Coupling DFT, SSCHA and SchNet NN for Hydrogen desorption calculations in Magnesium Hydride Nanoclusters

Andrea Pedrielli
Fondazione Bruno Kessler

pedrielli@fbk.eu

Based on the paper:

Understanding anharmonic effects on hydrogen desorption characteristics of MgnH2n nanoclusters by ab initio trained deep neural network

A. Pedrielli, P. E. Trevisanutto, L. Monacelli, G. Garberoglio, N. M. Pugno and S. Taioli, Nanoscale, 2022, 14, 5589 DOI: 10.1039/D1NR08359G

Summary

- Motivation
- State of the art
- Objectives
- Computational methods
- Results
- Discussion
- Outlooks

Motivation

- Hydrogen is promising energy vector but needs effective storage media.
- Bulk magnesium hydride (MgH_2) presents considerable gravimetric hydrogen storage capacity (7.6 wt%), being also abundant and relatively cheap.
- However, at ambient pressure, the desorption temperature is too high 553 K (280°C) for pratical applications.
- The desorption temperature can be modified by nanosizing of the material.
- We need to perform simulations to better understand the experimental data.

State of the art

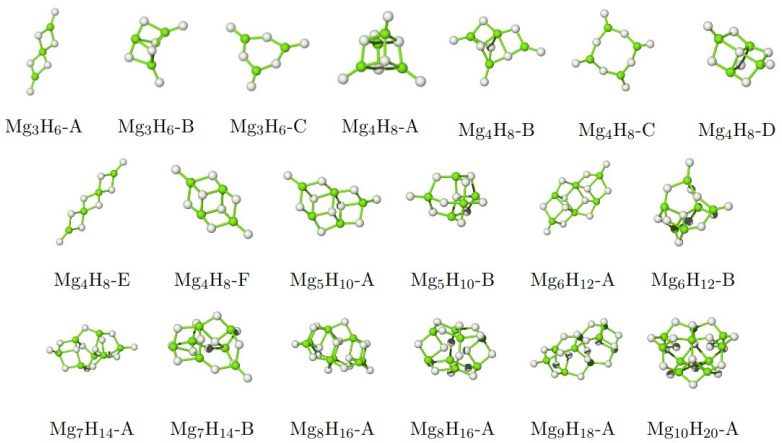
- The effect of nanosizing have been assessed by different computational methods such as DMC, CCSD(T) and DFT. DFT captures the main trends of the desorption energy.
- Amorphous NPs containing only a few atoms are destabilized, intermediate size NPS are stabilized and for large amorphous particles the desorption energy tends to a value lower than that of the bulk.
- In any case none of the studies in the literature included the anharmonic properties of the material.

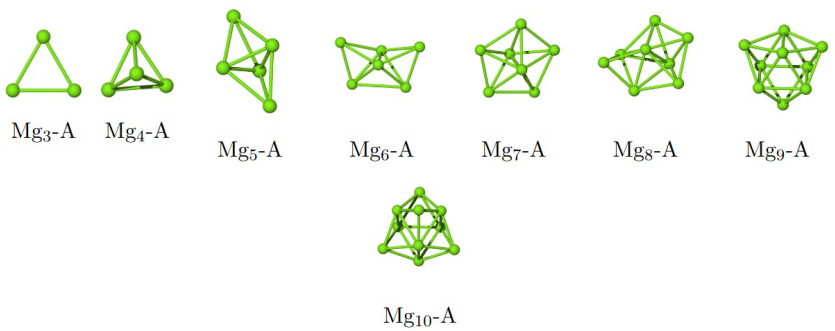
Objectives

- **Compute the Hydrogen desorption temperature of small Mg_nH_{2n} nanoparticles including anharmonic effects at DFT level**

  We use Stochastic Self Consistent Harmonic Approximation (SSCHA) based on DFT calculations of potential surface to determine the free energy of Mg and Mg_nH_{2n} NPs.

  → Even if stochastic we got many thousands of single points calculations!

