High-throughput database for the surface properties of elemental solids

Richard Tran[1], Zihan Xu[1], Balachandran Radhakrishnan[1], Xiangguo Li[1], Donald Winston[2], Joseph Montoyah[2], Wenhao Sun[2], Kristin A. Persson[2], Shyue Ping Ong[1]

[1]Department of NanoEngineering, University of California San Diego, 9500 Gilman Dr., Mail Code 0448, La Jolla, CA 92093-0448, USA. [2]Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

Motivation

- Work function and surface energy can explain surface phenomena such as crystal growth and used in the design of devices such as catalysis and Schottky barriers.
- A comprehensive/standardized database of these properties is needed to develop a general model for such phenomena and screen for optimal functional materials.
- Constructed the world's largest open, rigorously validated database for surface properties using high-throughput DFT calculations.

Surface energy (γ) and Wulff shapes

Methods:

- **For facets**: $\gamma_{hkl}^{DFT} = \frac{E_{slab}^{hkl} - E_{bulk}^{hkl} n_{slab}}{2A_{slab}}$, $\gamma_{hkl}^{BB} = E_{coh}\frac{N_{bb}}{CN}\frac{1}{2A_{slab}}$
- **Weighted value**: $\bar{\gamma} = \sum_{hkl} \gamma_{hkl} f_{hkl}^{A}$, where f_{hkl}^{A} is a fractional area on the Wulff shape

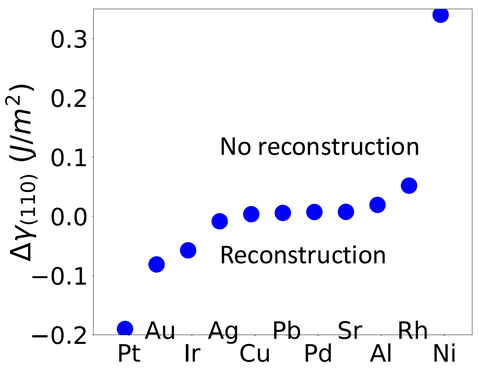
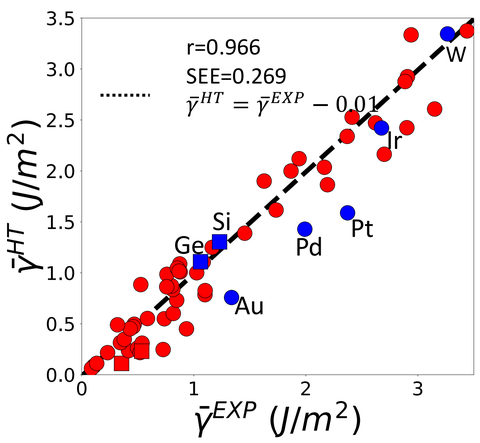


Fig 1. (top) Reconstruction energy for the fcc (110) 2x1 missing-row. ($\Delta\gamma_{110} = \gamma_{110}^{reconstruct} - \gamma_{110}^{relax}$)



Validation:

- $\bar{\gamma}^{HT}$ compares well with values obtained from liquid surface tension measurements ($\bar{\gamma}^{EXP}$).
- An accurate estimate of the Wulff shape is shown to require γ_{hkl} of max Miller index (MMI) greater than 1.
- Surface reconstructions found in the calculations are confirmed in experiments.
- In agreement with previously computed data (2-13% difference).

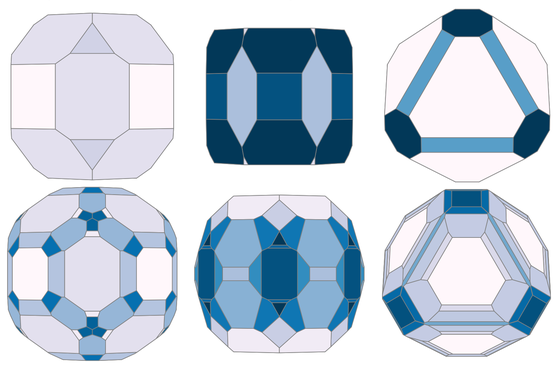


Fig 2 (top). Wulff shapes of Fe (left), Hf (center) and Pt (right) with an MMI of 1 (top) and MMI>1 (bottom).

Fig 3. (left) The calculated $\bar{\gamma}^{HT}$ provides an excellent estimate for $\bar{\gamma}^{EXP}$ measured using a sessile drop technique.

Work function (Φ)

Methods:

- **For facets**: $\Phi_{hkl} = V_{vac} - E_f$ where E_f is the Fermi energy and V_{vac} is the electrostatic potential at the vacuum region of the slab.
- **Weighted work function**: $\bar{\Phi} = \frac{\sum_{hkl} \Phi_{hkl} A_{hkl}}{\sum A_{hkl}} = \sum_{hkl} \Phi_{hkl} f_{hkl}^{A}$, provides an estimate for polycrystalline work functions.
- We modelled $\bar{\Phi}$ for metals using linear regression with a Pauling electronegativity to metallic radius ratio X/R.

