

Machine-learning-accelerated simulations to enable automatic surface reconstruction

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Supplementary Section 1: Abbreviations used

The following is the list of abbreviations utilized.

- DFT: Density-functional theory
- MC: Monte Carlo
- MCMC: Markov-chain Monte Carlo
- ML: Machine learning
- NFF: Neural network force field
- AL: Active learning
- AutoSurfRecon: Automatic Surface Reconstruction
- VSSR-MC: Virtual Surface Site Relaxation-Monte Carlo
- DAS: Dimer-atom stacking fault
- SD: Standard deviation
- MAE: Mean absolute error
- PCA: Principal component analysis
- DL: Double layer
- SL: Single layer
- LR: Learning rate
- SRS: Stephenson, Radny & Smith (potential)

Supplementary Section 2: Surface stability analysis

The stability of surfaces can be compared using the surface Gibbs free energy Ω_{surf} [1-3]:

$$\Omega_{\text{surf}} = G_{\text{slab}} - \sum_{\text{all } a} N_a \mu_a \quad (\text{S1})$$

where G_{slab} refers to the Gibbs free energy of the slab. For each element a , N_a refers to the number of a atoms in the slab, μ_a refers to the chemical potential of a .

For SrTiO_3 specifically, we have its surface Gibbs free energy:

$$\Omega_{\text{surf}}^{\text{SrTiO}_3} = G_{\text{slab}} - N_{\text{Sr}} \mu_{\text{Sr}} - N_{\text{Ti}} \mu_{\text{Ti}} - N_{\text{O}} \mu_{\text{O}} \quad (\text{S2})$$

The SrTiO_3 chemical potential is defined as the sum of the chemical potentials of the component elements:

$$\mu_{\text{SrTiO}_3} = \mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_{\text{O}}$$

At thermodynamic equilibrium, the chemical potential of the surface is equal to the bulk crystal Gibbs free energy:

$$\mu_{\text{SrTiO}_3} = g_{\text{SrTiO}_3}^{\text{bulk}}$$

Substituting, we obtain:

$$\Omega_{\text{surf}}^{\text{SrTiO}_3} = G_{\text{slab}} - N_{\text{Ti}} g_{\text{SrTiO}_3}^{\text{bulk}} - \Gamma_{\text{Sr}}^{\text{Ti}} \mu_{\text{Sr}} - \Gamma_{\text{O}}^{\text{Ti}} \mu_{\text{O}} \quad (\text{S3})$$

where $\Gamma_a^{\text{Ti}} = N_a - N_{\text{Ti}} \frac{N_a^{\text{bulk}}}{N_{\text{Ti}}^{\text{bulk}}}$ refers to the excess a component in the surface with respect to the number of Ti atoms and $\frac{N_a^{\text{bulk}}}{N_{\text{Ti}}^{\text{bulk}}}$ refers to the bulk stoichiometric ratio of a to Ti.

The bulk Gibbs free energy for a crystal can be decomposed into the following:

$$g_a^{\text{bulk}} = E_a^{\text{bulk}} + E_a^{\text{vib}} - T s_a + p v_a \quad (\text{S4})$$

where E_a^{bulk} is the static crystal energy obtained through DFT calculations, E_a^{vib} is the vibrational component, T is the temperature, s_a is the entropy of the crystal, p is the pressure, and v_a is the volume of the crystal. By performing approximations similar to [1, 2], changes in E_a^{vib} due to temperature roughly cancel out changes in $T s_a$ while $p v_a$ is negligible.

