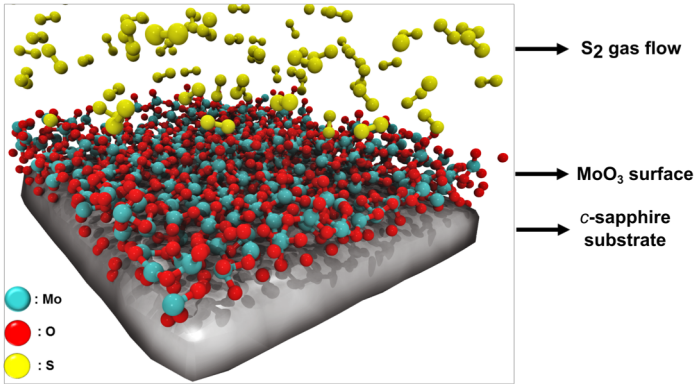
Reactive Force Field (ReaxFF) : Its concepts and application



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University of Southern California

Gaithersburg Marriot Washingtonian Center, November 12, 2018

Outline

1. **Basic concepts of ReaxFF**
   - Multi-scale computational modeling
   - ReaxFF general energy terms
   - Key features of ReaxFF
   - ReaxFF flow diagram
2. **Application of ReaxFF to complex nanoscale systems**
   - Chemical vapor deposition synthesis of MoS_2 layers
3. **Summary and future work**

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   - **ReaxFF general energy terms**
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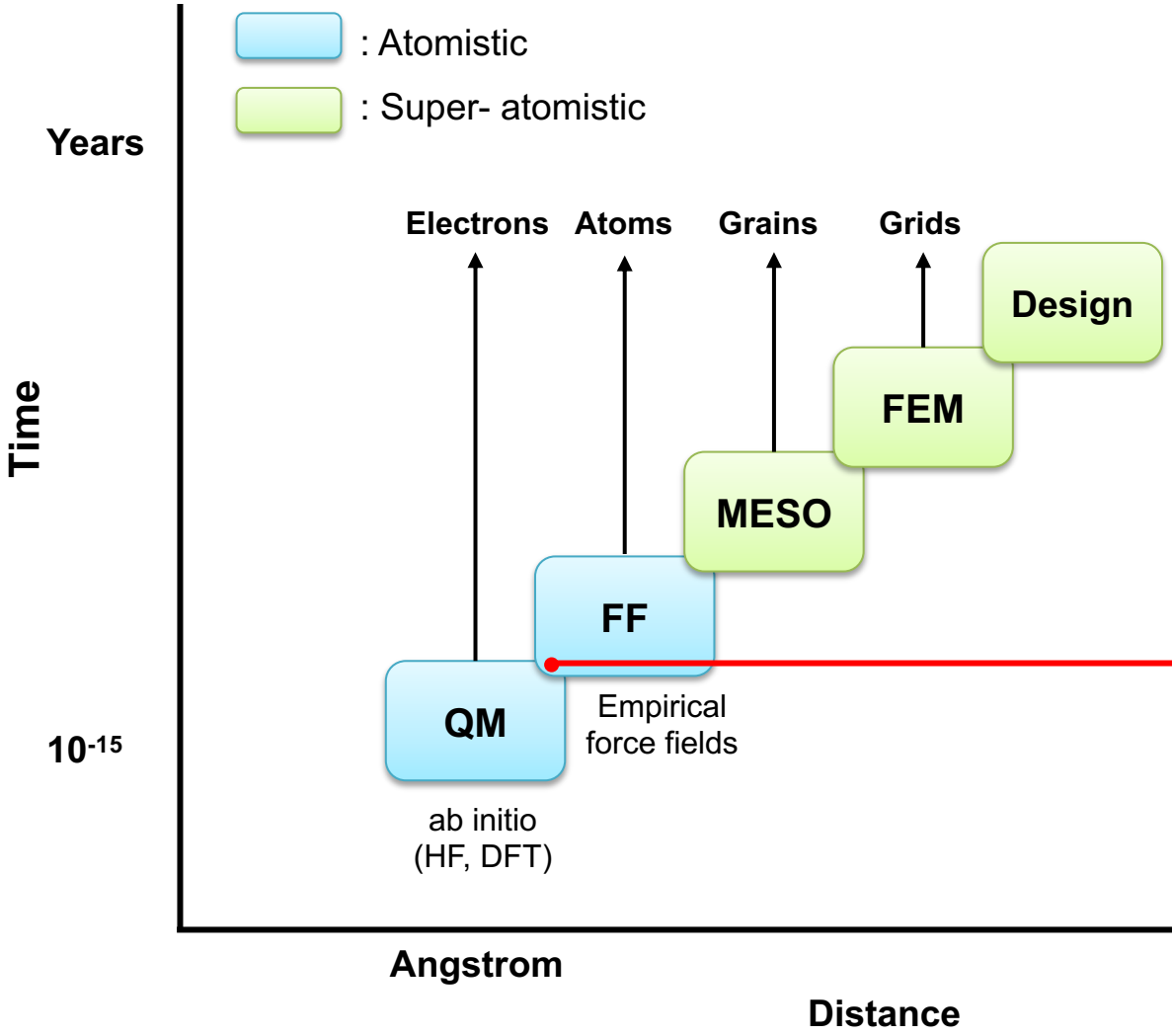
1. Basic concepts of ReaxFF

- **Multi-scale Computational Modeling**



QM methods:

-Fundamental; electronic level

-Computationally expensive

-Small systems (~100 atoms)

Classical FF methods:

