MATRENA
Doctoral Programme in Materials Research and Nanosciences

Diffusion on metal surfaces under high electric fields

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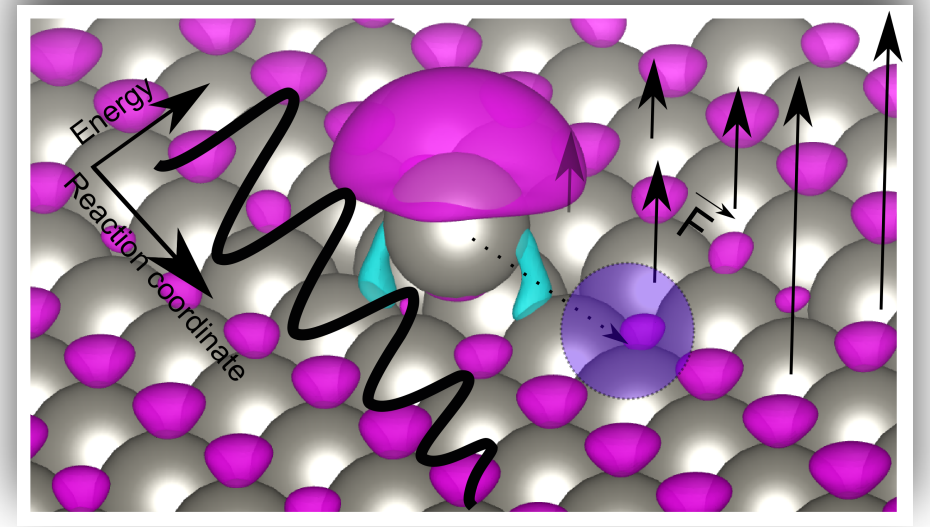
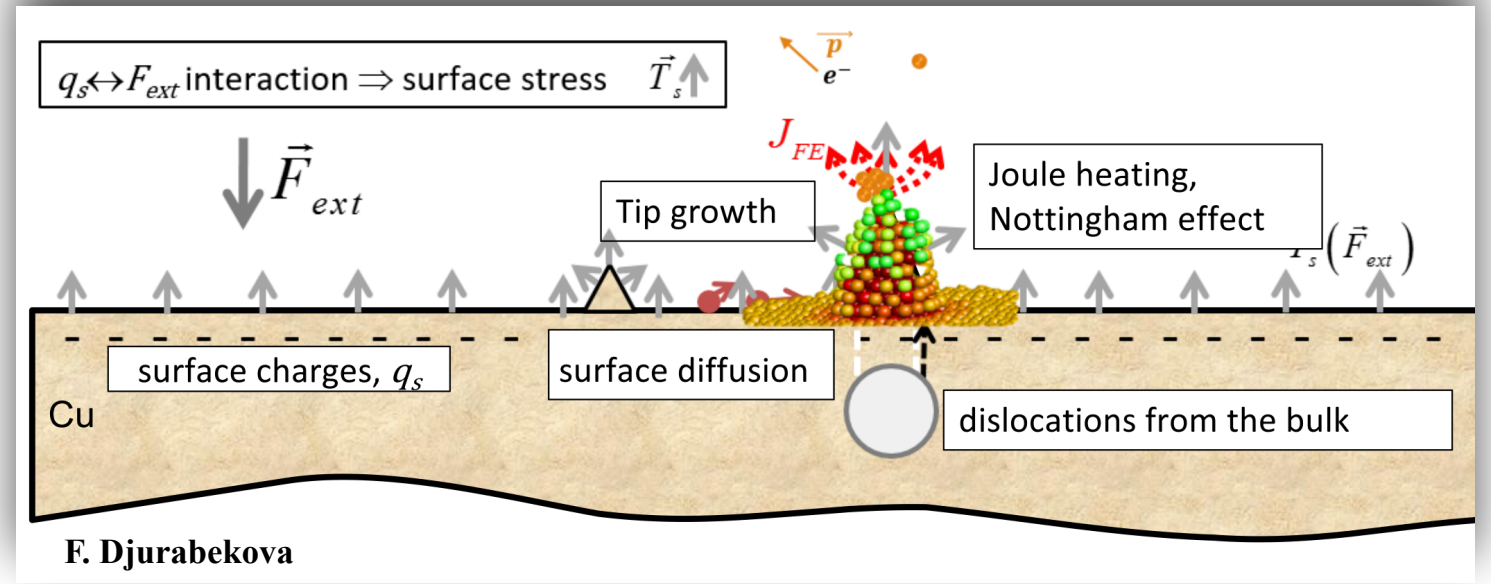