Thus, Gibbs free energies can be approximated by the DFT energies:

$$g_a^{\text{bulk}} \approx E_a^{\text{bulk}}$$

For later convenience in plotting the phase diagram, bulk-subtracted chemical potentials are introduced for Sr and Ti:

$$\mu'_{\text{Sr}} = \mu_{\text{Sr}} - g_{\text{Sr}}^{\text{bulk}} \approx \mu_{\text{Sr}} - E_{\text{Sr}}^{\text{bulk}} \quad (\text{S5})$$

$$\mu'_{\text{Ti}} = \mu_{\text{Ti}} - g_{\text{Ti}}^{\text{bulk}} \approx \mu_{\text{Ti}} - E_{\text{Ti}}^{\text{bulk}} \quad (\text{S6})$$

where $E_{\text{Sr}}^{\text{bulk}}$ and $E_{\text{Ti}}^{\text{bulk}}$ are obtained from DFT calculations.

Similarly, μ'_O is defined with the reference state as an isolated oxygen molecule:

$$\mu'_O = \mu_O - \frac{1}{2}E_{\text{O}_2} \quad (\text{S7})$$

where E_{O_2} is the DFT total energy of a single oxygen molecule.

Additionally, μ_O can be defined as a function of experimental conditions, O_2 partial pressure (p_{O_2}) and temperature (T), with the following equation:

$$\mu_O(T, p_{\text{O}_2}) = \frac{1}{2} \left[E_{\text{O}_2} + \mu_{\text{O}_2}(T, p_0) + k_B T \ln \left(\frac{p_{\text{O}_2}}{p_0} \right) \right] \quad (\text{S8})$$

where $p_0 = 1$ bar is the reference pressure and $\mu_{\text{O}_2}(T, p_0)$ is the reference chemical potential obtained from NIST [4].

We swap out μ_a for μ'_a and transform to obtain:

$$\Omega_{\text{surf}}^{\text{SrTiO}_3} = \phi - \Gamma_{\text{Sr}}^{\text{Ti}} \mu'_{\text{Sr}} - \Gamma_{\text{O}}^{\text{Ti}} \mu'_O \quad (\text{S9})$$

where

$$\begin{aligned} \phi &= G_{\text{slab}} - N_{\text{Ti}} g_{\text{SrTiO}_3}^{\text{bulk}} - \Gamma_{\text{Sr}}^{\text{Ti}} g_{\text{Sr}}^{\text{bulk}} - \Gamma_{\text{O}}^{\text{Ti}} \frac{E_{\text{O}_2}}{2} \\ &\approx E_{\text{slab}} - N_{\text{Ti}} E_{\text{SrTiO}_3}^{\text{bulk}} - \Gamma_{\text{Sr}}^{\text{Ti}} E_{\text{Sr}}^{\text{bulk}} - \Gamma_{\text{O}}^{\text{Ti}} \frac{E_{\text{O}_2}}{2} \end{aligned}$$

G_{slab} is approximated by the slab energy E_{slab} . For thermodynamic stability, $\mu'_{\text{Sr}} < 0$, $\mu'_O < 0$.

Note: In our main text, we denote μ'_{Sr} and μ'_O as μ_{Sr} and μ_O respectively for simplicity.

VSSR-MC samples according to the grand potential Ω_G , which is equivalent to Ω_{surf} after approximations:

$$\begin{aligned} \Omega_G^{\text{SrTiO}_3} &= E_{\text{slab}} - T s_{\text{slab}} - N_{\text{Sr}} \mu_{\text{Sr}} - N_{\text{Ti}} \mu_{\text{Ti}} - N_{\text{O}} \mu_{\text{O}} \quad (\text{S10}) \\ &= G_{\text{slab}} - p v_{\text{slab}} - N_{\text{Sr}} \mu_{\text{Sr}} - N_{\text{Ti}} \mu_{\text{Ti}} - N_{\text{O}} \mu_{\text{O}} \\ &\approx G_{\text{slab}} - N_{\text{Sr}} \mu_{\text{Sr}} - N_{\text{Ti}} \mu_{\text{Ti}} - N_{\text{O}} \mu_{\text{O}} \\ &= \Omega_{\text{surf}}^{\text{SrTiO}_3} \end{aligned}$$

References

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