-Empirical; parameters to be trained

-Large systems/high temperatures

-Rigid connectivity

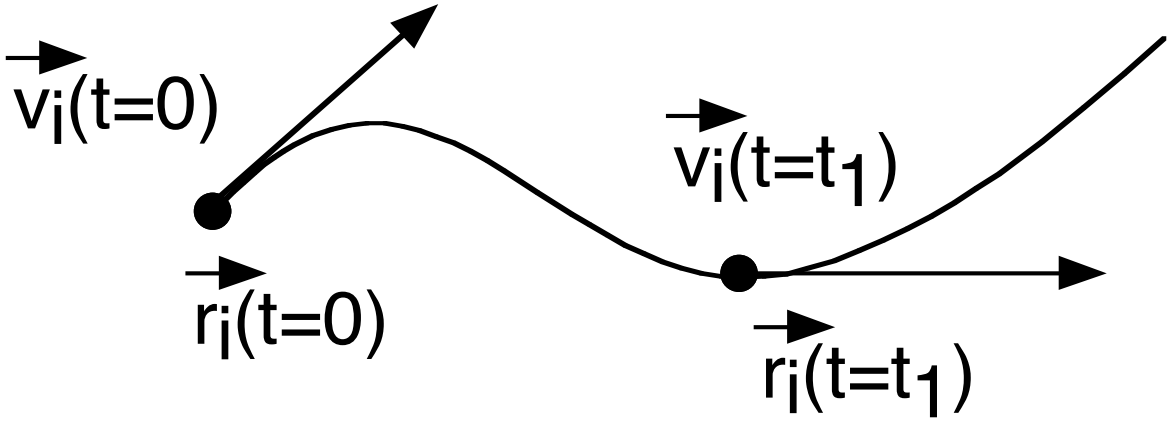
ReaxFF:

-QM-derived reactive force field (based on a bond-order scheme)

-Ability to describe chemical reactions

1. Basic concepts of ReaxFF

- **What is Molecular dynamics (MD) simulation?**



Numerically solve Newton's equation of motion

$$\vec{F}(t) = m\frac{d^2\vec{r}_i}{dt^2} = -\frac{d}{d\vec{r}_i}V(\vec{r}_i \ldots . \overrightarrow{r_N})$$

Interatomic potential; force field

1. Basic concepts of ReaxFF

- **ReaxFF general energy terms***

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

Bonded interactions **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.