Surface Diffusion and vacuum arcs

Introduction

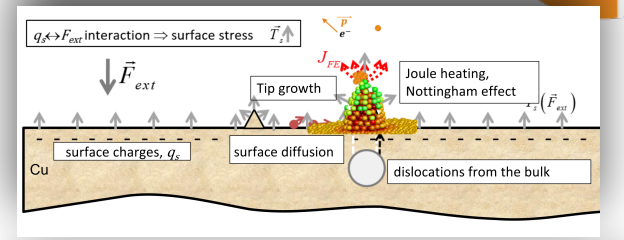
- **Vacuum breakdowns can be explained by the growth of sharp nano-tips on metal surfaces under electric field**

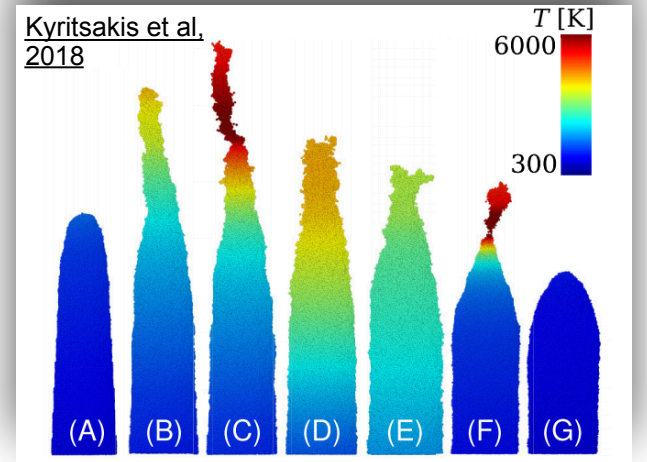


Introduction

- **Vacuum breakdowns can be explained by the growth of sharp nano-tips on metal surfaces under electric field**
  - **Very large nano-tips (90 nm high) may, on the other hand, emit enough electrons and neutrals to initiate a vacuum arc plasma**

Kyritsakis, Veske M, Eimre, Zadin, Djurabekova 2018 JOP D 51 225203





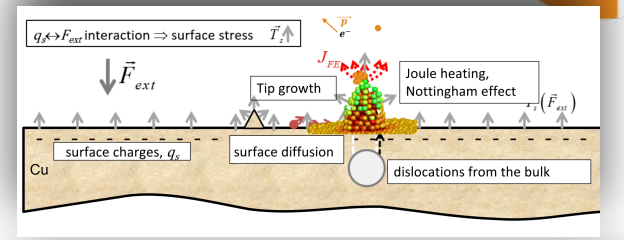
Introduction

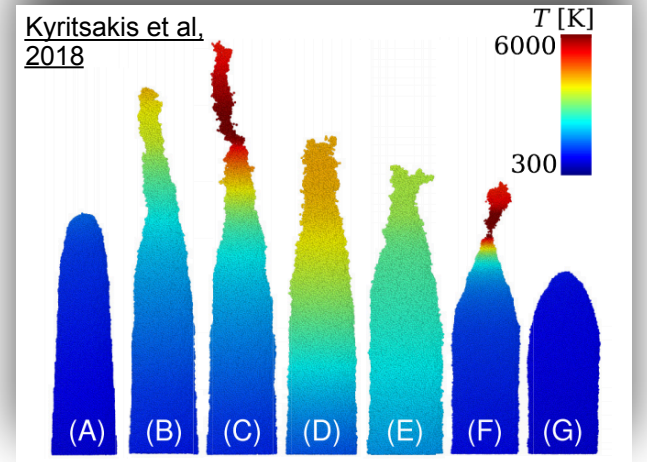
- Vacuum breakdowns can be explained by the growth of sharp nano-tips on metal surfaces under electric field
  - Very large nano-tips (90 nm high) may, on the other hand, emit enough electrons and neutrals to initiate a vacuum arc plasma

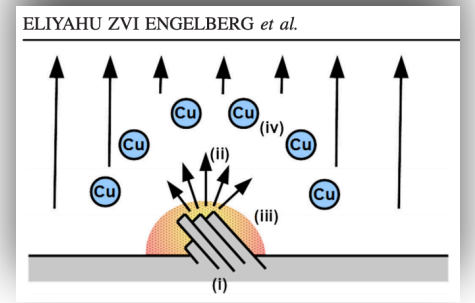
Kyritsakis, Veske M, Eimre, Zadin, Djurabekova 2018 JOP D 51 225203

