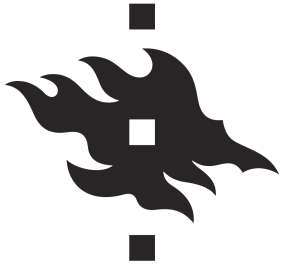


Interatomic Potential for Fe-Cr

taking surface properties into account

Intro

A study of stainless steels where the fundamental component is Fe-Cr alloy.

“Particularly, the mechanisms and kinetics (timescales) of segregation of Cr on the alloy surface are not well understood.”

“Our proposal aims to promote a study where kinetics of Cr is simulated properly also on surfaces and interfaces, and targeted experiments are precisely matched to simulations at the very beginning.”

“The controlling of Cr kinetics in the manufacturing process of Fe-Cr containing products is one of the key prerequisites for the cost effective way to produce novel high-quality end products.”

Embedded Atom Model and Tersoff

EAM:

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij})$$

F is the embedding energy which is a function of the atomic electron density *ρ*, *ϕ* is a pair potential interaction, and *α* and *β* are the element types of atoms *i* and *j*

Tersoff:

$$\begin{aligned}
E &= \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij} \\
V_{ij} &= f_C(r_{ij}) \left[f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right] \\
f_C(r) &= \begin{cases} 1 & : \quad r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{r - R}{D} \right) & : \quad R - D < r < R + D \\ 0 & : \quad r > R + D \end{cases} \\
f_R(r) &= A \exp(-\lambda_1 r) \\
f_A(r) &= -B \exp(-\lambda_2 r) \\
b_{ij} &= (1 + \beta^n {\zeta_{ij}}^n)^{-\frac{1}{2n}} \\
\zeta_{ij} &= \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) \exp\left[{\lambda_3}^m (r_{ij} - r_{ik})^m \right] \\
g(\theta) &= \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{\left[d^2 + (\cos\theta - \cos\theta_0)^2 \right]} \right)
\end{aligned}$$

f_R is a two-body term and *f_A* includes three-body interactions

the summations in the formula are over all neighbors *j* and *k* of atom *i* within a cutoff distance = *R* + *D*

also environment and angular functions

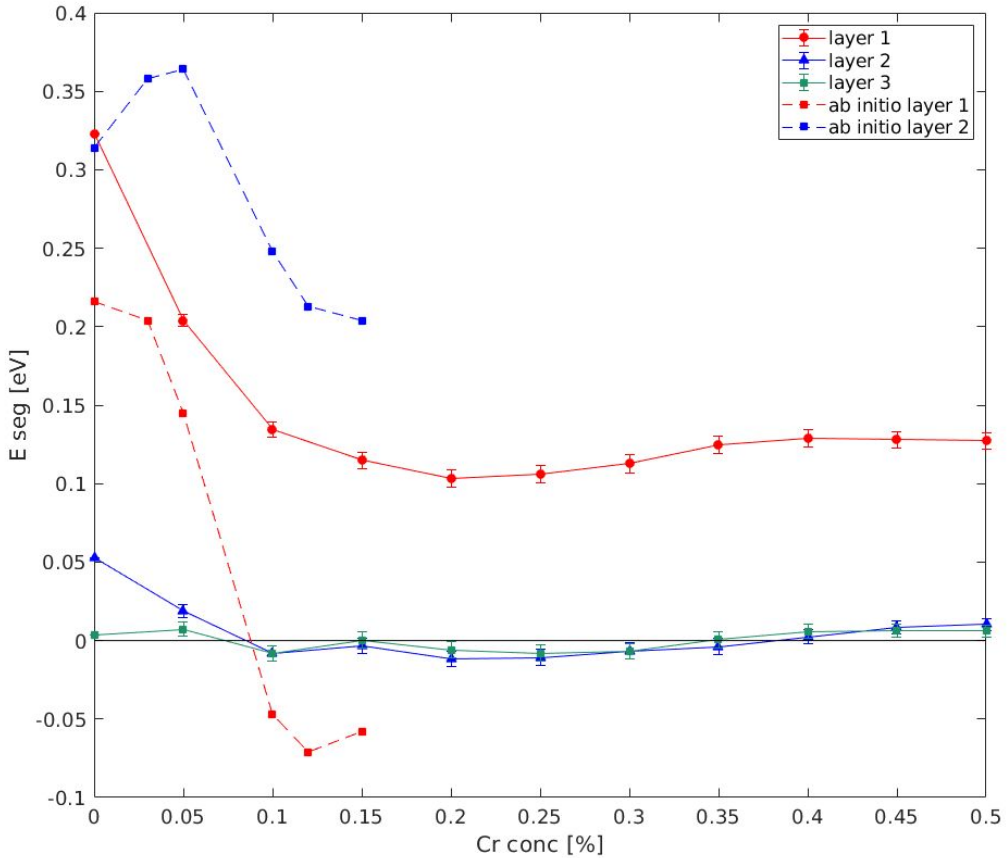
2018

Faults in existing potentials

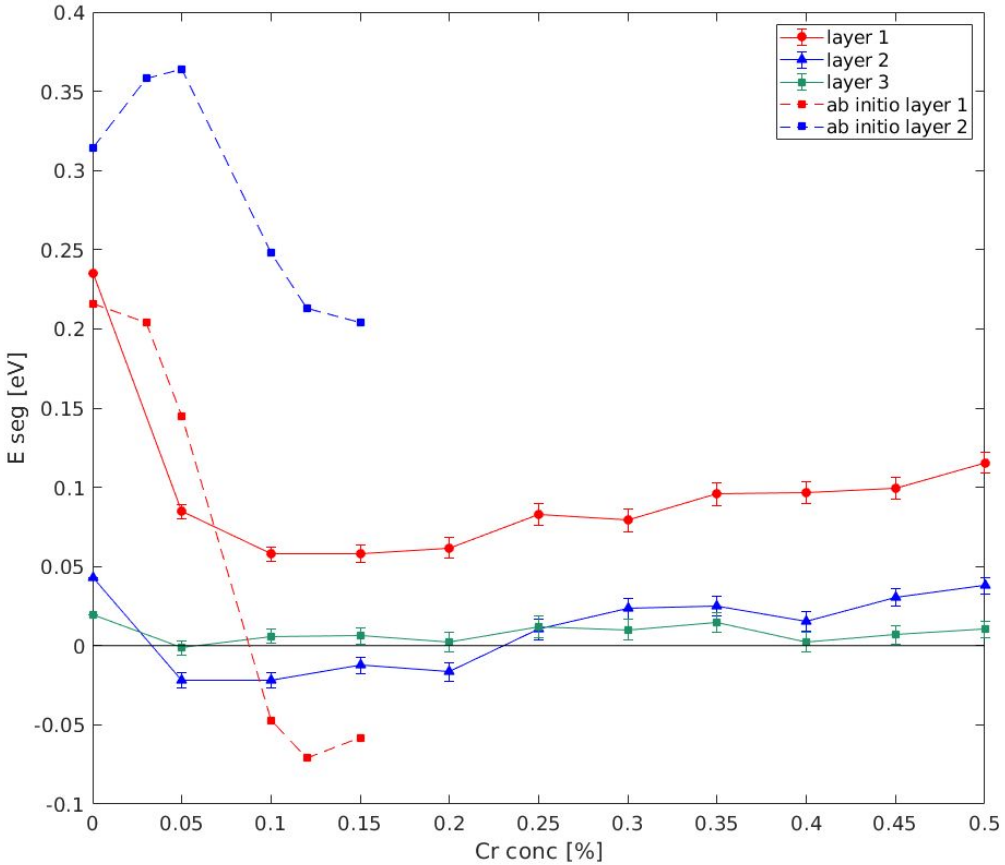
Segregation Energy

- Energy at a specific layer minus bulk energy (used LAMMPS box relax)
- Negative segregation energy means it would segregate to that layer
- DFT (ab initio) show segregation to the outer layer at 10% Cr
- Existing interatomic potentials: Segregation to second layer