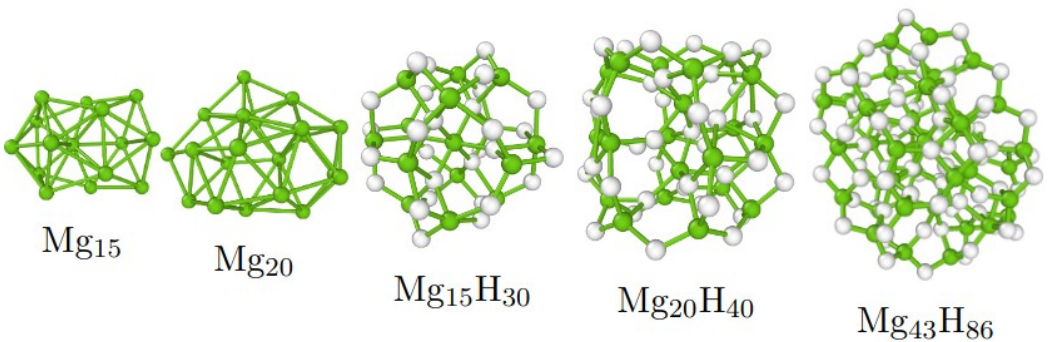




- **Exploit the DFT energy and forces to train a NN to be used with SSCHA for large NPs**

  As the SSCHA method needs many thousands of evaluations of forces and energies we employed the SchNet–package, a continuous filter layers convolutional Neural-Network (NN) package, integrating the latter in the Atomic Simulation Environment (ASE) together with the python implementation of the SSCHA code.

  → NN could be anyway trained on more accurate calculations of potential surface



Computational Methods

- **DFT within Quantum Espresso**

  P. Giannozzi et al. J.Phys.: Condens.Matter 21, 395502 (2009)

- **SSCHA method within python-sscha**

  Ion Errea, Matteo Calandra, and Francesco Mauri Phys. Rev. B 89, 064302 (2014)

  Lorenzo Monacelli et al. J. Phys.: Condens. Matter 33 363001 (2021)

- **NN model of potential energy surface with SchNetPack**

  K.T. Schütt et al. J. Chem. Theory Comput. , 15 (1): 448-455 (2019)

- **NN forces end energies calculation with The Atomic Simulation Environment ASE**

  Ask Hjorth Larsen et al.J. Phys.: Condens. Matter Vol. 29 273002 (2017)

- **Compute the Hydrogen desorption temperature of MgH_2 nanoparticles**

  The hydrogen desorption temperature Td in MgH_2 can be determined at constant pressure p = 1 bar:

$$f(T) = T - \frac{\Delta H(T)}{\Delta S(T)} = 0.$$

  where ΔH and ΔS are the changes in enthalpy and entropy of the reaction at constant temperature and volume, respectively. From the knowledge of ΔG = ΔH −TΔS, we computed the entropy S and the enthalpy H.

$$S(T) = -\left.\frac{\partial G(T)}{\partial T}\right|_p, \qquad H(T) = G(T) + TS(T).$$

  → We only need G of H_2 (done exactly), Mg_n and Mg_nH_{2n} NPs at different temperatures!

- **Stochastic Self Consistent Harmonic Approximation (SSCHA) to compute the free Energy**

  The Helmholtz free energy (HFE) of a solid, which includes the contributions arising from the static lattice zero-temperature internal energy, from the thermal electronic excitation and from the ionic vibrations, reads

$$F_{\mathscr{H}} = \mathrm{Tr}(\rho_{\mathscr{H}} \mathscr{H}) + \frac{1}{\beta} \mathrm{Tr}(\rho_{\mathscr{H}} \ln \rho_{\mathscr{H}})$$

  where $\mathscr{H} = K + V$ is the total Hamiltonian of the system written as the sum of kinetic energy operator (*K*) and of the many-body adiabatic potential energy (*V*) within the Born–Oppenheimer approximation.

