A Reactive Force Field for Molybdenum Disulfide Crystallization

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Motivation

Molybdenum disulfide, MoS_2, is a layered material from transition metal dichalcogenide (TMD) family. Its range of applications includes tribological coatings, materials for electronics, and catalysis.

TMD thin films are often prepared via deposition processes, that originally yield an amorphous material[1]. Tribological applications mostly rely on the ability of MoS_2 to crystallize in the course of exploitation. Other applications require MoS_2 to be crystallized in a certain way: in mild conditions for flexible stretchable photodetectors[2] or with specific defects for catalysis applications[3].

Accurate simulations at a large scale provide insights into collective events and structural changes in the course of transformation and isolate the effects of varying conditions. Those findings can be very useful for guiding experimental search of the treatment conditions.

Several ReaxFF[4] parameterizations exist for Mo-S system. They were used to study bending of MoS_2 layers[5], crystallization of a single layer of MoS_2[6,7], and formation MoS_2 from MoO_3 and sulfur[8]. None of those, however, yielded a layered MoS_2 in our attempts to crystallize it if it wasn't a single-layer setup. The structures we produced resembled a not-yet-discovered experimentally and non-stable within DFT defective rock-salt type MoS.

In our work on ReaxFF V-O parameterization we found a set that tended to produce layered VO_2 structures resembling MoS_2 layers. Using Chen et al[5,6] parameters for S atom, we developed this set into a full Mo-S parameterization. Our new Mo-S ReaxFF reproduces the energies of variuos crystalline Mo_xS_y phases and actually yields layered MoS_2 in crystallization simulations.

Methods

- DFT within VASP, PAW, PBE, E_{cut} = 500 eV
  van der Waals interactions – Grimme-D2
  U-correction 3.5 eV for Mo atom
- Molecular dynamics – LAMMPS, reax/c package
- ReaxFF parameters:
  Chenoweth et al[9] as a starting point for V-O
  Chen et al[7] – addition for S atom
- ReaxFF development – Monte-Carlo algorithm

Results

ReaxFF validation – crystalline models

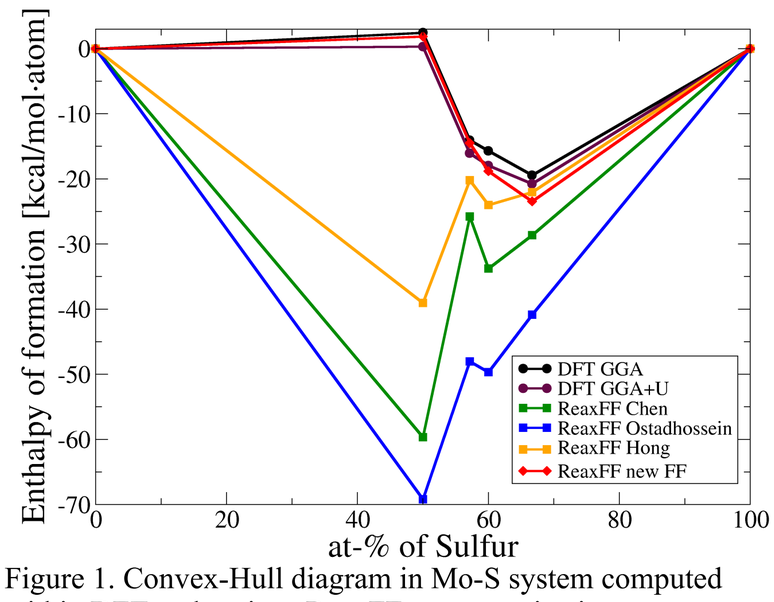

Figure 1. Convex-Hull diagram in Mo-S system computed within DFT and various ReaxFF parameterizations.

Table 1. Structural parameters of DFT- and ReaxFF-optimized MoS_2.

Method	Cell parameters [Å]	
	a	c
Experimental	3.169	12.324
DFT	3.189	12.401
DFT+U	3.199	12.407
ReaxFF new FF	3.209	11.901

- MoS_2 cell parameters – within 5% of experimental and DFT-computed values
- Enthalpies of formation of Mo_xS_y crystals within new FF matches DFT within 4 kcal/mol·atom
- State-of-the-art ReaxFF parameterizations overestimate the stability of hypothetical fcc-MoS.

