Adsorbate Partition Functions via Phase Space Integration: Quantifying the Effect of Translational Anharmonicity on Thermodynamic Properties

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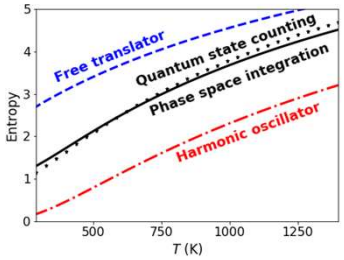
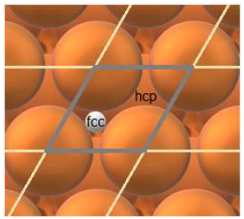
Introduction and Motivations

- The accuracy of adsorbate thermophysical properties is an important aspect of microkinetic mechanisms, which have become increasingly popular for predicting reaction networks in heterogeneous catalysis.
- A new method for computing anharmonic thermophysical properties on metal surfaces is presented, which improves upon standard methods by including anharmonicity.
- The method has been implemented for a H atom on a Cu(111) surface.



Methods

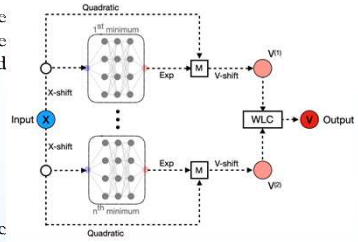


1. We produced training data for the potential energy surface (PES) of H on Cu(111) by performing DFT calculations using the Argonne National Laboratory's Theta system.
2. A minima-preserving neural network (MP-NN) PES surrogate was constructed from the training data. It is specifically designed to preserve accuracy near the minima (adsorbate binding sites). The architecture of the surrogate allows for multiple minima, in which case the output is a weighted linear combination (WLC) of surrogates in the form of NN-based multiplicative corrections to a quadratic function.

3. Classical Monte Carlo phase space integration (PSI) is used to integrate over the MP-NN surrogate and obtain the partition function,

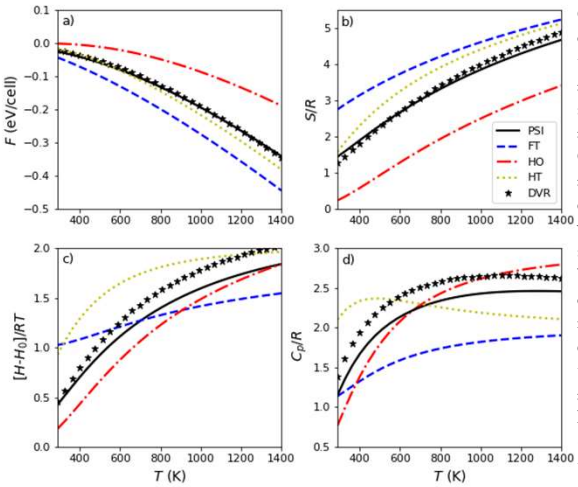
$$q \approx \frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3}\frac{\Omega}{N}\sum_{i=1}^{N} e^{-\beta V_s(x,y,z)},$$

from which the thermodynamic properties are directly derived.

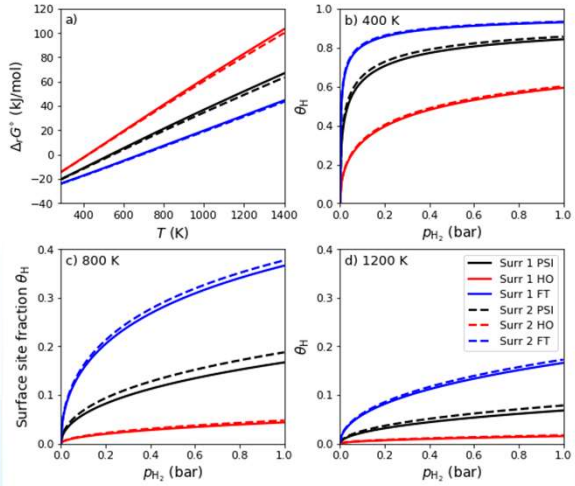


4. The results are benchmarked against direct state counting results, acquired with discrete variable representation (DVR).

Results

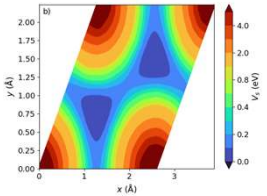


Our results show that contributions of translational anharmonicity are significant for H adsorbed on a Cu(111) surface. The approach is in excellent agreement with the quantum state counting benchmark (DVR) over the temperature range of interest, especially compared to the commonly used analytical models, the harmonic oscillator (HO) and the free translator (FT).

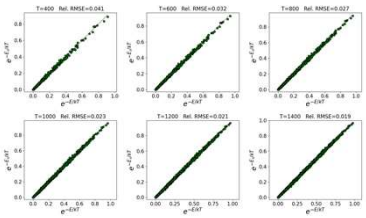


The free energy of dissociative adsorption of H_2 was calculated, as well as the Langmuir isotherms at 400, 800 and 1200 K in a partial pressure range of 0-1 bar. It shows that surface coverages depend heavily on the model used for obtaining the free energy, as the anharmonic effects lead to significantly higher predicted surface site fractions of hydrogen (1.6-4.6 higher in the temperature range of interest).

MP-NN PES Surrogate



This 2D slice in MP-NN surrogate potential energy space (at the optimized position in the direction normal to the surface) shows that the local PES around the fcc binding site has a broad range of energetically accessible area. This illustrates why neither the HO (assuming infinite energy barriers) nor the FT (no barriers) are good approximations in this case, while the PES landscape is well captured with PSI.



The integrand root mean square error directly translates to the partition function error bars at the respective temperature.

Significance and Impact

The method is to be a part of the Sandia National Laboratories' ECC computational framework for automated chemistry, an effort to provide accurate microkinetic mechanisms. As we transition into the exascale, accurate methods that require computational power become relevant and useful tools to considerably improve chemical process predictions.

Future Directions

- Our method has been implemented in our open-source package, AdTherm.
- Rotations are being incorporated into the method, extending the it to be applicable for multiatomic adsorbates.
- Anharmonic, coverage-dependent partition functions, building on this approach, are underway.

AdTherm

Publication

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