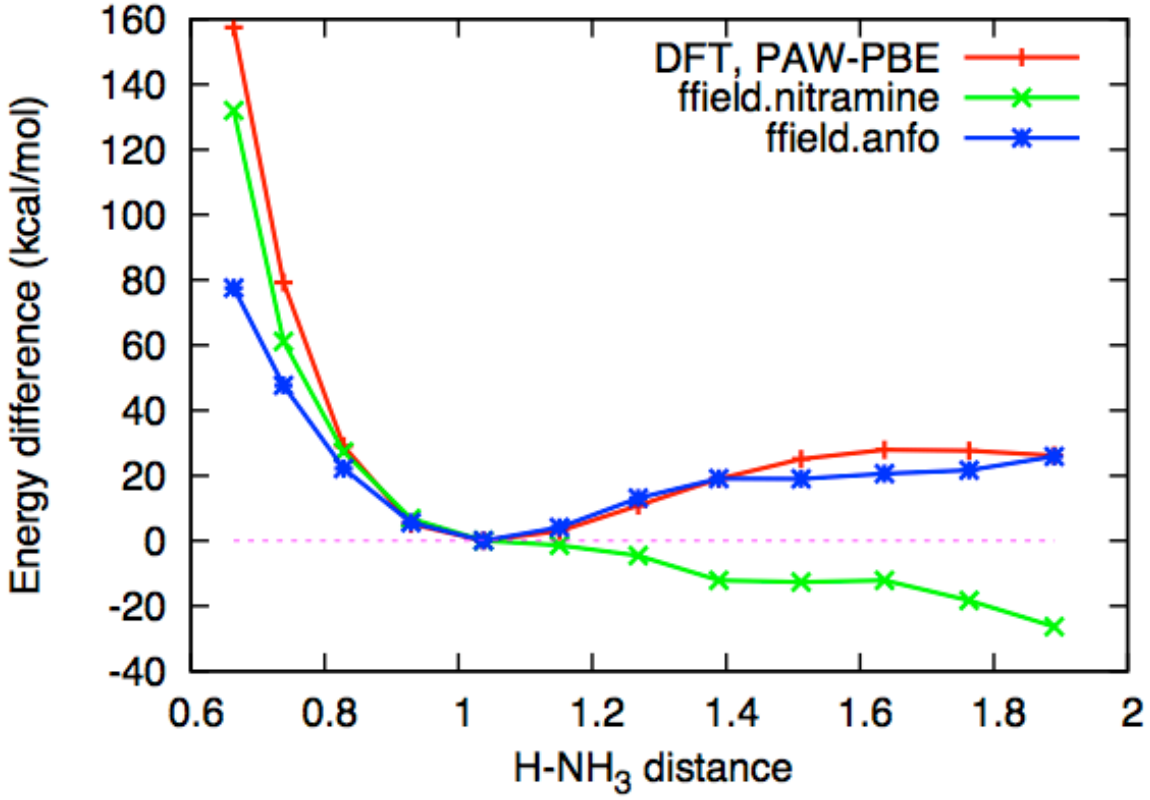


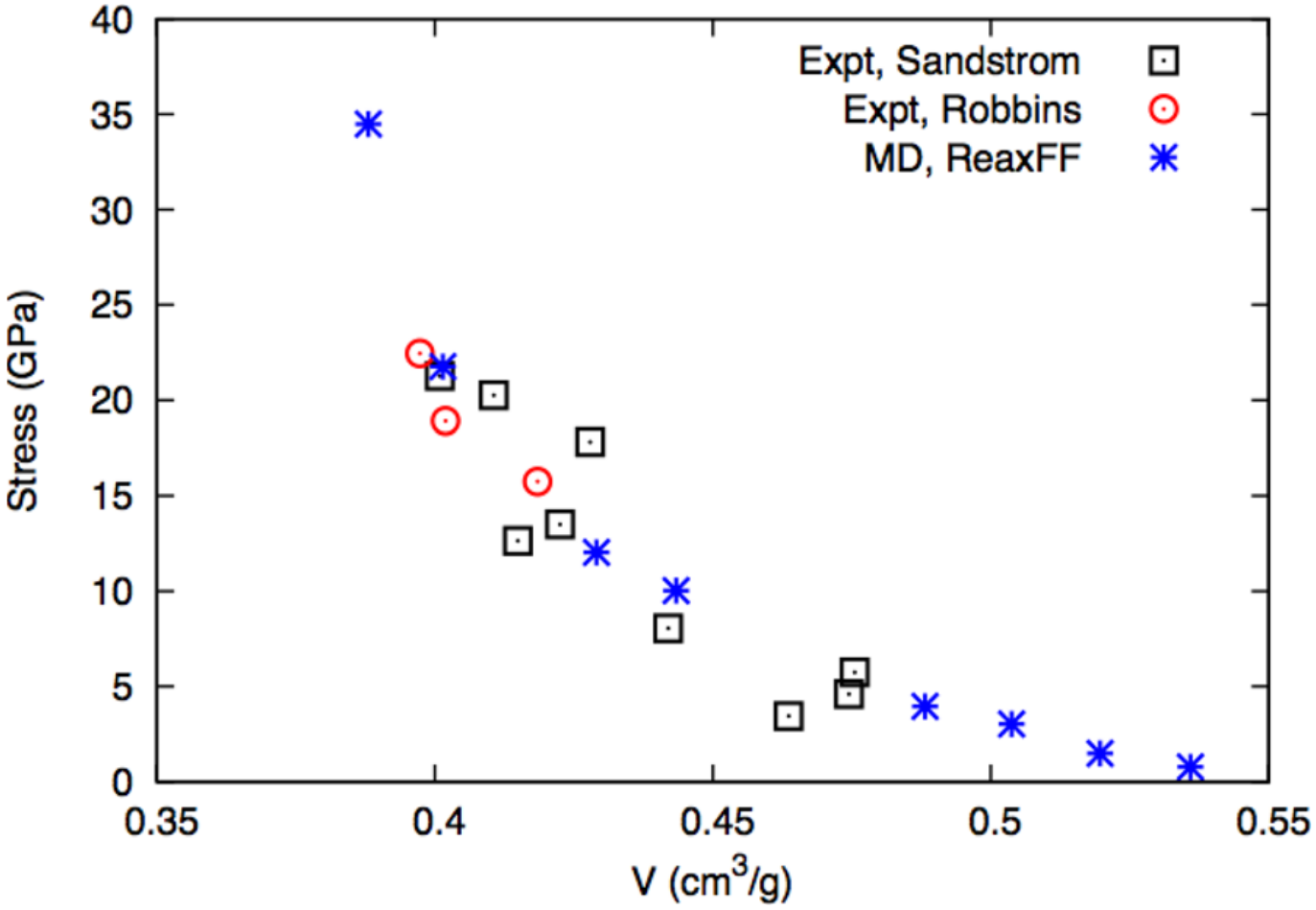

- We developed a new ReaxFF parameterization for AN
  - Reproduces stable stable $NH_4$-$NO_3$ lattice
  - Trained against energy barrier, heats of formation, lattice constants



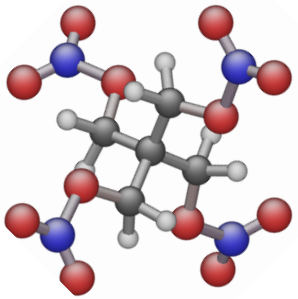
T.-R. **Shan**, A. C. T. **van Duin**, A. P. **Thompson**, J. Phys. Chem. A 118, 1469 (2014)

