Vibrational properties of Molybdenum Sulphides at finite T combining *ab initio* methods and Machine Learning

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1. Introduction

Molybdenum sulphides belong to the family of **transition metal chalcogenides** (TMCs), compounds that thanks to their chemical-physical properties, are promising candidates in several topical fields of research, especially that of electrocatalysis for the **hydrogen evolution reaction** (HER) from water[(1)]. Studying TMCs' vibrational properties is fundamental to identify the **structure-property relations** that are of great help for the development of these materials as catalysts.

To obtain results comparable with experimental evidences a treatment at finite temperature is needed. By increasing the temperature the anharmonic nature of the interactions in matter gets more and more influent on its vibrational behaviour. Furthermore, many thermal properties are affected by anharmonicity; for instance, phonon thermal conductivity is meaningless within a purely harmonic context, and it is usually retreived by introducing in the potential contributions which go beyond the harmonic approximation and that are then also responsible for the anharmonicity.

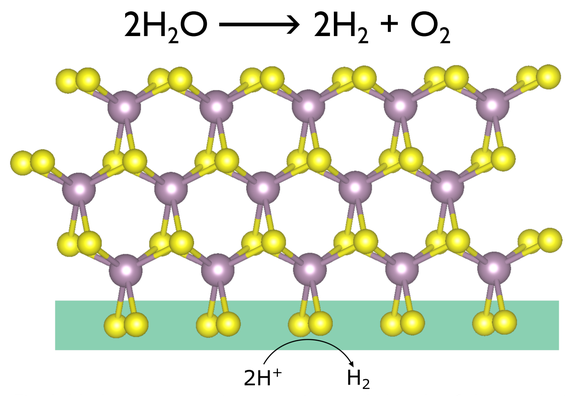

Fig. 1: Hydrogen evolution reaction and sketch of the catalysis with hexagonal MoS_2.

2. Methods

Study at 0 K: usual *ab initio* approach

1. **Ground state** computed with **DFT**
2. **Phonons** and **Raman** with **DFPT**

DFT, DFPT

Study at finite T: Machine Learning + TDEP

1. Create the **dataset** for the MLIP
2. Train and test the **MLIP**
3. Sample with **ML-Molecular Dynamics**
4. Extract **anharmonic phonons** with **TDEP**[(2)]
5. Run **DFPT** for **dielectric data**
6. Feed dielectric into **TDEP** for finite-T **Raman**

Moleular Dynamics

TDEP

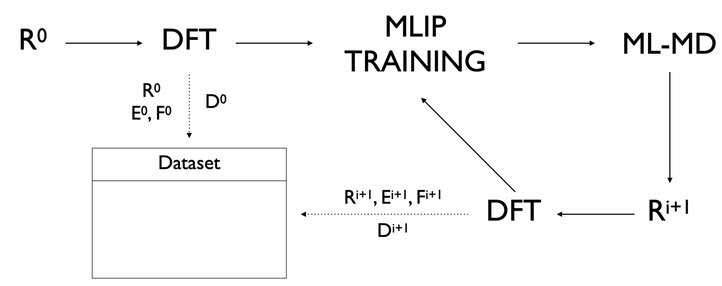

Fig. 2: Iterative scheme of the Machine Learning Assisted Canoninal Samplig algorithm.

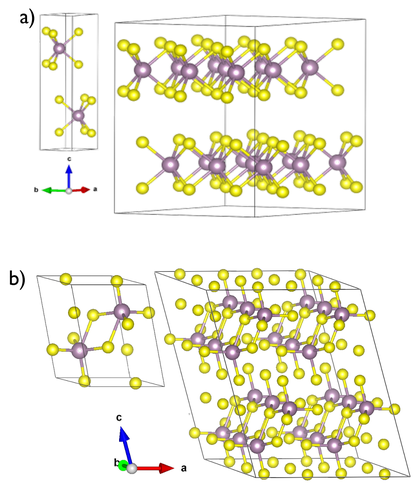

Fig. 3: a) Unit cell and supercell of hexagonal MoS_2; b) unit cell and supercell of monoclinic MoS_3 (yellow: S, purple: Mo).

3. Methods: Temperature Dependent Effective Potential

Temperature Dependend Effective Potential is a method to retrieve vibrational and thermodinamical information about a system at a specific temperature from a set of (*ab initio*-)molecular dynamics configurations. The best harmonic potential is obtained by minimizing the difference between (AI)MD and the model's forces.

$$\min_{\Phi}\left(\frac{1}{N_t}\sum_{i,t}\left|\mathbf{F}_{i,t}^{\mathrm{MD}}-\mathbf{F}_i^{\Phi}\right|^2\right)$$

$$U(\{\mathbf{u}_i\})=U(0)+\frac{1}{2}\sum_i \mathbf{u}_i\underbrace{\left[\sum_j \Phi_{ij}^{(2)}\mathbf{u}_j\right]}_{\equiv\mathbf{F}_i^{\Phi(2)}}+\frac{1}{6}\sum_i \mathbf{u}_i\underbrace{\left[\sum_{j,k}\Phi_{ijk}^{(3)}\mathbf{u}_j\mathbf{u}_k\right]}_{\equiv\mathbf{F}_i^{\Phi(3)}}+\dots$$

4. Methods: Machine-Learned Interatomic Potential

The machine-learned interatomic potential is a function of the geometrical and chemical variables of the system that returns its energy (and analytical derivatives). We use **Moment Tensor Potential**[(3)] (MTP):

$$E(\mathbf{x})=\sum_i^{atoms} V_i(\mathbf{x}_i) \qquad V_i(\mathbf{x}_i)=\sum_\alpha \xi_\alpha B_\alpha(\mathbf{x}_i)$$

atomic contribution
linear coeffs.

$$B_\alpha(\mathbf{x}_i)\sim\sum_j f_\alpha(|r_{ij}|z_iz_j)\mathbf{r}_{ij}\otimes\dots\otimes\mathbf{r}_{ij}$$

descriptor
radial function
tensorial part

The MLIP needs a **dataset** to be trained and tested. We generate one with the algorithm called **Machine Learning Assisted Canonical Sampling**[(4)].

5. Results

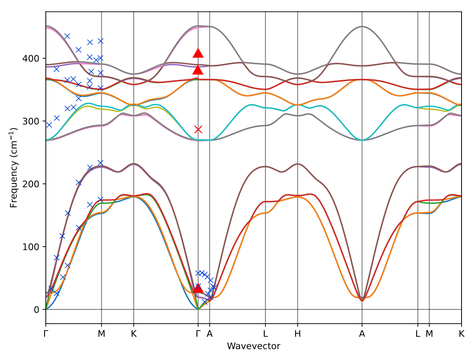

Fig. 4: Phonon band structure of MoS_2 computed with DFPT (solid lines), and from experimental[(5)] neutron scattering (blue crosses), IR (red cross) and Raman (triangles).

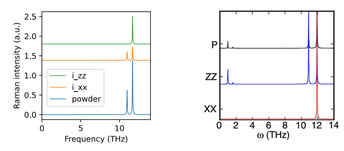

Fig. 5: *Ab initio* Raman spectrum of MoS_2 computed with DFPT (left), and from literature[(5)].

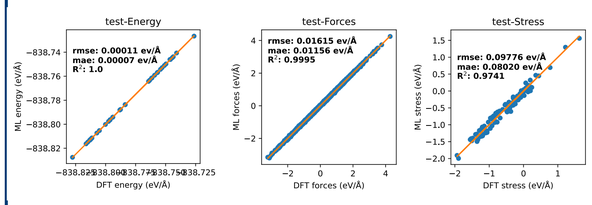

Fig. 7: Fit of the DFT data for MoS_2 with MTP.

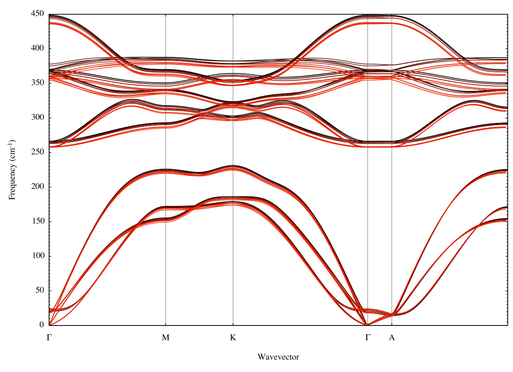

Fig. 8: Phonon band structure of MoS_2 computed with TDEP between 100 and 600 K (from bright to dark).

The 0 K and finite-T studies were conducted on MoS_2 and MoS_3.

- Partial agreement with literature (no available data for MoS_3);
- Very good MTP fit;
- Low-temperature TDEP reproduces well the DFT data;
- Instability in MoS_3 phonons (Y-X) at 0 K;
- 100 and 200 K no more Y-X instabilities; new instabilities at higher T.

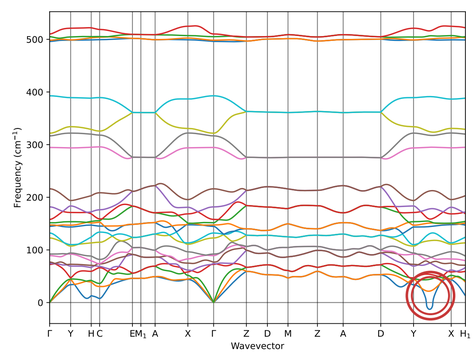

Fig. 6: Phonon band structure of MoS_3 computed with DFPT. An instability is present in the segment Y-X.

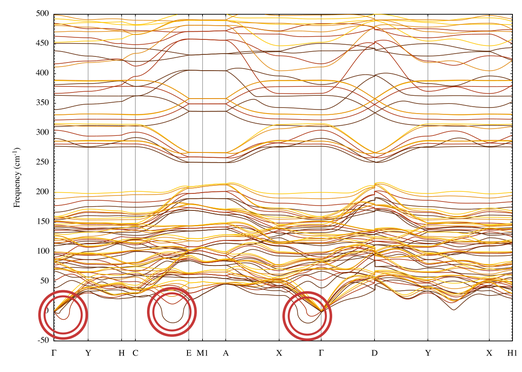

Fig. 9: Phonon band structure of MoS_3 computed with TDEP between 100 and 400 K (from bright to dark). Note the absence of instability in Y-X (see fig. 6), but new ones at high T.

6. Conclusion and perspectives

- MTP can give very good results, with possibilities of improvement by refining the hyperparameters;
- TDEP also proves very powerful to explore the thermal and vibrational properties at high temperature.
- Next steps:
  (i) get a well-working MLIP <u>for both</u> MoS_2 and MoS_3;
  (ii) find and study defected systems.

References

(1) D. Xiao et al., Phys. Rev. Lett. 108, 196802 (2012)

(2) O. Hellman et al,. Phys. Rev. B 87, 104111 (2013)

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(4) A. Castellano et al., Phys. Rev. B 106, L161110 (2022)

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