

CyberMAGICS Workshop: Reactive Molecular Dynamics

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RMD hands-on: Marco Olguin, Tian Sang, Nitish Baradwaj,
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CyberMAGICS Workshop, June 5, 2025



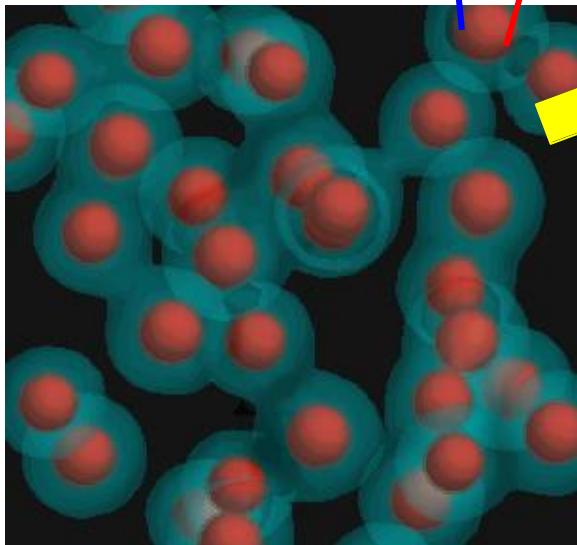
**HOWARD
UNIVERSITY**

Hierarchy of Molecular Dynamics Methods

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_{\mathbf{r}_i} E_{\text{MD}}(\{\mathbf{r}_i\})$$

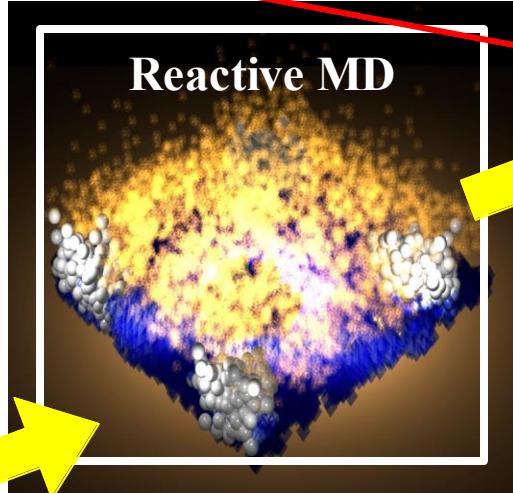
$$\min E_{\text{QM}}(\{\psi_n(\mathbf{r})\})$$

Electron wave function

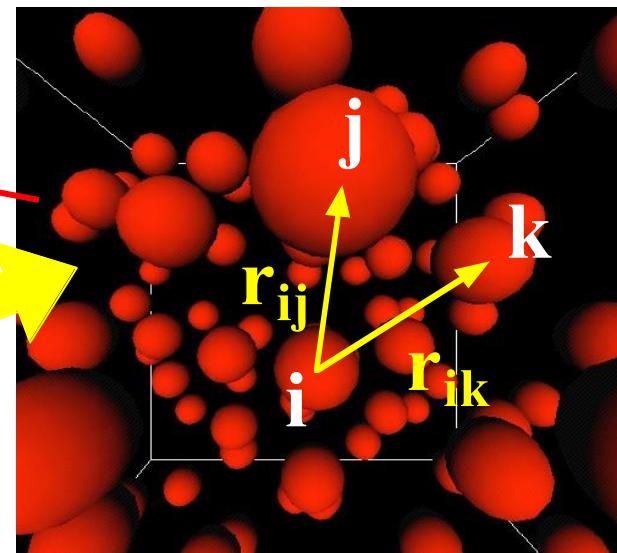


Quantum Mechanics (QM)

Atom

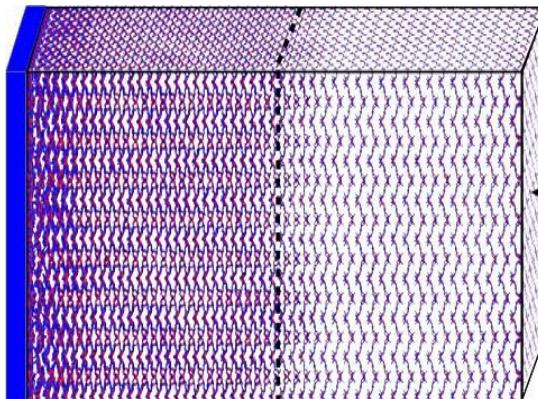


Molecular Dynamics (MD)

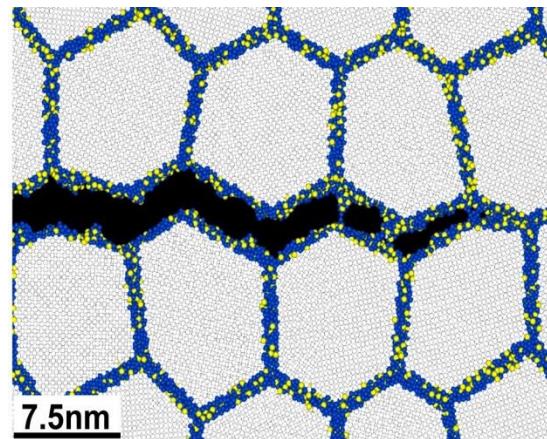


- **MD with empirical interactions $\sim O(N)$**
Long-time (10^9 steps) & large size (10^{12} atoms)
- **DFT quantum MD $\sim O(N^3)$**
Short-time (10^4 steps) & small size (~ 400 atoms)
- **Divide-and-Conquer QMD $\sim O(N)$: Al/Li nanoparticle in water using 16K atoms for 30,000 steps**