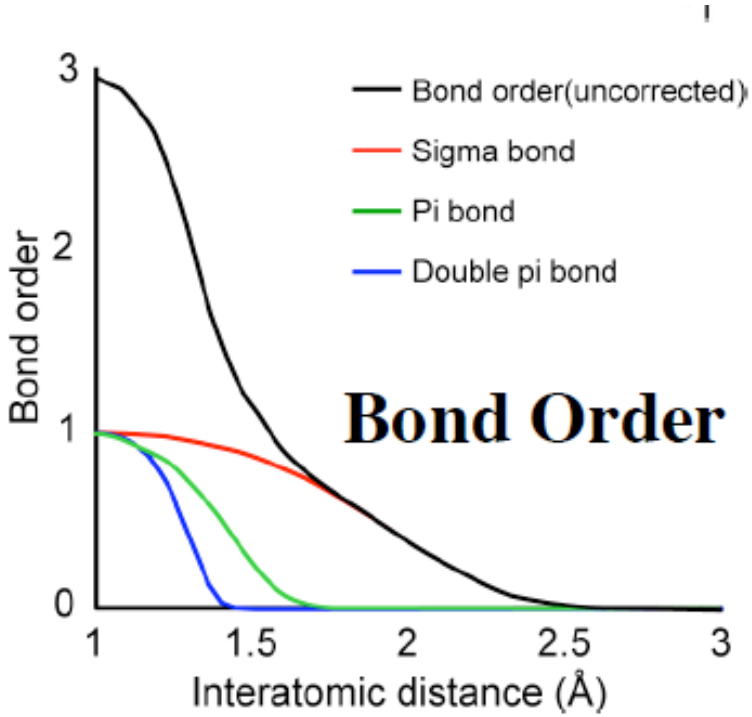
1. Basic concepts of ReaxFF

- **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

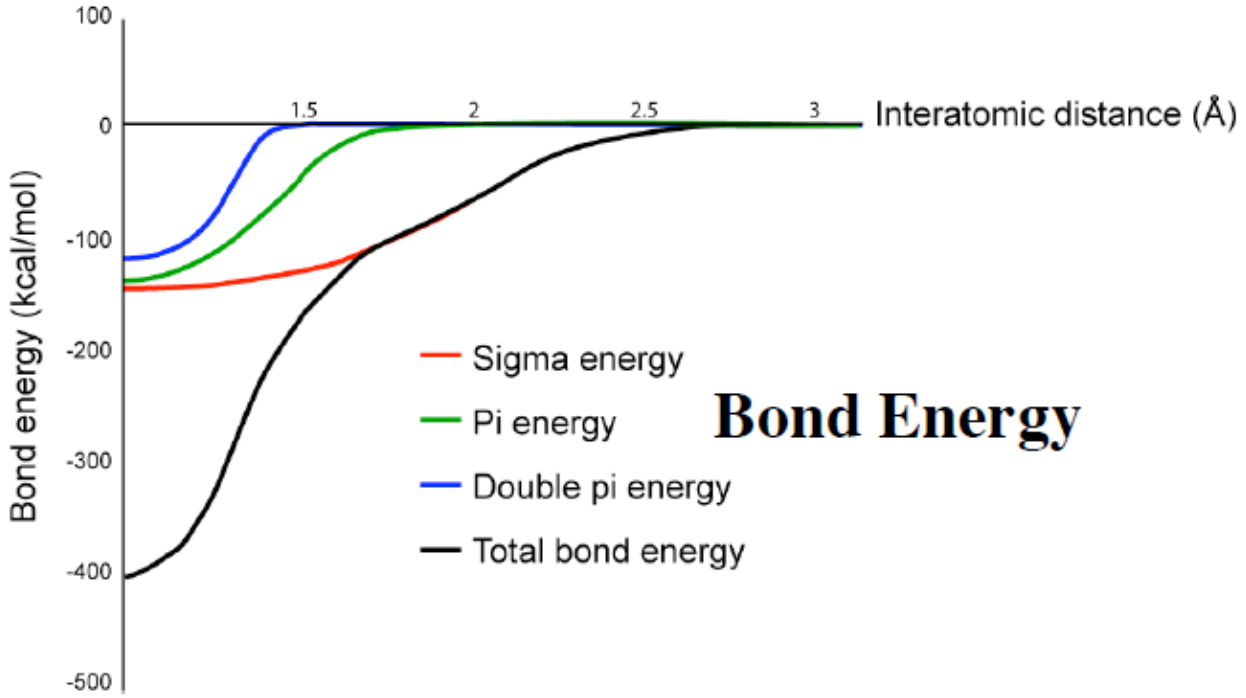


*Russo, Michael F., and Adri CT van Duin. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **269** (2011): 1549-1554.

1. Basic concepts of ReaxFF

- **Key features of ReaxFF – 2***
  - All bonded-interactions are made of bond-order dependent.

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



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1. Basic concepts of ReaxFF

- **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.

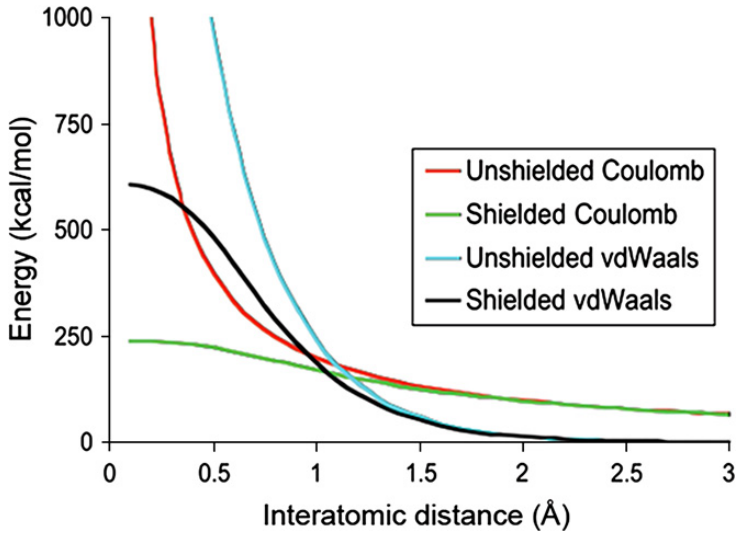
$$E_{vdWaals} = Tap \cdot D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\}$$

A shielded Morse potential

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

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

A shielded Coulomb potential



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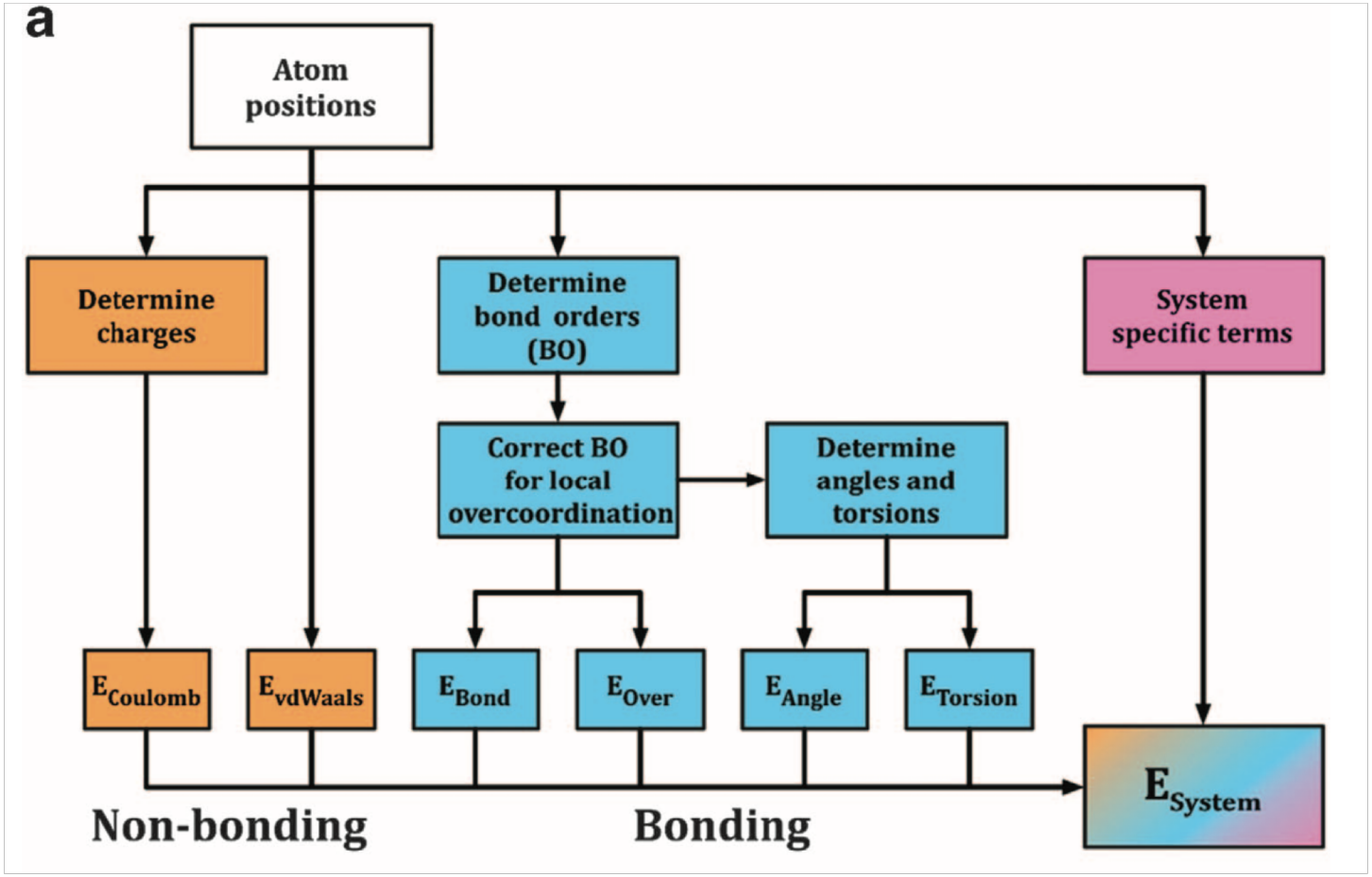
Rappe, Anthony K., and William A. Goddard III. *The Journal of Physical Chemistry* **95 (1991): 3358-3363.