  - The nucleation points, small asperities on the surface, may possibly be caused by dislocation movement close to the surface and dislocation activity in surfaces under high field has been correlated to breakdowns in a recent statistical model

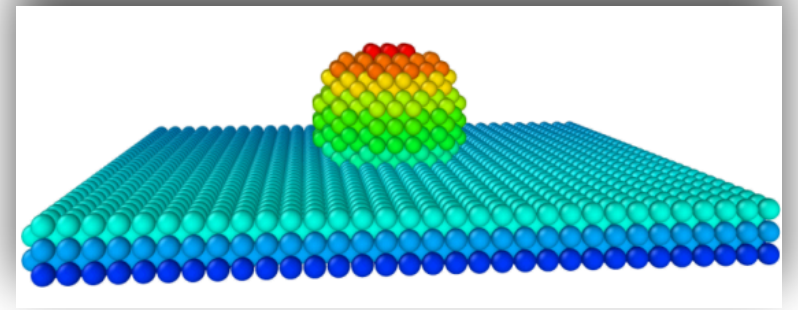
Engelberg, Ashkenazy, Assaf PRL, 2018

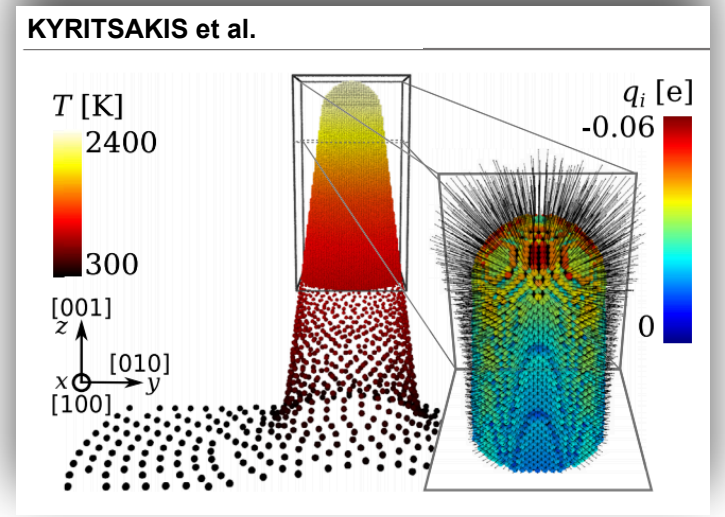






Our ultimate goal

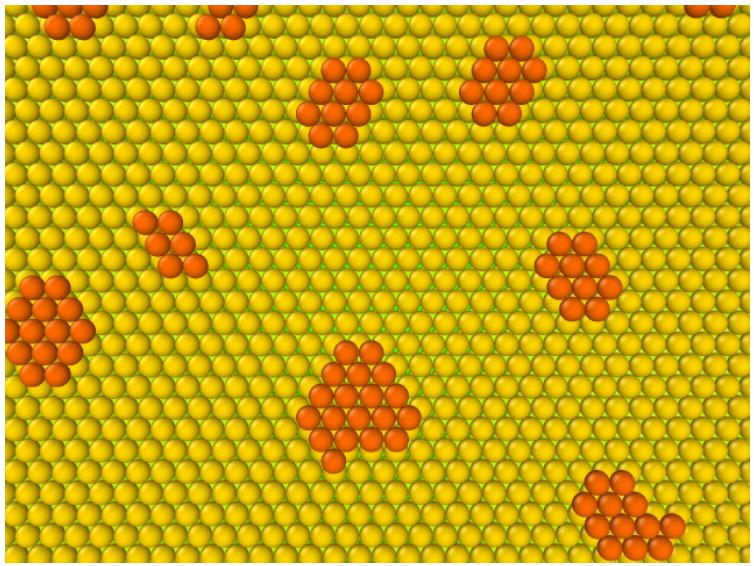




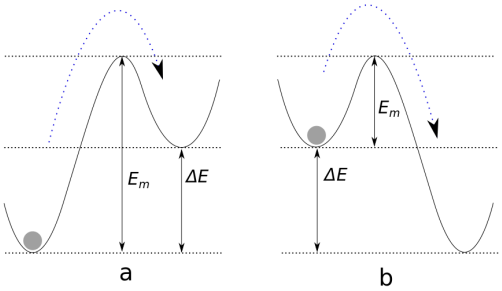
- We want to simulate the growth of nano-tips under electric field
  - Challenges:
    - long-term evolution model is needed
    - Fundamental theory of surface diffusion under electric field

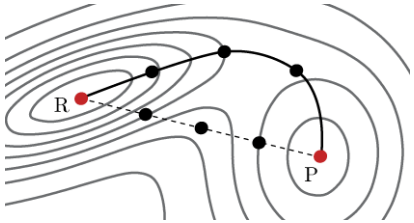
Surface Diffusion on metals

Diffusion of adatoms



- Adatom needs to overcome an energy barrier Em
  - Em are calculated with Nudged Elastic Band (NEB) with interatomic potentials





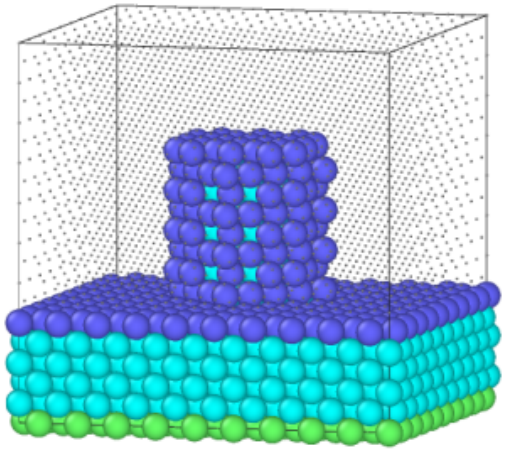
- Probability for an adatom to make a jump:

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

Kinetic Monte Carlo models: Long-term evolution via diffusion

- Long-term self-diffusion can be studied
- Probabilistic approach

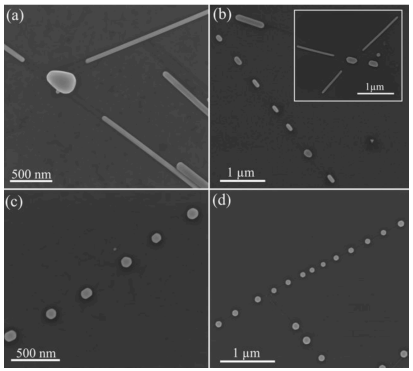
$$\Gamma = \nu e^{\left(\frac{-E_m}{k_b T}\right)}$$

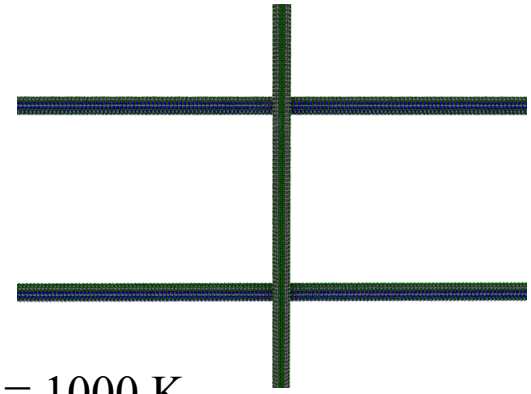


- Our code Kimocs:
  - metal surfaces
  - rigid lattice
  - energy barriers precalculated with NEB using MD potentials + predicted by the neural network

Diffusion on a Nanoscale: Research with Kimocs

- Gold nanowires





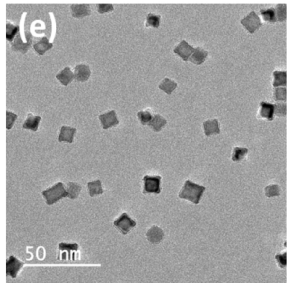
T = 1000 K

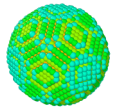
Vigonski et al. "Au nanowire junction breakup through surface atom diffusion." Nanotechnology 29.1 (2017): 015704.

- Copper nano-tips flattening

Jansson, Baibuz, Djurabekova, (2016). Long-term stability of Cu surface nanotips. Nanotechnology, 27(26), 265708. ISO 690