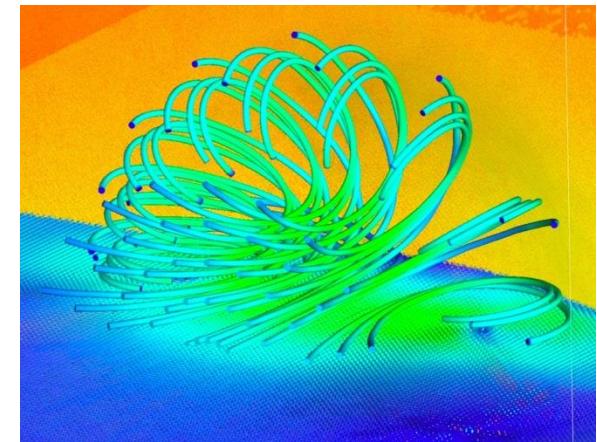
Large-Scale Reactive MD Simulations



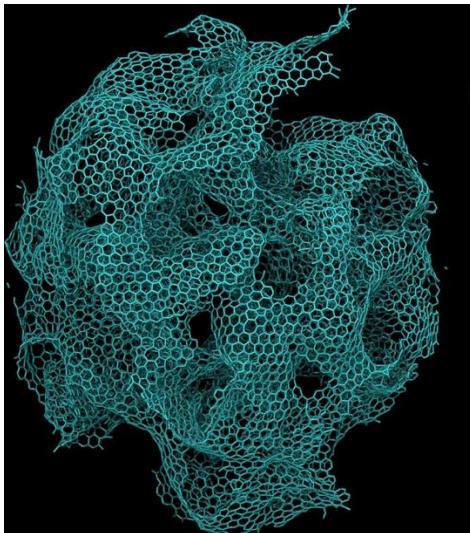
Shock-induced chemical reaction



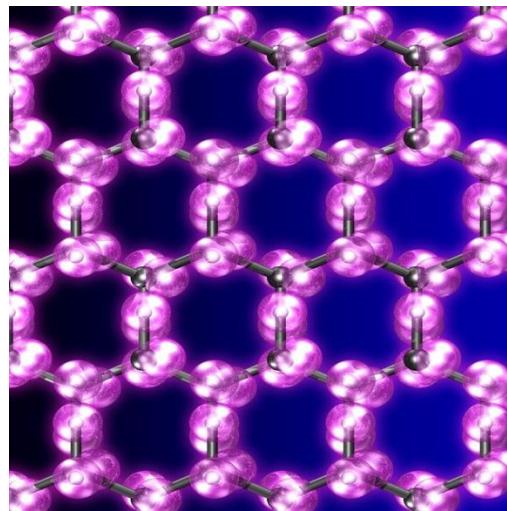
Stress corrosion cracking



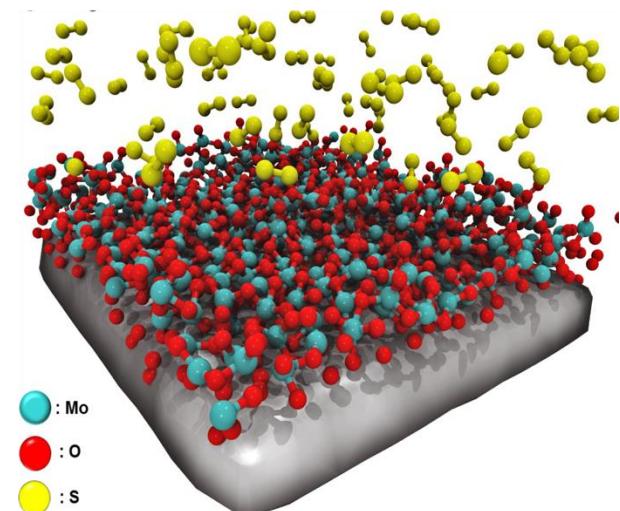
Underwater bubble collapse



Oxidation of nanoparticle



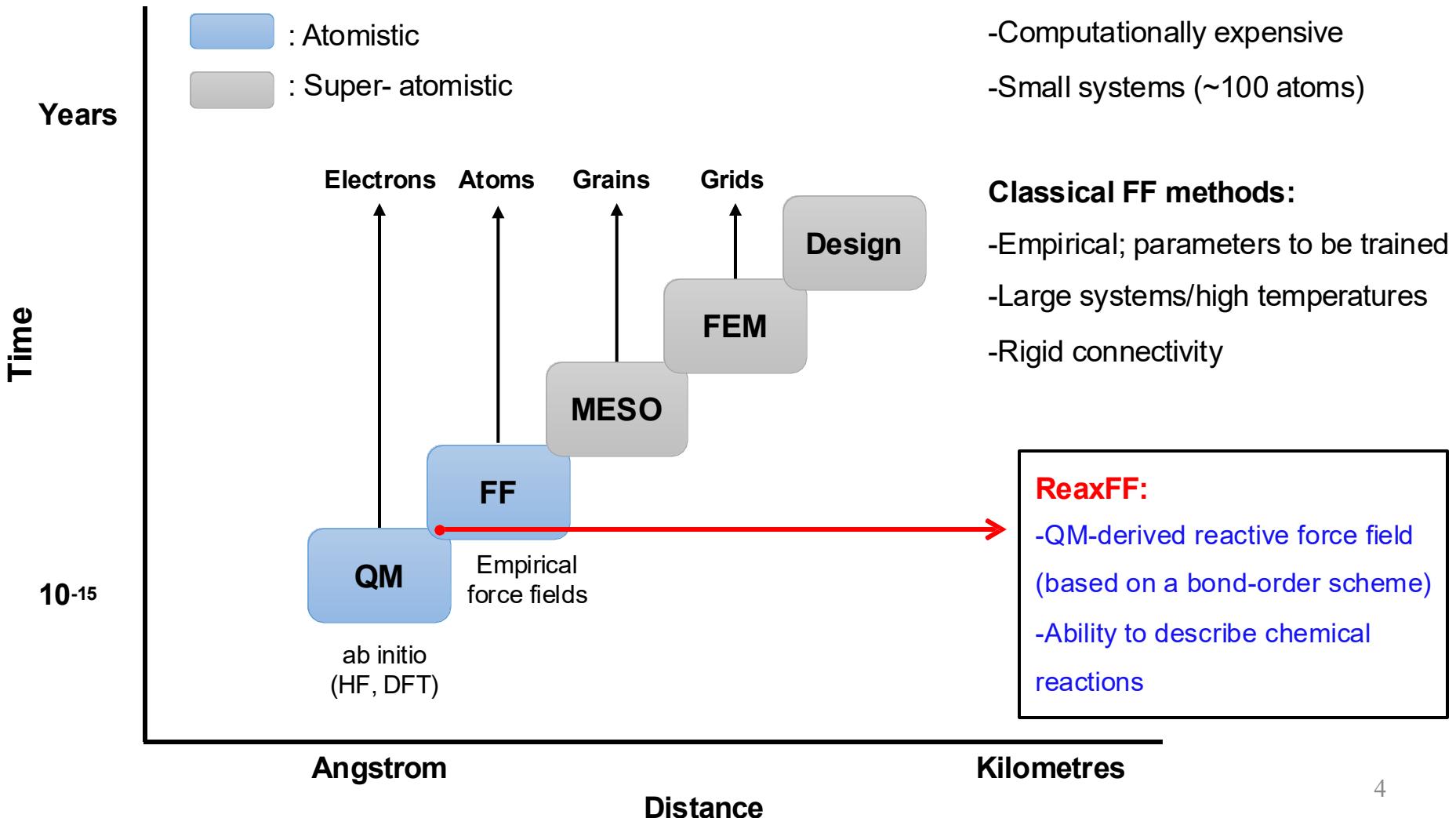
Dielectric polymers



2D material synthesis

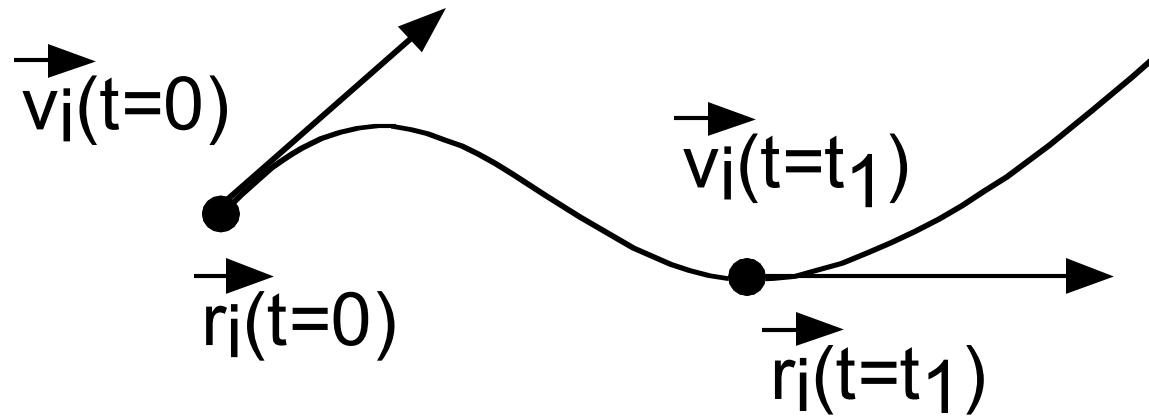
Basic Concepts of ReaxFF Forcefield

• Multi-scale Computational Modeling



Basic Concepts of ReaxFF Forcefield

- What is Molecular dynamics (MD) simulation?



Numerically solve Newton's
equation of motion

$$\vec{F}(t) = m \frac{d^2 \vec{r}_i}{dt^2} = - \frac{d}{d \vec{r}_i} V(\vec{r}_i \dots \vec{r}_N)$$

Interatomic potential; force field

Basic Concepts of ReaxFF Forcefield

- ReaxFF general energy terms*

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

The equation is shown with two blue curly braces underneath. The first brace groups the terms E_{bond} , E_{over} , E_{val} , and E_{tors} . The second brace groups the terms E_{vdWaals} and E_{Coulomb} . Below the first group is the red text "Bonded interactions", and below the second group is the red text "Non-bonded interactions".

E_{bond} : Bond energy; two-body attractive term

E_{over} : Over-coordination energy; penalty for overcoordinating atoms

E_{val} : Angle strain energy; three-body term

E_{tors} : Torsion energy; four-body term

E_{vdWaals} : van der Waals interactions

E_{Coulomb} : Coulomb interactions

*van Duin, Adri CT, et al. *The Journal of Physical Chemistry A* **105** (2001): 9396-9409.

Basic Concepts of ReaxFF Forcefield

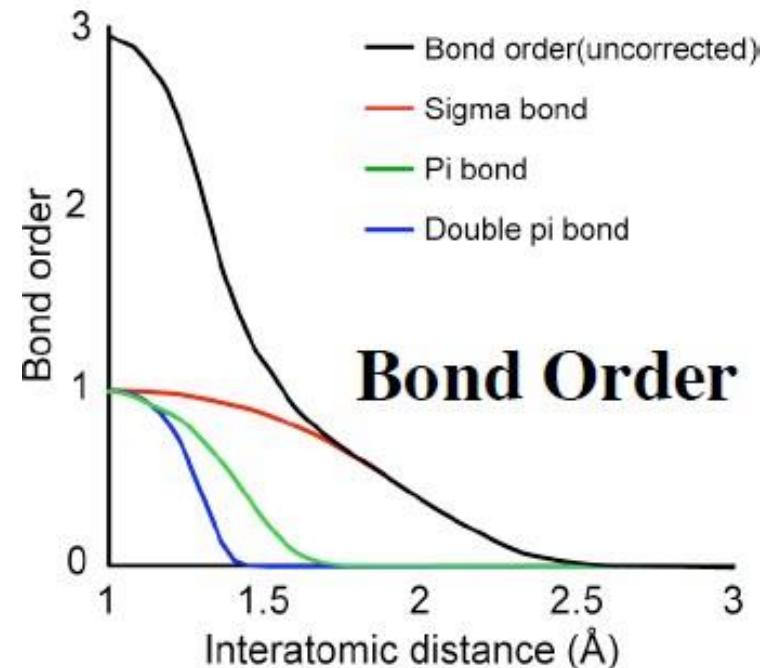
- Key features of ReaxFF – 1*

- A bond order is calculated and updated every step, thus allowing for chemical reactions during MD simulations.

A bond-order/distance relationship

$$BO_{ij} = \exp \left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_o^\sigma} \right)^{p_{bo,2}} \right] + \exp \left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_o^\pi} \right)^{p_{bo,4}} \right] + \exp \left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}} \right)^{p_{bo,6}} \right]$$

C-C bond order



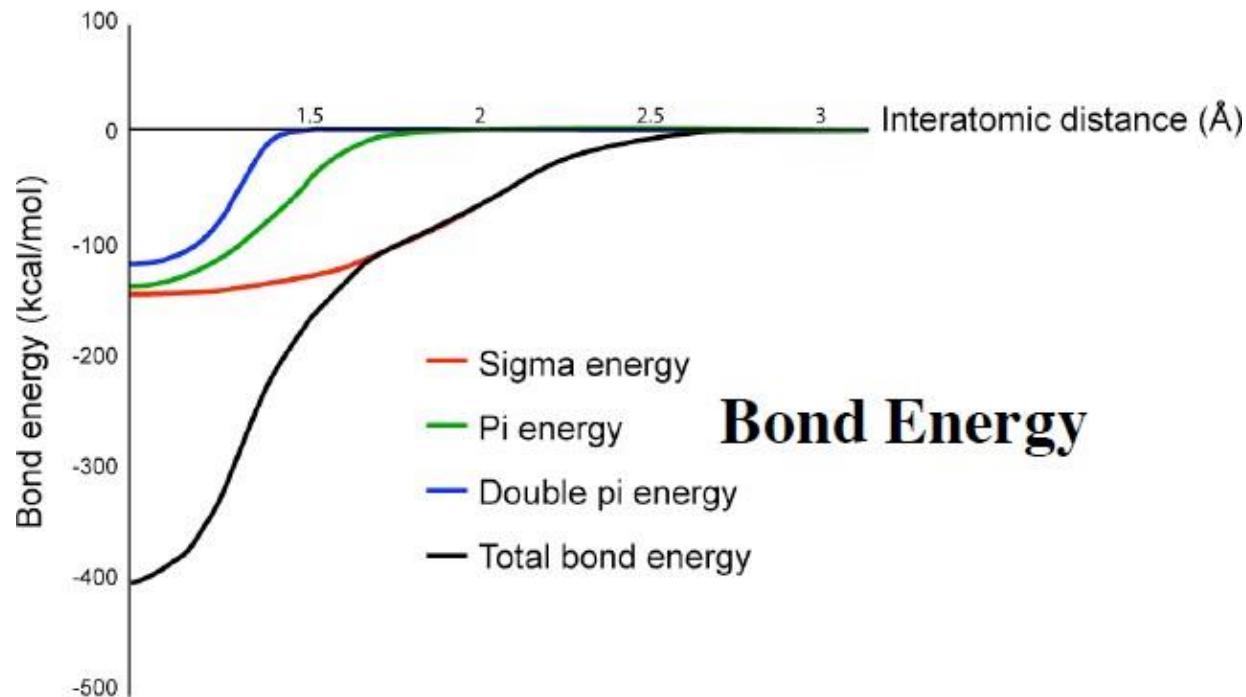
*Russo, Michael F., and Adri CT van Duin. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

Basic Concepts of ReaxFF Forcefield

- Key features of ReaxFF – 2*

- All bonded-interactions are made of bond-order dependent.

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot f(BO_{ij}^\sigma) - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$



*Russo, Michael F., and van Duin, Adri. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

Basic Concepts of ReaxFF Forcefield

- Key features of ReaxFF – 3*

- Non-bonded interactions (van der Waals and Coulomb) are calculated between every atom pair. (*i.e.*, no exception)
- ReaxFF employs the QEq method,** a geometry-dependent point charge calculations scheme, to update point charges for the entire system.

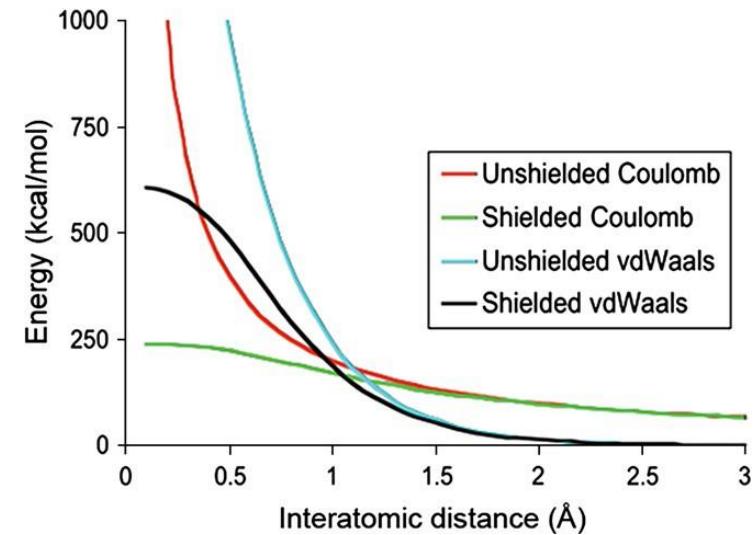
$$E_{vdWaals} = Tap \cdot D_{ij} \cdot \left\{ \exp \left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 \cdot \exp \left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\}$$

A shielded Morse potential

$$f_{13}(r_{ij}) = \left[r_{ij}^{p_{vdW1}} + \left(\frac{1}{\gamma_w} \right)^{p_{vdW1}} \right]^{\frac{1}{p_{vdW1}}}$$

$$E_{Coulomb} = C \cdot \frac{q_i \cdot q_j}{[r_{ij}^3 + (1/\gamma_{ij})^3]^{1/3}}$$

A shielded Coulomb potential



*Russo, Michael F., and Adri CT van Duin. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