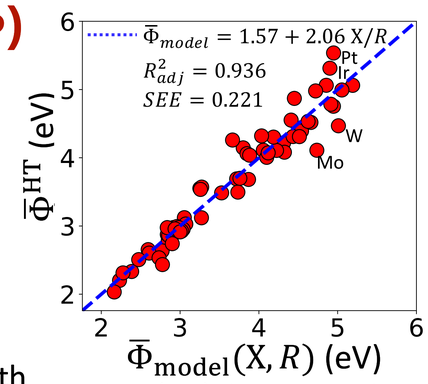


Fig 5. (top) Linear regression with X/R provides an excellent model for average metallic work function ($\bar{\Phi}$).

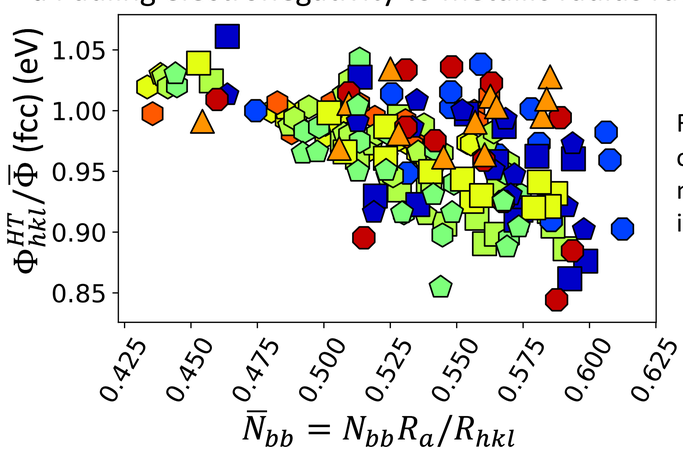


Fig 6. Work function of fcc metals vs number of broken bonds ($\overline{N_{bb}}$) (normalized). Φ_{hkl}^{HT} is negatively correlated to $\overline{N_{bb}}$ for most metals in accordance with Smoluchowski smoothing.

Validation and modelling:

- $\bar{\Phi}$ compared well to experimental values obtained from polycrystalline specimens (Φ_{poly}^{EXP}). DFT values are on average lower.
- Results of different functionals compared well with our values (r>0.9 with LDA, GGA-PBE and RPBE).
- Most systems follow Smoluchowski smoothing[3] for work function when plotting Φ_{hkl} against the number of broken bonds.
- X/R is an excellent descriptor for $\bar{\Phi}$ (metals). This ratio is analogous to the charge to distance (Q/R) ratio of Gauss's Law for the potential of a conducting sphere.

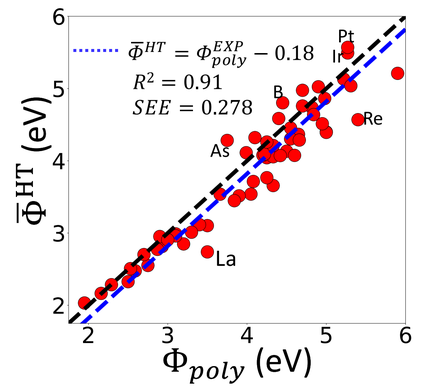


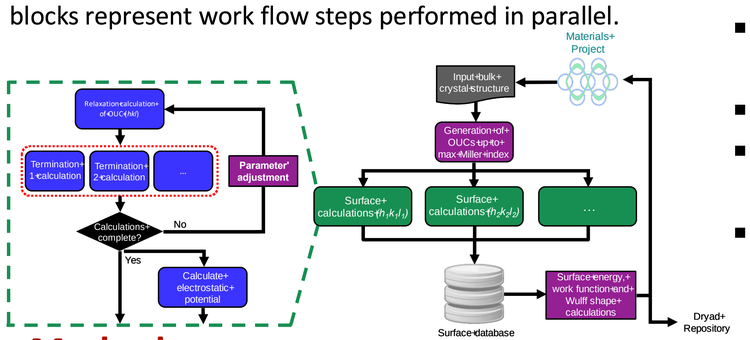
Fig 7. (top) $\bar{\Phi}^{HT}$ provides an estimate for experimental values of polycrystals (Φ_{poly})

Conclusions

- We developed new method of comparing calculated values of work function (Φ_{hkl}) and surface energy (γ_{hkl}) to experimental values obtained from polycrystals (Φ_{poly}) and liquid surface tension measurements ($\bar{\gamma}^{EXP}$) by using a weighted average based on the Wulff shape geometry.
- Our data was validated using previous DFT and experimental values and follows well-known trends such as reconstruction and Smoluchowski smoothing.
- We developed a model to predict $\bar{\Phi}$ for metals using atomic parameters.

Workflow and database

Fig 4. Schematic of the high-throughput infrastructure. Dashed blocks represent work flow steps performed in parallel.



Database includes:

- Surface properties of over 142 crystals of over 72 elements.
- Metals and non-metals.
- Elemental solid polymorphs available on MP.
- Facets of MMI up to 2 and 3 for all non-cubic and cubic crystals respectively.
- Well-known reconstructions.

Methods:

- DFT calculations were performed using the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional.
- All slabs have a minimum slab and vacuum thickness of 10 Å.
- Automated high-throughput workflow implemented using the FireWorks library.

References

1. Tran, R. *et al*. *Sci. Data*, **2016,** Data Descripter: Surface energies of elemental crystals. *3* (160080), 1–13.
2. Tran, R. *et al*. Anisotropic work function of elemental crystals. (in preparation).
3. Smoluchowski, R. *Phys. Rev*, **1941**, *60*(9), 661–674.

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