# ReaxFF for ANFO

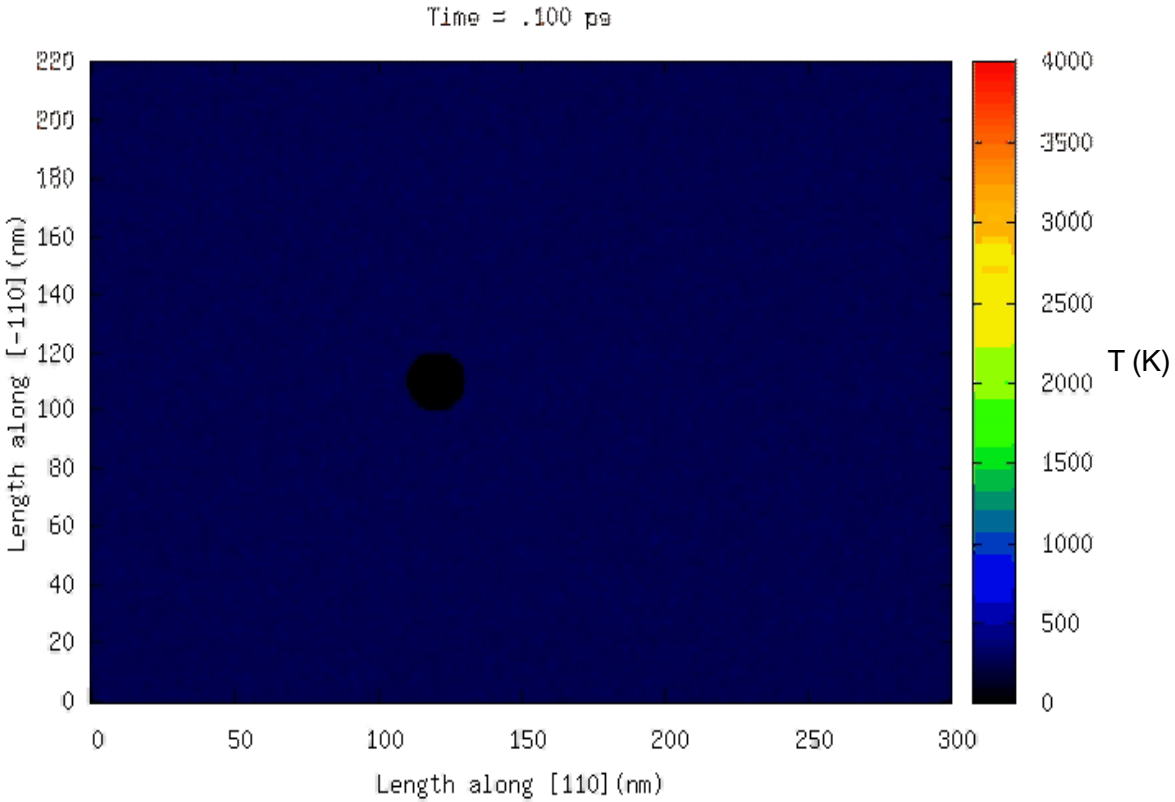
- Unreacted Hugoniot agrees well with experiments



# ReaxFF for PETN



- Normal NEMD shock runs from 0 – 64 ps
  - Observed hotspot formation due to void collapse
- Shock-front ABC runs from 64 – 500 ps:
  - Observed hot spot growth due to coupling to exothermic chemical reactions