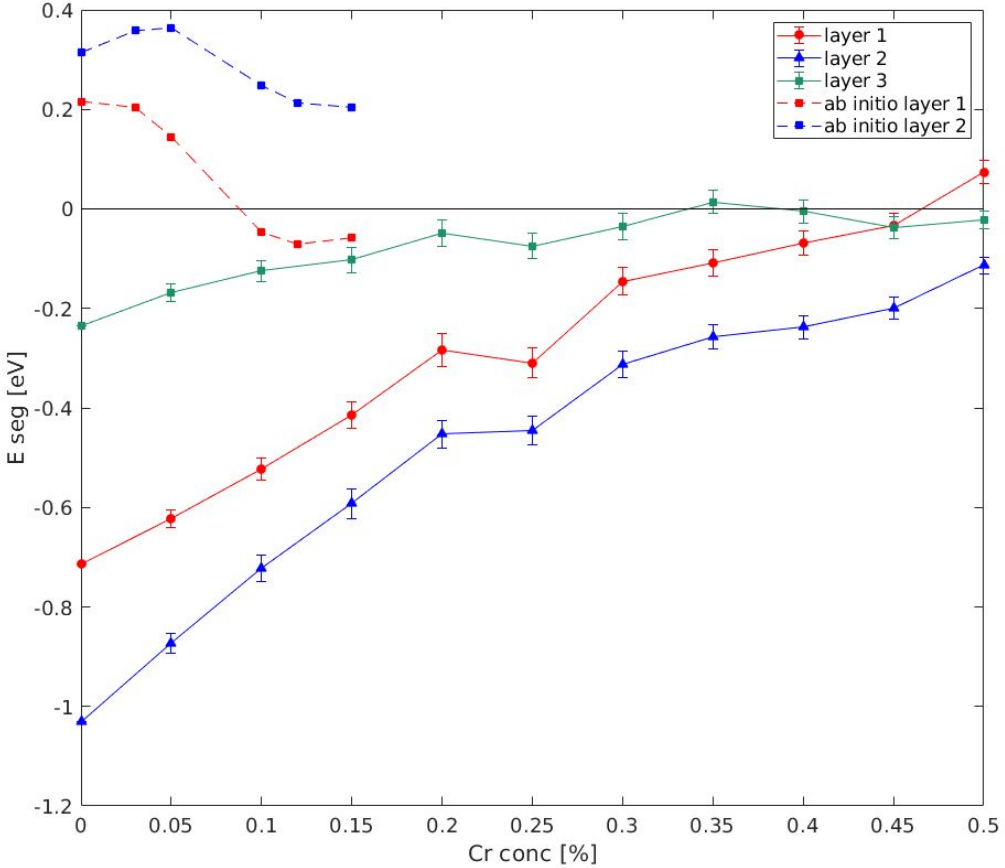
CD-EAM Segregation Energy



2B-EAM Segregation Energy



Tersoff Segregation Energy



SRO β parameter

Erhart et. al: Short-range order and precipitation in Fe-rich Fe-Cr alloys: Atomistic off-lattice Monte Carlo simulations

