A Reactive Force Field for Alumina Systems

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Introduction

Alumina, more specifically γ-Al_2O_3, plays a central role in catalyic processes. γ-Al2O3 is widely used as a support for catalytic compounds such as ZSM-5. The need for binders and supporting materials arrises as most catalytic active compounds lack essential chemical and mechanical properties such as strength, surface density and acidity to be applicable in industrial conditions.

The system sizes of the catalyst/binder interface often contain thousands of atoms, making it prohibitively expensive for Ab Initio methods. Falling back on regular force field methods is not possible since the model should be reactive to account for the catalytic reactions. ReaxFF is therefore proposed to model this system. This emperical force field method is orders of magnitude cheaper to calculate than Ab Initio methods while still being reactive. This work proposes a new force field for these alumina systems obtained through a novel optimization procedure.

ReaxFF

The energy of ReaxFF[1] can be expressed using a global equation containing multiple contributions and corrections:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{charge}} + E_{\text{specific}}$$

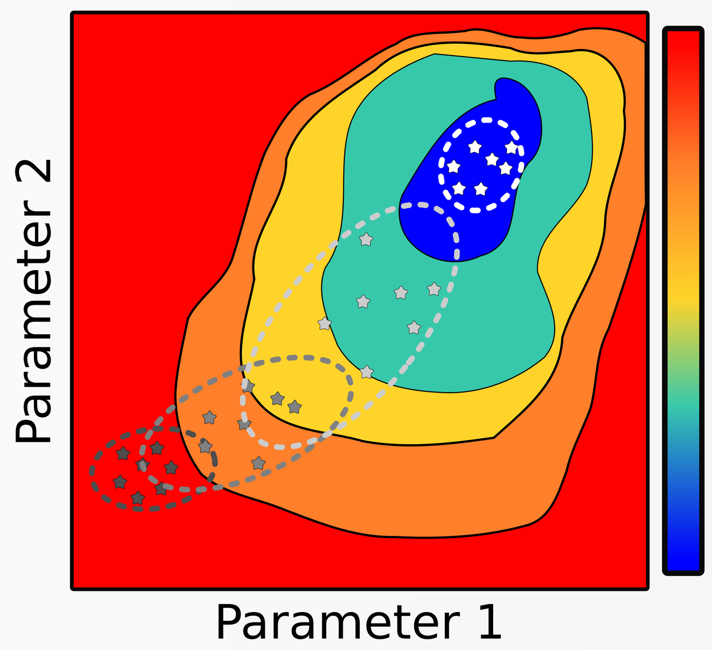
By introducing a Bond Order (BO) dependence in the local (covalent) terms, ReaxFF succeeds in introducing bond breaking and formation for a multitude of elements.

$$\begin{aligned}\text{BO}'_{ij} &= \text{BO}'_{ij,\sigma} + \text{BO}'_{ij,\pi} + \text{BO}'_{ij,\pi\pi} \\ &= \exp\left(p_{\text{bo},1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{p_{\text{bo},2}}\right) + \exp\left(p_{\text{bo},3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{p_{\text{bo},4}}\right) \\ &\quad + \exp\left(p_{\text{bo},5}\left(\frac{r_{ij}}{r_0^{\pi\pi}}\right)^{p_{\text{bo},6}}\right)\end{aligned}$$

Optimization

Covariance Matrix Adaptation - Evolutionary Strategy

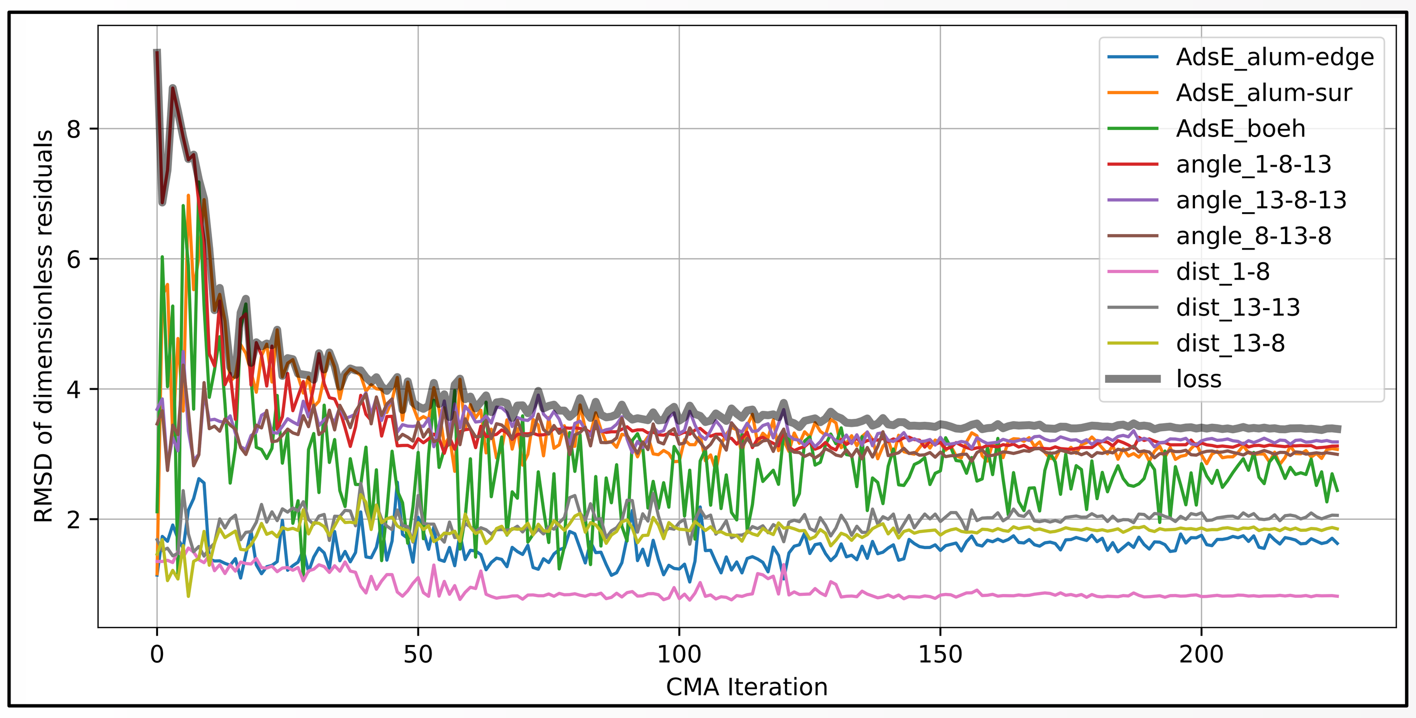
CMA-ES[2] is an optimization method that adapts the covariance matrix in an iterative manner to map the response surface of the specified objective function.



BalancedLoss

A new loss function **BalancedLoss** is proposed to remove the need of weights in the training set. BalancedLoss can be understood as a MaxError function over user-defined categories, but is smooth so that optimizers are well-behaved.

$$L_{\text{BalancedLoss}} = \ln\left(\sum_{a}^{C} \exp\frac{R_a}{\alpha}\right)\alpha \;,\; R_a = \sqrt{\frac{1}{N}\sum_{i}^{N}\frac{x_{i,\text{ reaxff}} - x_{i,\text{ ref}}}{\sigma_i}}$$



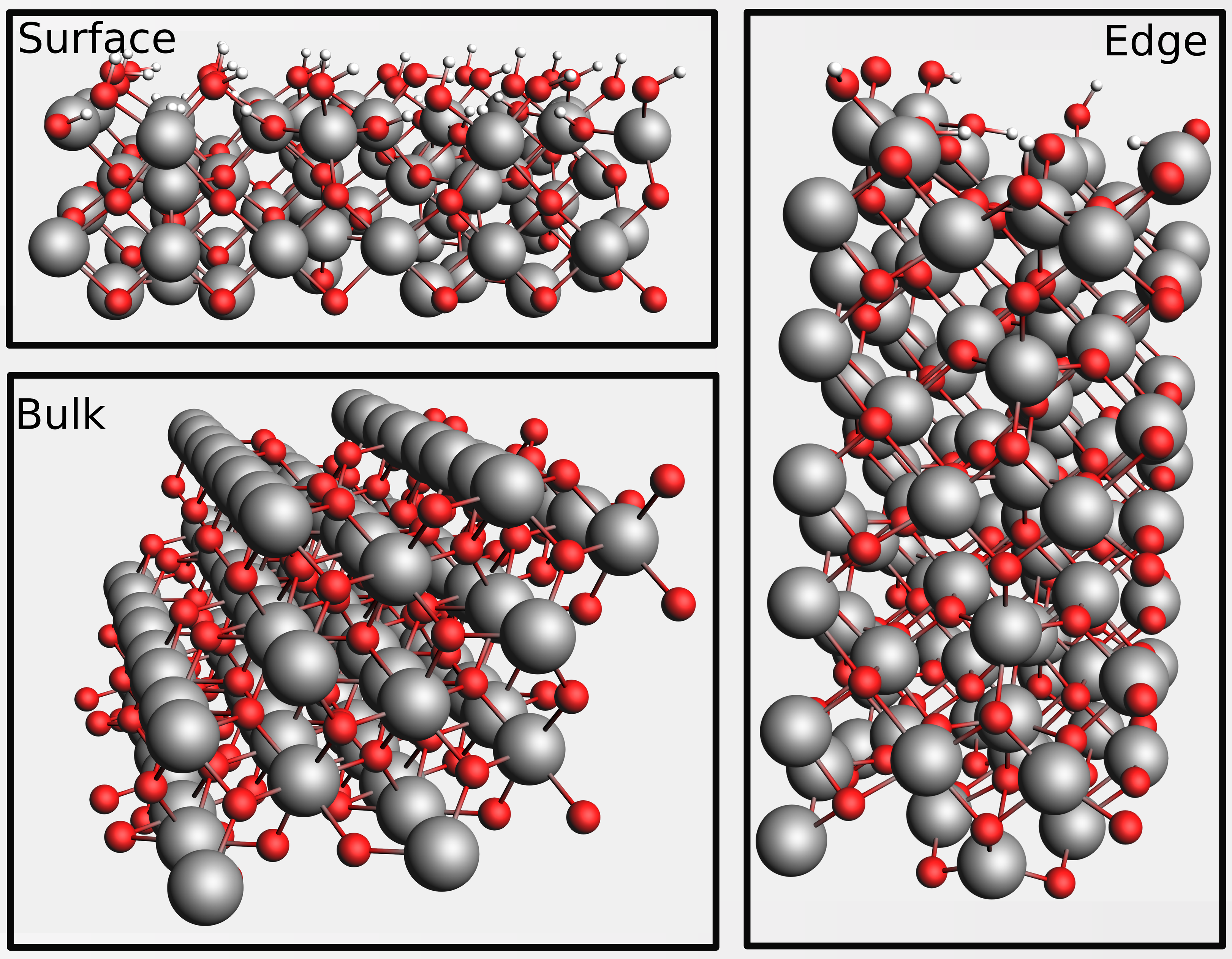
Training Set

Computational Details

- PAW
- dDsC correction
- 600 eV cutoff
- 10^{-5} eV SCF convergence
- fixed lattice parameters

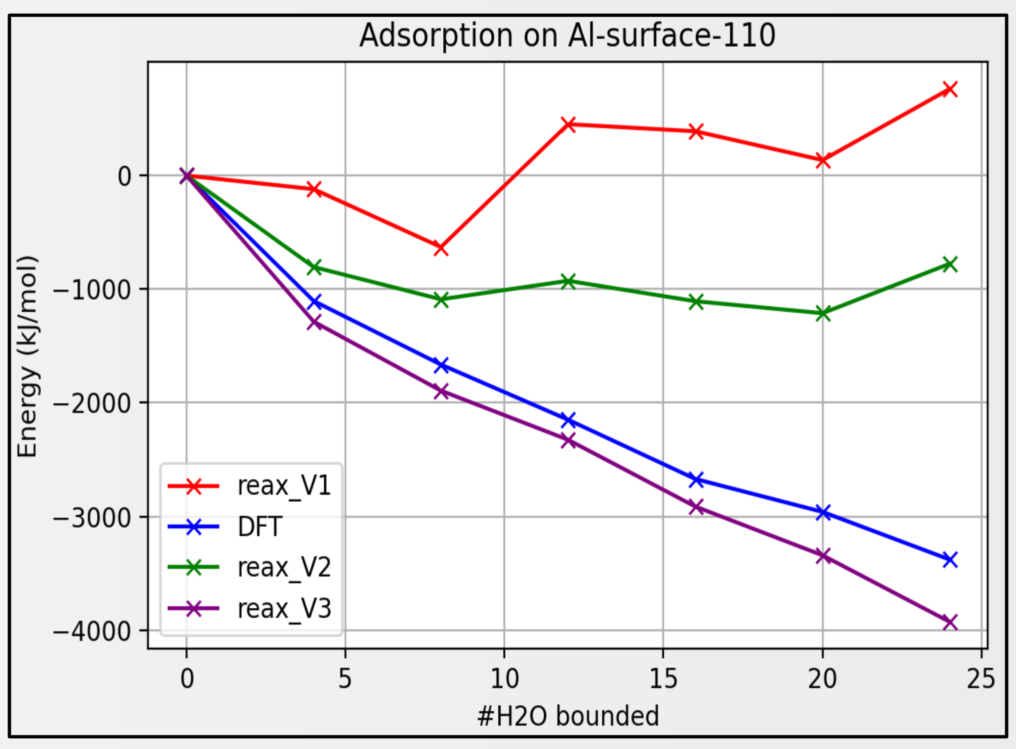
Structure	Hydration levels
γ-Al_2O_3(100-110)	8
γ-Al_2O_3(100)	4
γ-Al_2O_3(110)	7
γ-Al_2O_3(111)	4
Boehmite (101)	2
Boehmite (010)	1
Boehmite (001)	2
Boehmite (100)	3
Bulk α-Al_2O_3	1
Bulk boehmite	1
Bulkγ-Al_2O_3	1
monomere	1
water	1

VASP



Force Field Results

Without refitting, water adsorption using ReaxFF is endothermic while in reality it is strongly exothermic. A first reparametrization on geometric features improves this property, but only after adding energetic reference data the water adsorption is well reproduced.



Conclusion

A force field that can accurately describe water adsorption/desorption on alumina has been developed. During optimization, no water-parameters nor Al-Si parameters are altered, assuring that the description of water and alumina/ZSM5 interactions is still accurately described. The introduction of the new loss-function BalancedLoss allows to obtain lower errors than regular RMSD or SSE as well as provides important insights in the optimization and limitations of ReaxFF.

References:
[1]C. T. van Duin, S. Dasgupta, F. Lorant and W. A. Goddard, The Journal of Physical Chemistry A, 2001, 105, 9396–9409
[2]Christian Igel, Nikolaus Hansen, Stefan Roth; Covariance Matrix Adaptation for Multi-objective Optimization. Evol Comput 2007; 15 (1): 1–28. doi: https://doi.org/10.1162/evco.2007.15.1.1

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