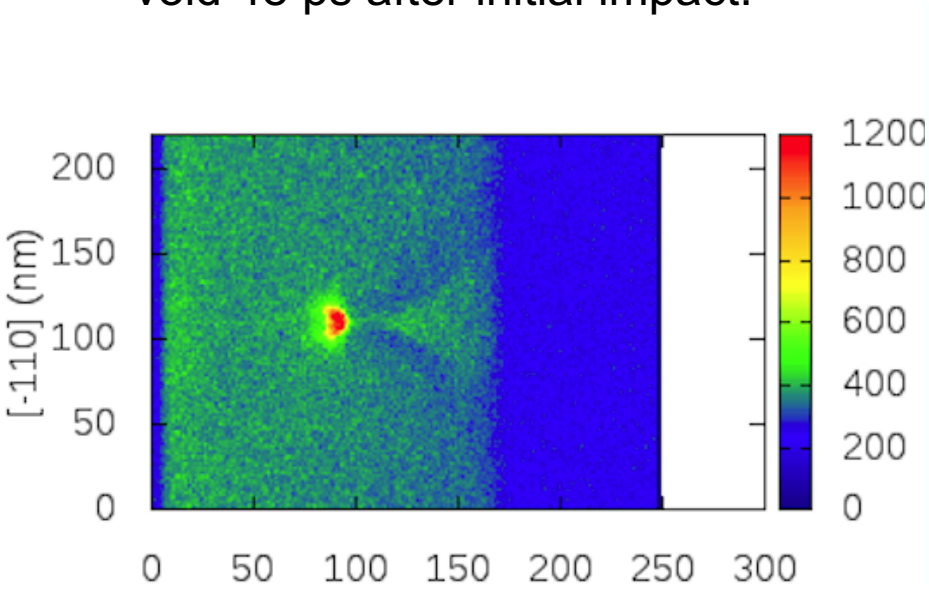

$H_2O$

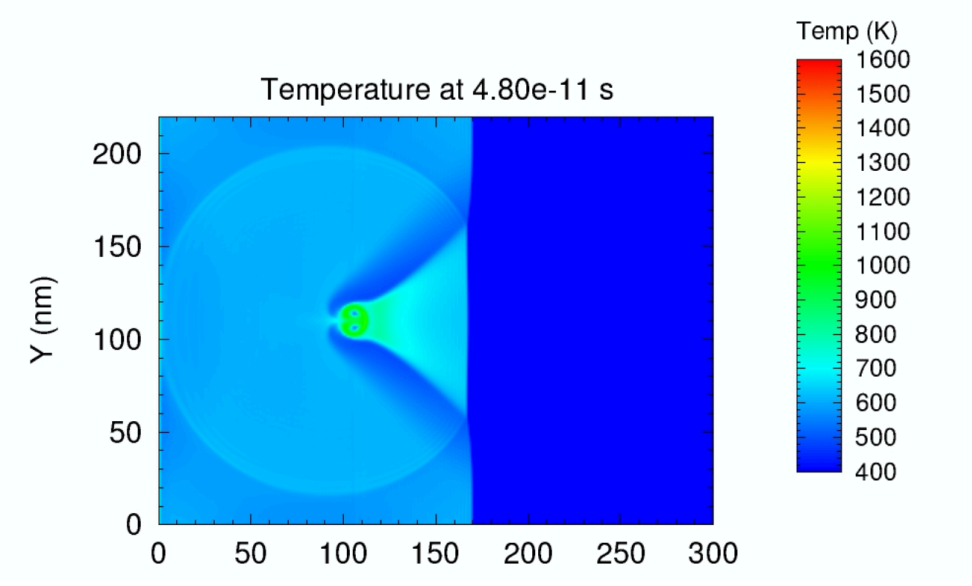
$N_2$

# ReaxFF for PETN

- Effect of secondary shockwave

  Temperature maps from (a) ReaxFF molecular dynamics simulation (LAMMPS) and (b) continuum hydrodynamics simulation (CTH) illustrating hot spot formation in the PETN crystal containing a 20 nm void 48 ps after initial impact.




Shan, Wixom, Thompson, "Extended Asymmetric Hot Region Formation due to Shockwave Interactions Following Void Collapse in Shocked High Explosive", *Phys. Rev. B* **94** 054308 (2016)

# Talk Outline

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- **SNAP**
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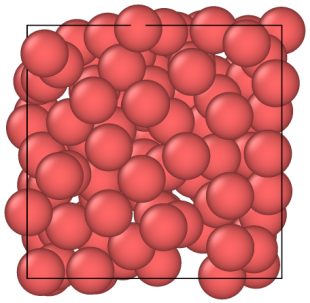
# SNAP: Spectral Neighbor Analysis Potentials



Geometric descriptors of atomic environments

Energy as a function of geometric descriptors

$$E^{SNAP} = \sum_{i=1}^{N} E_i^{SNAP} + \sum_{j<i}^{N} \phi_{ij}^{rep}\left(r_{ij}\right)$$

$$E_i^{SNAP} = \beta_0 + \sum_{k \in \{J<J_{\max}\}} \beta_k B_k^i$$

- **GAP (Gaussian Approximation Potential):** Bartok, Csanyi et al., *Phys. Rev. Lett, 2010.* Uses 3D neighbor density bispectrum and **Gaussian process regression**.
- **SNAP (Spectral Neighbor Analysis Potential):** Our SNAP approach uses GAP's neighbor bispectrum, but replaces Gaussian process with **linear regression**.
  - More robust
  - Lower computational cost
  - Decouples MD speed from training set size
  - Enables large training data sets, more bispectrum coefficients
  - Straightforward sensitivity analysis

**A. P. Thompson** , L.P. Swiler, C.R. Trott, S.M. Foiles, and G.J. Tucker, "Spectral neighbor analysis method for automated generation of quantum-accurate interatomic potentials," *J. Comp. Phys.*, **285** 316 (2015) .