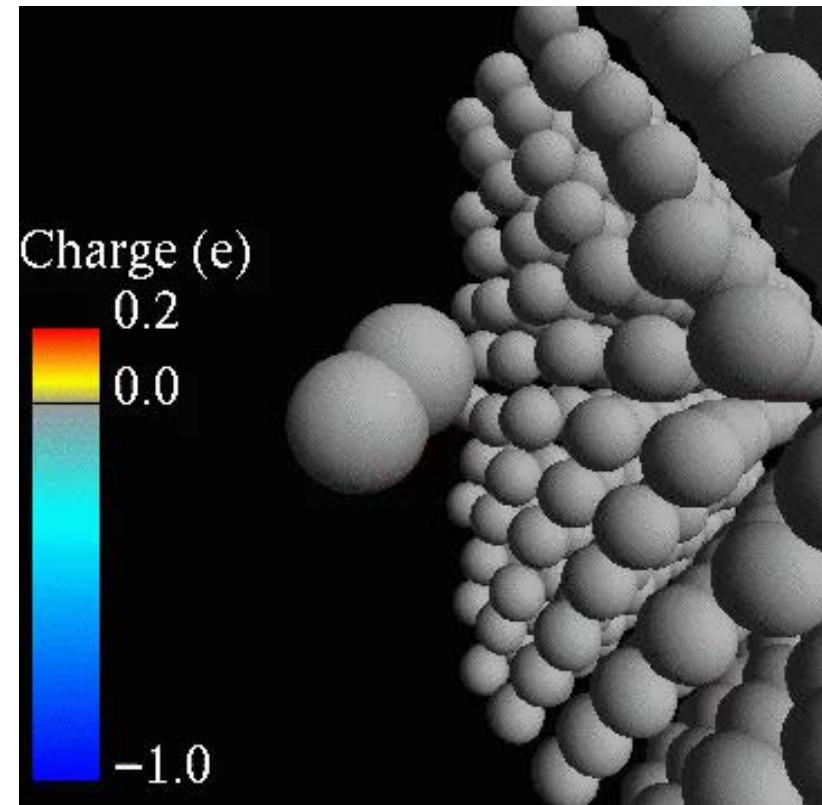
Rappe, Anthony K., and William A. Goddard III. *The Journal of Physical Chemistry* **95 (1991): 3358-3363.

Basic Concepts of ReaxFF Forcefield

Key features of ReaxFF – 4**

- Charge-equilibration (QE_q)
→ Charge transfer

Determine atomic charges
 $\{q_i \mid i = 1, \dots, N\}$ every MD step
to minimize $E_{\text{ES}}(\mathbf{r}^N, q^N)$ with
charge-neutrality constraint:
 $\sum_i q_i = 0$

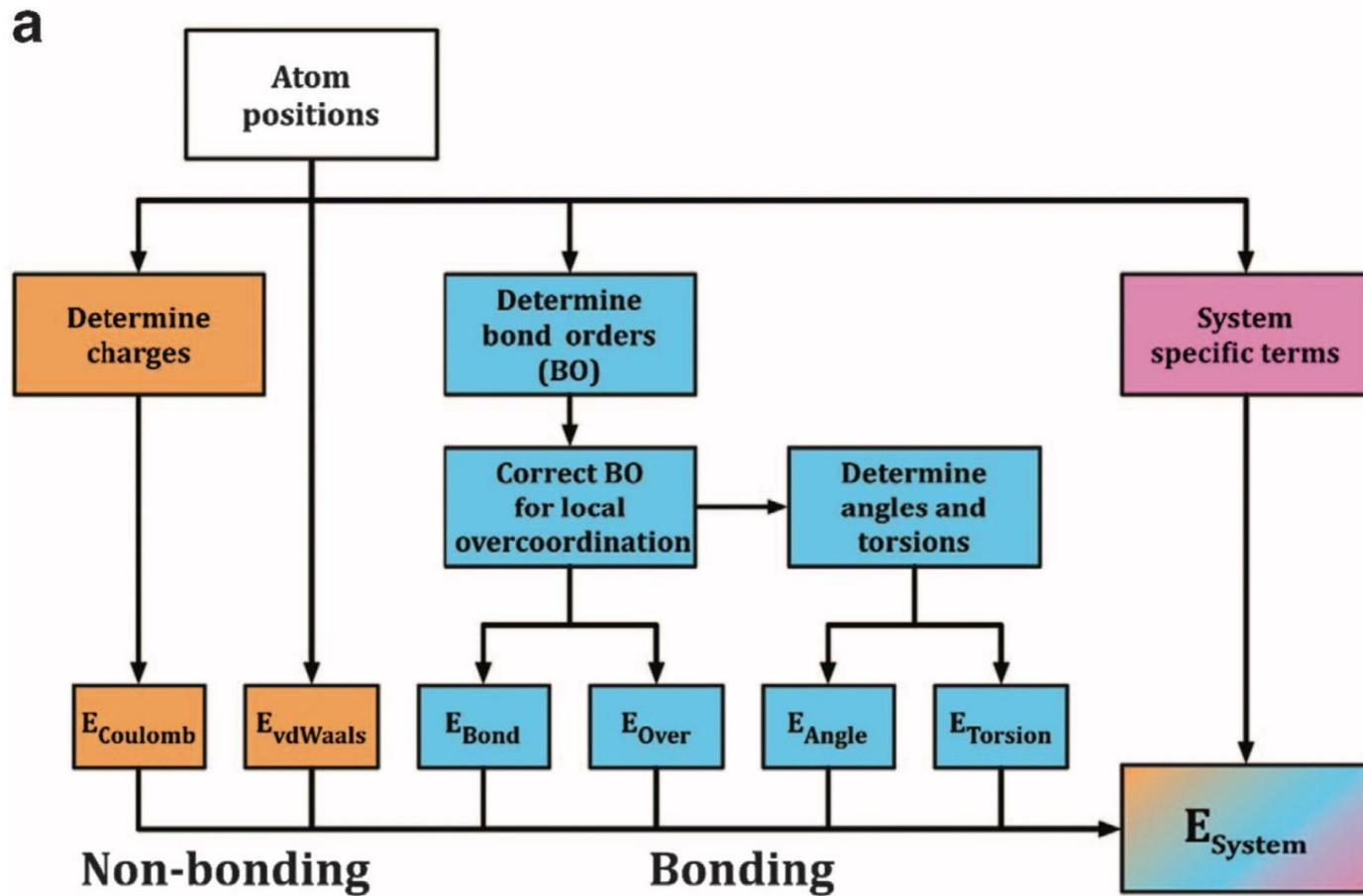


O₂ dissociation on Al(111)

$$E_{\text{ES}}(\mathbf{r}^N, q^N) = \sum_i \chi_i q_i + \frac{1}{2} \sum_{i < j} J_{ij} q_i^2 + \sum_i \int d\mathbf{x} \int d\mathbf{x}' \frac{\rho_i(q_i; \mathbf{x} - \mathbf{r}_i) \rho_j(q_j; \mathbf{x}' - \mathbf{r}_j)}{|\mathbf{x} - \mathbf{x}'|}$$

Basic Concepts of ReaxFF Forcefield

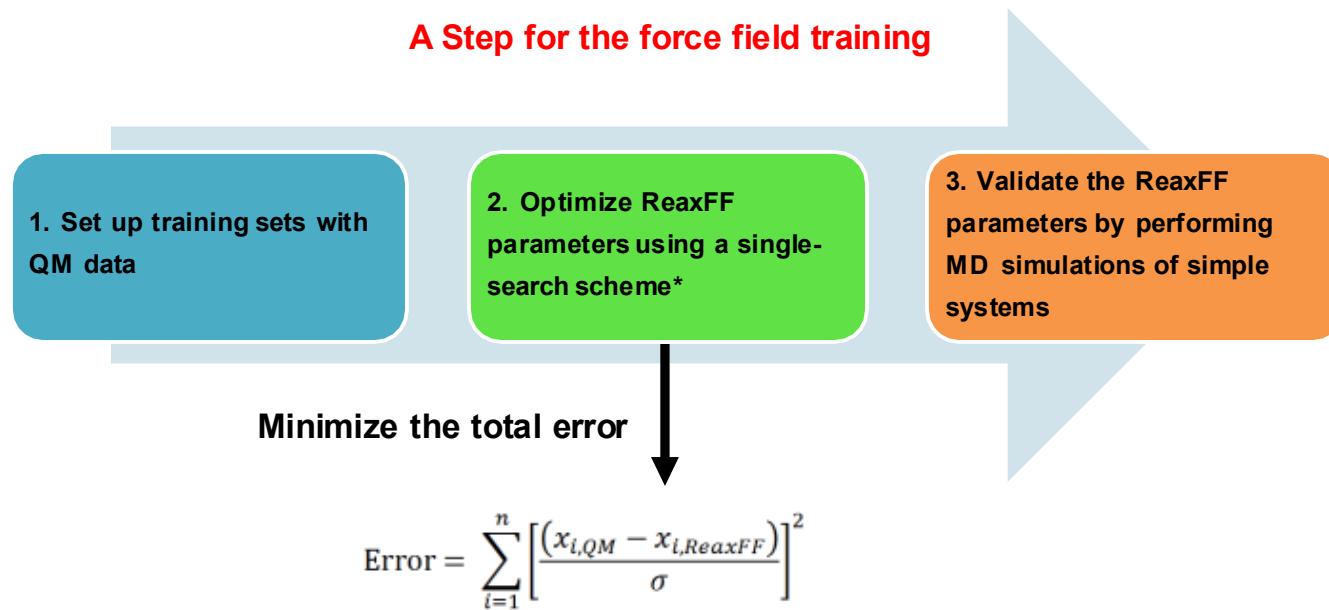
- ReaxFF flow diagram*



*Senftle, Thomas, et al. *npj Computational Materials* **2** (2016).

Basic Concepts of ReaxFF Forcefield

- How to get ReaxFF reactive force field parameters?
 - Do search Google Scholar:
<https://scholar.google.com/>
 - Develop your ReaxFF force field parameters (non-trivial)

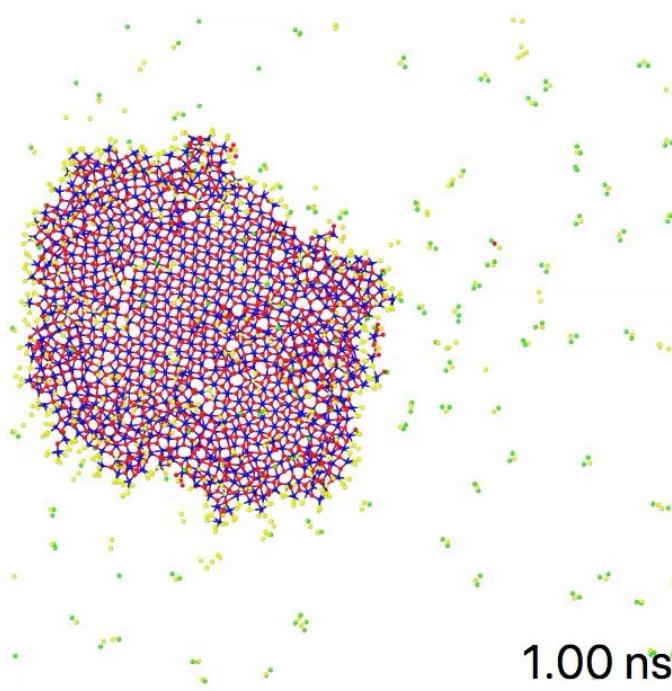


* van Duin, A. C. T.; Jan, M.; de Graaf, B. *J. Chem. Soc., Faraday Trans.* **1994**, 90, (19), 2881-2895.