$$\alpha_{Cr}^{(k)} = 1 - \frac{Z_{Fe}^{(k)}}{Z_{tot}^{(k)}(1 - c_{Cr})}$$

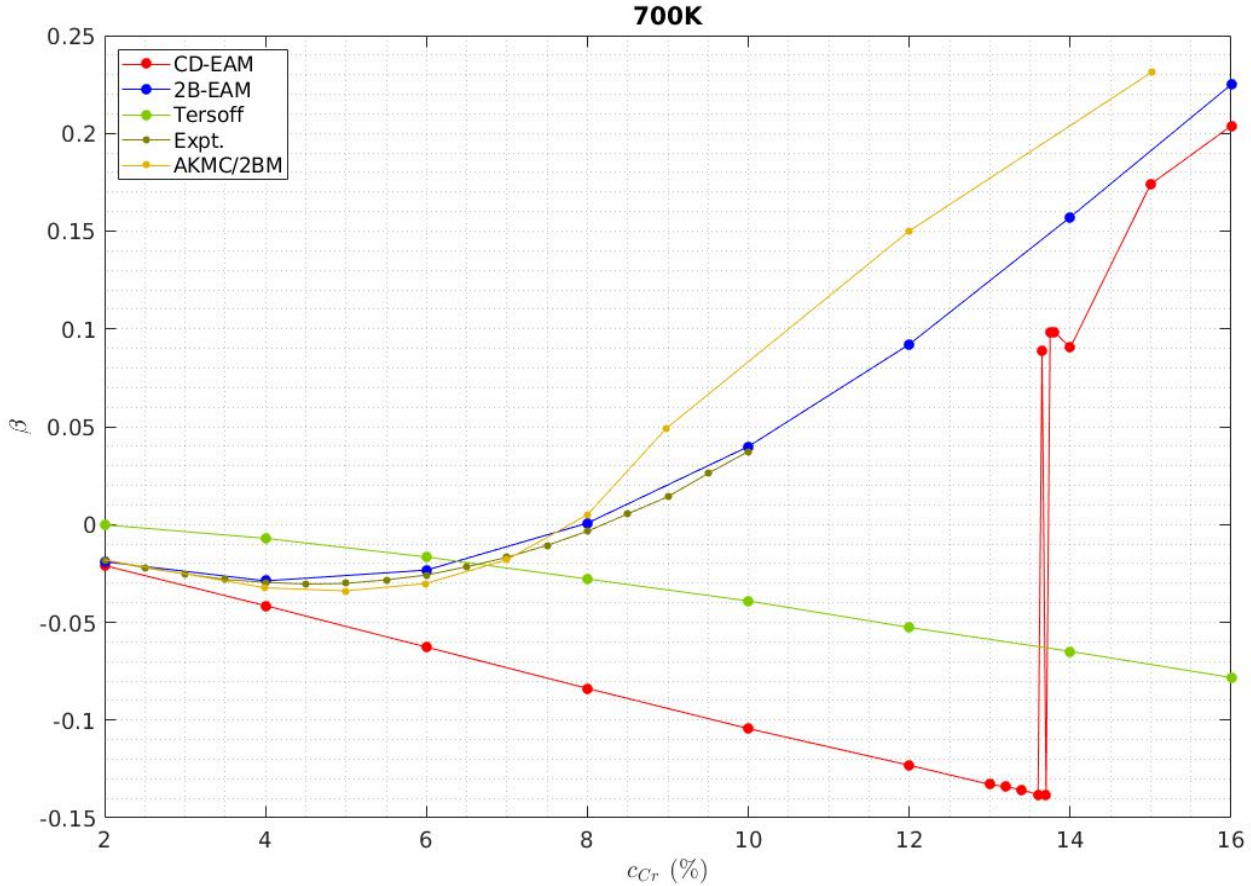
$$\beta = \frac{8\alpha_{Cr}^{(1)} + 6\alpha_{Cr}^{(2)}}{14}$$

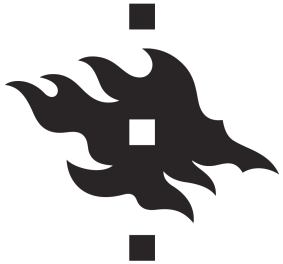
Z_Fe: mean of Fe atoms on the *k*:th neighbouring shell of a Cr atom, *c_Cr*: chromium concentration

Negative *β* → Cr tend to be far from each other

Positive *β* → Cr tend to form clusters

β = 1 → only Cr as neighbours and *β* = 0 → random distribution according to concentration


700K
CD-EAM
2B-EAM
Tersoff
Expt.
AKMC/2BM
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
-0.15
β
2
4
6
8
10
12
14
16
c_{Cr} (%)



2019

Testing new tersoff parametrizations

List of potentials

EAM used for comparison:

2B-EAM Bonny et. al: Iron chromium potential to model high-chromium ferritic alloys

CD-EAM Stukowski et. al: Efficient implementation of the concentration-dependent embedded atom method for molecular-dynamics and Monte-Carlo simulations

Tersoff used for comparison:

Old Tersoff Henriksson et. al: Atomistic simulations of stainless steels: a many-body potential for the Fe–Cr–C system

Potentials being tested - Pekko's 28 parametrizations:

1st set = Cr-Fe.tersoff.zbl_20181225032444 ... Cr-Fe.tersoff.zbl_20190128054313

2nd set = Cr-Fe.tersoff.zbl_20190606204342 ... Cr-Fe.tersoff.zbl_20190619003319

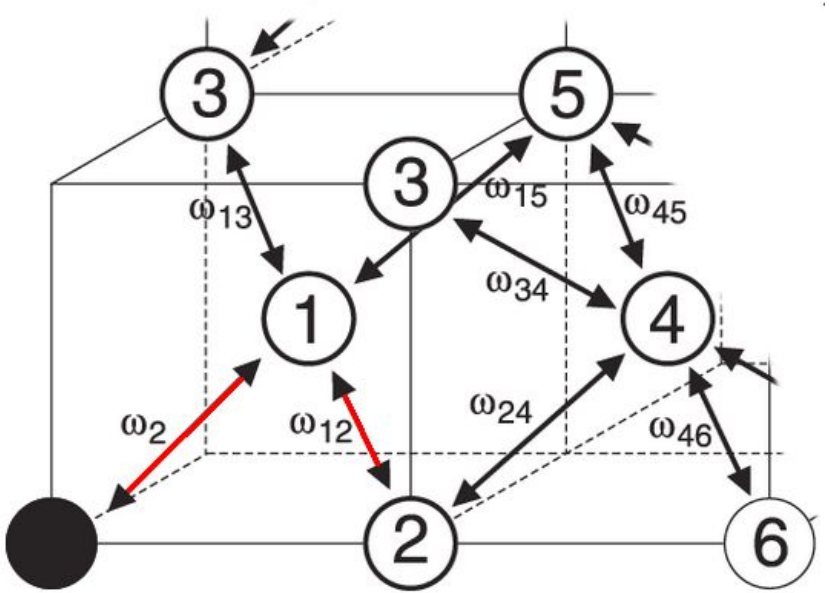
3rd set = Cr-Fe.tersoff.zbl_20190630030601 ... Cr-Fe.tersoff.zbl_20190729133304

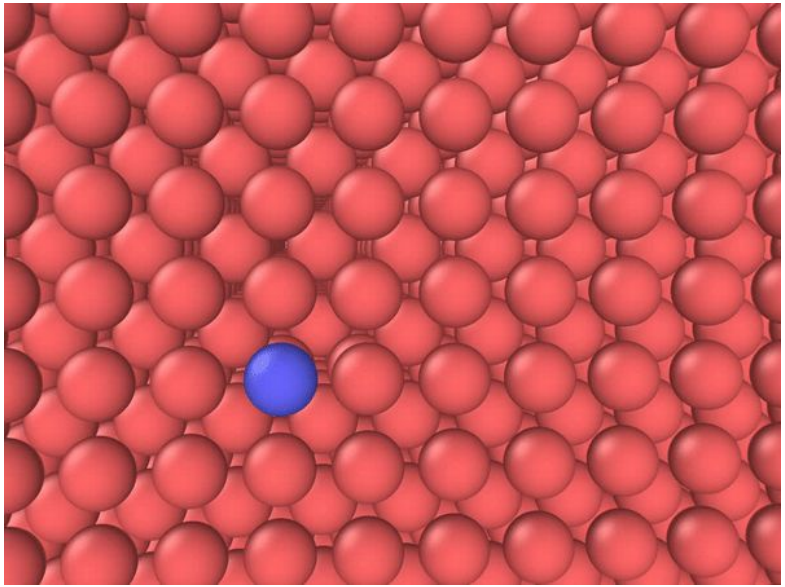
Diffusion barriers using NEB

- Algorithm to find minimum energy transitions between equilibrium states
- Gives energy barrier associated with a transition state, e.g. for an atom to perform a diffusive hop from one energy basin to another
- Used LAMMPS neb command

Diffusing atoms

Migration barrier notation *ωij*: atom moving from site *j* to a vacant site *i*





Cr atom’s closest neighbour diffusion

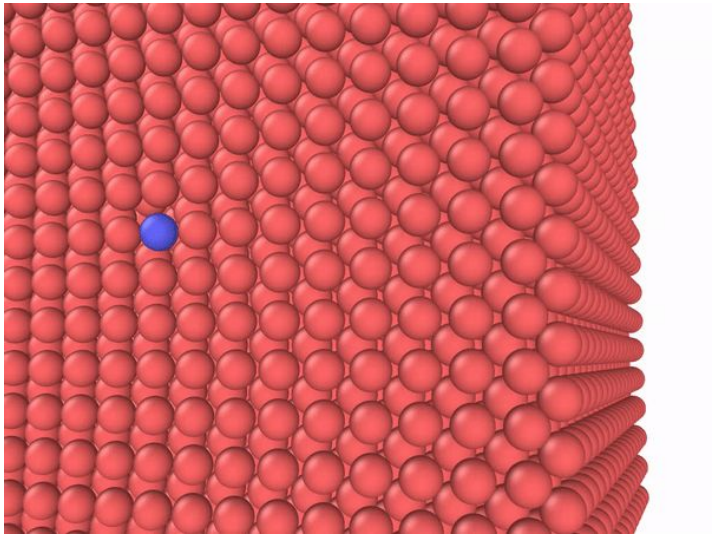
Messina et. al: Exact ab initio transport coefficients in bcc Fe-X (X=Cr, Cu, Mn, Ni, P, Si) dilute alloys
DFT comparison **ω12 = 0.69 eV**, **ω21 = [0.64; 0.66] eV**

Potential	ω12 [eV]	ω21 [eV]
2B-EAM	0.6511	0.6260
CD-EAM	0.6467	0.6160
Old Tersoff	0.4666	0.7413
Subset of 1st set	~ 0.8	~ 0.73
Rest of Pekko’s	~ 1.1	~ 0.9

Cr diffusion

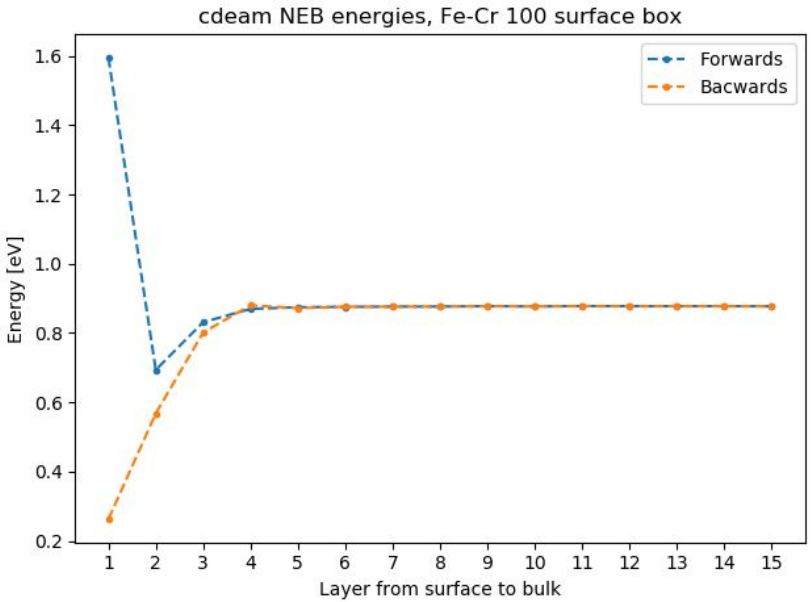
Messina et. al DFT bulk **ω2 = [0.53; 0.62] eV**
2B-EAM ω2 = 0.55 eV CD-EAM ω2 = 0.9 eV from https://journals.aps.org/prb/pdf/10.1103/PhysRevB.79.104207

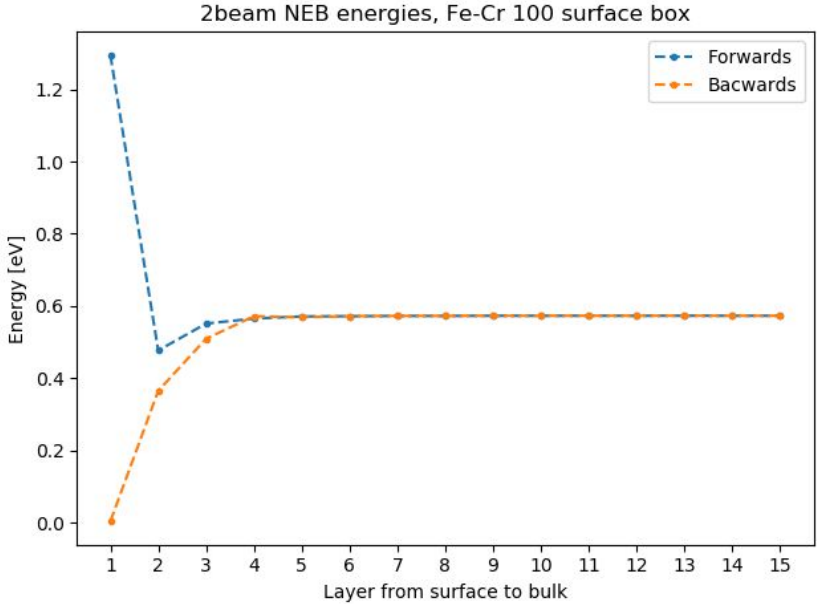
Potential	ω2 [eV]	Energy barrier from surface to second layer [eV]
2B-EAM	0.5725	0.0035
CD-EAM	0.8772	0.2624
Old Tersoff	0.7267	1.1866
1st set	> 1	~ 0.8
2nd set	~ 0.6	~ 0
3rd set	~ 0.8	~ 0



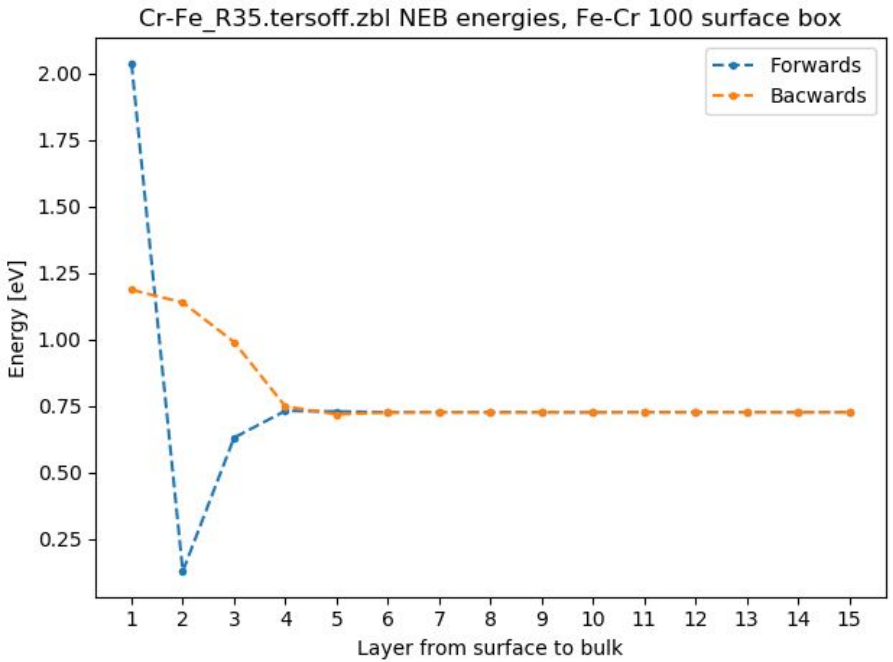
EAM Energy Barriers

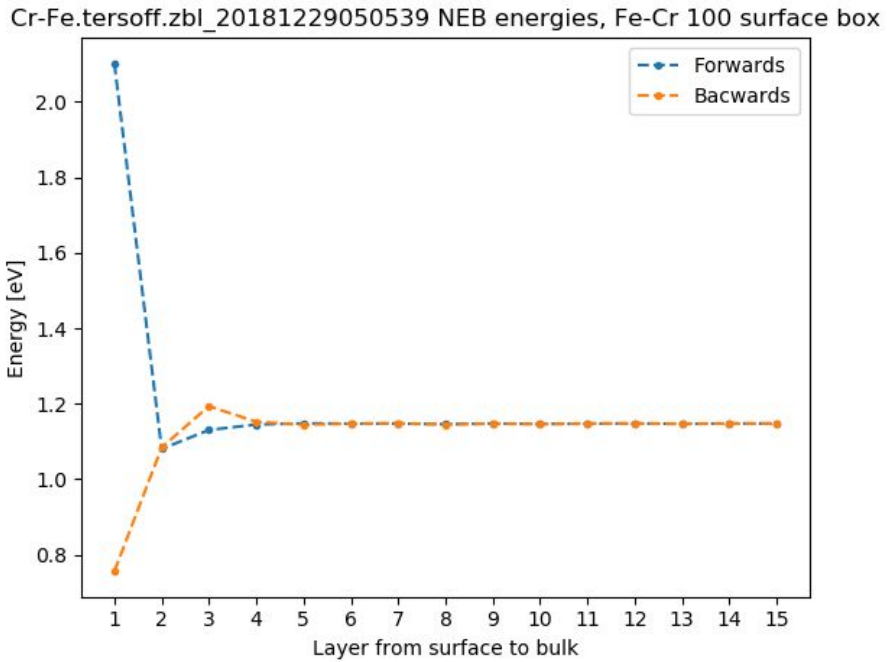
Note: Forwards direction is towards the surface.



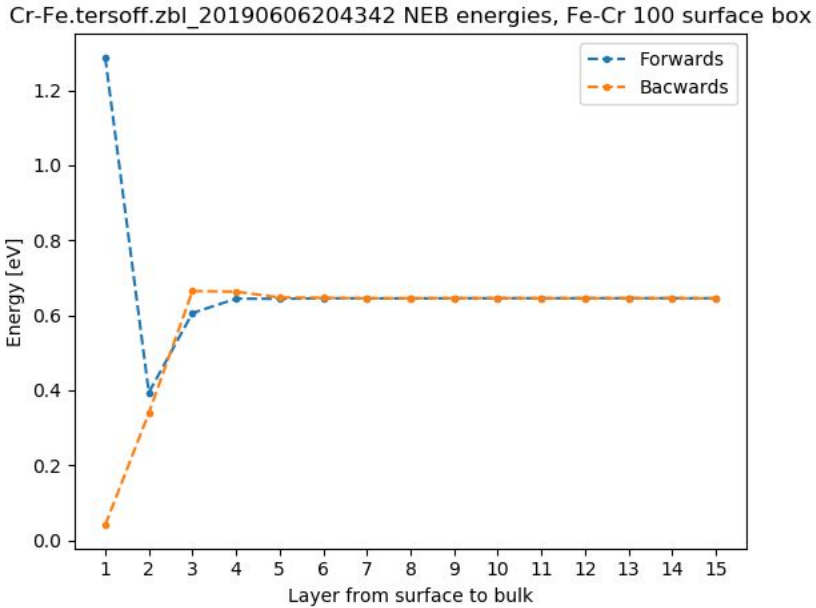


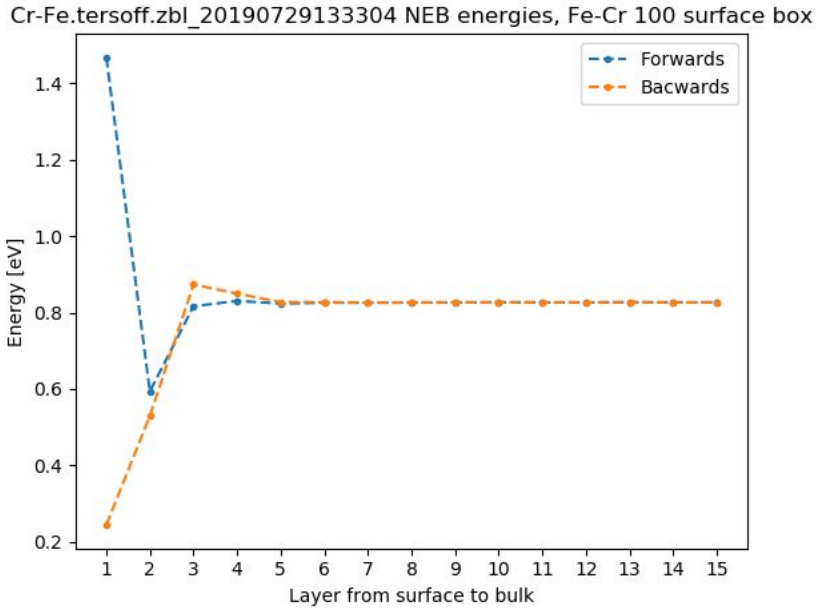
Old Tersoff and 1st set NEB





2nd and 3rd set NEB





Conclusion

- There are surface related properties not well described by existing potentials
- EAM works well and are fast for bulk purposes
- With the NEB simulations as a basis Pekko’s 2nd set of Tersoff seem to be the best of the three
- Potentials are very similar within the sets, so other factors can weigh in on choosing the final one