1. Basic concepts of ReaxFF

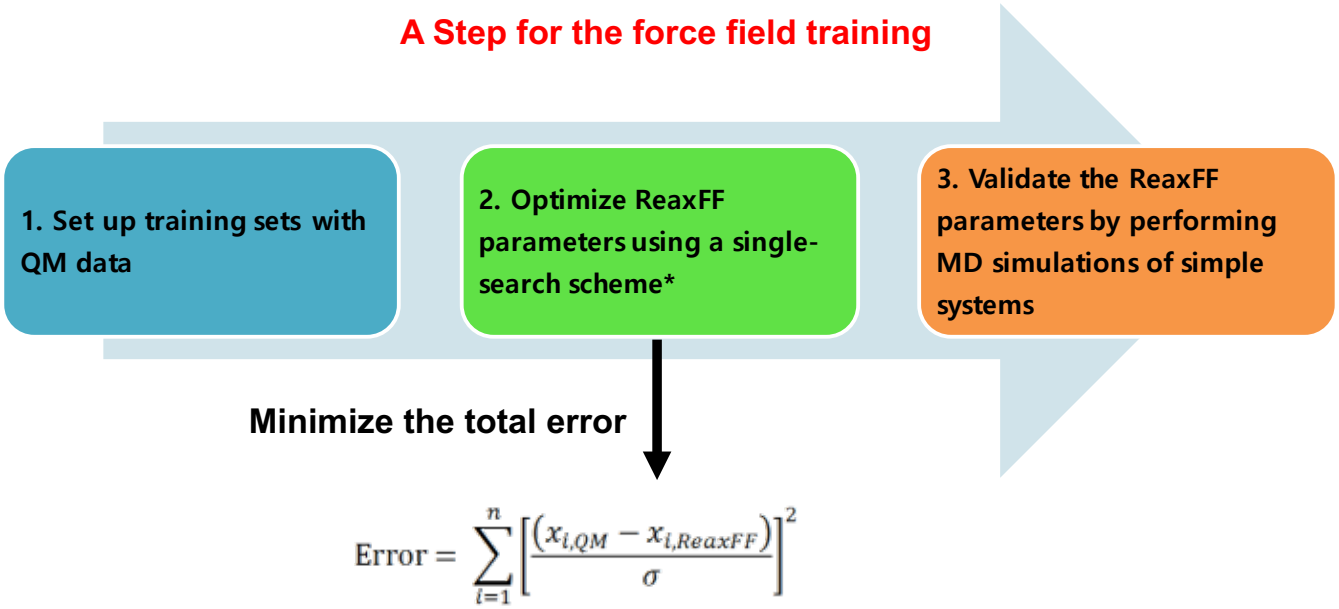
- **ReaxFF flow diagram***



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

1. Basic concepts of ReaxFF

- **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.

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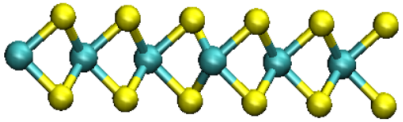
I. Background/motivation

- **Computational synthesis of layered materials**

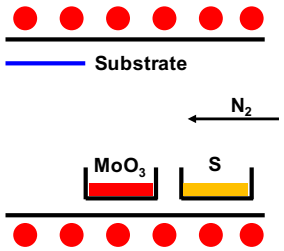


Mono-layered MoS_2
- has unique electric and optoelectronic characteristics [1]
- can be applied to next-generation electronic devices

Synthesis Method?

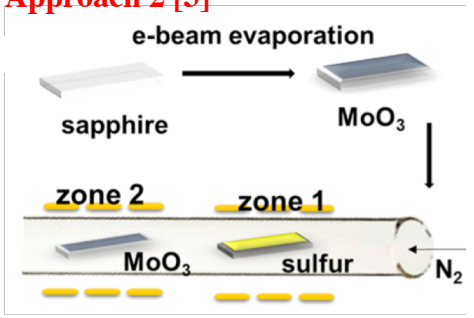
Chemical Vapor Deposition (CVD)

Approach 1 [2]



MoO_3 powder + S powder

Approach 2 [3]



Pre-deposited MoO_3 surface + S powder

Research Problem?