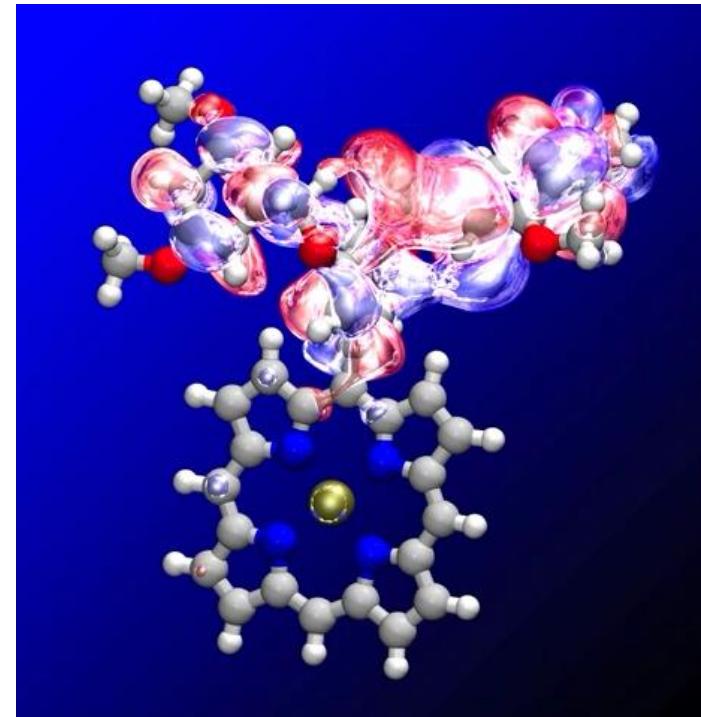
Reactive and Quantum MD Software

RXMD: Reactive molecular dynamics software for desktop to supercomputing platforms

QXMD: Quantum dynamics software with non-adiabatic extensions



Sulfurdization of MoO_3 nanoflake



Electron transfer in light-harvesting molecule

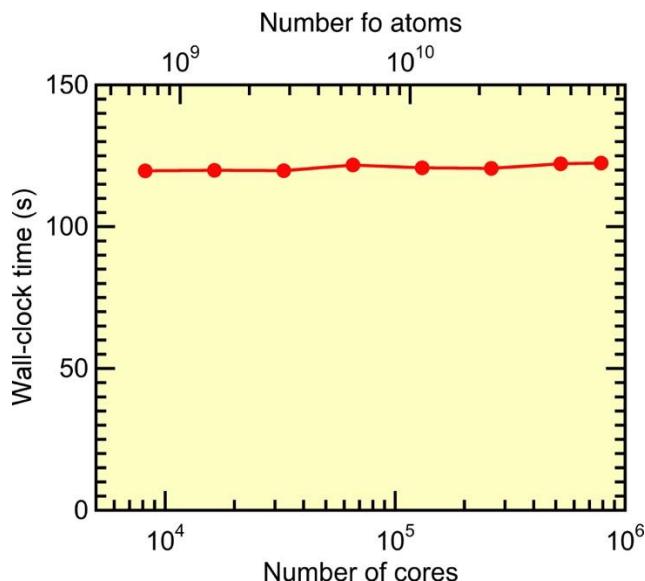
Extended-Lagrangian Method

- Eliminated speed-limiting iteration for charge-equilibration (QE_q) in ReaxFF by adapting an extended-Lagrangian scheme proposed for QMD

$$L_{\text{XRMD}} = L_{\text{RMD}} + \frac{\mu}{2} \sum_i \dot{\theta}_i^2 - \frac{\mu \omega^2}{2} \sum_i (\theta_i - q_i)^2$$

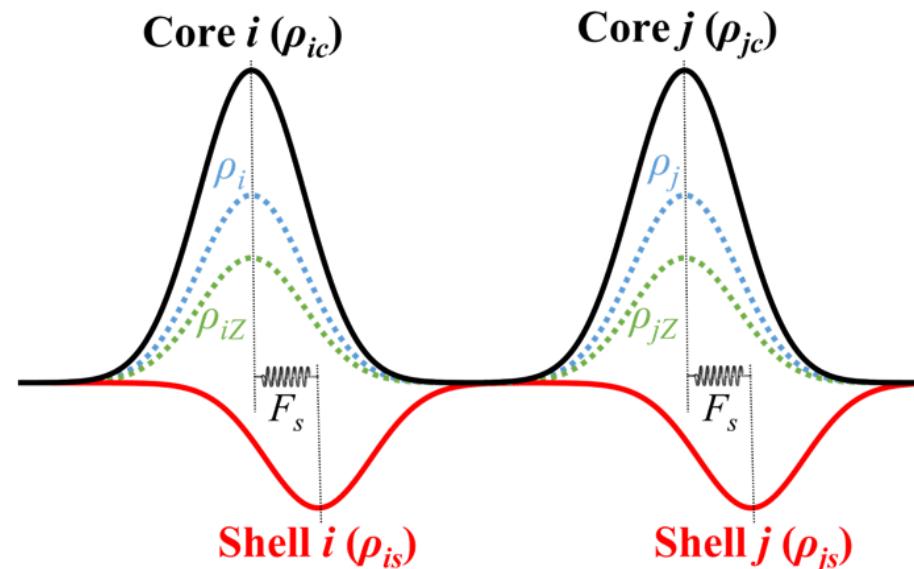
Auxiliary charge: dynamic variable
Physical charge

- Extended-Lagrangian RXMD achieves 8.6x speed up with the same energy conservation as fully converged QE_q
- Parallel efficiency 0.977 on 786,432 Blue Gene/Q cores for 67.6 billion atoms



Polarizable Charge Equilibration (PQEeq) Method

- PQEeq method has been implemented in RXMD to study dielectric response as a function of time, electric field and temperature.
- Each atom is partitioned into two charged sites, i.e., core and shell
- The core consists of variable charge ρ_i and with fixed charge ρ_{iZ}
- The shell is connected with the core by an isotropic harmonic spring with force constant F_s



self energy of *i*-atom

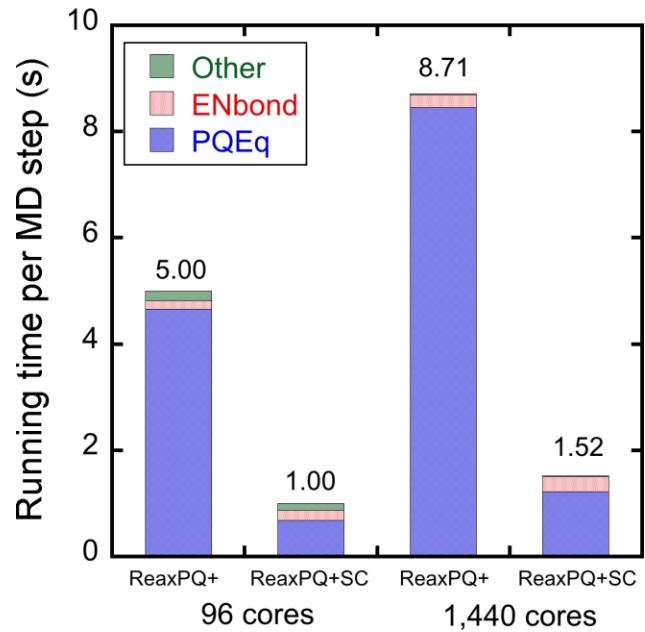
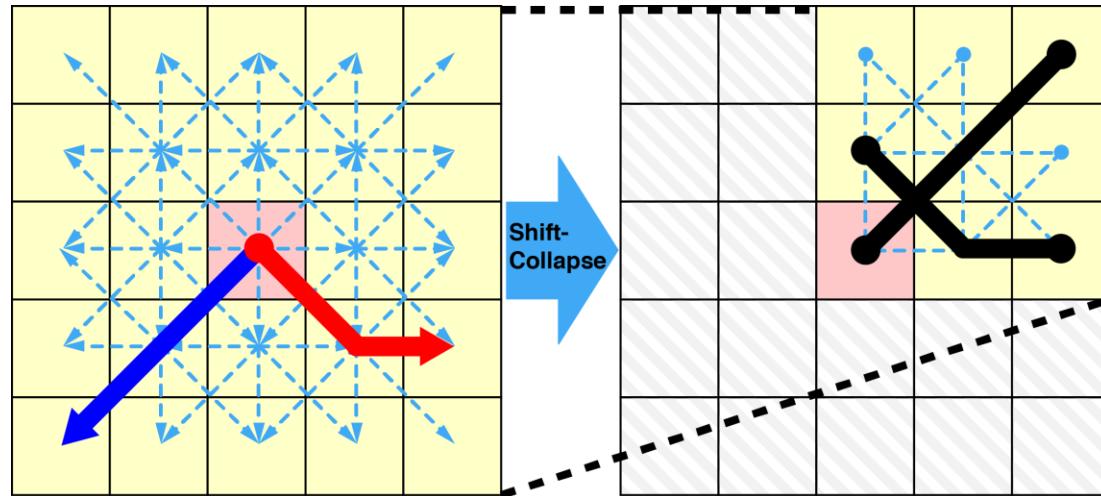
$$E(\{\vec{r}_{ic}, \vec{r}_{is}, q_i\}) = \sum_i^N \left\{ E_i^0 + \chi_i^0 q_i + \frac{1}{2} J_{ii}^0 q_i^2 + \boxed{\frac{1}{2} K_s r_{ic,is}^2} \right\}$$

core-shell interaction on *i*-atom

$$+ \sum_{i>j} [C(\vec{r}_{ic,jc})q_{ic}q_{jc} - C(\vec{r}_{ic,js})q_{ic}Z_j - C(\vec{r}_{is,jc})q_{jc}Z_i + C(\vec{r}_{is,js})Z_iZ_j]$$

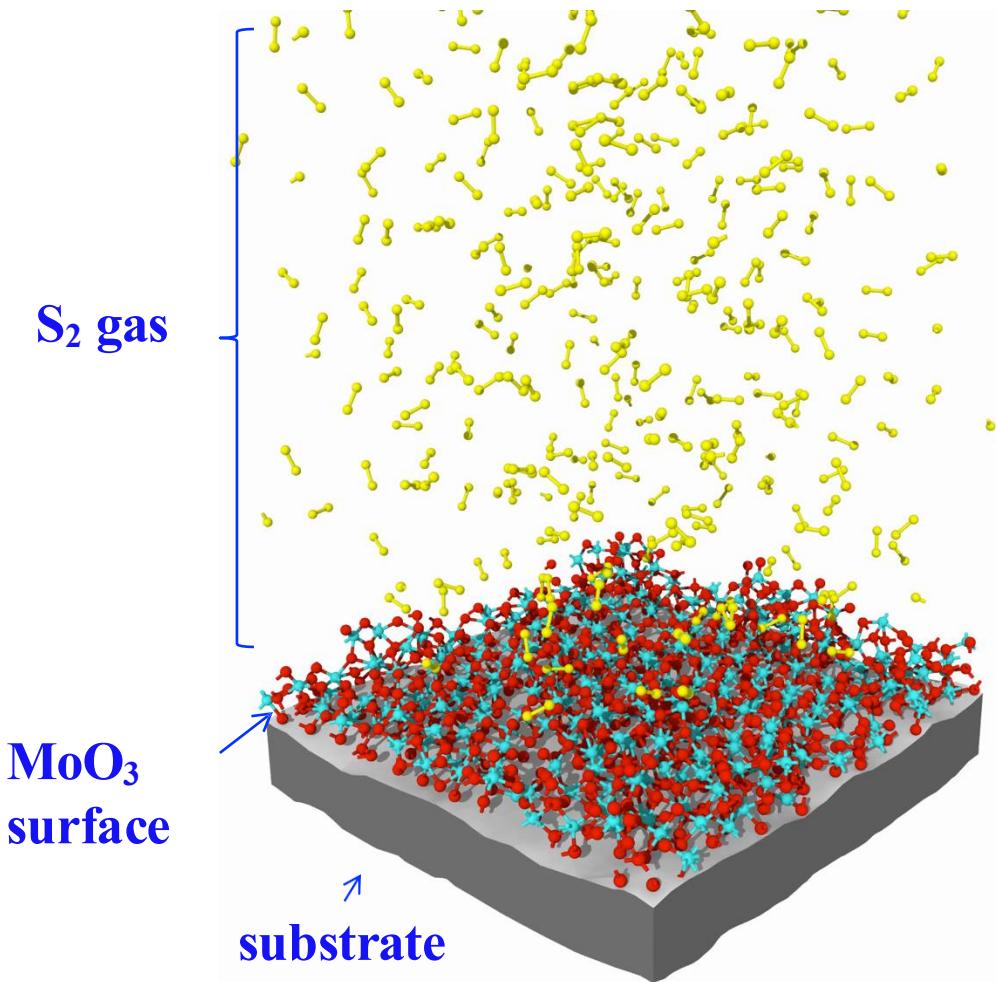
core-shell interaction between *i*- and *j*-atoms

Shift-Collapse (SC) Algorithm for Time-to-Solution



- SC algorithm generates optimal computation pattern for general finite-range n -tuple energy/force computations.
- SC-accelerated PQEq+SC achieves 5.0x speedup compare to the original PQEq.

