Washington University in St. Louis
Arts & Sciences

Prof. Anouk Rijs
Chair, PCCP editorial board

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Thank you for the invitation to contribute to the *2023 PCCP Emerging Investigators Themed Issue*. Herein, I have attached my first independent manuscript, "**Surface Phase Diagrams from Nested Sampling**," prepared by my postdoctoral research associate, Dr. Mingrui Yang, my collaborator, Prof. Livia B. Pártay, and myself for submission to the *Physical Chemistry Chemical Physics* journal. Our work reports the development of a new computational method to predict surface phase diagrams from nested sampling. The Bayesian-inference-based nested sampling algorithm enables the direct and efficient computation of the partition function of surface systems, allowing one to determine surface thermodynamic properties at finite temperatures. This proof-of-concept work features the first application of nested sampling to study two-component gas-surface systems, providing a new methodology for constructing surface phase diagrams, and serving as a stepping stone towards accurate modeling of surface phase equilibria under non-standard conditions.

Atomic-scale modeling of surface phase equilibria at finite temperatures has always been challenging due to the complexity of surface configurational space and, therefore, the difficulty in computing the free energy of surfaces. In this proof-of-concept work, we predict coverage-temperature surface phase diagrams and identify phase transitions of adsorbates on both flat and stepped facets of the face-centered cubic Lennard-Jones solid. These phase transitions typically feature an enthalpy-driven condensation at higher temperatures and an entropy-driven reordering process at lower temperatures. We capture both energetic and entropic (especially configurational) contributions to the surface phase transitions with nested sampling. Overall, we demonstrate the ability and potential of nested sampling for predicting the structure of hard-to-measure *operando* surfaces, *e.g.*, that govern the activity and selectivity of heterogeneous catalysts. We are excited to share this new computational method with the community through our contributions to the open-source nested sampling package `pymatnest`.

We confirm that neither the manuscript nor any parts of its content are currently under consideration or published in another journal. All authors have approved the manuscript and agree with its submission to *Physical Chemistry Chemical Physics*.

Please find below a suggestion of (six) referees who – in our opinion – can expertly judge our work, none of whom we have ever collaborated with:

1. Karsten Reuter (reuter@fhi.mpg.de) – Fritz Haber Institute, Max Planck Society
2. Anastassia Alexandrova (ana@chem.ucla.edu) – University of California, Los Angeles
3. Yuanyuan Zhou (yuzhou@dtu.dk) – Technical University of Denmark
4. Sharani Roy (sharani.roy@utk.edu) – University of Tennessee, Knoxville
5. Bilge Yildiz (byildiz@mit.edu) – Massachusetts Institute of Technology
6. Bryan Goldsmith (bgoldsm@umich.edu) – University of Michigan

Sincerely,
Robert B. Wexler