



Polarisation characteristics of adatoms diffusing on $W\{110\}$ surface under applied electric field

Ekaterina Baibuz
Andreas Kyritsakis
Ville Jansson
Flyura Djurabekova

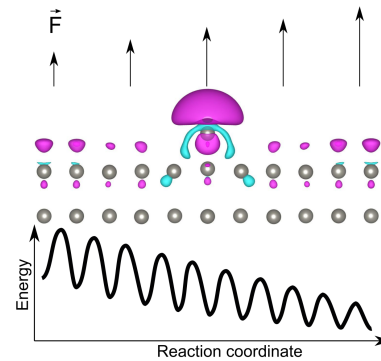


Motivation



Motivation

- ▶ We want to find out if atoms can form sharp features on metal surfaces under electric field via self-diffusion
- ▶ We use Kinetic Monte carlo model to simulate this process
- ▶ Kinetic Monte carlo model needs to know energy barriers of jumping atoms in all possible local atomic environments(LAE) and how energy barriers are modified by the electric field

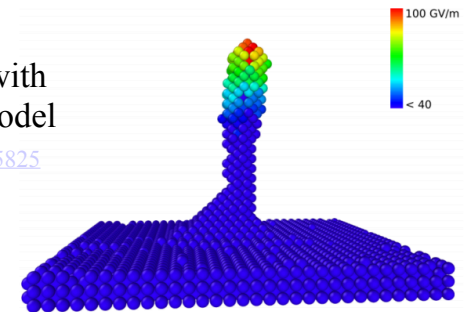


DFT calculations of W adatom on W {110} surface under electric field

<https://arxiv.org/abs/1808.07782>

KMC simulations with an approximated model

<https://arxiv.org/abs/1909.05825>



(d) $t = 7.6$ ns

Probability to make a jump:

$$\Gamma = \nu e^{\left(\frac{-E_m}{k_b T}\right)}$$

Energy barriers are changed by field:

$$E_m(F) = E(F = 0) - \Delta E$$



Background



Self-diffusion under electric field

- ▶ We know that atoms diffuse towards higher electric fields from experiments e.g
 - ▶ [T. T. Tsong and G. L. Kellogg, Phys. Rev. B 12, 1343 \(1975\)](#)
- ▶ We know how energy barriers of jumping atoms are modified by the electric field:
 - ▶ [Kyritsakis, A., Baibuz, E., Jansson, V., & Djurabekova, F. \(2018\)](#)

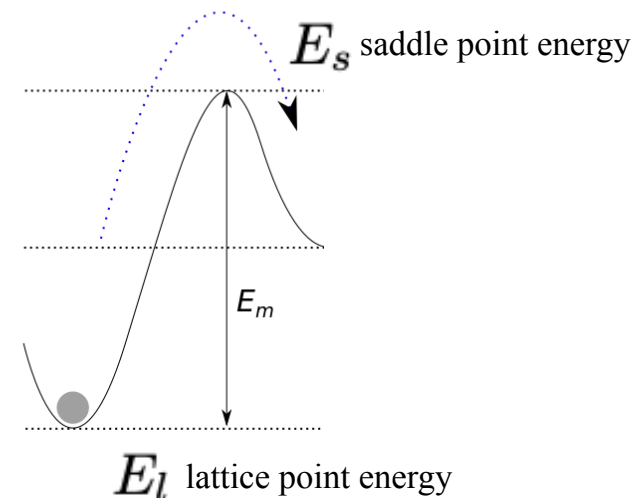
$$E_m(F) = E(F = 0) - \Delta E$$

$$E_m \equiv E_s - E_l = E_m(0) - \mathcal{M}_{sl}F - \frac{1}{2}\mathcal{A}_{sl}F^2$$

$\mathcal{M}_{sl} \equiv \mathcal{M}_s - \mathcal{M}_l$ difference between dipole moments of saddle and lattice points

$\mathcal{A}_{sl} \equiv \mathcal{A}_s - \mathcal{A}_l$ difference between polarisabilities of saddle and lattice points

$E_m(0)$ energy barrier without field



Energy barrier of a jumping atom is modified by field according to the change of polarisation characteristics of its vicinity during the jump

- Previously, we calculated polarisation characteristics of a single adatom on W {110} surface and the effect of electric field on its barrier to jump from one lattice point to the closest neighbouring one [[Kyritsakis, A., Baibuz, E., Jansson, V., & Djurabekova, F. \(2018\)](#)]

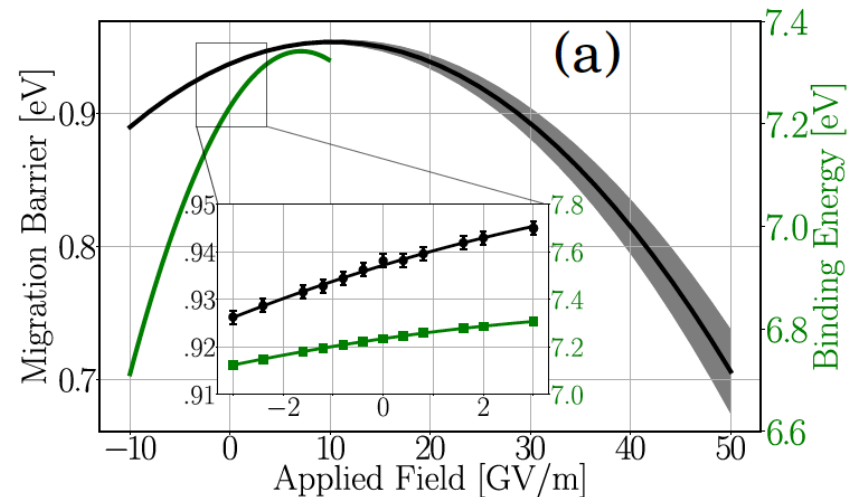
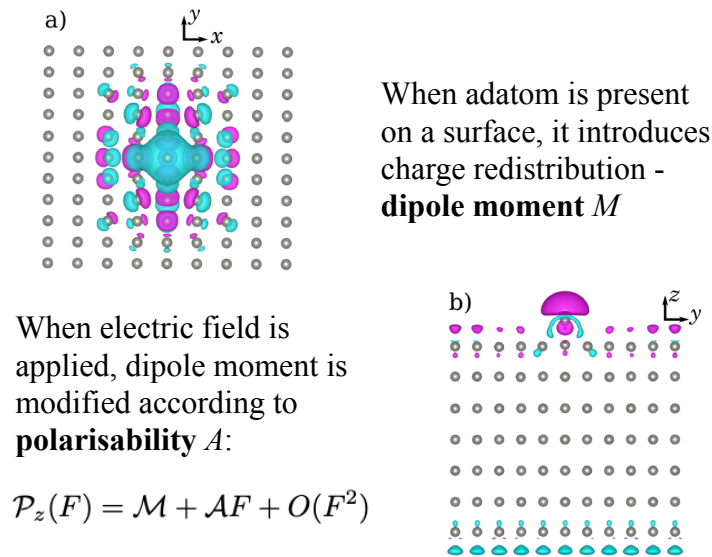


FIG. 1. Charge redistribution induced by (a) the presence of an adatom, (b) a positive 1 GV/m applied field (anode) on a system with adatom (atoms fixed at their original zero-field positions for illustration purposes). The open surface of the slab is {110} oriented. Cyan and magenta colored areas correspond to increased and decreased electron densities, respectively, that exceed 1% of the maximum electron density of the reference system for (a) and 0.1% for (b).

$$E_m \equiv E_s - E_l = E_m(0) - \mathcal{M}_{sl}F - \frac{1}{2}\mathcal{A}_{sl}F^2$$





Research question

Is the electric field effect on an energy barrier of a jumping atom the same in various local atomic environments?

More specifically, can we use the same \mathcal{M}_{sl} and \mathcal{A}_{sl} values for all possible jumps in our KMC model?



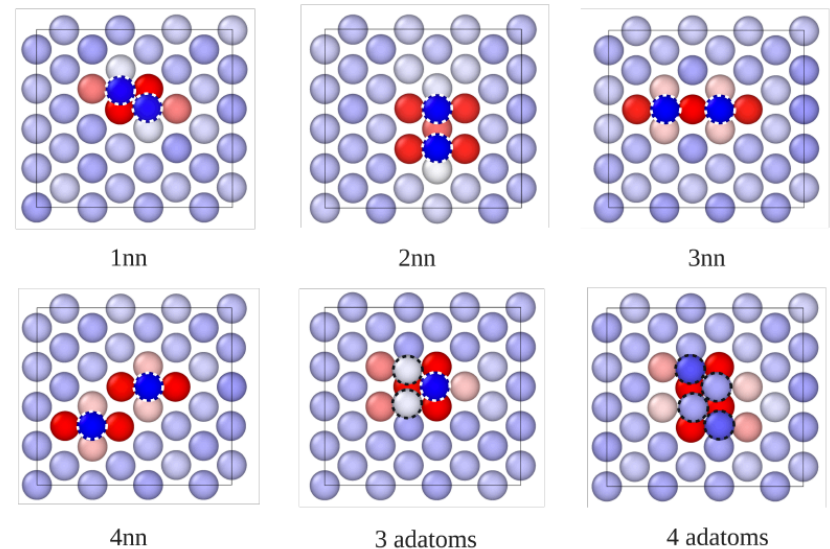
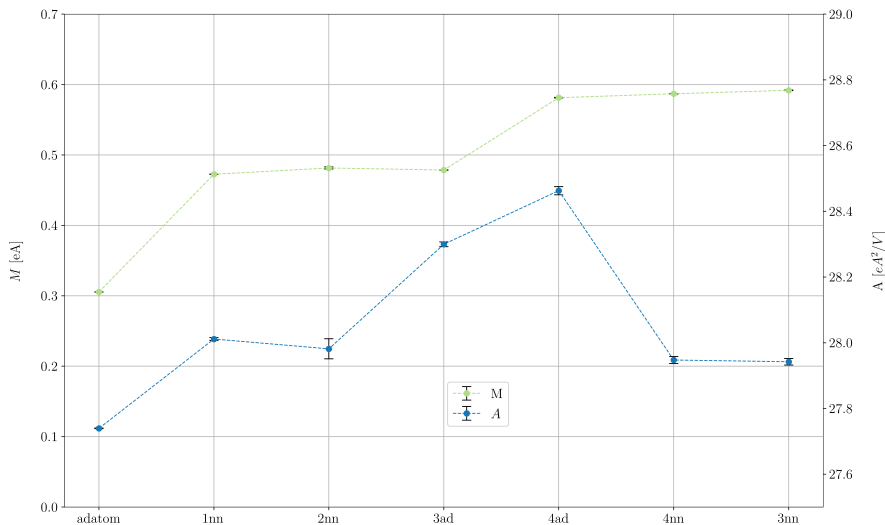


Highlights from our findings

We performed Density Functional Calculations under electric field and found that polarisation characteristics of W {110} surface with up to 4 adatoms grouped together differ quite a bit depending on arrangement of atoms on a surface

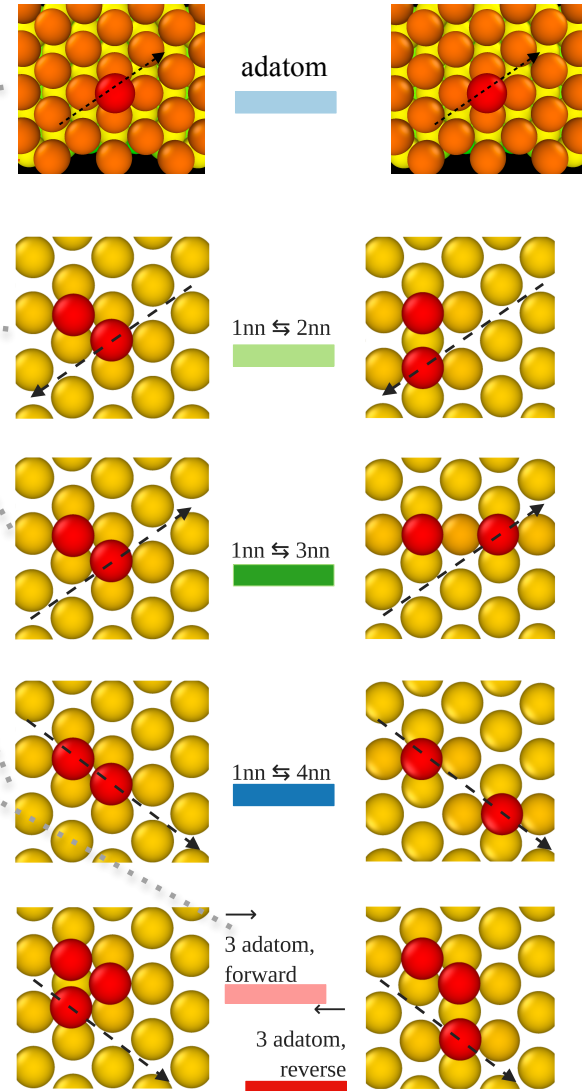
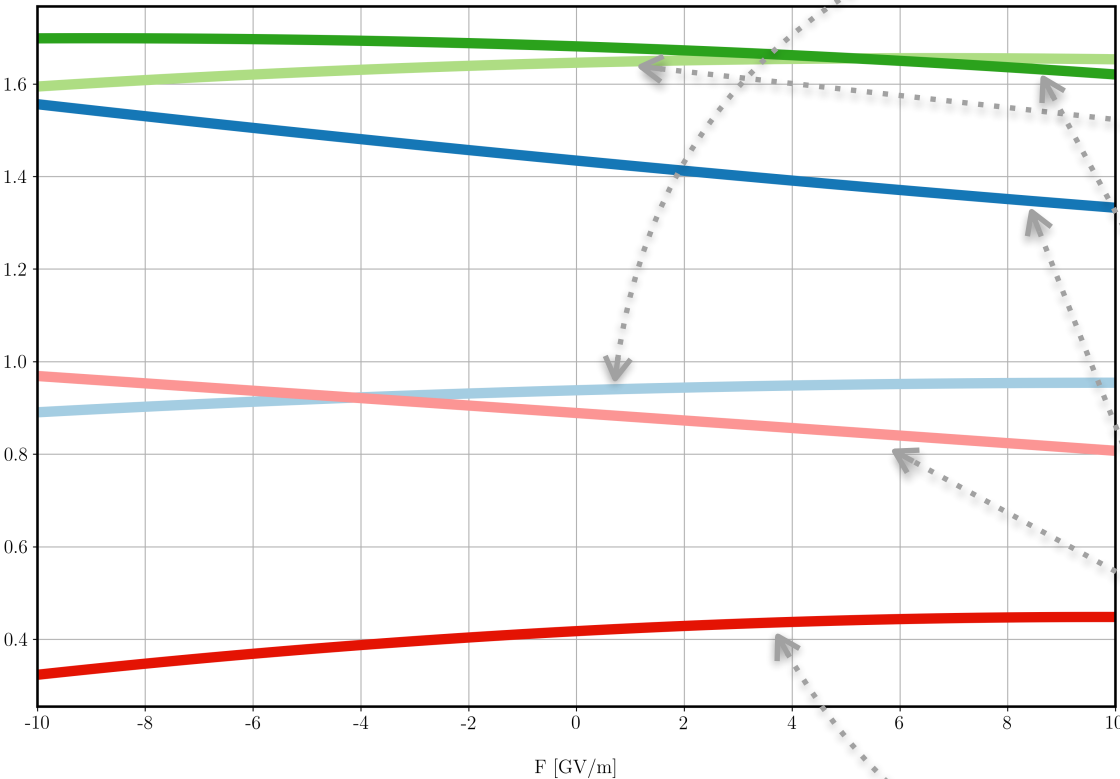
Systems under study

Figure 2: Studied systems of W adatoms on W {110} surface: *1nn* is a slab with two adatoms at lattice sites within the first-nearest neighbours distance from each other; *2nn* - two adatoms at the second-nearest neighbouring lattice positions; *3nn* - at the third-nearest neighbouring positions; *4nn* - fourth-nearest neighbouring positions; *3 adatoms, forward* is a slab with 3 adatoms clustered together; *3 adatoms, reverse* is a system after one of the adatoms from *3 adatoms, forward* has jumped away from the other two; *4 adatoms* - a slab with 4 adatoms island. Color of each atom correspond to its charge, which was extracted with the Bader analysis from the charge density outputted by VASP. Only adatoms and a surface layer atoms are shown. Unit cells of VASP calculations are shown with rectangles.



We found that energy barriers are also modified way too different by the electric field

Jumps under study

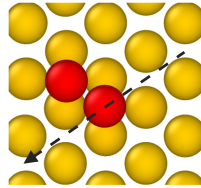
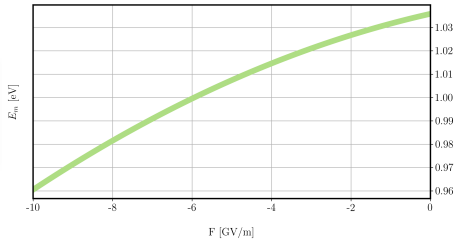


Cathode

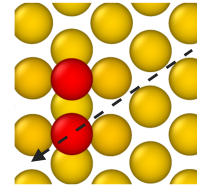
Lastly, we found that barriers are changed differently by anode and cathode fields

Anode

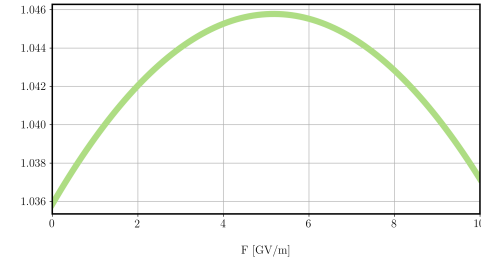
Barrier lowered by field



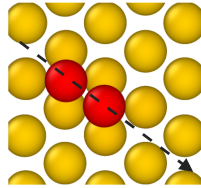
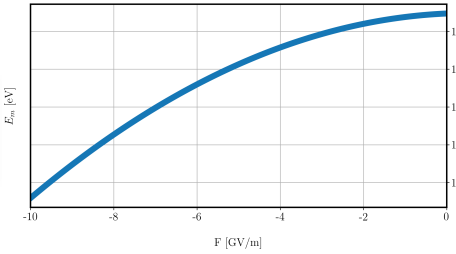
1nn \leftrightarrow 2nn



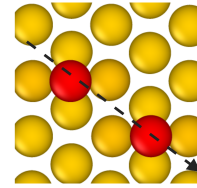
Barrier has a maximum value at $F \sim 5$ GV/m



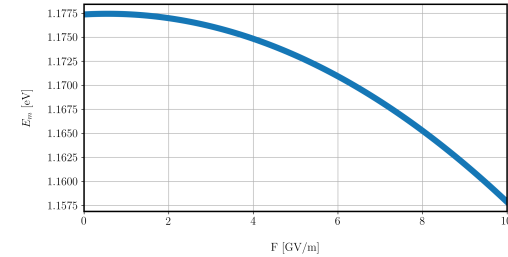
Barrier lowered by field



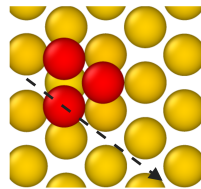
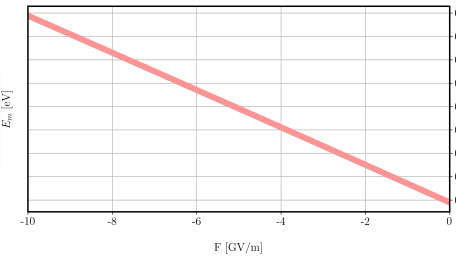
1nn \leftrightarrow 4nn



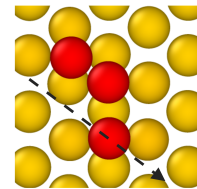
Barrier lowered by field



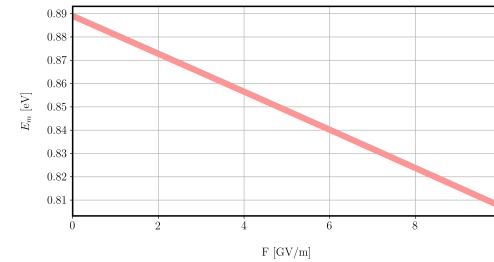
Barrier grows with field



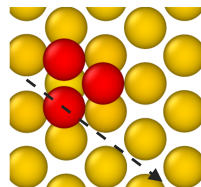
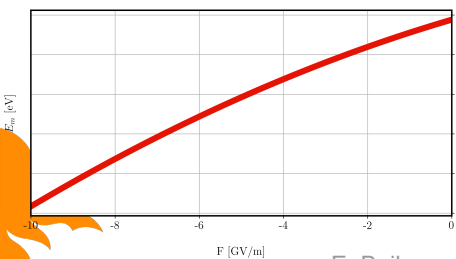
→
3 adatom, forward



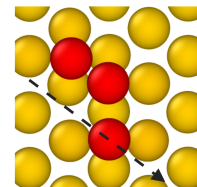
Barrier lowered by field



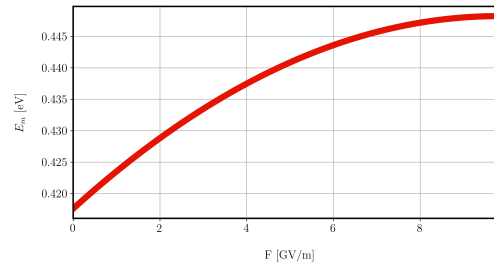
Barrier lowered by field



←
3 adatom, reverse



Barrier grows with field





Conclusions

- ▶ We studied polarisation characteristics, namely dipole moment and polarisability, of various atomic arrangements on W {110} surface by means of Density Functional Theory
- ▶ We found that polarisation characteristics depend on LAE in a nontrivial way. More cases of LAE are needed to draw any conclusion about how exactly effect of electric field depends on arrangement of adatoms on a surface. Here, Machine Learning would be a handy tool as the number of possible LAE is enormously large even for the case of a small cutoff.
- ▶ We found that LAE plays a role on how electric field affects the barriers of a jumping atom. Even though an approximation of a single pair of $(\mathcal{M}_{sl}, \mathcal{A}_{sl})$ proved to work quantitatively in our [previous work](#), for a higher accuracy models, all possible combinations of $(\mathcal{M}_{sl}, \mathcal{A}_{sl})$ most likely need to be calculated