# Bispectrum Components as Descriptor

- Neighbors of each atom are mapped onto unit sphere in 4D

$$(\theta_0, \theta, \phi) = \left(\theta_0^{max}\, r/r_{cut}\,, \cos^{-1}(z/r), \tan^{-1}(y/x)\right)$$

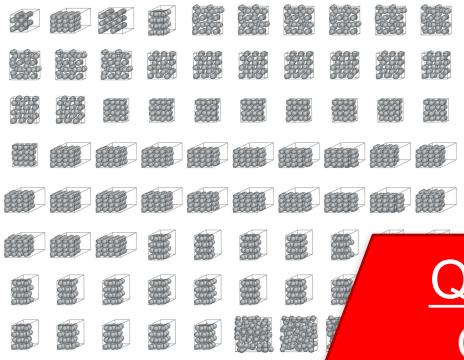
- Expand density around each atom in a basis of ***4D hyperspherical harmonics***,
- Bispectrum components of the 4D hyperspherical harmonic expansion are used as the geometric descriptors of the local environment
  - Preserves universal physical symmetries
  - Rotation, translation, permutation
  - Size-consistent

$$u^j_{m,m'} = U^j_{m,m'}(0,0,0) + \sum_{r_{ii'}<R_{cut}} f_c(r_{ii'}) w_i U^j_{m,m'}(\theta_0, \theta, \phi)$$

$$B_{j_1,j_2,j} = \sum_{m_1,m_1'=-j_1}^{j_1} \sum_{m_2,m_2'=-j_2}^{j_2} \sum_{m,m'=-j}^{j} (u^j_{m,m'})^* H^{jmm'}_{\substack{j_1 m_1 m_1' \\ j_2 m_2 m_2'}} u^{j_1}_{m_1,m_1'} u^{j_2}_{m_2,m_2'}$$

Symmetry relation: $\dfrac{B_{j_1,j_2,j}}{2j+1} = \dfrac{B_{j,j_2,j_1}}{2j_1+1} = \dfrac{B_{j_1,j,j_2}}{2j_2+1}$

# SNAP Fitting Process
# FitSnap.py



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"Hyper-parameters"
- Cutoff distance
- Group Weights
- Number of Terms
- Etc.

QUEST
QDFT
Training
Data

Dakota
optimization,
sensitivity

fitsnap.py
Communicate with LAMMPS; weighted regression to obtain SNAP coefficients

LAMMPS

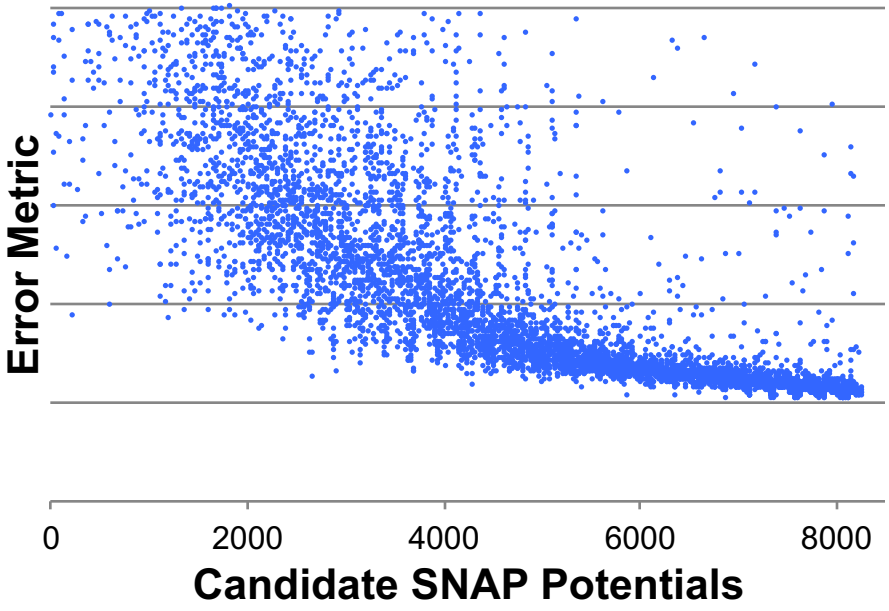
Metrics
- Force residuals
- Energy residuals
- Elastic constants
- Etc.