Synthesis of clean and uniform mono-layered MoS_2 is still challenging.

Research Question?

What is the reaction mechanism of sulfidation of MoO_3 surface at the atomic level?

Research Goal:

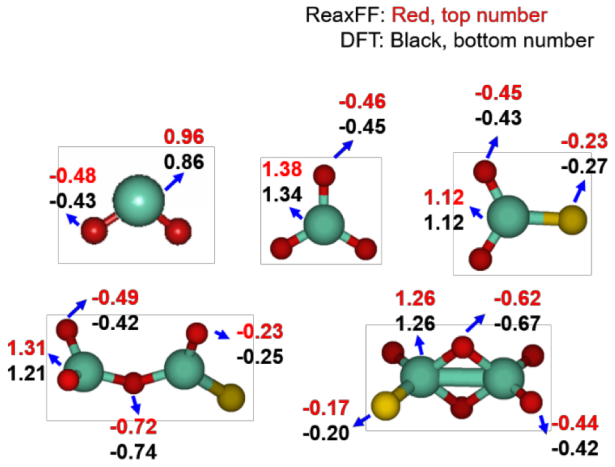
Develop a ReaxFF reactive force field for Mo/O/S systems to gain atomistic-scale insights into the sulfidation of MoO_3 surfaces.

[1] Gupta, Ankur, Tamilselvan Sakthivel, and Sudipta Seal. "Recent development in 2D materials beyond graphene." *Progress in Materials Science* 73 (2015): 44-126.
[2] Lee, Yi-Hsien, et al. "Synthesis of Large-Area MoS2 Atomic Layers with Chemical Vapor Deposition." *Advanced Materials* 24.17 (2012): 2320-2325.
[3] Taheri, Payam, et al. "Growth mechanism of largescale MoS2 monolayer by sulfurization of MoO3 film." *Materials Research Express* 3.7 (2016): 075009.

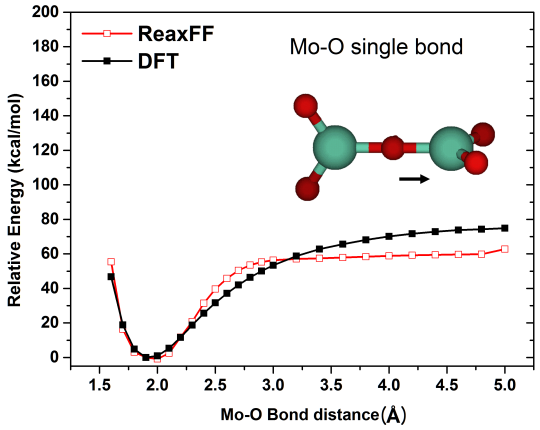
II. Methods

- **How do we develop ReaxFF reactive force field parameters?**

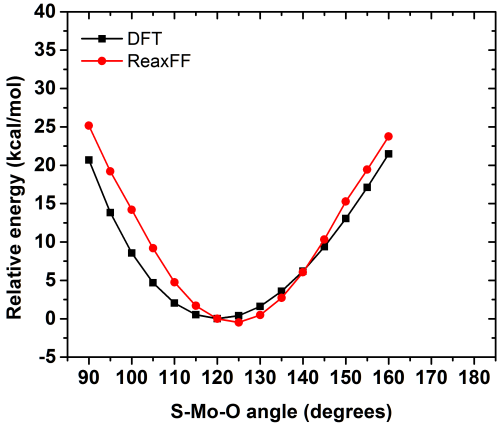
❑ **Atomic charges**



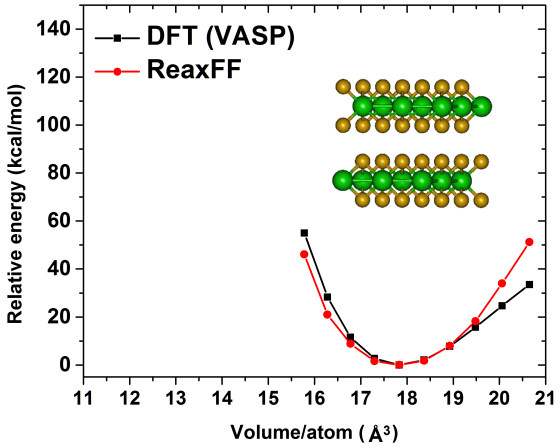
❑ **Full bond dissociation curve**



❑ **Angle distortion energy**

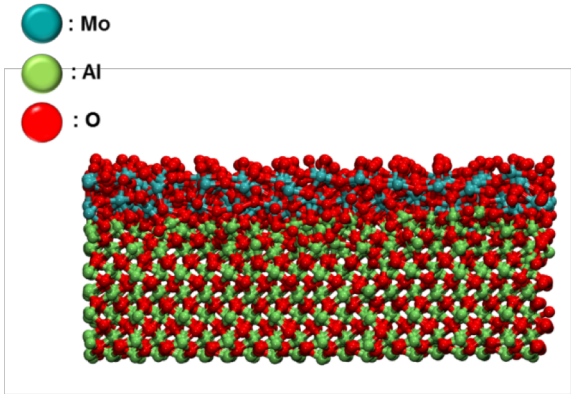


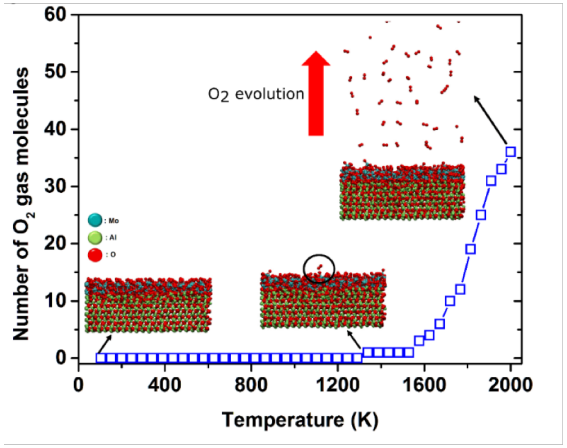
❑ **Equations of state for crystal systems**



