Supplementary Information to

ReaxFF Reactive Force-Field Study of Molybdenum Disulfide (MoS_2)

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Optimization of ReaxFF for two-dimensional MoS_2:

We have performed DFT simulations on both small molecules and periodic structures to generate the required data for the fitting of the new ReaxFF forcefield.

Table S1: Parameters optimized during the training of $ReaxFF_{MoS_2\text{-}2017}$

Fitted parameters	Remarks
Mo atomic parameters	γ_{vdw}, χ_{EEM}, η_{EEM}
Mo-S bond	$E_{diss.1}$; $E_{diss.-2}$;P_{be1}; P_{be2}; P_{be2}; P_{bo3}; P_{bo4}; P_{bo1}; P_{bo2}
Mo-S off-diagonal	Evdw; Rvdw; alfa; cov.r; cov.r_2; cov.r_3
S-Mo-S angle	θ_0; κ_a; κ_b; p_{conj}; p_{v2}; k_{penal}; p_{v3}
Mo-S-Mo angle	θ_0; κ_a; κ_b; p_{conj}; p_{v2}; k_{penal}; p_{v3}
S-S-Mo angle	θ_0; κ_a; κ_b; p_{conj}; p_{v2}; k_{penal}; p_{v3}
S-Mo-Mo angle	θ_0; κ_a; κ_b; p_{conj}; p_{v2}; k_{penal}; p_{v3}
H-S-Mo and H-Mo-S angle	θ_0; κ_a; κ_b; p_{conj}; p_{v2}; p_{v3}

The parameters which were optimized within the FF-training steps are listed in Table S1. The Mo-S containing compounds and the condensed-phase periodic structures based on which we performed FF-optimization are listed in Table S2.

Table S2: Molecular and periodic structures used for force field optimization

Molecule species	Periodic specious	
MoS_6	MoS_2	Equation of state for hexagonal 2H&1T-MoS_2 along *a*-direction
MoS_4H_2		Equation of state of bi-layer MoS2 along *c*-direction
MoS_3H_2		Surface Coverage of MoS_2 with Mo and S Edge
Mo_2S_6		H_2 adsorption on Mo and S edge of MoS_2
MoS_2		Bended and swap mismatch MoS_2 interacting with 1-2 vacancy

DFT and ReaxFF calculations for bond dissociation and valence angle distortion:

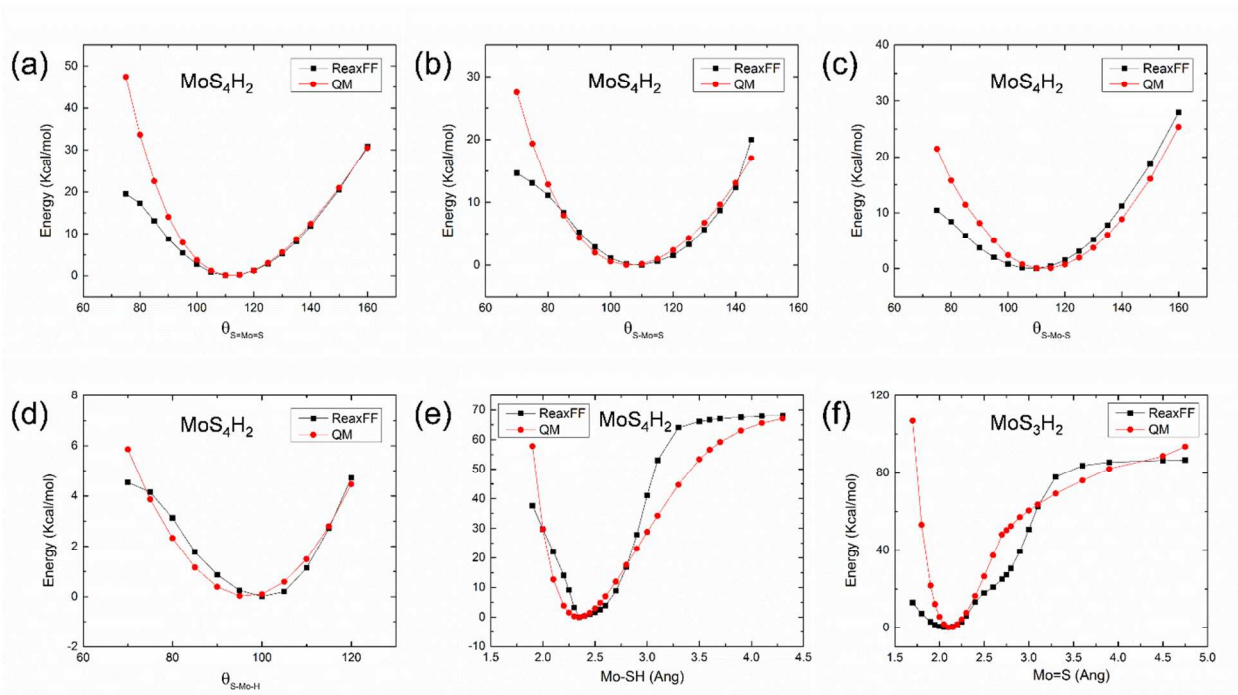

Figure S1: Angle distortion and bond-dissociation energies in MoS_4H_2 and MoS_3H_2 molecule, ReaxFF vs. DFT results

Additional reaction energies obtained from ReaxFF simulations are reported in Figure S2 and compared with their corresponding values from DFT calculations.

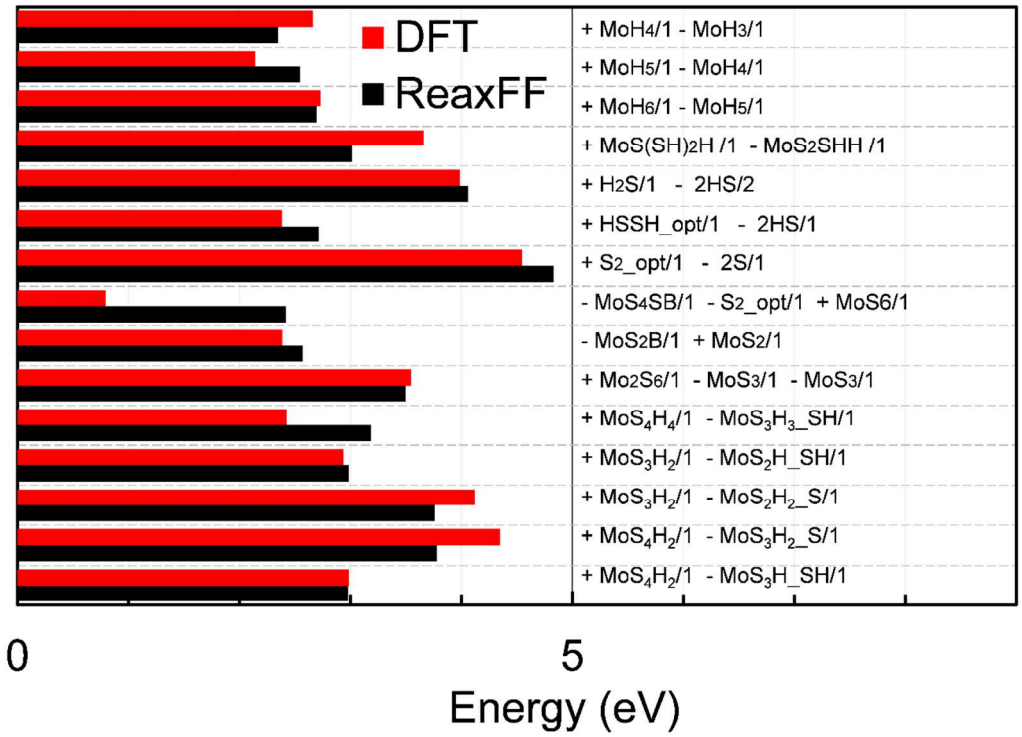

Figure S2: ReaxFF and DFT reaction energies associated with different Mo-S-H clusters.