RMD Simulations of MoS₂ Monolayer Synthesis



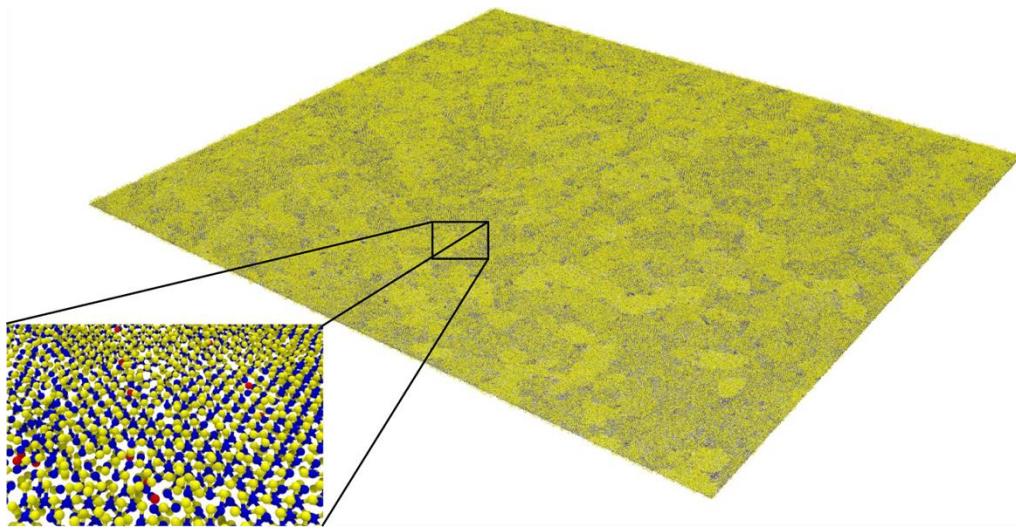
High-temperature
sulfurdization of MoO₃
monolayer with S₂ gas

**Step 1. O₂ evolution
from a MoO₃ surface**

**Step 2. SO/SO₂
formation from a
MoO_{2.6} surface**

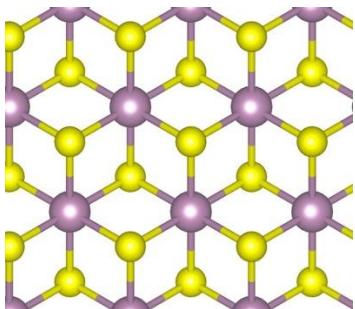
**Step 3. Mo-S bond
formation on MoO_xS_y**

MoS₂ Crystal Growth Simulation



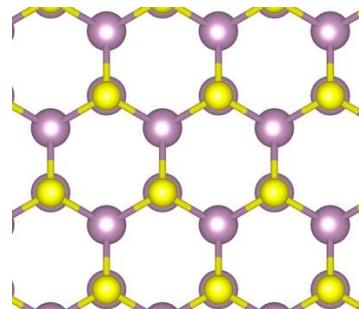
- Number of atoms:
4,305,600 atoms (1,497,600 O; 2,347,200 S and 460,800 Mo)
- System dimensions:
 $211.0 \times 196.3 \times 14.5$ (nm³)
- Timestep: 0.75 fs.

1T Structure



 Sulfur

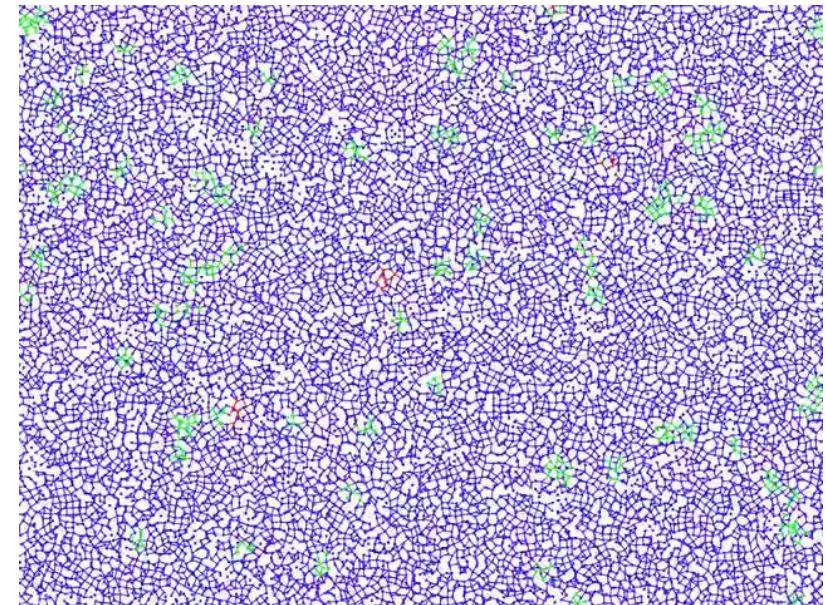
2H Structure



 Molybdenum

The pre-sulfurized MoS slab is thermalized at 3000K for 1 nsec, quenched to 1000K, then subjected to temperature cycle to improve its crystallinity.

Grain Growth by Annealing

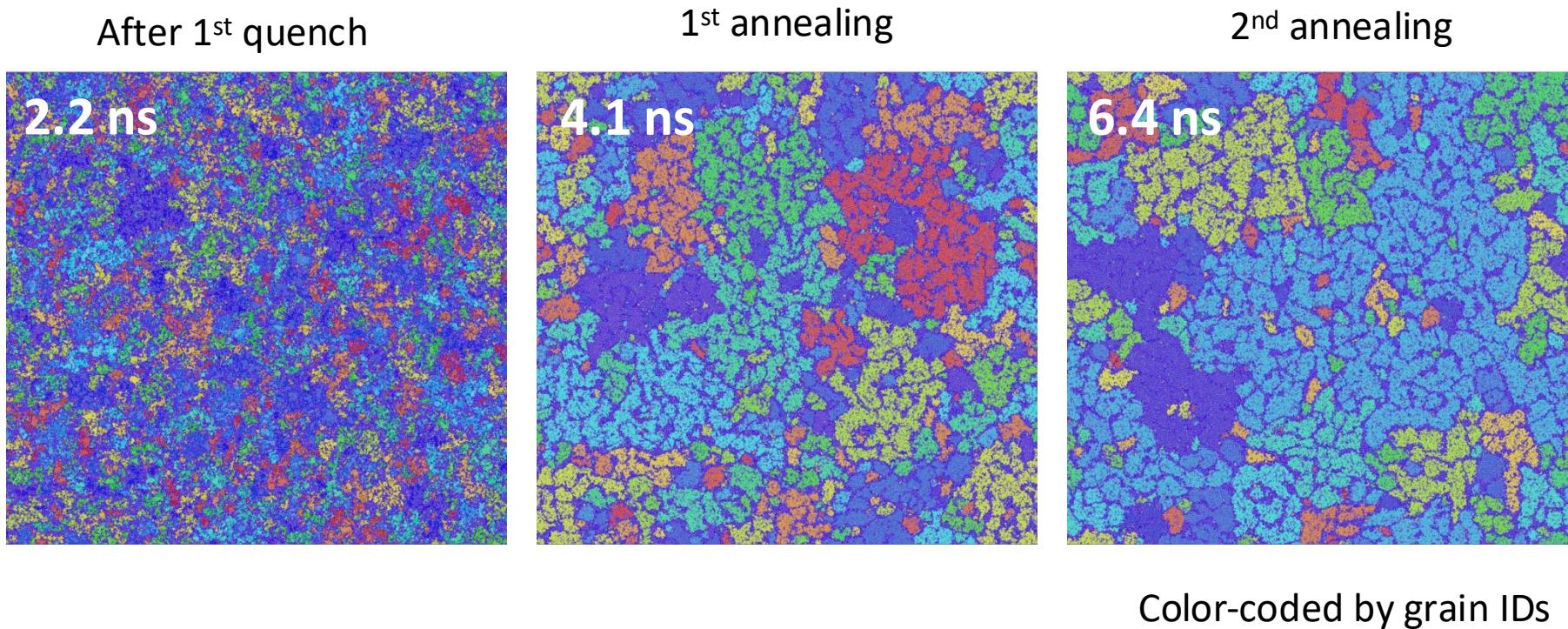


Zoom-in view

● 1T ● 2H ● disordered

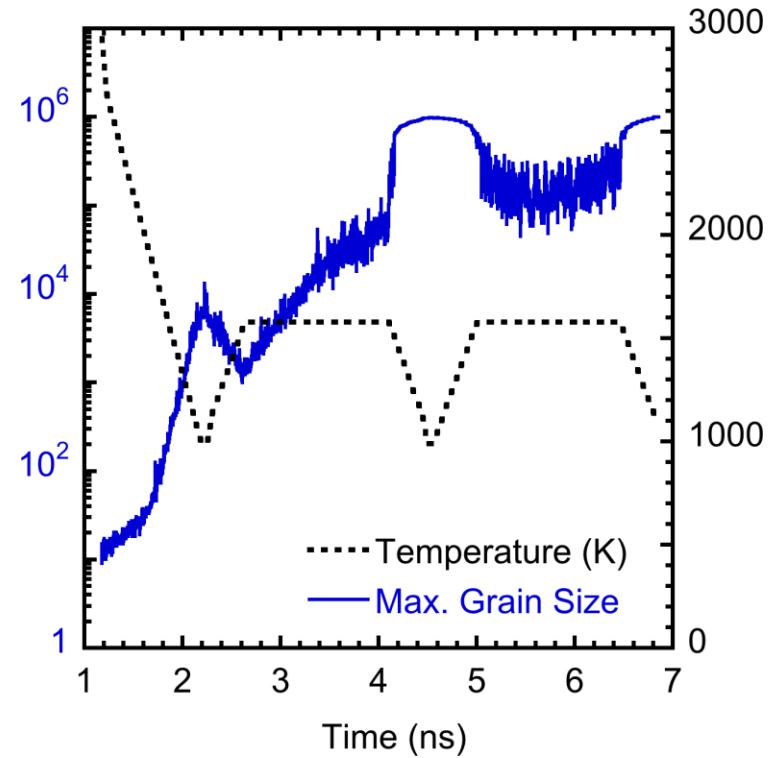
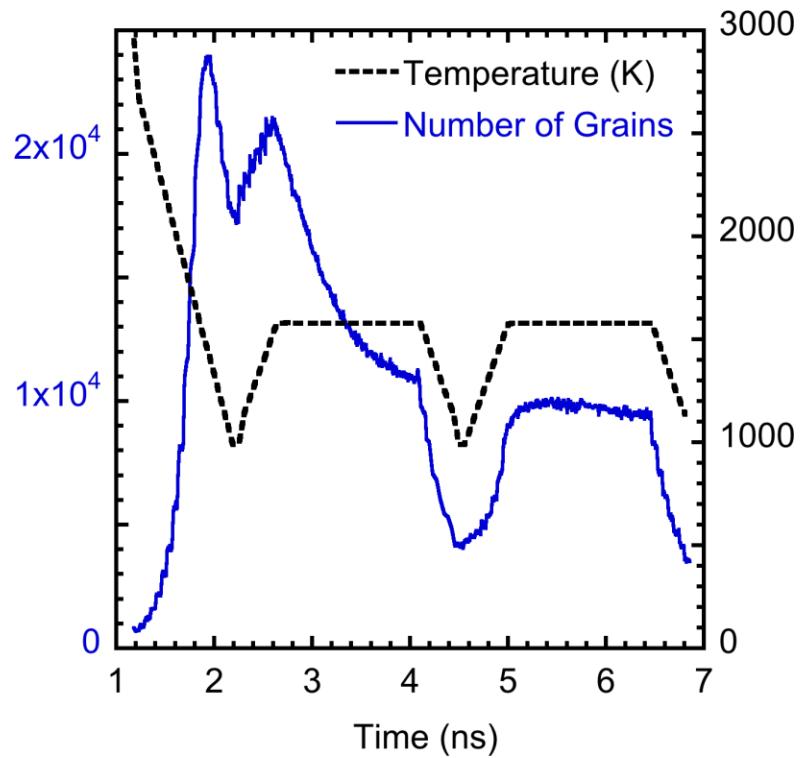
- Atoms in the sulfidized slab are classified into 1T, 2H and disordered phases.
- Areas of connected 2H phase atoms indicates MoS_2 crystal grains, separated by 1T or disordered phases.