  $\rho_{\mathscr{H}} = e^{-\beta\mathscr{H}}/[\mathrm{Tr}(e^{-\beta\mathscr{H}})]$ is the density matrix, where β = 1/(kBT), kB is the Boltzmann constant, and T the temperature. $\mathcal{F}_{\mathscr{H}}[\mathcal{H}]$ is obtained for using trial density matrix $\rho_{\mathcal{H}}$.

The Gibbs–Bogoliubov variational principle states that for an arbitrary harmonic trial Hamiltonian $\mathcal{H} = K + \mathcal{V}$, the Harmonic free energy fulfills the following inequality

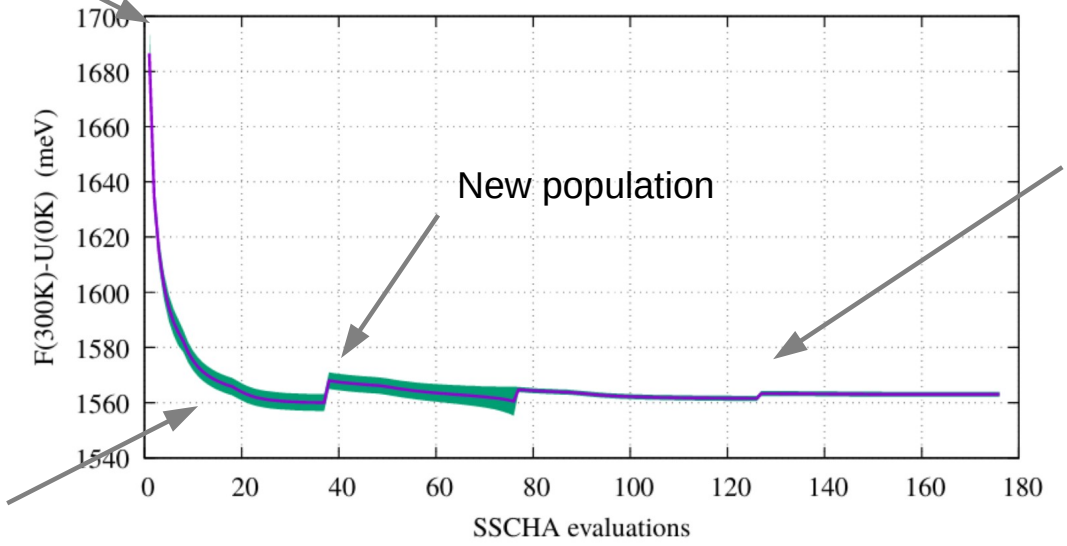
$$F_{\mathscr{H}} \leq \mathcal{F}_{\mathscr{H}}[\mathcal{H}] = F_{\mathcal{H}} + \int d\mathbf{R}[\, V(\mathbf{R}) - \mathcal{V}(\mathbf{R})]\rho_{\mathcal{H}}(\mathbf{R})$$

where **R** identifies the ion positions. In the SSCHA method the minimization o $\mathcal{F}_{\mathscr{H}}[\mathcal{H}]$ is performed by a stochastic evaluation of the free energy and its gradient by varying the free parameters of an Hamiltonian characterised by an harmonic trial potential $\mathcal{V}$. $F_{\mathcal{H}}$ and $\rho_{\mathcal{H}}(\mathbf{R})$ have the analytic forms.

During the minimization, the atomic coordinates are allowed to relax in order to obtain the finite temperature atomic positions.

We need a starting dynamical matrix. Then we need the calculation of the energies and the forces for each of the configurations of the population, that are composed by a few thousands of configuration each.

Starting population
2000 of configurations

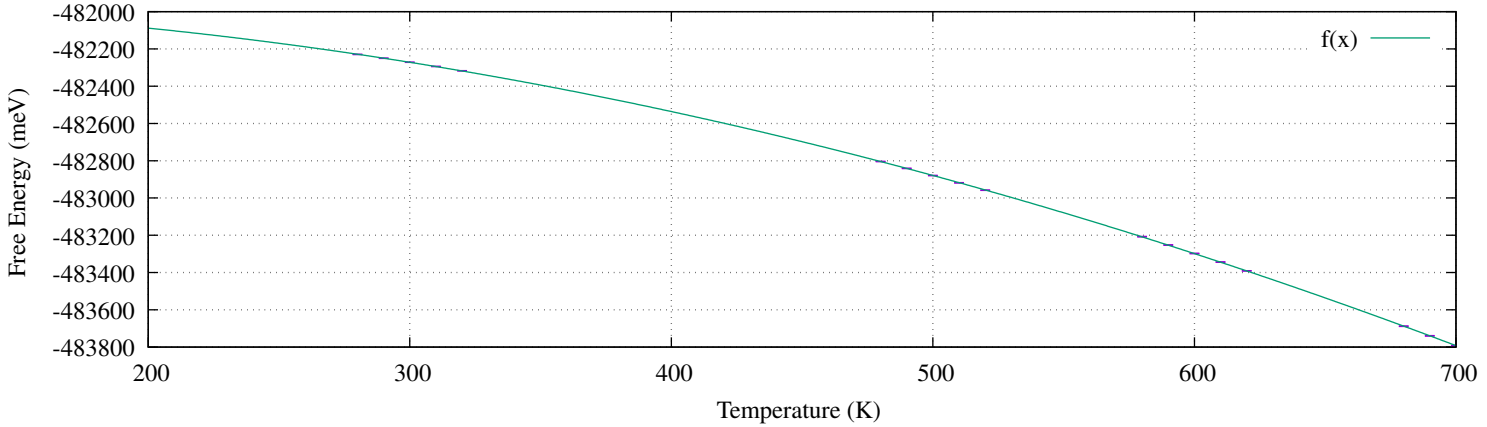


New population

Larger populations
(10000 – 20000) =
smaller error

Minimization with
reweighting

SSCHA proceeds through a series of repeated evaluation steps, the first being the generation of the stochastic population and the calculation of the energy and forces for each element of the population, the second being the minimization of the free energy using a reweighting procedure. The resampling is performed when the stochastic population due to the reweighting procedure is no more representative of the starting one.