ReaxFF validation – amorphous models

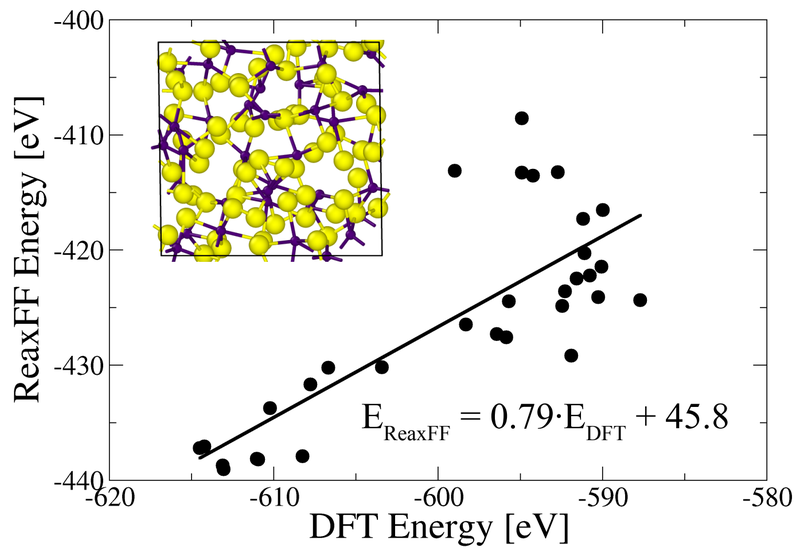

Figure 2. Energies of 105-atom amorphous MoS_2 models, generated via melt-quench within ReaxFF and optimized within DFT. Black line – linear fit, red line – linear fit, slope of 1.

- ReaxFF energies of amorphous MoS_2 correspond well to their DFT energies
- 1 "ReaxFF eV" ≈ 0.8 "DFT eV" in am-MoS_2
- Overall – good performance of the new FF vs. DFT

Results

MoS_2 crystallization – small models

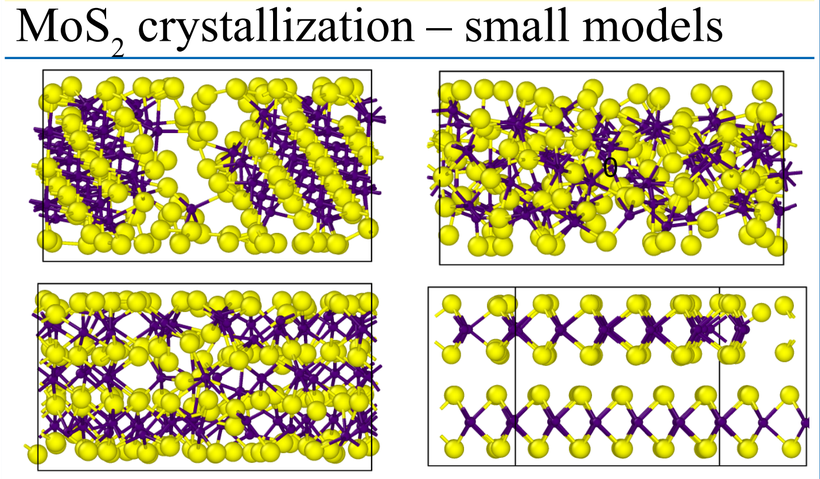

Figure 3. MoS_2 crystallization with different ReaxFF parameter sets: top left – Ostadhossein[5], top right – Chen[7], bottom left – Hong[8], bottom right – our new parameterization.
216 atom model, 2 layers of MoS_2, LJ walls in z-direction; melted at 5000K and then quenched at 10 K/ps.

MoS_2 crystallization – big models

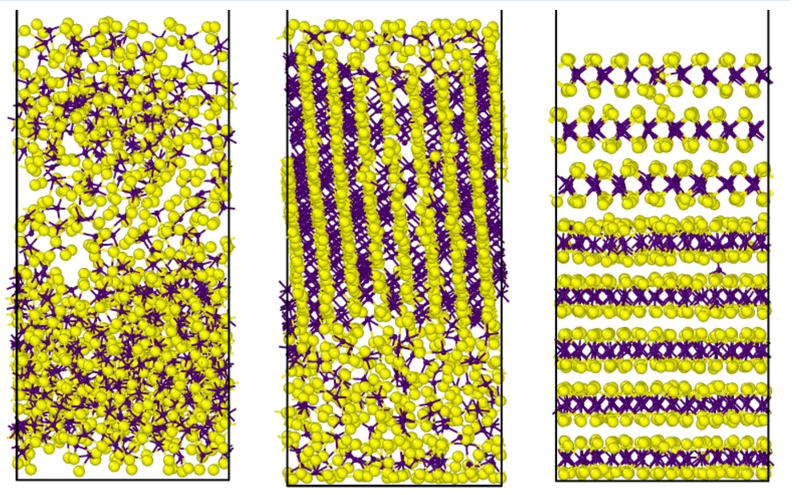

Figure 4. MoS_2 crystallization with different ReaxFF parameter sets: left– Chen[7], middle – Hong[8], right – our new parameterization.
1344 atom model, 8 layers of MoS_2, LJ walls in z-direction; melted at 5000K, cooled to 2000K at 10 K/ps and then held at 2000K with top wall wiggling to mimic tribological conditions.

- State-of-the-art force fields: structures resembling rock salt MoS plus sulfur-rich phase
- Our new force field – 2H-MoS_2 layers

Conclusions

Our new ReaxFF parameter set for Mo-S system:

- Reproduces cell parameters of 2H-MoS_2
- Reproduces DFT stabilities of crystalline Mo_xS_y
- Reproduces stabilities for amorphous MoS_2
- Yields crystallization of layered MoS_2 structures in multiple layer setup, even in relatively big system

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Acknowledgments
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