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# A topological screening heuristic for low-energy, high-index surfaces

Wenhao Sun[a,b,*], Gerbrand Ceder[a,b,c]

[a] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[b] Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[c] Department of Materials Science and Engineering, UC Berkeley, Berkeley, California 94720, USA

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ABSTRACT

Robust *ab initio* investigations of nanoparticle surface properties require a method to identify candidate low-energy surface facets *a priori*. By assuming that low-energy surfaces are planes with high atomic density, we devise an efficient algorithm to screen for low-energy surface orientations, even if they have high (*hkl*) miller indices. We successfully predict the observed low-energy, high-index $\{10\bar{1}2\}$ and $\{10\bar{1}4\}$ surfaces of hematite $\alpha$-$Fe_2O_3$, the {311} surfaces of cuprite $Cu_2O$, and the {112} surfaces of anatase $TiO_2$. We further tabulate candidate low-energy surface orientations for nine of the most common binary oxide structures. Screened surfaces are found to be generally applicable across isostructural compounds with varying chemistries, although relative surface energies between facets may vary based on the preferred coordination of the surface atoms.

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## 1. Introduction

Many important interfacial properties of nanoparticles, such as reactivity [1], photocatalytic activity [2], crystal-growth direction [3], and intercalation rates for battery electrodes [4], depend on which surface facets are exposed on the particle morphology. At equilibrium, this morphology is given by the Wulff construction, which can be predicted from first-principles by calculating which surface orientations bound the nanocrystal with the lowest surface energy. This process determines which surfaces are stable, and are therefore relevant for more sophisticated investigations of surface properties or reactions. The first step in an *ab initio* investigation of nanoparticle interfacial properties is the selection of which surface orientations to calculate. Ideally, one would choose the stable surface facets observed in experimental nanoparticle morphologies, but when these are unavailable, surface investigations have typically been constrained to the low-index surfaces (Miller indices *hkl* all being either 0 or ± 1). However, particle morphologies can often exhibit stable high-index surfaces, such as the $\{10\bar{1}2\}$ and $\{10\bar{1}4\}$ surfaces of rhombohedral crystals such as hematite $Fe_2O_3$ [5] and Calcite $CaCO_3$ [6]. High-index surfaces can also be stabilized electrochemically, as in the (730) surfaces of FCC platinum [7], or via adsorbates, such as the (311) surfaces of cubic $Cu_2O$ [8]. Most surface properties are strongly orientation-dependent, so if stable high-index surfaces are not considered in a computational investigation, then calculated surface properties may be largely irrelevant.

One might consider searching for low-energy, high-index surface orientations by calculating the energy of surfaces attained by a brute force enumeration of surface orientations [9]. However, this process can be combinatorically prohibitive, as combinations of Miller indices up to index *N* yield $O(N^3)$ surface orientations, each with potentially multiple unique terminations. It can also be wasteful, as usually only a small handful of surface facets are energetically competitive to appear on the Wulff construction. Furthermore, it may actually be conceptually flawed to search for low-energy surfaces by Miller index, as Miller indices are defined with respect to the conventional unit-cell lattice, which is not unique, and is a ‘human’ convention, rather than a physical one. Atomic positions are a physically-relevant crystallographic feature to search for low-energy surfaces by, but the lattice does not include this information.

In this paper, we propose an efficient, physically-motivated screening heuristic for low-energy surfaces that does not depend on how the unit-cell is defined. Our heuristic is based on the hypothesis that low-energy surfaces tend to be planes with high atomic density. This is a reasonable assumption for two reasons: 1) because planes with greater atomic density have the potential for more in-plane bonds, which reduces the surface energy. 2) The Gibbs-Thomson model relates excess chemical potential to plane curvature, indicating that flat planes have the lowest free-energy. While this argument is generally exercised at the microscopic level, the geometric argument operates on a similar principle at the atomic level.

Our heuristic is described as follows. Planes can be defined by any set of three atoms. By identifying all the possible unique planes formed by sets of three atoms within a crystal structure, and identifying which Miller indices are most highly represented by this survey, we identify the highest-density planar orientations, which are promising candidates

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[*] Corresponding author.
*E-mail address:* wenhaosun@lbl.gov (W. Sun).

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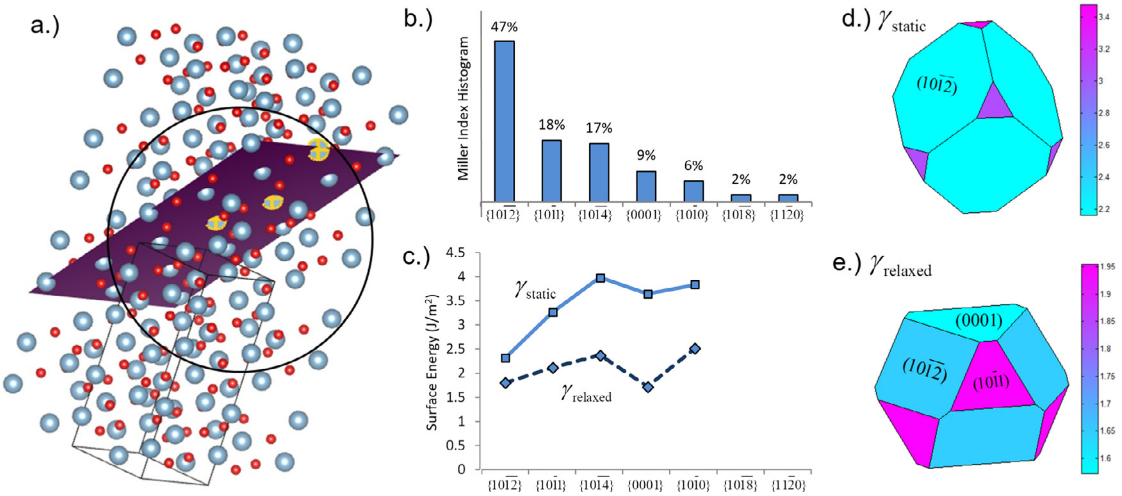