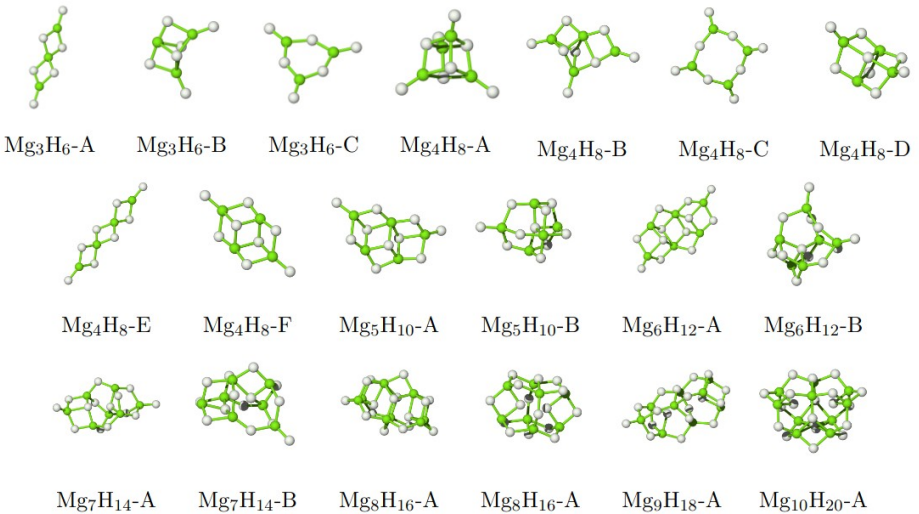


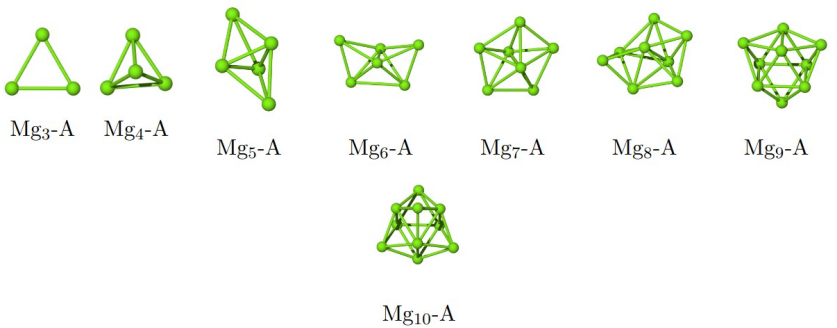
The calculations have been performed at 300 K, 500 K, and 600 K.

The free energy calculation has been extended in the range ±20 K around each calculated point, using the stochastic population generated at the reference temperature by taking advantage of the reweighing procedure.

- **Ab initio calculation of the Born-Oppenheimer potential surfaces and forces**

We performed the evaluation of the potential energy, forces and dynamical matrix by means of DFT calculations, using: Quantum ESPRESSO code. PBE exchange-correlation functional. The van der Waals dispersion Grimme D3 semiempirical correction. Cubic cell of 2 nm side for all structures. Makov–Payne correction for the cutoff interactions among periodic replicas. Number of calculations 2000-20000 for different populations.





- **The integration of machine learning, SchNet**
- From one side we have a lot of calculations done for the small NPs, from the other side we want to study lager NPs.
- We have employed SchNet, which is a continuous filter layers convolutional Neural-Network (NN) package
- These layers can model unevenly spaced data.
- Rotationally invariant energy predictions and a smooth, differentiable potential energy surface.
- It has remarkable flexibility and scalability is another distinguishing factor.

- **Training and test of the SchNet model**

- The training set contains 2 $\times 10^5$ Mg_n and Mg_nH_{2n} cluster configurations ($3 \leq n \leq 10$) with their relevant DFT forces and total energies. We used the data obtained from the population at 300 K and 500 K.

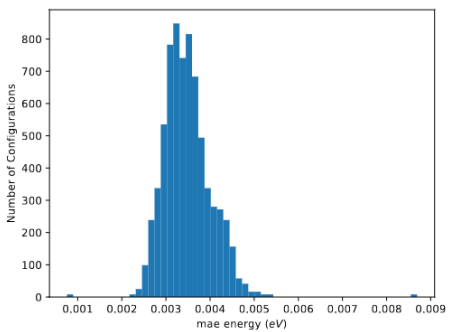
- The validation set contains $4x10^3$ configurations.

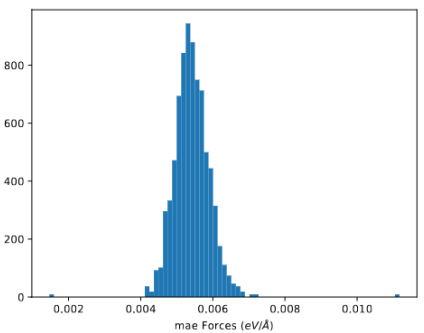
- Our NN is generated with 5 interaction blocks, 128 features and, for the Gaussian expansion, we used a range of 0.25 nm to cover all the interatomic distances occurring in the data.

- For the loss function we have also added the root-mean-square (RMS) error of the forces to the DFT total energies, with a trade-off between energy and forces loss. The convergence is obtained when the loss function is less than 10^{-4}.

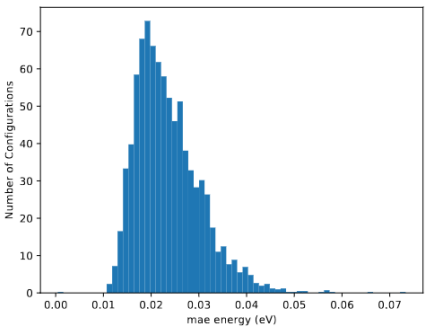
- A Mg_n cluster test set of 2 $\times 10^5$ configurations (4 $\times 10^5$ for Mg_nH_{2n}) was used for the determination of the Maximum Absolute Error (MAE) between ML predictions and the configurations of the test set.