Grain Growth by Annealing



- Highly disordered structure is obtained by the rapid quenching at 2.2ns.
- Grain growth and crystallinity improvement at 6.4 ns due to the active grain boundary migration.

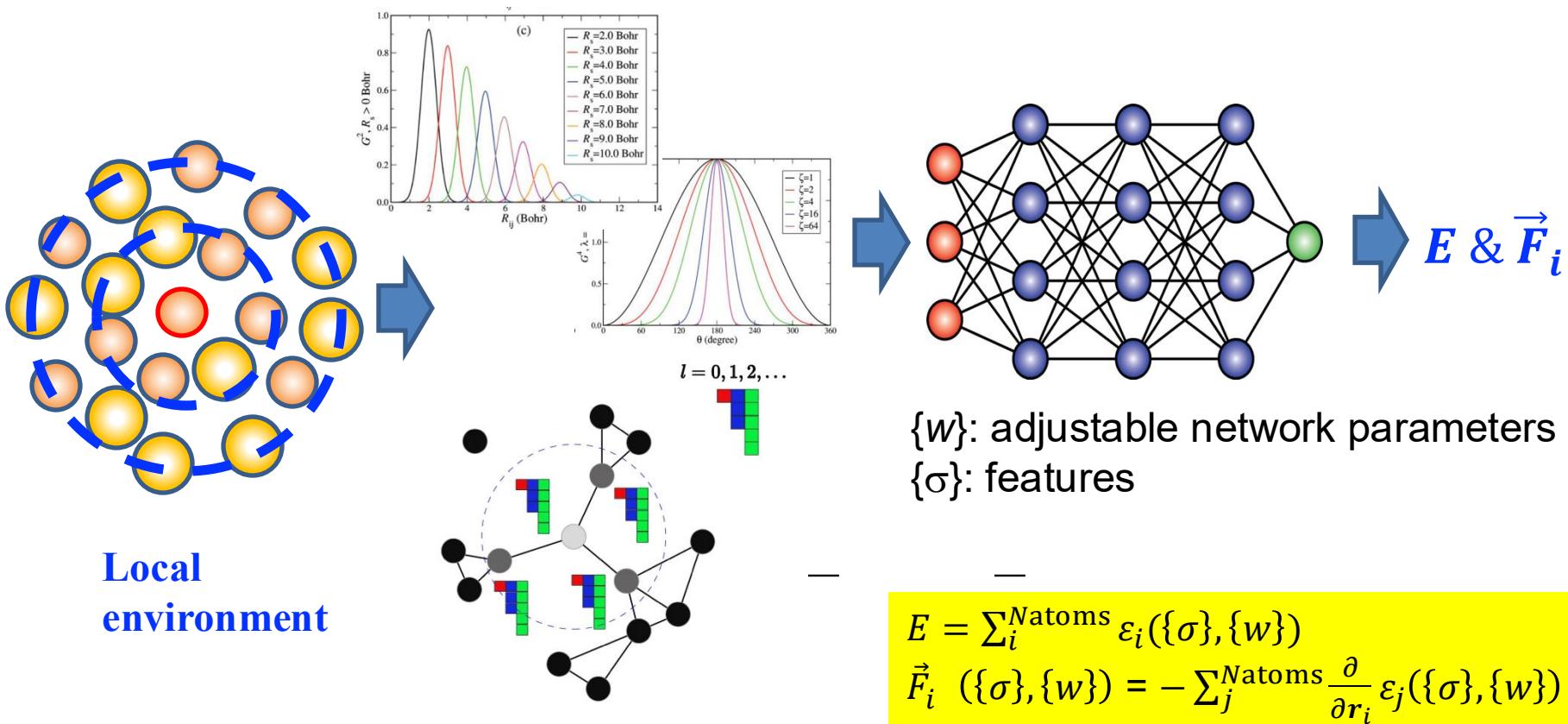
Grain Growth by Annealing



- Rapid decrease in the number of grains and increase in the size of grain during the 1st annealing.
- The largest grain continues to grow with a lower rate during the 2nd annealing step.

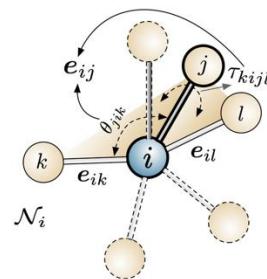
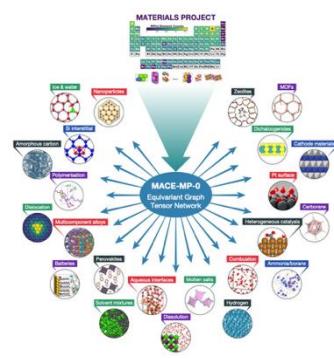
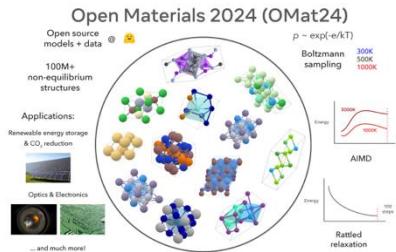
Machine Learning Interatomic Potentials (MLIPs)

- Use Machine Learning to encode local atomic environment to features, such as atom-centered symmetry functions and geometrical tensors
- Neural network to predict atomic energy and force, as well as incorporate QM



Universal MLIPs

- MLIPs that are capable to simulate a variety of materials, covering almost the entire periodic table
- Universal (or foundational) MLIPs based on transformer, attention and graph neural network architectures



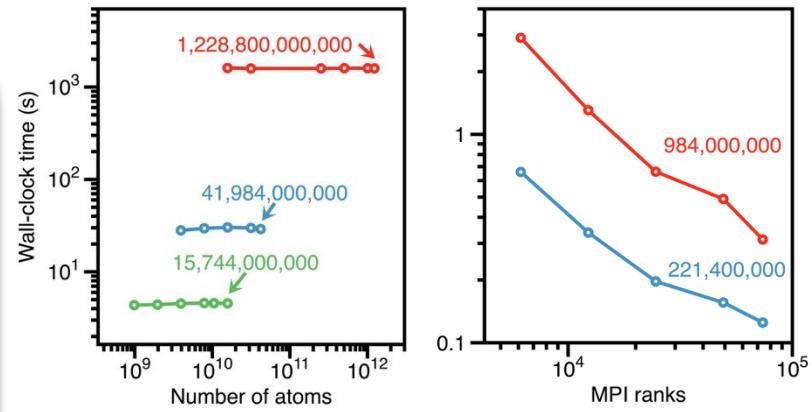
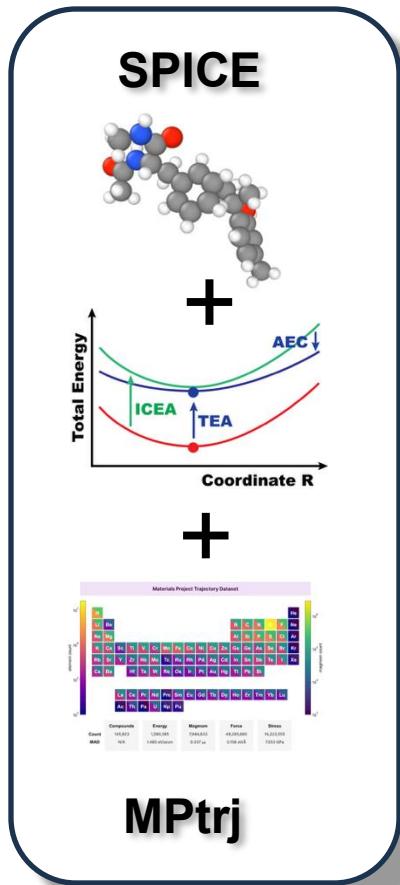
Model ①	CPS ↑	F1 ↑	DAF ↑	Prec ↑	Acc ↑	MAE ↓	R ² ↑	KSRME ↓	RMSD ↓	Training Set	P
eSEN-30M-MP	0.800	0.831	5.26	0.804	0.946	0.033	0.822	0.3398	0.0142	146k (1.58M) (MPtrj)	3
SevenNet-I3i5	0.709	0.76	4.629	0.708	0.92	0.044	0.776	0.55	0.0182	146k (1.58M) (MPtrj)	1.
MatRIS v0.5.0 MPtrj	0.680	0.809	5.049	0.772	0.938	0.037	0.803	0.861	0.0156	146k (1.58M) (MPtrj)	5
GRACE-2L-MPtrj	0.678	0.691	4.163	0.636	0.896	0.052	0.741	0.525	0.0186	146k (1.58M) (MPtrj)	11
DPA3-v2-MPtrj	0.647	0.786	4.822	0.737	0.929	0.039	0.804	0.959	0.0164	146k (1.58M) (MPtrj)	4
MACE-MP-0	0.640	0.669	3.777	0.577	0.878	0.057	0.697	0.647	0.0194	146k (1.58M) (MPtrj)	4
AlphaNet-MPtrj	0.562	0.799	4.863	0.743	0.933	0.041	0.745	1.31	0.0227	146k (1.58M) (MPtrj)	11
eqV2 S DeNS	0.526	0.815	5.042	0.771	0.941	0.036	0.788	1.676	0.0138	146k (1.58M) (MPtrj)	3
ORB MPtrj	0.476	0.765	4.702	0.719	0.922	0.045	0.756	1.725	0.0185	146k (1.58M) (MPtrj)	2
M3GNet	0.430	0.569	2.882	0.441	0.813	0.075	0.585	1.412	0.0217	62.8k (188k) (MPF)	2
CHGNet	0.391	0.613	3.361	0.514	0.851	0.063	0.689	1.717	0.0216	146k (1.58M) (MPtrj)	4