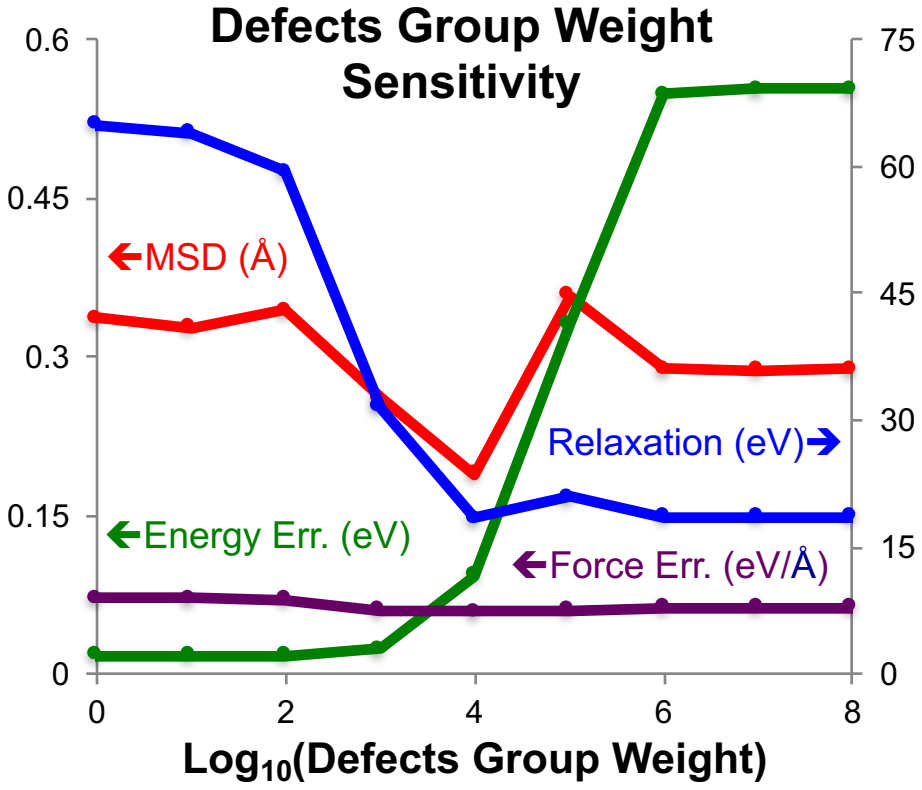
Bispectrum components & derivatives, reference potential

# FitSnap.py: Robust Software Framework

- Fitting previously based on a fragile collection of shell scripts, Python scripts, and C++ code.
- All scripts and codes were brought under version control and systematically combined and re-written into a unified tool: fitsnap.py.

**Hyper-parameter Optimization**




Key advantages of fitsnap.py

- Minimal file I/O
- Use of NumPy/SciPy
- Caching and reuse of data
- File-based input
- Supports parallel LAMMPS

# Ta SNAP potential was fit to a DFT-based training set containing 'usual suspects'

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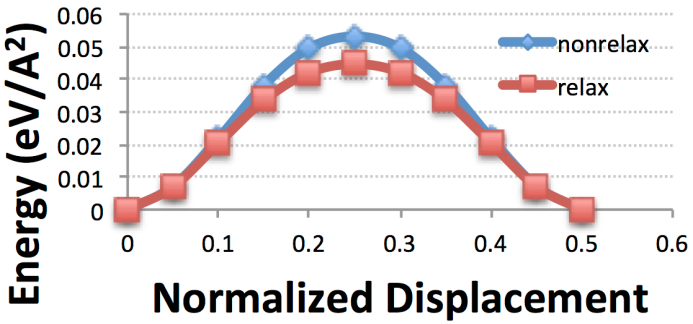
For each configuration in training set, fit total energy, atomic forces, stress

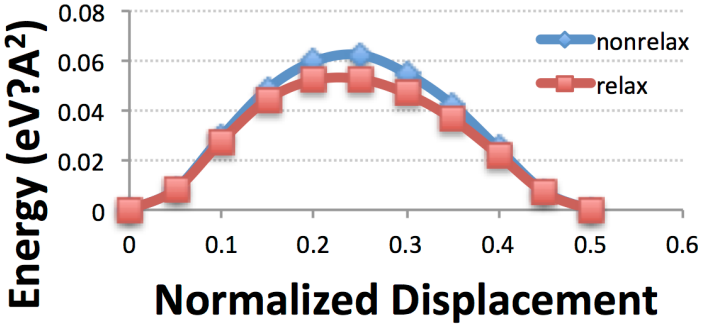
- Equilibrium lattice parameter
- Elastic constants ($C_{11}$, $C_{12}$, and $C_{44}$) and bulk modulus (B)
- Free surface energies: (100), (110), (111), and (112)
- Generalized planar stacking fault curves: {112} and {110}
- Energy-Volume (Contraction and Dilation) - BCC, FCC, HCP, and A15
- Lattices with random atomic displacements
- Liquid structure

Example: DFT-based Generalized Stacking Fault Energies

(110)

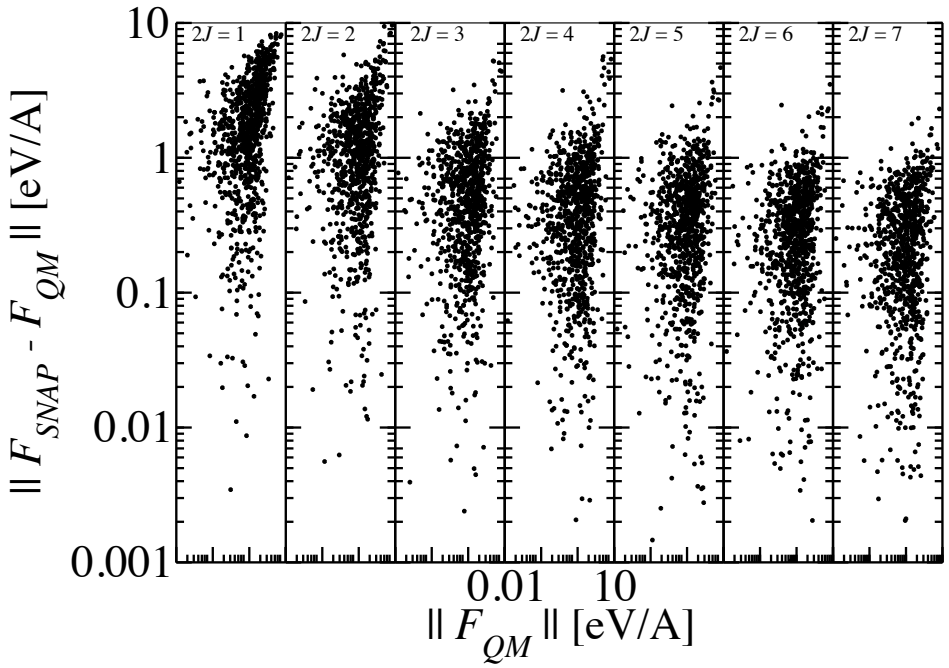



(112)