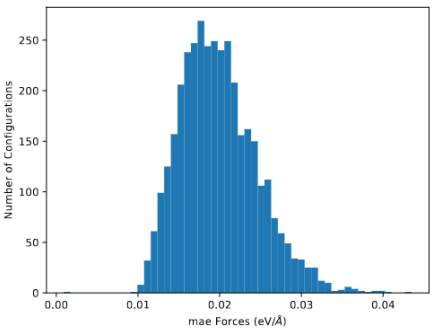
- **Test of the SchNet model**





Magnesium



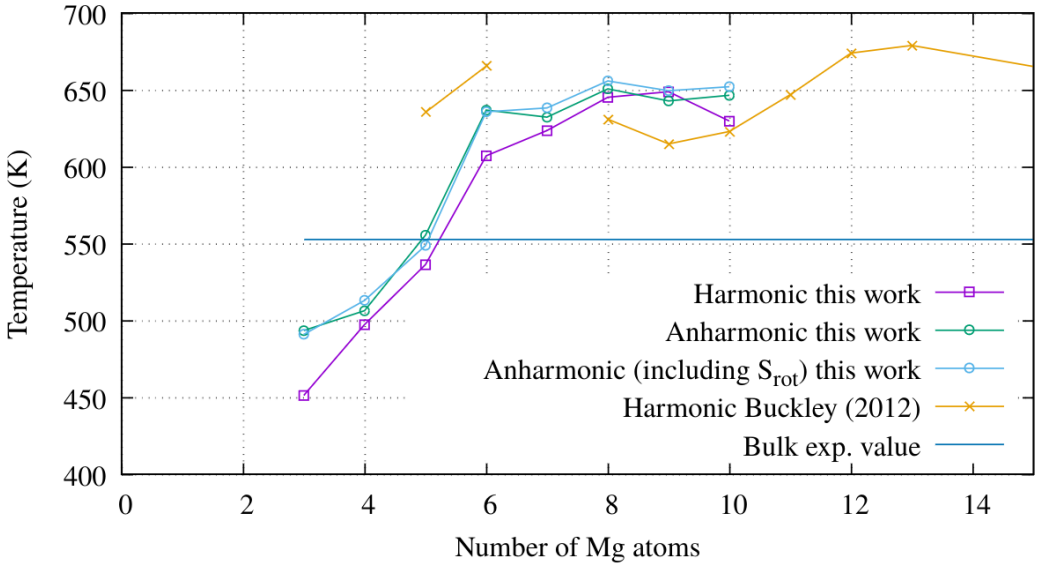


Magnesium Hydride

We used the data obtained from the population at 300 and 500 K. The Maximum Absolute Error (MAE) mean values for the Mg_n clusters are rather small, that is 0.004 eV for the energy and 0.005 eV/A for the forces at the peak maximum energies and forces are, respectively, 0.02 eV and 0.02 eV/A around the maximum of the peak distributions.