MatBench Discovery*



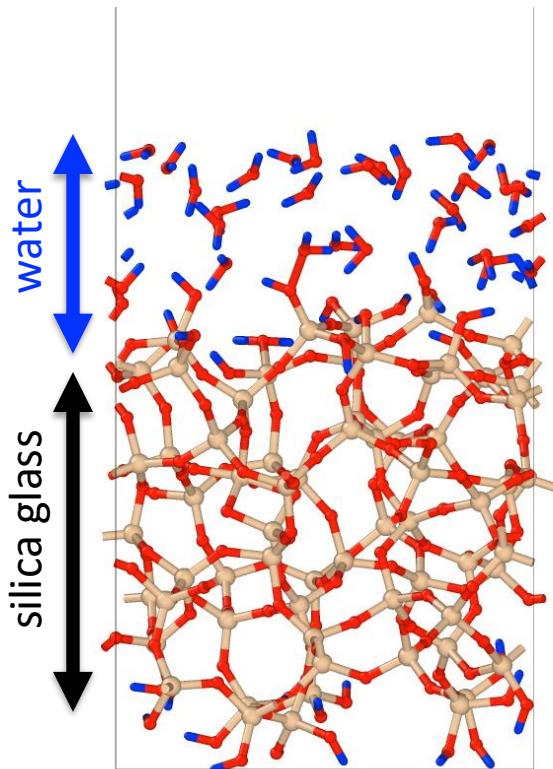
Allegro-FM: Exascale Equivariant Foundation Model

Goal: Develop a MLIP to seamlessly learn large-scale heterogenous datasets and directly deployable to exascale computing platform

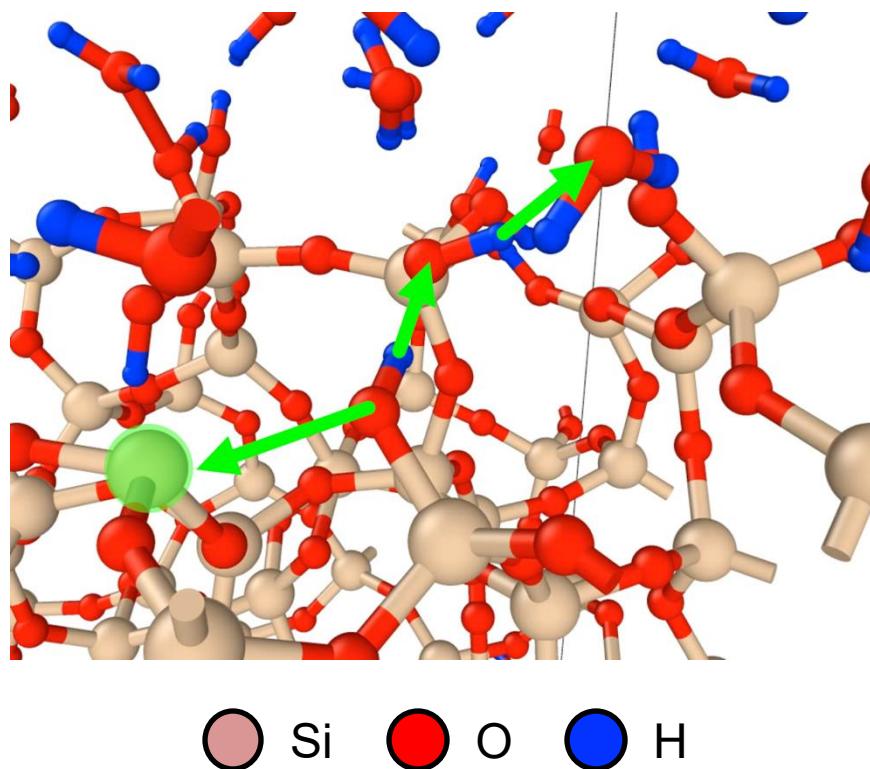


- Parallel efficiency (0.996 weak and 0.981 strong) up to a 1.2 trillion-atom system using full-Aurora Intel GPUs
- 1-billion atoms system for 30K steps (3×10^{14} force evaluations) in 24 hours

Proton Transfer on Hydrated Silica Surface



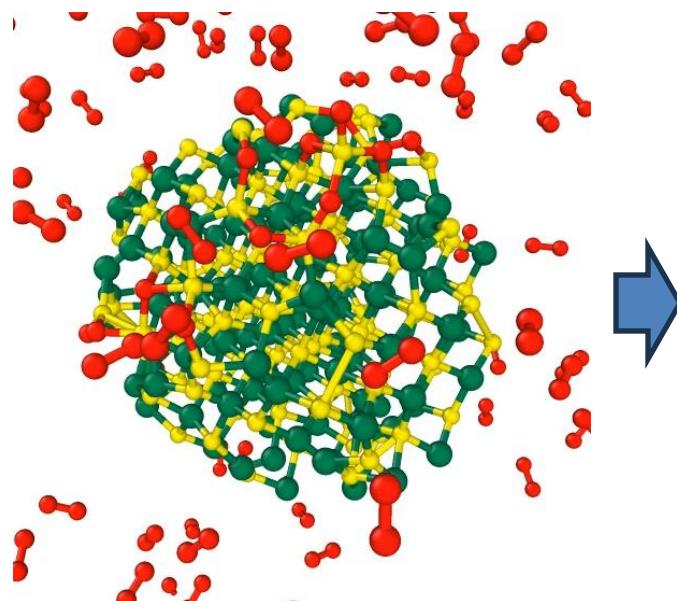
Proton transfer on silica glass surface



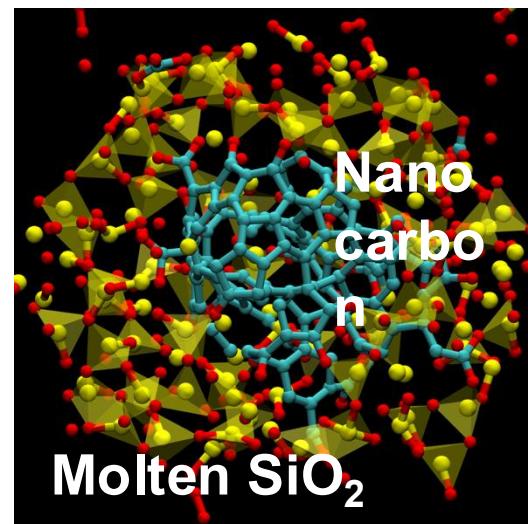
Hydrated silica surface at 300 K

Nanocarbon Synthesis by SiC Nanoparticle Oxidation

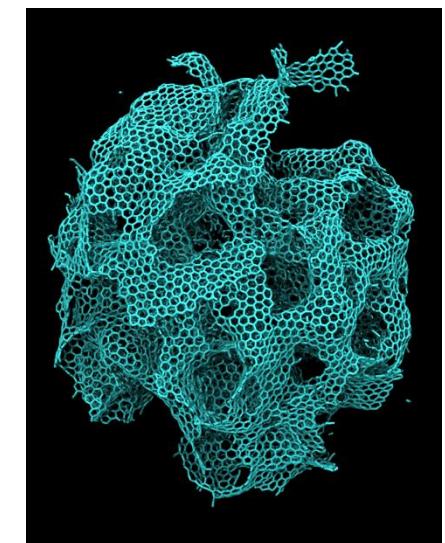
- Formation of nanocarbon and molten silica layer by oxidizing SiC nanoparticle at 2,000 K



● Si ● C ● O

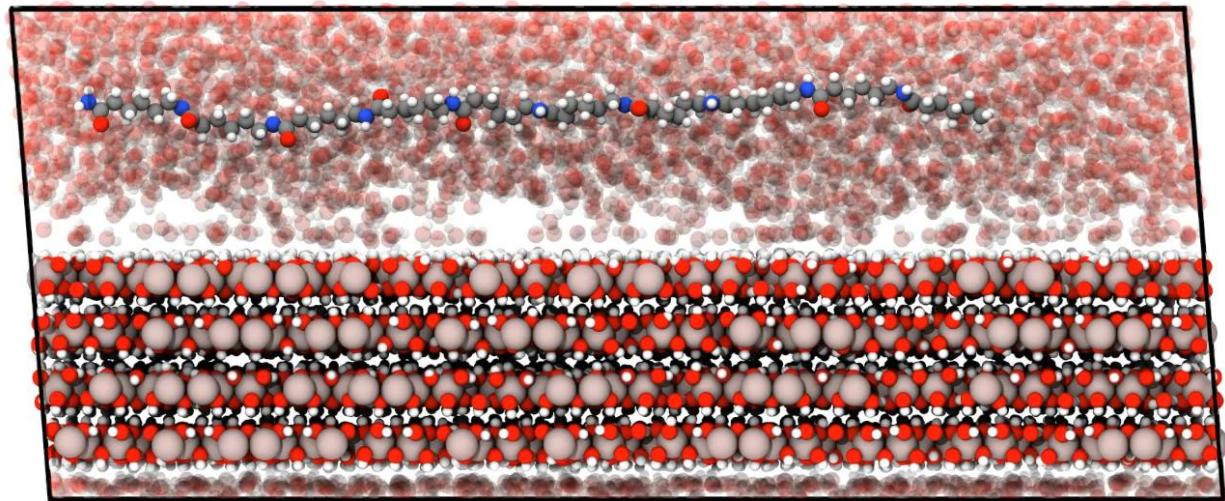
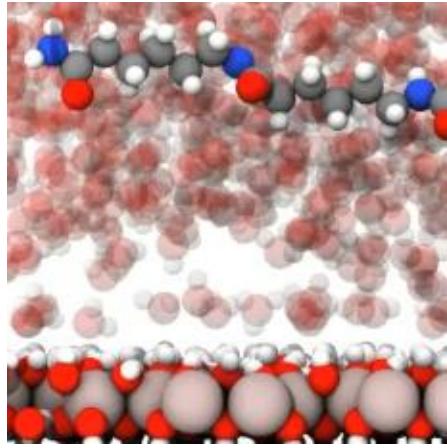


Allegro-FM



3D nanocarbon
structure with ReaxFF

Nylon-6 Chain in Water-filled Gibbsite Cavity

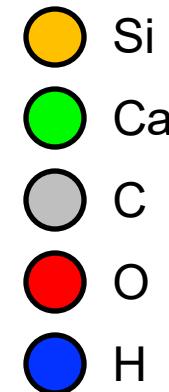
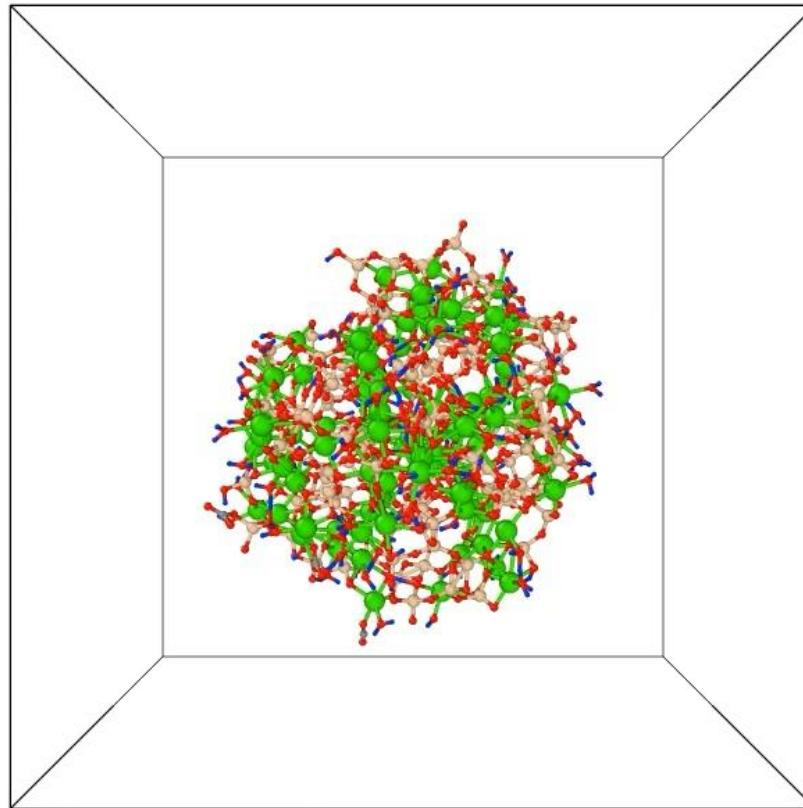