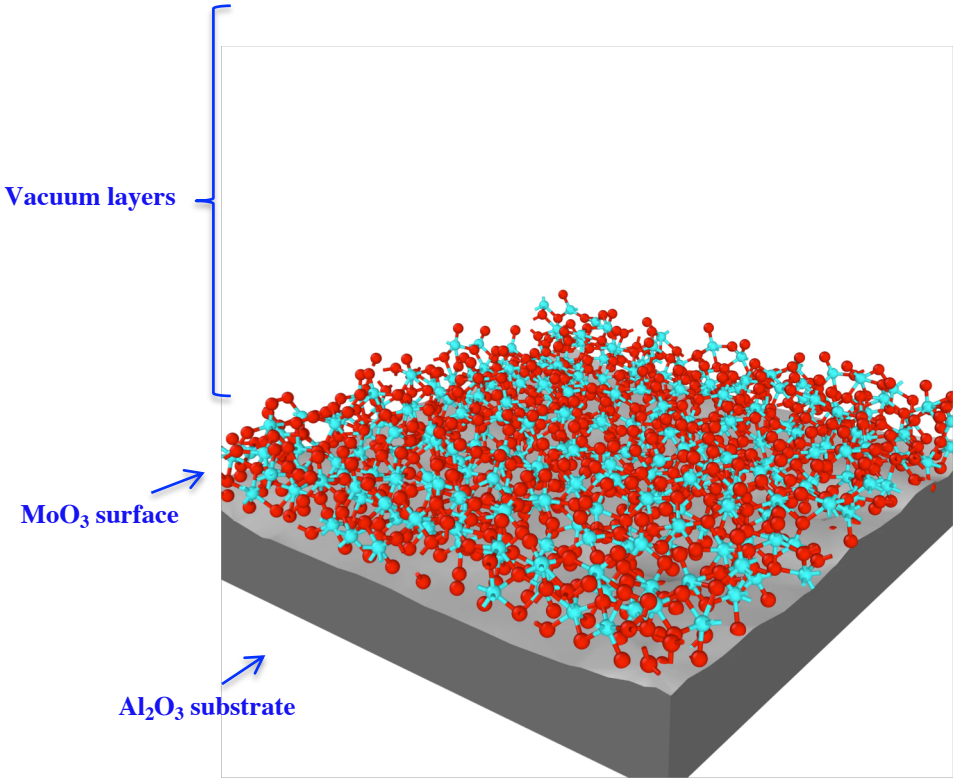
III. RMD simulations: a three-step sulfidation process

- **Step 1. O_2 evolution from a MoO_3 surface**





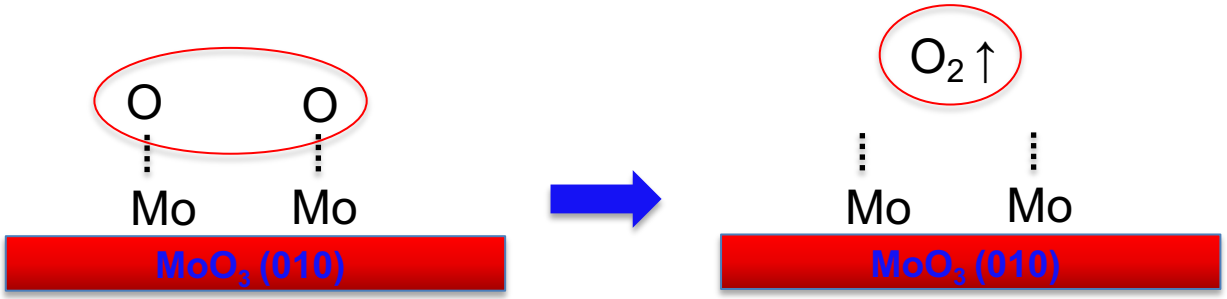
RMD simulation of O_2 evolution from a MoO_3/Al_2O_3 surface



➢ At elevated temperatures (T > 1300 K), a MoO_3 surface is self-reduced by O_2 evolution.