# Effect of Higher-order Bispectrum Components

- Liquid force errors decrease with increasing J
- Diminishing returns beyond J = 7/2




| 2J | N | Ferr |
|---|---|---|
| 1 | 2 | 2.09 |
| 2 | 5 | 1.39 |
| 3 | 8 | 0.66 |
| 4 | 14 | 0.53 |
| 5 | 20 | 0.44 |
| 6 | 30 | 0.35 |
| 7 | 40 | 0.30 |

# SNAP potential yields good agreement with DFT results for some standard properties

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| | DFT | SNAP | Zhou (EAM) | ADP |
|---|---|---|---|---|
| Lattice Constant (Å) | 3.320 | 3.316 | 3.303 | 3.305 |
| B (Mbar) | 1.954 | 1.908 | 1.928 | 1.971 |
| C' = (1/2)($C_{11}$ – $C_{12}$) (Mbar) | 50.7 | 59.6 | 53.3 | 51.0 |
| $C_{44}$ (Mbar) | 75.3 | 73.4 | 81.4 | 84.6 |
| Vacancy Formation Energy (eV) | 2.89 | 2.74 | 2.97 | 2.92 |
| (100) Surface Energy (J/m$^2$) | 2.40 | 2.68 | 2.34 | 2.24 |
| (110) Surface Energy (J/m$^2$) | 2.25 | 2.34 | 1.98 | 2.13 |
| (111) Surface Energy (J/m$^2$) | 2.58 | 2.66 | 2.56 | 2.57 |
| (112) Surface Energy (J/m$^2$) | 2.49 | 2.60 | 2.36 | 2.46 |
| (110) Relaxed Unstable SFE (J/m$^2$) | 0.72 | 1.14 | 0.75 | 0.58 |
| (112) Relaxed Unstable SFE (J/m$^2$) | 0.84 | 1.25 | 0.87 | 0.74 |

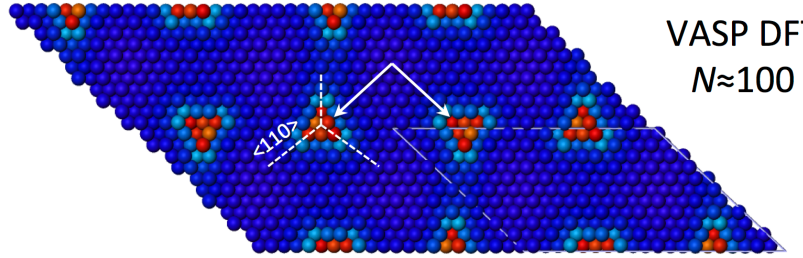
# SNAP potentials predict correct Peierls barrier for Ta screw dislocations

Sandia National Laboratories

A. P. Thompson , L.P. Swiler, C.R. Trott, S.M. Foiles, and G.J. Tucker, *J. Comp. Phys.*, **285** 316 (2015) .

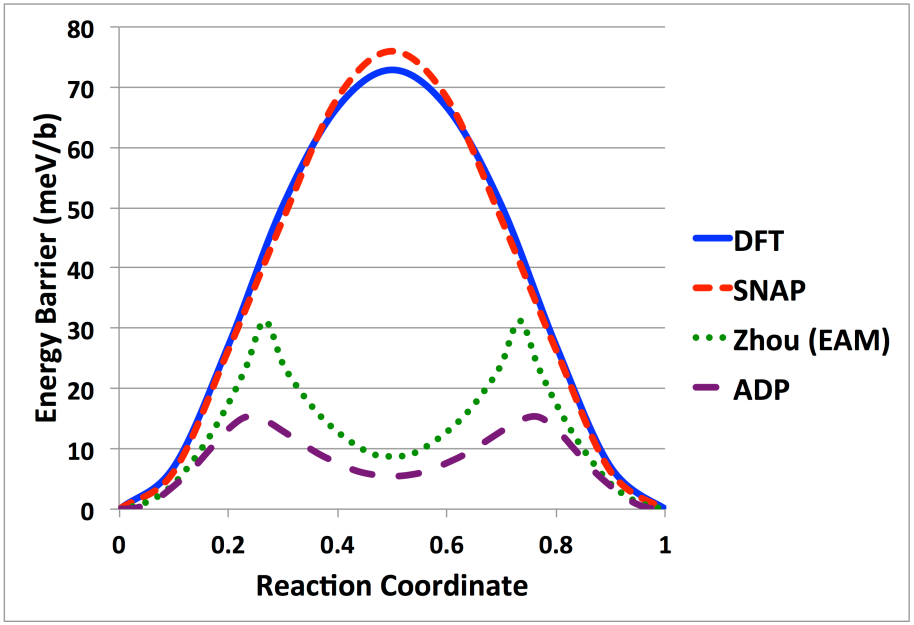
- Peierls barrier is the activation energy to move a screw dislocation
- Many simple interatomic potentials incorrectly predict a metastable state
  - Leads to erroneous dynamics
- SNAP potential agrees well with DFT calculations
  - Future work will explore dislocation dynamics based on this potential