● ● ● ● ●
Al C H O N

- A Nylon-6 chain (10 monomers) in water-filled nanocavity of gibbsite (aluminum hydroxide)
- ~40,000 atoms at 298 K and 1 bar pressure

Carbon Mineralization with Tobermorite Nanoparticle

- A tobermorite (calcium silicate hydrate) nanoparticle immersed in a H_2O and CO_2 mixture and thermalized at 900K
- Formation of H_2CO_3 and HCO_3^- and dissolution of calcium ions

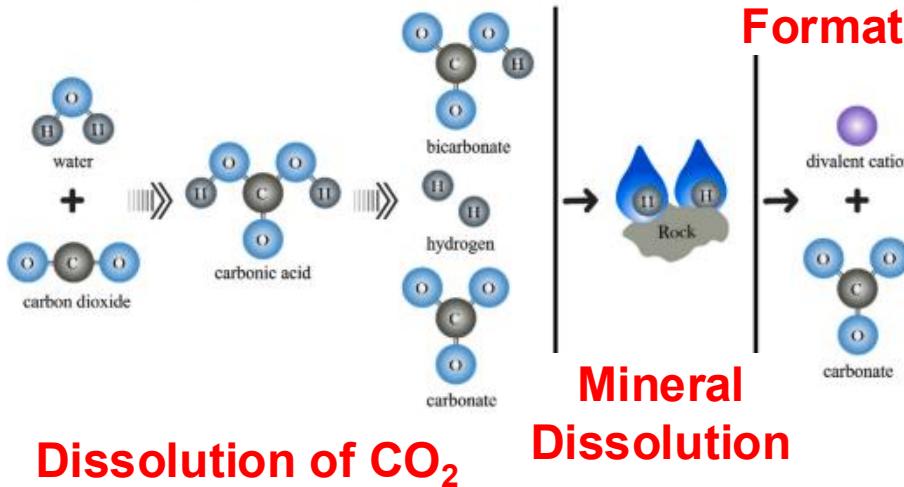


H_2O and CO_2 molecules
are not shown for clarity

Carbon Mineralization with Tobermorite Nanoparticle

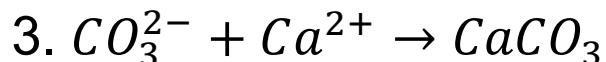
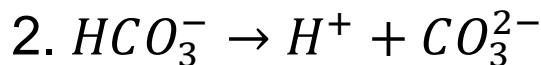
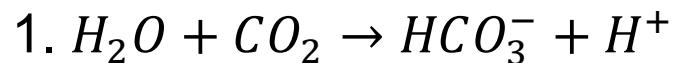
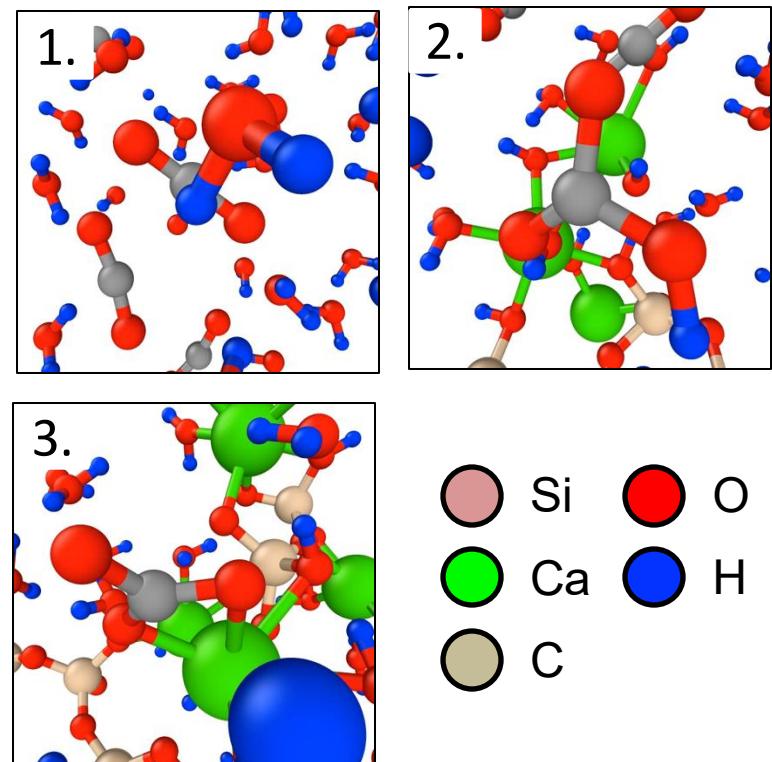
- Multistep carbon mineralization reaction and carbonate precipitation on nanoparticle surface

Carbon mineralization process*



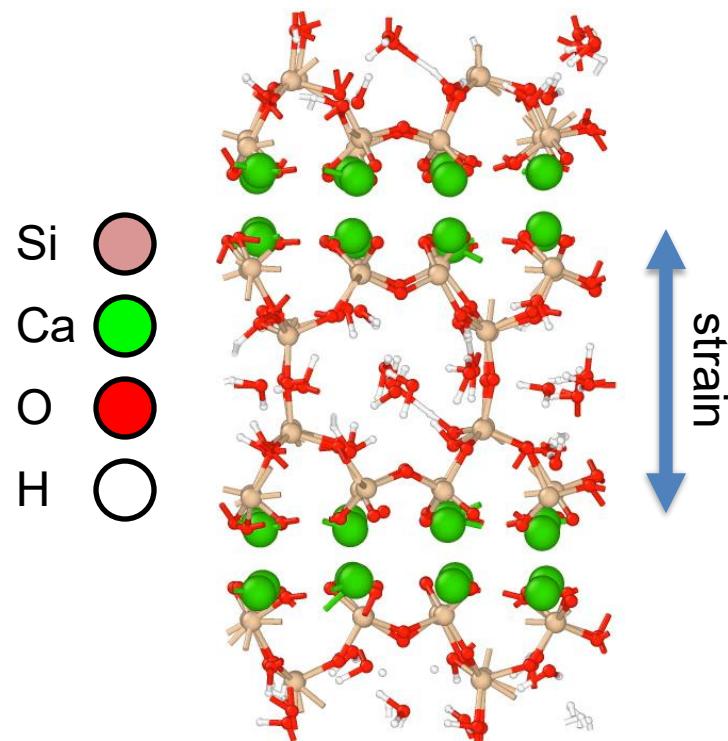
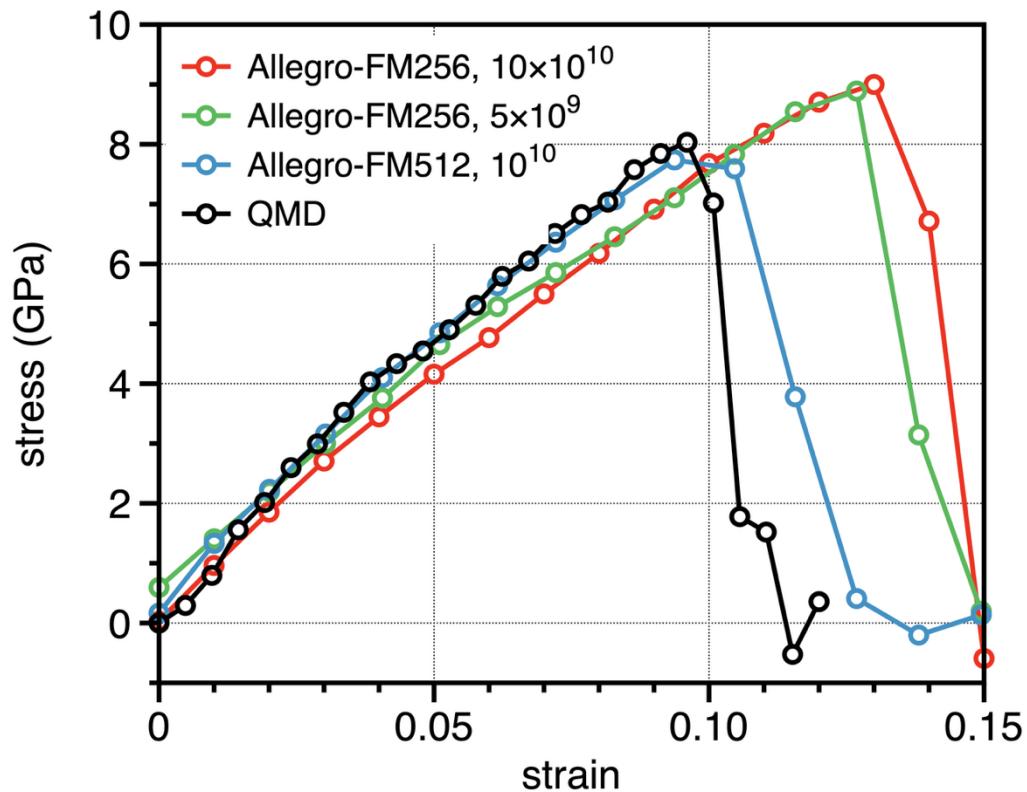
Carbonate Formation

Mineral Dissolution



Tensile Loading on T11 Crystal

- Stress-strain profile agrees well with Allegro-FM and QMD
- Brittle fracture with cleavage plane at the calcium layer



Moving Forward

Review: The ReaxFF reactive force-field: development, applications and future directions*

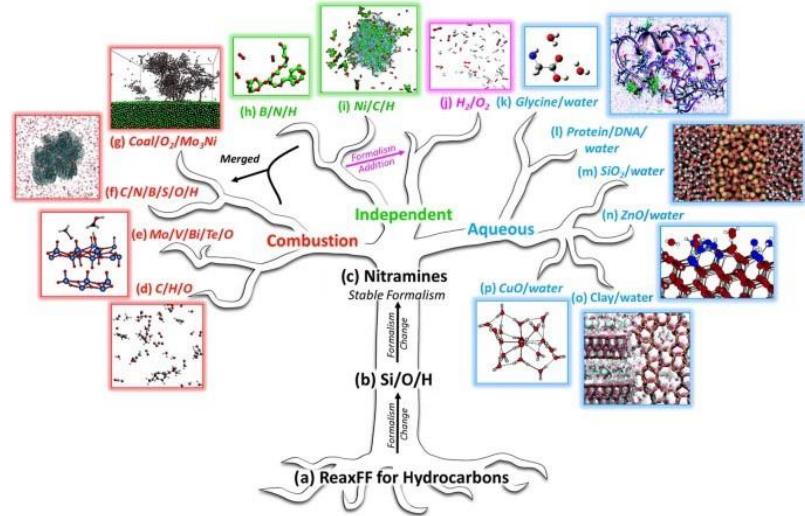
<https://www.nature.com/articles/npjcompumats201511>

List of published ReaxFF force fields

https://www.scm.com/doc/ReaxFF/Included_Forcefields.html

Interatomic potential repository

<https://www.ctcms.nist.gov/potentials/>



ReaxFF development tree*

Recent advances in RMD:

- eReaxFF: A Pseudoclassical Treatment of Explicit Electrons within Reactive Force Field Simulations <https://pubs.acs.org/doi/10.1021/acs.jctc.6b00432>
- JAX-ReaxFF: A Gradient Based Framework for Extremely Fast Optimization of Reactive Force Fields <https://chemrxiv.org/engage/chemrxiv/article-details/60e0d9496b8d89786e6b8a06>
- Allegro-FM: Towards Equivariant Foundation Model for Exascale Molecular Dynamics Simulations <https://arxiv.org/abs/2502.06073>