III. RMD simulations: a three-step sulfidation process

- **Reaction mechanism of the O_2 evolution at high temperatures by RMD simulations**



$$2 - \underbrace{Mo = O_t}_{\text{O-termination}}{}^{*} \rightarrow 2 - \underbrace{Mo =}_{\text{Mo-dangling bond}}{}^{*} + O_2 \uparrow$$

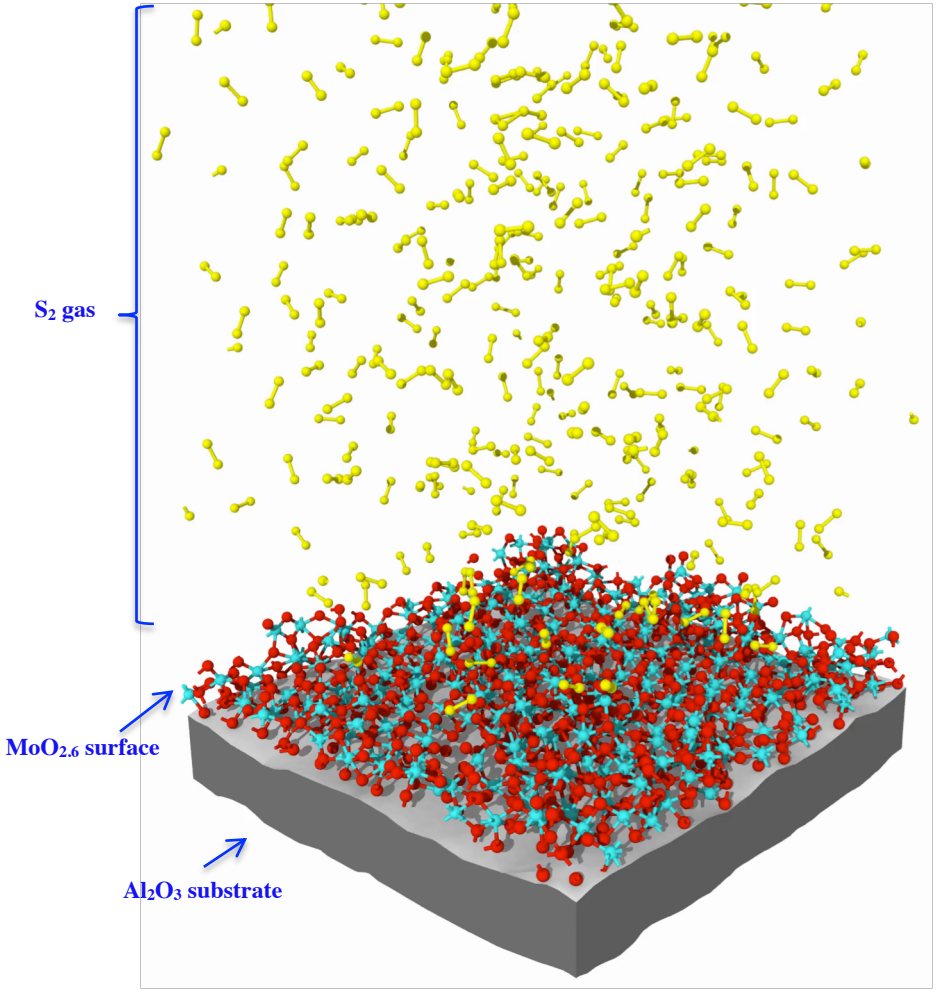
* Surface species

: At high temperatures, a MoO_3 surface undergoes self-reduction by disordered O-termination sites, leading to Mo-dangling bonds.

III. RMD simulations: a three-step sulfidation process

- **Step 2. SO/SO_2 formation from a $MoO_{2.6}$ surface**

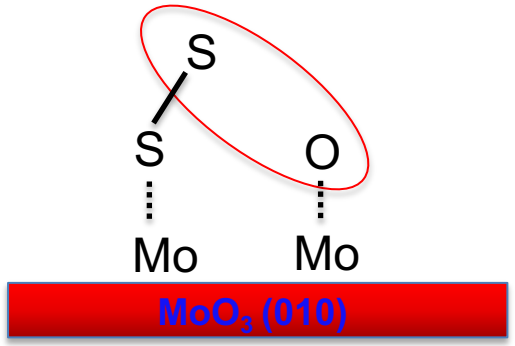
RMD simulation of CVD synthesis of MoS_2 layers (up to 1.2 ns)

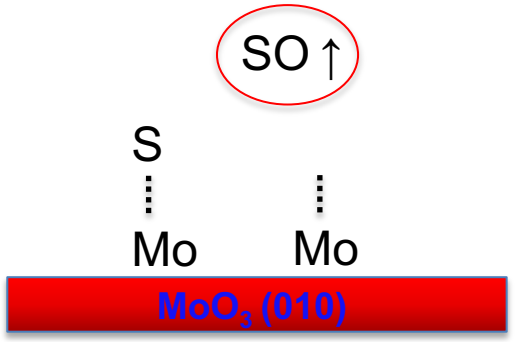


- A $MoO_{2.6}$ surface, reduced by the previous step, is exposed to S_2 gas molecules for CVD simulations
- $MoO_{2.60}$ surface was further reduced and partially sulfurized by forming SO and SO_2 products.

III. RMD simulations: a three-step sulfidation process

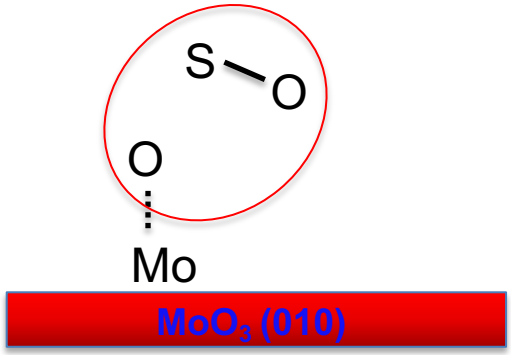
❑ Reaction mechanisms of the SO/SO_2 formation by RMD simulations