Screw Dislocation Dipole in Tantalum

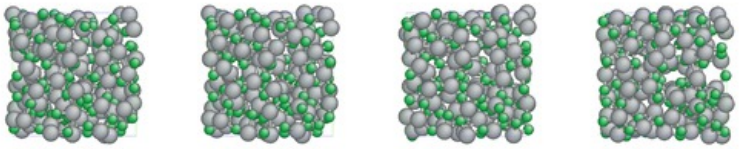


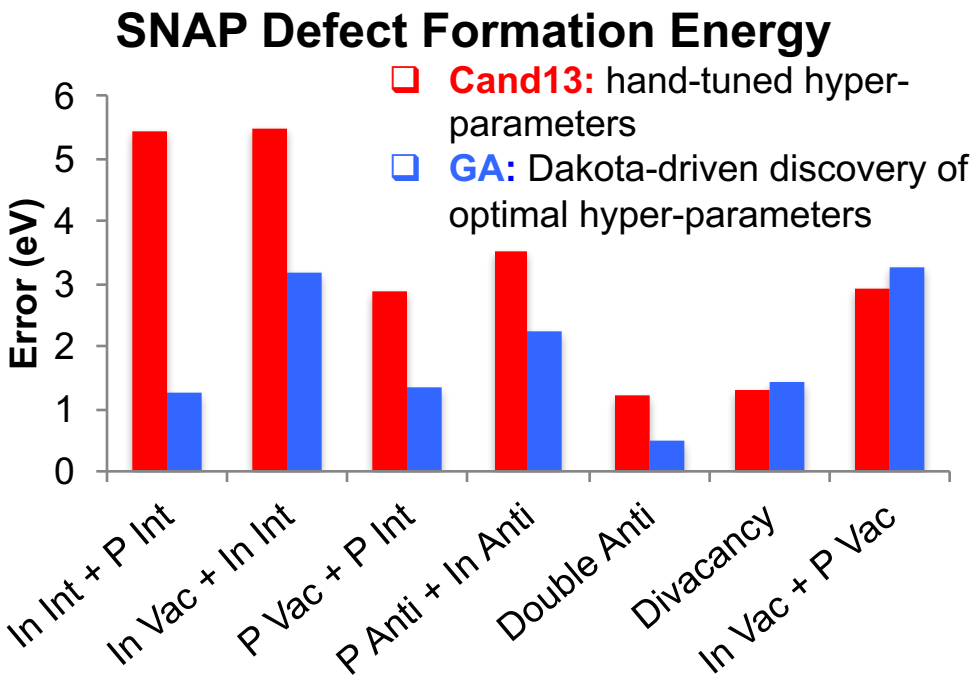

VASP DFT
$N \approx 100$

Weinberger, Tucker, and Foiles, PRB (2013)



# SNAP Indium Phosphide






**Additional Challenges**

- Two elements
- Different atom sizes
- Diverse structures
- Defect formation energies
- Sensitive to curvature

**Innovations**

- Differentiate elements by: density weight, linear coefficients, neighbor cutoff
- Trained against relaxed defect structures
- Trained against deformed defect structures

**Result**

- Good overall fit
- Defect energy error > 1 eV

# SNAP Silica: Promising Start

(Stan Moore, Paul Crozier, Peter Schultz)

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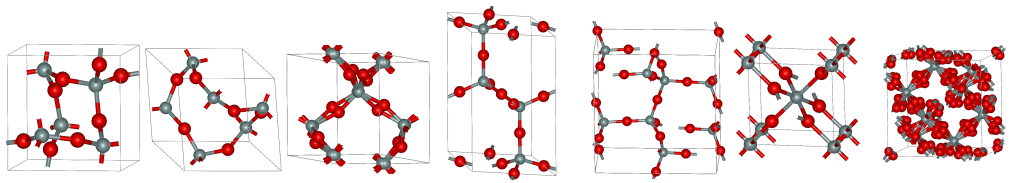
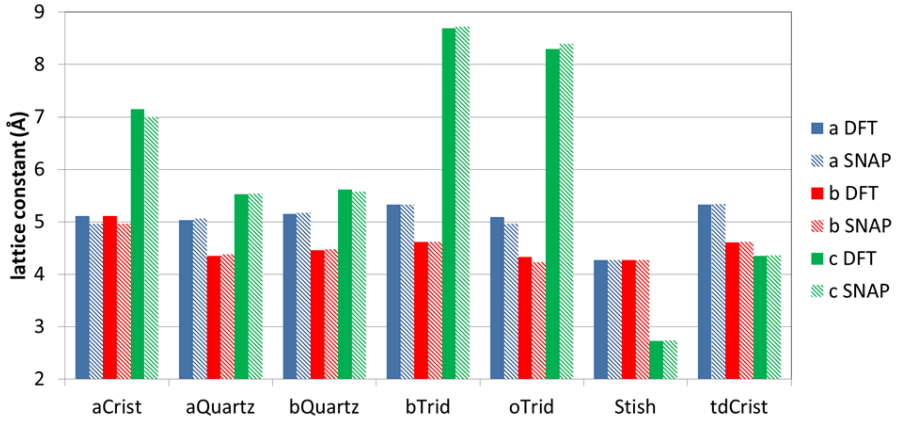
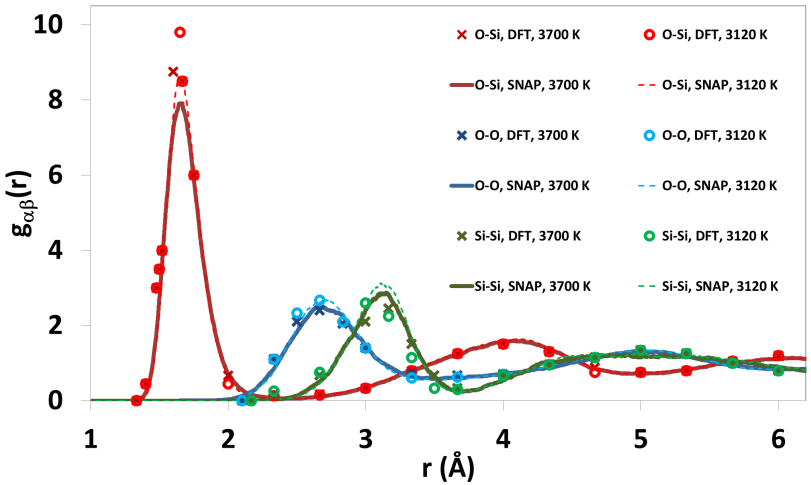
Less than 3% error in predicted lattice parameters of 7 crystal polymorphs






Good agreement with QM liquid structure for SiO2




## Additional Challenges

- Electrostatics
- Started with no training data
- Goal: quantum-accurate prediction of Si/SiO2 interface

## Innovations

- Generated training data adaptively, on-the-fly
- Added fixed point charges, long-range electrostatics

## Result (so far)

- Good agreement with QM for SiO2 crystal polymorphs
- Good agreement with QM liquid structure for SiO2

# Talk Outline

- Molecular Dynamics
- Interatomic Potentials
- ReaxFF
- SNAP
- **Outlook**

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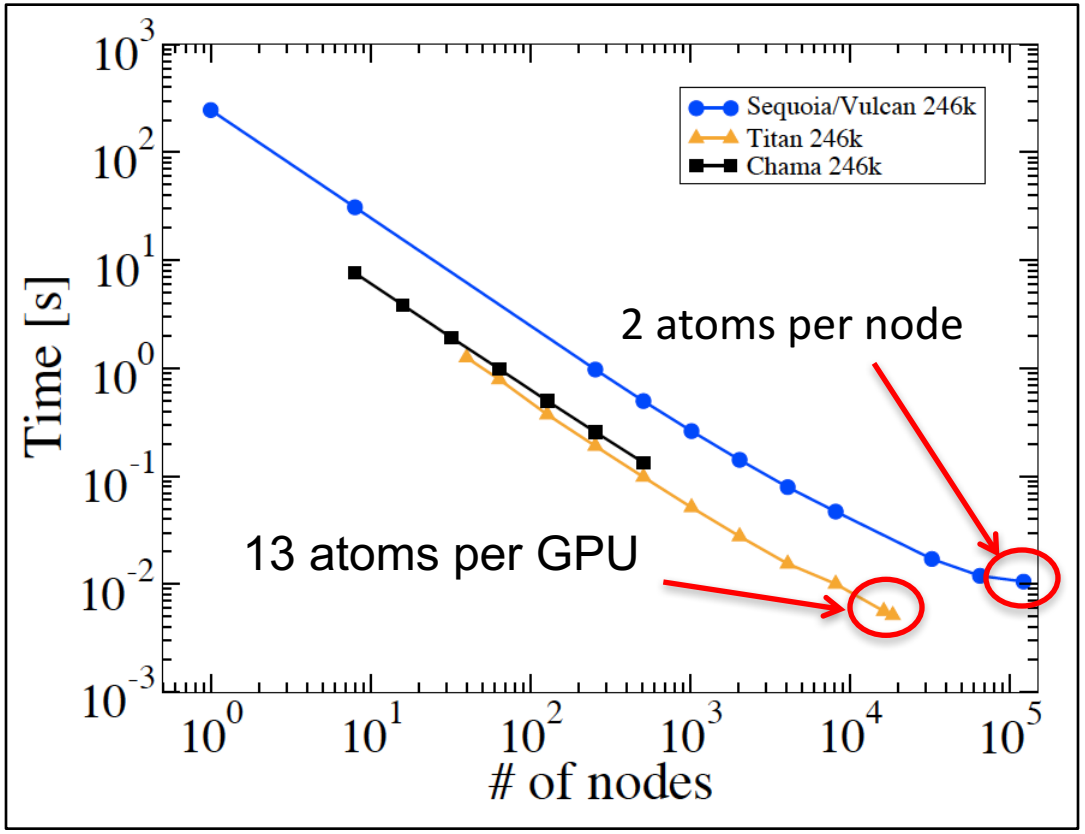
# Bigger Computers ⟷ More Expensive Potentials

**Strong-scaling LAMMPS MD Benchmark with SNAP Tantalum Potential**



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# Bigger Computers ⟷ Better Potentials

**Quantum-Accurate MD Simulations Leveraging Exascale Computing Resources**

1. Generation of large QM training datasets
2. UQ analysis via simulations with ensembles of potentials
3. On-the-fly potential development combining quantum-accurate MD with on-demand generation of QM training data
4. Database-driven MD simulations with forces interpolated directly on dynamic database of quantum calculations

# Conclusions

- Ever-increasing demand for interatomic potentials that can quantitatively match quantum methods and other data sources
- Driving continued development of both traditional potentials and automated machine learning potentials

- This work is inherently multidisciplinary, requiring expertise in computational materials science, electronic structure methods, scientific computing, and statistical analysis.

## Collaborators

| | | |
|---|---|---|
| Ray Shan | Stephen Foiles | Mitch Wood |
| Steve Plimpton | Garritt Tucker | Paul Crozier |
| Reese Jones | Christian Trott | Stan Moore |
| Laura Swiler | Peter Schultz | Adam Stephens |