Comparison of ReaxFF versus DFT energetics for 2D MoS_2 structures:

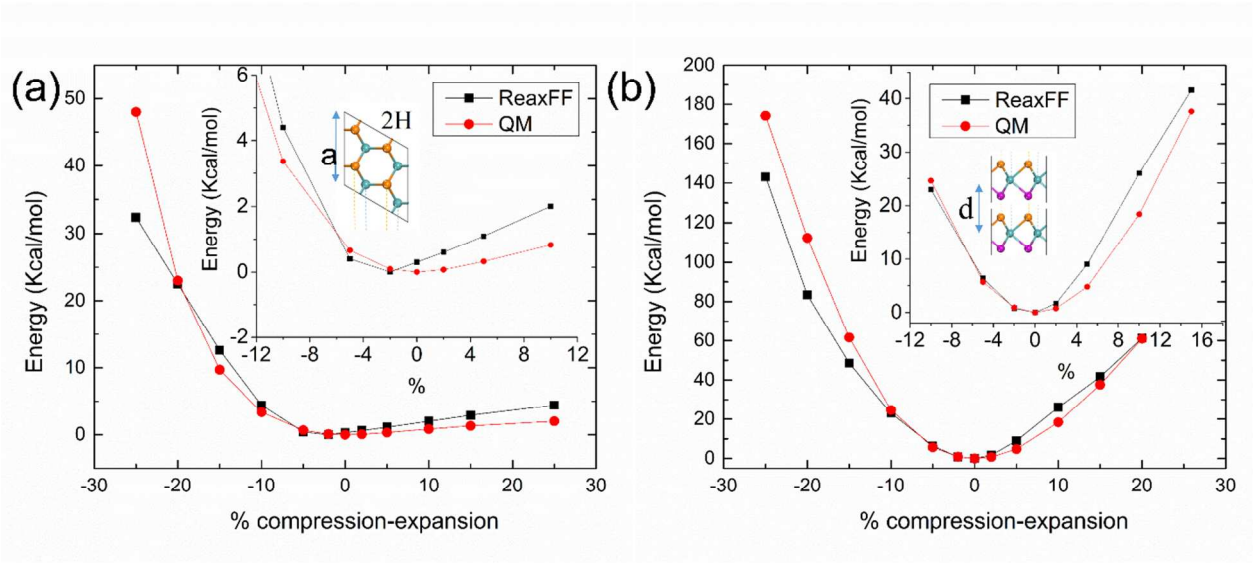

Figure S3: Equation of state of single layer MoS_2 (along *a*-direction) and double layer MoS_2 (along *c*-direction)

Mechanical Properties of SL 2H-MoS_2 structures

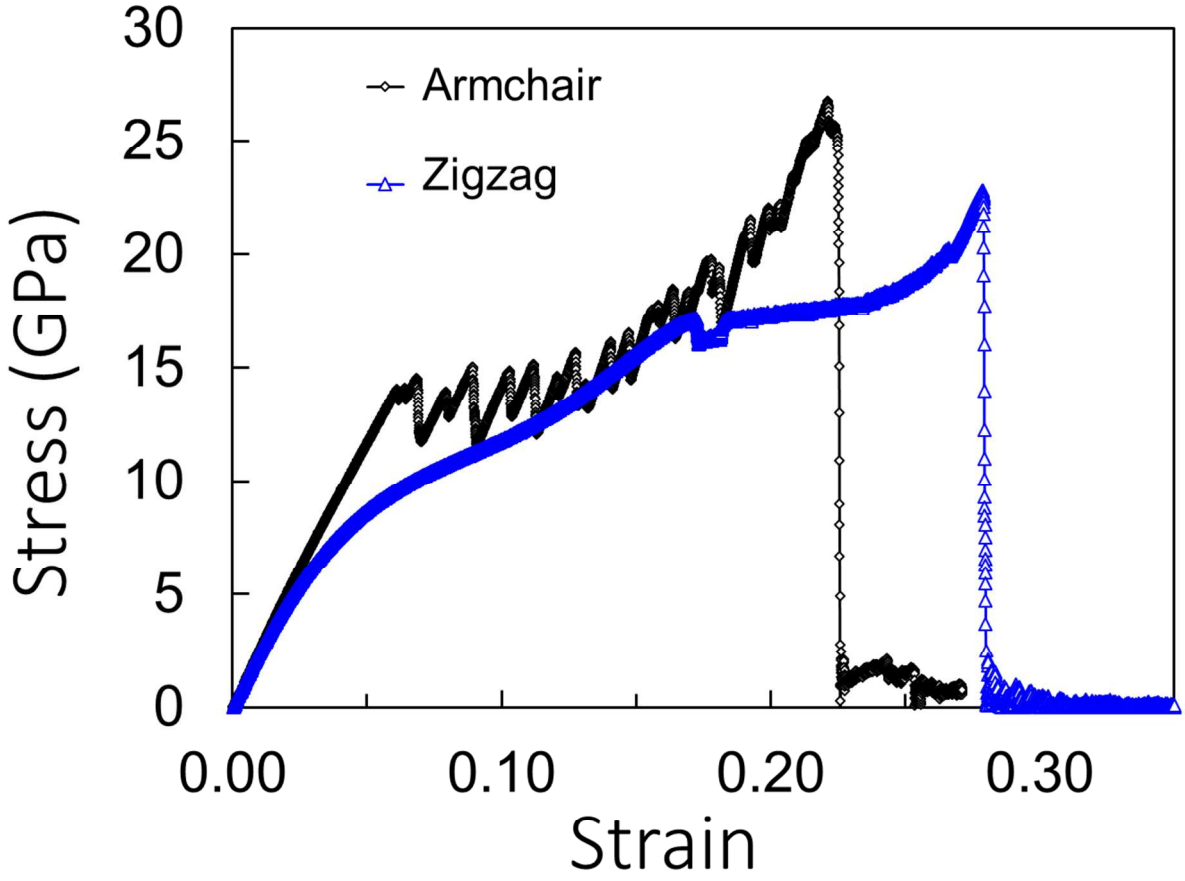

Figure S4: Uniaxial stress–strain responses of pristine 2H MoS_2 sheet at room temperature.

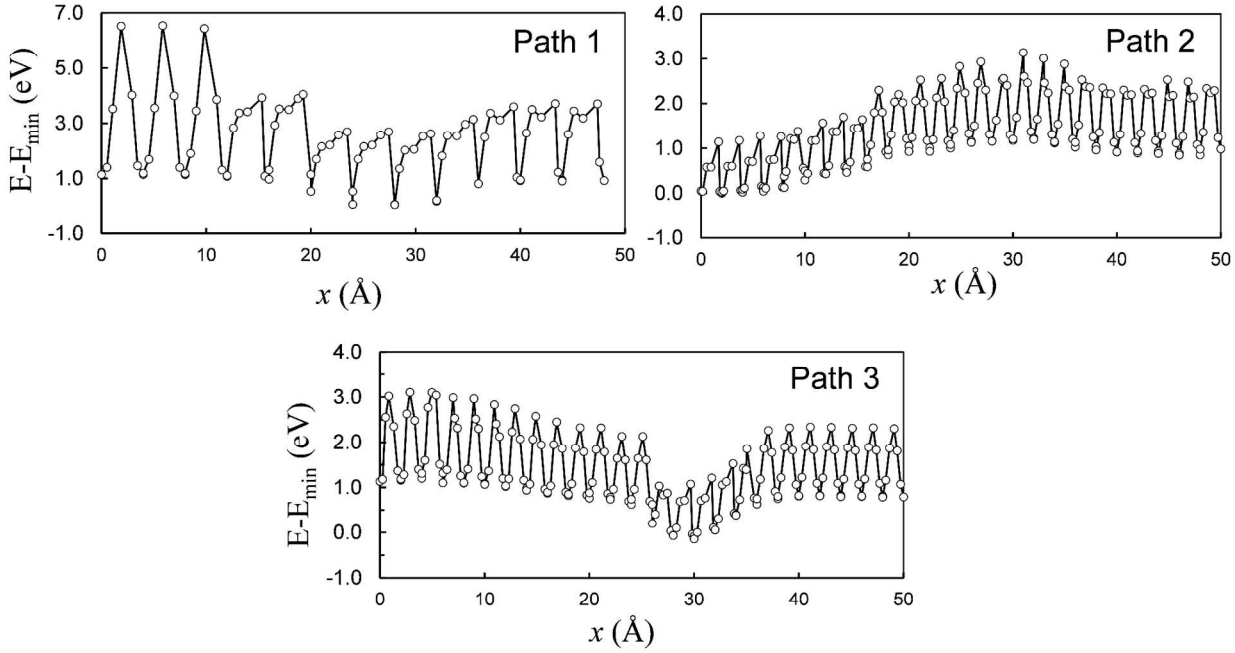

Figure S5: Evolution of vacancy migration energy of (a) an upper-surface vacancy along a straight path (path1) (b) a lower-surface vacancy along a zigzag path (path2) and (c) an upper-surface vacancy along a zigzag path (path3)

Table S3: Optimized parameters of ReaxFF for Mo/S/H interaction.

```
Reactive MD-force field: H/S/Mo for MoS2 project JPC-Letters January
2017
 39       ! Number of general parameters
   50.0000 !p(boc1)
    9.5469 !p(boc2)
   26.5405 !p(coa2)
    1.5105 !p(trip4)
    6.6630 !p(trip3)
   70.0000 !kc2
    1.0588 !p(ovun6)
    4.6000 !p(trip2)
   12.1176 !p(ovun7)
   13.3056 !p(ovun8)
  -10.1292 !p(trip1)
    0.0000 !Lower Taper-radius (swa)
   10.0000 !Upper Taper-radius (swb)
    0.0000 !not used
   33.8667 !p(val7)
    6.0891 !p(lp1)
    1.0563 !p(val9)
    2.0384 !p(val10)
    6.1431 !not used
    6.9290 !p(pen2)
    0.3989 !p(pen3)
    3.9954 !p(pen4)
    0.0000 !not used
    5.7796 !p(tor2)
   10.0000 !p(tor3)
    1.9487 !p(tor4)
    0.0000 !not used
    2.1645 !p(cot2)
    1.5591 !p(vdW1)
    0.1000 !Cutoff for bond order*100 (cutoff)
    2.1365 !p(coa4)
    0.6991 !p(ovun4)
   50.0000 !p(ovun3)
    1.8512 !p(val8)
    0.0000 !not used
    0.0000 !not used
    0.0000 !not used
    0.0000 !not used
    2.6962 !p(coa3)
  3    ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma
            alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
            ro(pipi);p(lp2);Heat
increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
            p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.
 H    0.7853   1.0000   1.0080   1.5904   0.0419   1.0206  -0.1000
1.0000
```

```
      9.3557   5.0518   1.0000   0.0000 121.1250   5.3200   7.4366
1.0000
     -0.1000   0.0000  62.4879   1.9771   3.3517   0.7571   1.0698
0.0000
    -15.7683   2.1488   1.0338   1.0000   2.8793   0.0000   0.0000
0.0000
 S    1.8328   2.0000  32.0600   1.8815   0.3236   0.7530   1.6468
6.0000
      9.0000   4.9055   4.0000  30.0000 112.1416   6.5745   9.0000
2.0000
      1.0000   3.4994  65.0000  12.0000  22.1978  15.3230   0.9745
0.0000
    -15.7363   2.8802   1.0338   6.2998   2.8793   0.0000   0.0000
0.0000
 Mo   2.4695   5.6375  95.9400   1.8471   0.3413   0.7020   0.1000
6.0000
     13.1958  44.8826   4.0000   0.0000   0.0000   1.5954   6.5231
0.0000
      0.1000   0.0000 152.6300   3.4529   0.0722   3.1767   0.8563
0.0000
    -17.9815   3.1072   1.0338   8.0000   3.4590   0.0000   0.0000
0.0000
 6      ! Nr of bonds; at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(b
                     p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
  1  1 156.0973   0.0000   0.0000  -0.1377   0.0000   1.0000   6.0000
0.8240
         2.9907   1.0000   0.0000   1.0000  -0.0593   4.8358   0.0000
0.0000
  1  2 183.1582   0.0000   0.0000  -0.7544   0.0000   1.0000   6.0000
0.3725
        11.7366   1.0000   0.0000   1.0000  -0.0595   4.6177   1.0000
0.0000
  2  2  86.8868  69.1367   0.0000  -0.9993  -0.4781   1.0000  17.8574
0.0999
         0.2799  -0.1677   8.2557   1.0000  -0.1131   6.1440   1.0000
0.0000
  1  3  77.9675   0.0000   0.0000  -0.5019  -0.3000   0.0000  36.0000
0.1374
         0.0697  -0.3027  15.0243   1.0000  -0.0500   5.9618   1.0000
0.0000
  2  3  64.9870  33.5938 137.6546   1.0000  -0.2304   1.0000  19.1688
0.2000
         1.3265  -0.1497   7.0000   1.0000  -0.1447   6.6437   1.0000
0.0000
  3  3  51.8235   0.0000   0.0000   0.8271  -0.3000   0.0000  16.0000
0.2670
         0.2248  -0.3000  16.0000   1.0000  -0.1908   7.3978   0.0000
0.0000
 3    ! Nr of off-diagonal terms. at1;at2;Dij;RvdW;alfa;ro(sigma);r
  1  2   0.1017   1.7755   9.6088   1.3696  -1.0000  -1.0000
  1  3   0.1939   1.3679  11.7159   1.4389  -1.0000  -1.0000
  2  3   0.1000   1.8000   9.8235   2.3403   1.6147  -1.0000
```

```
 15    ! Nr of angles. at1;at2;at3;Thetao,o;p(val1);p(val2);p(coa1);
  1  1  1   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000
1.0400
  1  2  1  92.1229  42.8350   0.6163   0.0000   1.0235   0.0000
1.0010
  1  2  2  70.9476   9.9024   0.6923   0.0000   0.2031   0.0000
2.9811
  2  3  2  70.5456  50.0000   0.6721   0.0984   1.0000   0.0000
1.4973
  3  2  3  30.0000  22.6920   8.0000   0.0000   3.6520   0.0000
3.2979
  2  2  3  90.0000  20.5180   0.8991   0.0000   3.5892   0.0000
1.3043
  2  3  3  43.1709  41.4967   7.9750   0.0000   2.4076   0.0000
3.6697
  1  2  3  89.0008  22.3751   0.6748   0.0000   0.6873   0.0000
4.0000
  2  2  2  84.2345  15.5790   3.7715   0.0000   1.3066   0.0000
1.6270
  1  3  3  57.6230   6.3083   5.0722   0.0000   0.6873   0.0000
1.5510
  1  3  2  30.5534   0.0100   7.3018   0.0000   1.6873   0.0000
2.9513
  1  3  1  78.0184  11.1868   7.8000   0.0000   0.9375   0.0000
1.1193
  2  1  2   0.0000   7.5000   2.0000   0.0000   0.0000   0.0000
1.0400
  2  1  3   0.0000   7.5000   2.0000   0.0000   0.0000   0.0000
1.0400
  3  1  3   0.0000   7.5000   2.0000   0.0000   0.0000   0.0000
1.0400
 4    ! Nr of torsions. at1;at2;at3;at4;;V1;V2;V3;p(tor1);p(cot1);n
  0  1  1  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
0.0000
  0  1  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
0.0000
  2  2  2  2   2.4661  71.9719   0.0100  -8.0000   0.0000   0.0000
0.0000
  1  2  2  1   0.0000  50.0000   0.0000  -8.0000   0.0000   0.0000
0.0000
 1    ! Nr of hydrogen bonds. at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3
  2  1  2   1.5000  -2.0000   1.7976   3.0000
```