- Iron nanocubes under deposition



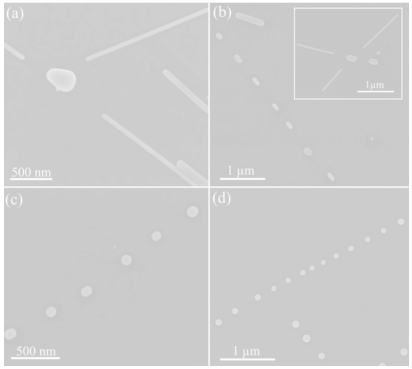


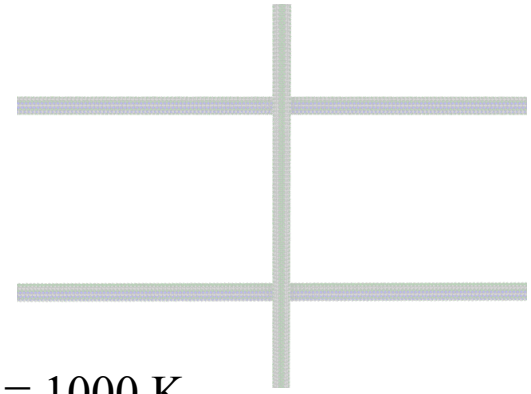
J. Zhao, E. Baibuz et al., ACS Nano (2016)

Zhao et al. "Formation mechanism of Fe nanocubes by magnetron sputtering inert gas condensation." ACS nano 10.4 (2016): 4684-4694.

Diffusion on a Nanoscale: Research with Kimocs

- Gold nanowires

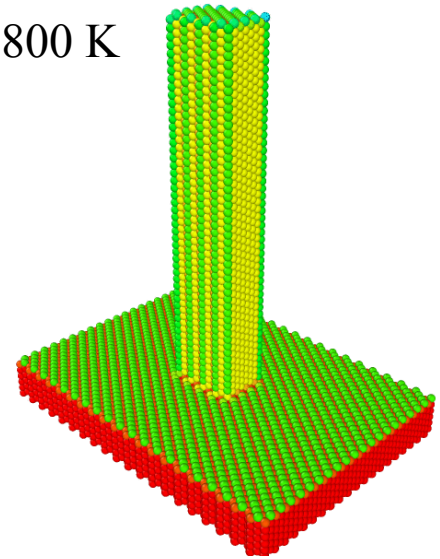




T = 1000 K

- Copper nano-tips flattening

T = 800 K



V. Jansson (2015)

- Under high T - flattens
- low T - stable within μs

- Iron nanocubes under deposition

J. Zhao, E. Baibuz et al., ACS Nano (2016)

Vigonski et al. "Au nanowire junction breakup through surface atom diffusion." Nanotechnology 29.1 (2017): 015704.

Jansson, Baibuz, Djurabekova, (2016). Long-term stability of Cu surface nanotips. Nanotechnology, 27(26), 265708. ISO 690

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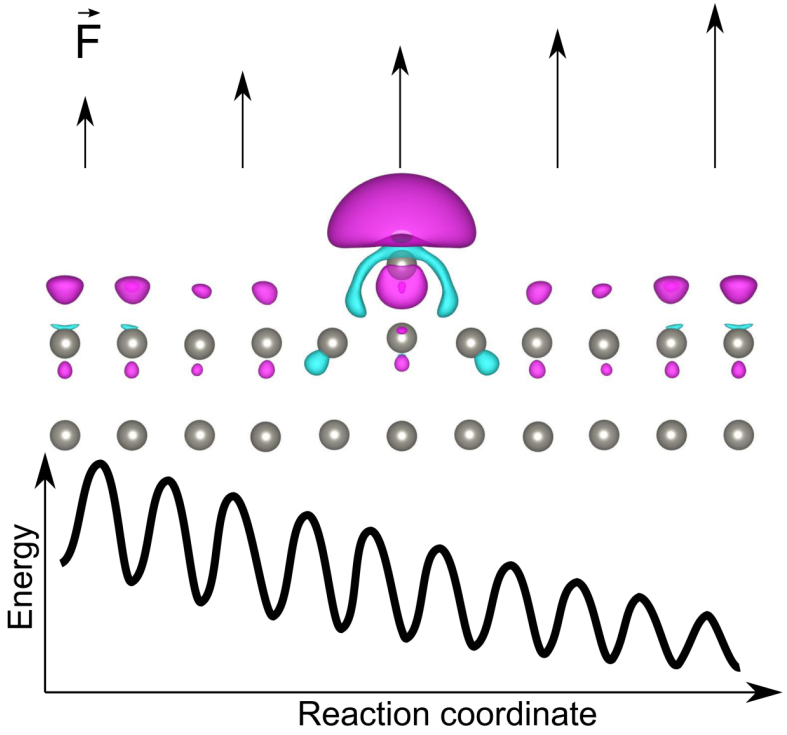
Surface Diffusion on metals under electric field

Surface diffusion under electric field: general knowledge

- Diffusion becomes easier when the field is applied
  - * the story is not as simple
- If there is a field gradient:
  - Atoms diffuse towards higher electric fields



Back to 70s: Tsong et al.

- Observed directional diffusion of W adatom on W {110} surface
- Explained diffusion via adatom's dipole moment and polarisability
- Obtained a formula for energy barrier *Em* vs field *Fz* under the field gradient
  - **effective polarisability concept**

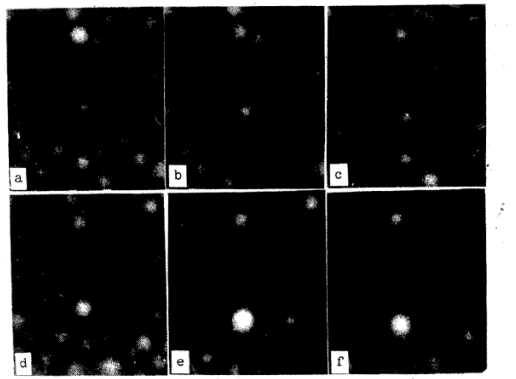


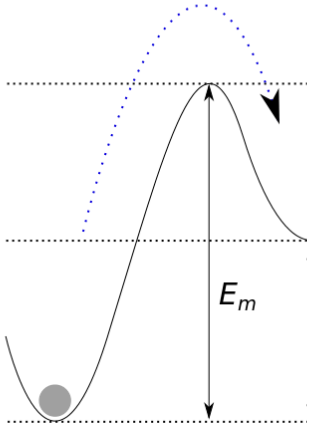
FIG. 4. Continuous observation of the directional walk of a W adatom on a W (110) plane at ~3.8 V/Å and ~295°K.

T. T. Tsong and G. L. Kellogg, Phys. Rev. B 12, 1343 (1975).

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

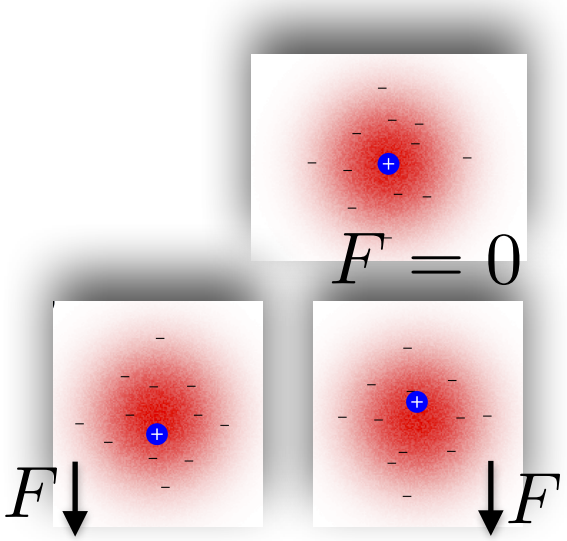
$$\Delta E = \mu_{sp}F_{sp} - \mu_{ls}F_{ls} + 0.5(\alpha_{sp}F_{sp}^2 - \alpha_{ls}F_{ls}^2)$$

F_{sp} - local electric field at the saddle point, F_{ls} - at the lattice site, μ - permanent dipole moment (at 0



Tsong et al: Effective Dipole moment and Polarisability of Adatom

- isolated atom under field ***F***
  - dipole moment **M**: $M_0 = 0$
  - polarisability *A*: $M(F) = AF$



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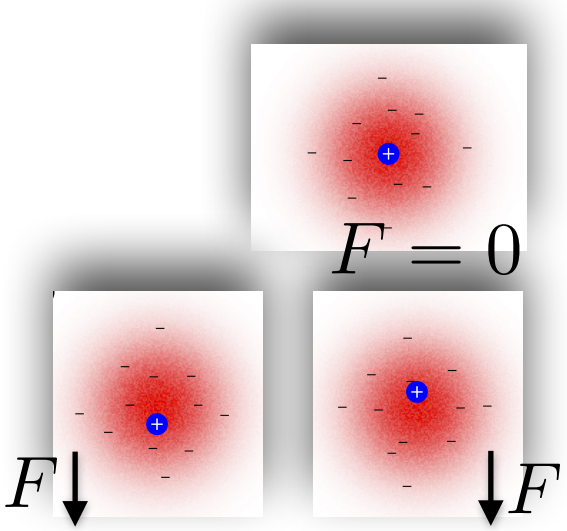
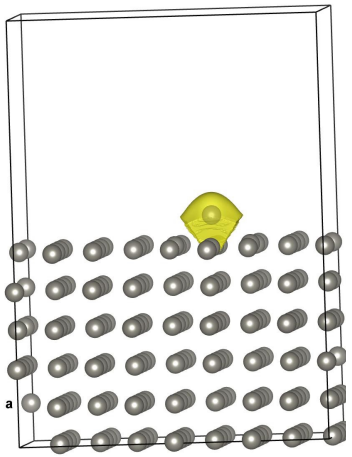


- adatom on a surface:
  - **effective** d.p: $M_0 \neq 0$
  - **effective** polarisability:

$$M(F) = M_0 + AF$$



Our theory

Kyritsakis, A., Baibuz, E., Jansson, V., & Djurabekova, F. (2019). Atomistic behavior of metal surfaces under high electric fields. *Physical Review B*, *99*(20), 205418.

- W on W {110}

Atomistic behavior of metal surfaces under high electric fields

A. Kyritsakis,[1,*] E. Baibuz,[1] V. Jansson,[1] and F. Djurabekova[1]

[1] *Helsinki Institute of Physics and Department of Physics, University of Helsinki, PO Box 43 (Pietari Kalmin katu 2), 00014 Helsinki, Finland*

(Dated: May 17, 2019)

Combining classical electrodynamics and density functional theory (DFT) calculations, we develop a general and rigorous theoretical framework that describes the energetics of metal surfaces under high electric fields. We show that the behavior of a surface atom in the presence of an electric field can be described by the polarization characteristics of the permanent and field-induced charges in its vicinity. We use DFT calculations for the case of a W adatom on a W{110} surface to confirm the predictions of our theory and quantify its system-specific parameters. Our quantitative predictions for the diffusion of W-on-W{110} under field are in good agreement with experimental measurements. This work is a crucial step towards developing atomistic computational models of such systems for long-term simulations.

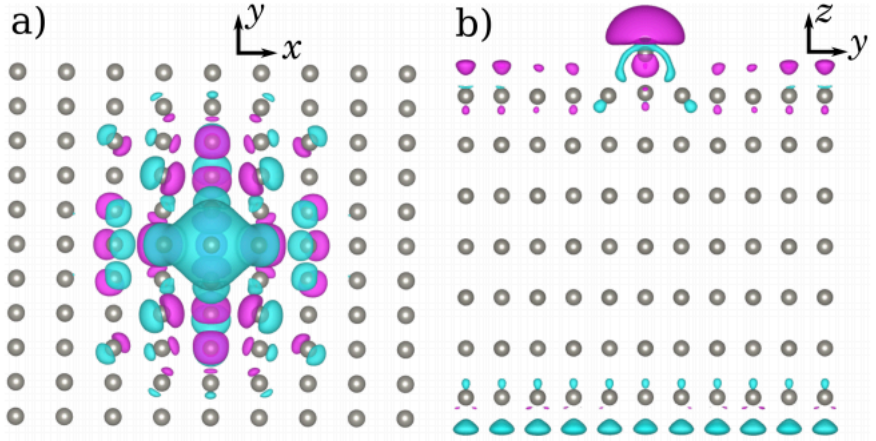
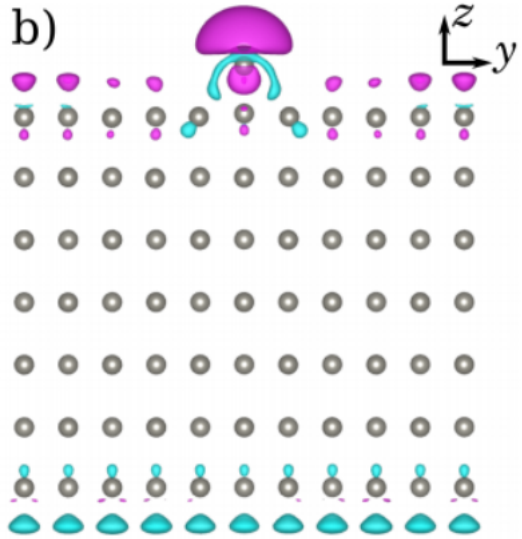


FIG. 1. Charge redistribution induced by (a) the presence of an adatom, (b) a positive 1 GV/m applied field (anode) on a system with adatom (the atoms are fixed to their original zero–field positions for illustration purposes). The open surface of the W slab is of the {110} kind. Cyan and magenta colored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

Our theory

Kyritsakis, A., Baibuz, E., Jansson, V., & Djurabekova, F. (2019). Atomistic behavior of metal surfaces under high electric fields. *Physical Review B*, *99*(20), 205418.

- Started from energies
  - The interaction of a charge with an applied electric field changes total energy of the system



L. Landau and E. Lifshitz, Electrodynamics of continuous media

$$E(F) = E(0) - \int_0^F \mathcal{P}_z(F')dF'$$

Taylor expansion: $\mathcal{P}_z(F) = \mathcal{M} + \mathcal{A}F + O(F^2)$

- Total energy of the system:

$$E(F) = E(0) - \mathcal{M}F - \frac{1}{2}\mathcal{A}F^2 + O(F^3)$$

Density Functional Theory

- solves Schrödinger equation for the electron density (with approximations)
  - interactions between atoms is via pseudo potential
  - electric field can be included in the Hamiltonian
- finds:
  - ground state energy
  - charge density

$$H\Psi = E\Psi$$

$H($  $)$

$\Psi($  $)$

 ions

 electrons

From lecture notes by P. Rinke

Energy of the system vs. electric field

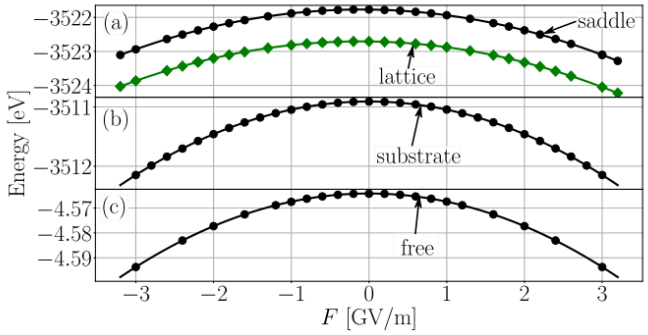
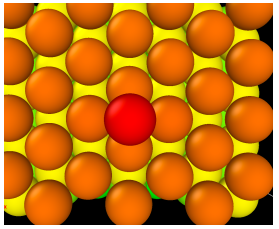
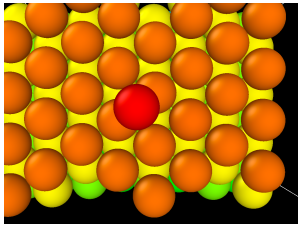


FIG. 2. Total energy of the four W systems simulated by DFT, vs the applied field. Black dots and green diamonds in (a) correspond to the system with an adatom at the saddle point and at the lattice site respectively. Black dots in (b) and (c) correspond to the flat reference and isolated atom systems, respectively. The corresponding solid-line curves indicated by arrows are obtained by eq. (3) with parameters that are fitted to the same DFT data.

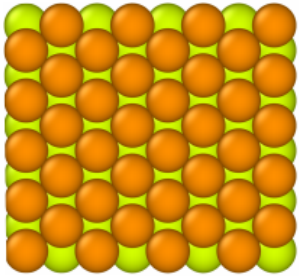
- Lattice site



- Saddle point



- Substrate



$$E(F) = E(0) - \mathcal{M}F - \frac{1}{2}\mathcal{A}F^2 + O(F^3)$$

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Charge density of the system vs electric field

- Dipole moment of the system:

$$\boldsymbol{\mu}(\boldsymbol{r}) = \int_V \rho(\boldsymbol{r_0})(\boldsymbol{r_0} - \boldsymbol{r}) d^3\boldsymbol{r}_0$$

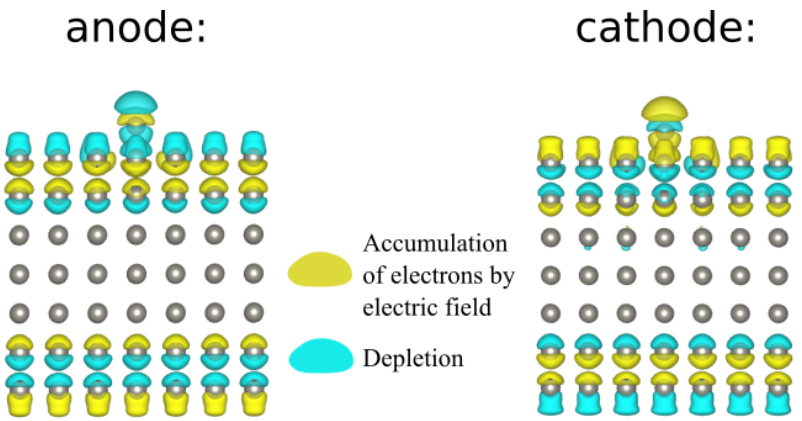
- