Anharmonic vibrational properties of Molybdenum Sulphides from Machine Learning-driven canonical space sampling

Samuel Longo[1], Matthieu J. Verstraete[1]
[1]Université of Liège, Physics Dep., Nanomat group, Allée du six Août 19, 4000 Liège

samuel.longo@uliege.be

Molybdenum Sulphides (MSs) represent one of the most promising non-toxic and inexpensive alternatives to the Pt-based catalysts for the Hydrogen Evolution Reaction (HER). The design of such catalysts is still mainly limited by the difficulty in determining their structure [1]. Vibrational spectroscopy is a powerful tool to unveil their local structural features and can assist in the study of the catalytic mechanisms. We investigate the temperature-dependent vibrational properties of MoS_2, such as phonons and Raman activity, by combining state-of-the-art Machine Learning-Interatomic Potentials (MLIPs) with Molecular-Dynamics (MD) simulations. More specifically, we use the Temperature Dependent Effective Potential [2] (TDEP) to extract the anharmonic interatomic force constants, the phonon lifetimes and the Raman activity from canonical sampling at a given temperature. To attain an accurate sampling, it is performed via Machine Learning-Molecular Dynamics (MLMD) simulations, where the MLIP (we use the Moment Tensor Potential, MTP [3]) replaces the computationally demanding *ab initio* calculation of the atomic forces. The MLIP itself is trained on a MoS_2 DFT dataset generated via a self-consistent iterative scheme of phase space exploration called Machine Learning Assisted Canonical Sampling (MLACS) [4]. Accordingly, the training datapoints are obtained as snapshots of MLMD, by retraining the MLIP at each augmentation of the dataset, to improve its accuracy, until the error converges. The accuracy of the training set (*ab initio*) and the enforcement of a temperature during the MLMD runs, ensure that the resulting interatomic force constants account for anharmonicity effects. The Raman spectra we obtained and their temperature dependence are in good agreement with experimental values, confirming the effectiveness of both the MTP model and the TDEP method.

References

[1] Phong D. Tran et al., Nature Materials, 6 (2016) 640-646.
[2] Olle Hellman et al., Physical Review B, 10 (2013) 104111.
[3] Ivan S. Novikov et al., Machine Learning: Science and Technology, 2 (2020).
[4] Aloïs Castellano et al., Physical Review B, 16 (2020) L161110.

Figures

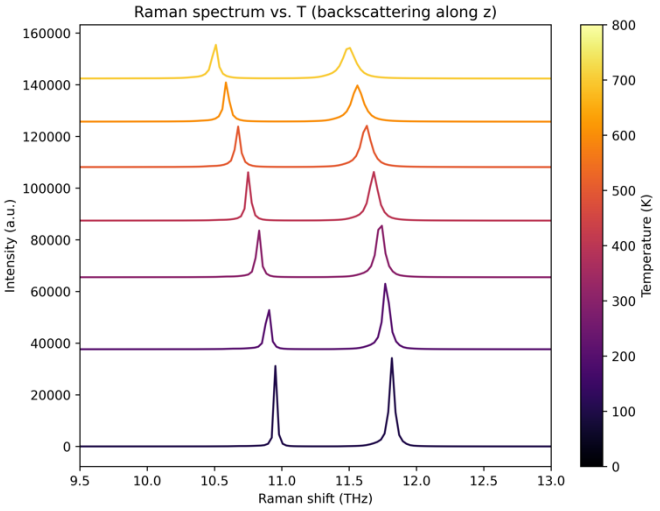
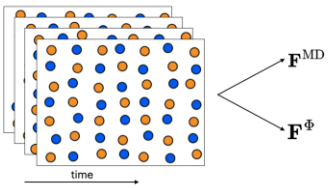


Figure 1. Raman spectra of MoS_2 vs. Temperature

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



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

Figure 2. Tdep model truncated to the third order and scheme of optimization.