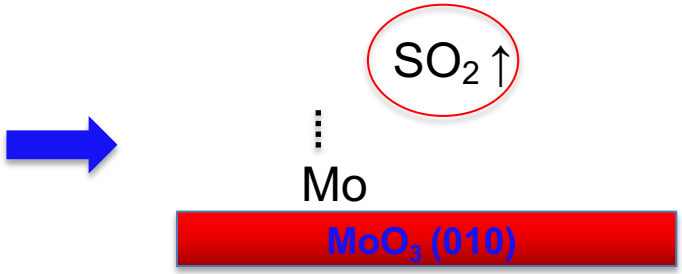




$$-\underbrace{Mo = S_2}_{S_2\text{-termination}}^{*} + \underbrace{-Mo = O_t}_{\text{O-termination}}^{*} \rightarrow \underbrace{-Mo - S}_{\text{S-termination}}^{*} + \underbrace{-Mo = *}_{\text{Mo-dangling bond}} + \mathbf{SO(g)} \uparrow$$

* Surface species

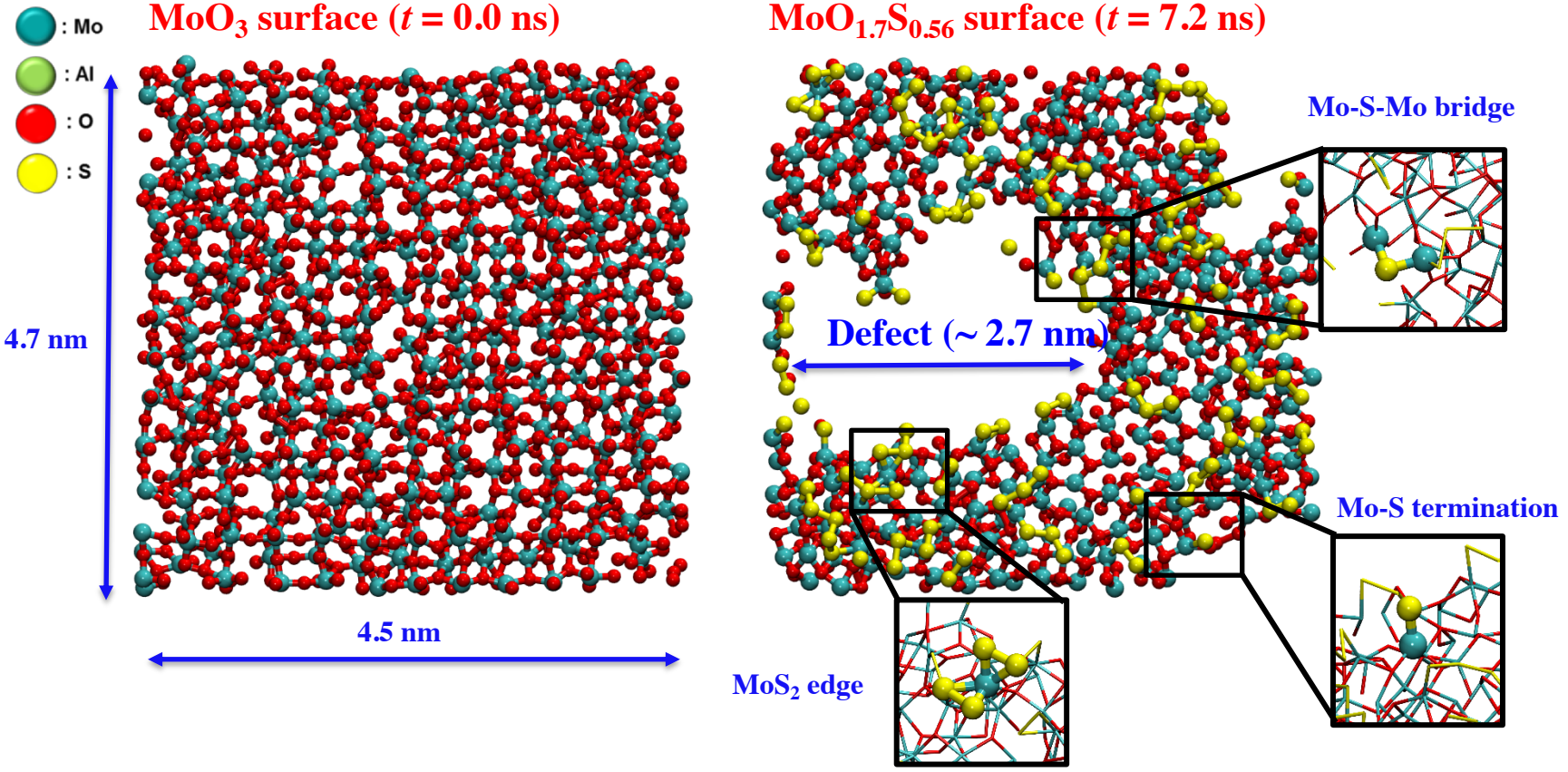




$$\underbrace{-Mo = O_t}_{\text{O-termination}}^{*} + \mathbf{SO(g)} \rightarrow \underbrace{-Mo =}_{\text{Mo-dangling bond}}^{*} + \mathbf{SO_2(g)} \uparrow$$

III. RMD simulations: a three-step sulfidation process

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



- Surface defect was generated because of O removals and follow-up Mo redistribution.
- Mo/S configurations at 7.2 ns are qualitatively consistent with a portion of MoS_2 structures (Mo-S termination, Mo-S-Mo bridge, and MoS_2 edge)

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3. Summary and future plan

- **RMD simulations coupled with ReaxFF enable us to study physical and chemical properties of complex nanoscale system.**

- **Large-scale and long-time RMD simulations will be performed to investigate:**
  1. **Further growth of MoS_2-like structures**
  2. **Healing of surface defects for further introduction of sulfur precursor**

Funding:

U.S. DEPARTMENT OF ENERGY | Office of Science