**Fig. 1.** The low-energy, high-index surface screening heuristic a.) Surface orientations are sampled by enumerating triplets of atoms in a sphere around the symmetrically-distinct atoms in a unit cell. b.) The frequency of sampled orientations is collected in a histogram, where highly sampled surfaces correspond to greater planar atomic densities, shown for the corundum $\alpha$-$Al_2O_3$ structure. c.) Static and relaxed surface energies of orientations obtained using the screening heuristic. Greater atomic planar densities generally correlate with lower surface energies. d.) Wulff construction from static surface energies. e.) Wulff construction made from relaxed surface energies.

for the lowest-energy surfaces. Our proposed algorithm is successful at identifying multiple observed low-energy, high-index planes for several important oxide structures. Because our algorithm is based on the crystal structure, but not the chemistry, we perform an analysis for the applicability of screened surfaces across isostructural compounds with varying chemistries, and how chemistry changes the relative surface energies between facets. Our screening heuristic is powerful and computationally inexpensive, and should precede any *ab initio* investigation of surface properties where the equilibrium particle morphology is unknown.

## 2. Methodology

We aim to develop a quantitative descriptor for high-density planes that is easy to identify computationally, and does not require explicit construction of surface slabs to achieve. We begin by reasoning that a complete sampling of planes formed by three atoms will naturally be biased towards surface orientations with high-density. Here, we start with a description of the algorithm, illustrated in Fig. 1a, including a discussion of subtleties to be aware of in order to minimize the identification of spurious high-index surfaces.

1. **For a given unit cell, identify all symmetrically unique atoms.** This eliminates the dependence of the algorithm on the orientation of the chosen lattice, or the number of primitive unit cells within this orientation. This further ensures that environments of atoms on high-symmetry Wyckoff positions are not oversampled.
2. **For each symmetrically unique atom, construct a sphere of cutoff radius $r_0$.** The radius of this sphere should encompass enough atoms to attain a reasonable sampling of the local short-range atomic environment. The number of triplets of atoms scales as ${}_{N}C_2$, where $N$ is the number of atoms in the sphere. We find that an $r_0$ that encompasses 50 atoms is sufficient to identify most low-energy high-index surfaces.
3. **Within this sphere, identify all sets of three atoms that include the original atom.** In the cases of complex ions, such as $CO_3^{2-}$, $SO_4^{2-}$, $PO_4^{3-}$, $AlH_4^{-}$, $NH_4^{+}$, etc, only the center atom is considered. If all atoms are considered for these cases, then surface orientations representing the surfaces of ionic polyhedra become oversampled, rather than just the preferred cleavage surfaces of the cationic/anionic sublattice.
4. **Determine the Miller indices of the plane formed by the sets of three atoms**, defined with respect to the desired unit cell, which is typically the conventional one. To do this generally, for Bravais lattices of any symmetry, one begins by forming two vectors from the three atoms. The Miller indices of the *vectors* can be found from $v_{\text{Miller}} = L^{-1}v$ where $L$ is the lattice of the desired unit cell, and $v$ is the vector formed between two of the three atoms, defined with respect to the same standard basis as the lattice. The Miller index of the plane formed by these two vectors is the cross product of the two Miller vectors. Miller indices with irreducible fractional indices are discarded, as one cannot create a slab with irreducible fractional indices that satisfies periodic boundary conditions.
5. **Build a histogram of sampled surface orientations. The orientations that occur the most frequently are the ones with the greatest planar atomic density.** Miller indices that are equivalent by symmetry (i.e. in a family) should be grouped together. The family of a Miller index can be constructed by applying all the point group operations of the reciprocal lattice to the Miller index.

We next apply this surface screening algorithm to a selection of binary oxides that have been experimentally observed to exhibit high-index surfaces. We compute the surface energy, $\gamma$, using the equation

$$\gamma = \frac{1}{2A}\left(E_{slab} - NE_{bulk}\right) \tag{1}$$

where $A$ is the area of the surface unit cell, $E_{\text{slab}}$ is the energy of the slab supercell, $E_{bulk}$ is the bulk energy per atom, and $N$ is the number of atoms in the surface slab. The $\frac{1}{2}$ pre-factor accounts for the two surfaces of a slab. If the surface can exchange molecular or atomic species with an external reservoir, then the surface grand potential is:

$$\gamma = \frac{1}{2A}\left(E_{slab} - NE_{bulk} - \sum_i N_i\mu_i\right) \tag{2}$$

where excess or deficient atoms are accounted for by a chemical potential term for the $N_i$ atoms of species $i$ with chemical potential $\mu_i$.

For this work we only consider stoichiometric oxide surface slabs, constructed from planar cleavages of a bulk crystal, where the surface energy is given by Eq. (1). In real oxide surfaces, surface reconstructions may occur, where the surface structure changes to accommodate the energetic cost of broken bonds [10]. Surfaces may also become non-stoichiometric under highly oxidizing or reducing oxygen environments, changing the surface energy according to Eq. (2), thereby influencing which surface facets appear on the equilibrium morphology [11,12]. Although explicit calculations of non-stoichiometric or reconstructed surfaces are beyond the scope of this work, we will demonstrate that the surface orientations screened using our planar-density heuristic are

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