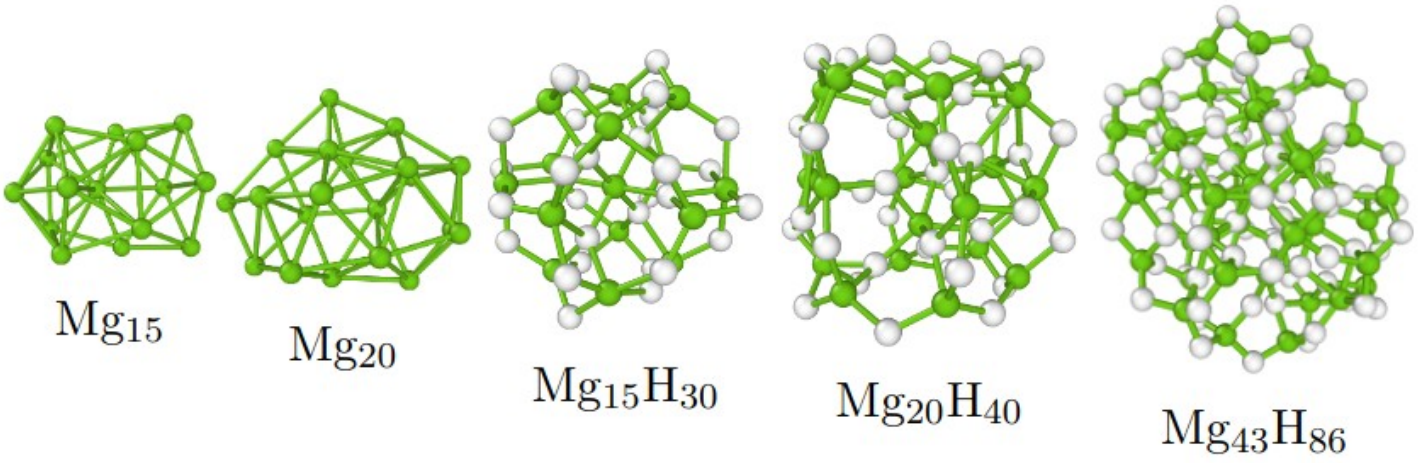
The trained SchNet best model was embedded in the ASE calculator, which provides the total energies and forces to be used in the SSCHA minimization procedure.

Results



- Td is an increasing function of the cluster size for the considered NPs
- The effect of anharmonicity on Td is up to 40 K
- The inclusion of the rotational entropy leads to almost negligible corrections

- **Extension to larger NPs**
- To start the structural optimization of Mg_nH_{2n} NPs ($n \geq 10$), we used the geometries of Ti_nO_{2n} NPs ($n = 15, 20, 43$)



Nanoparticle	$U(0)$ (meV)	$F(300)$ (meV)	$F(300)$ - $U(0)$ (meV)	$S(300)$ (meV/K)	T_d (K)
Mg_{10}-A (AI)	1027	1006	-21	0.290	
Mg_{10}-A (ML)	1027	1006	-20	0.289	
$Mg_{10}H_{20}$ (AI)	883	1226	343	0.308	646
$Mg_{10}H_{20}$ (ML)	883	1224	341	0.310	645

- The difference between the results obtained using the SchNet + SSCHA (*S[chnet]SCHA* framework) and the DFT + SSCHA one are very small, including the desorption temperature.

Nanoparticle	$U(0)$ (meV)	$F(300)$ (meV)	$F(300)$ - $U(0)$ (meV)	$S(300)$ (meV/K)
Mg_{15}	956	983	27	0.236
Mg_{20}	883	996	113	0.354
$Mg_{15}H_{30}$	797	1187	389	0.341
$Mg_{20}H_{40}$	721	1132	411	0.383

We were able to perform the calculation of the free energy on NPs up to $Mg_{20}H_{40}$ atoms on a laptop. The calculation takes a few hours.

Discussion

- The general trend of our results is similar to that found in the literature for small nanoparticles up to $Mg_{10}H_{20}$.
- The anharmonic contribution is not negligible as it can be up to 40K.
- The data of energies and forces can be used for the training of NN, as the number of ab initio calculations is feasible but large for large systems.
- SchNet is suitable for the description of these materials and the coupling with SSCHA has been implemented using the ASE package.

Outlooks

- The use of the *S[chnet]SCHA* framework could allow to study the anharmonic properties and the hydrogen desorption of very large nanoparticles with ab initio accuracy.
- The SchNet model could be even trained on more accurate quantum chemical methods.
- The desorption temperature calculation could be done recursively from an initial guess.
- The data mining for the exploration of the low energy configurations could be again based on SchNet models.

Thanks for the attention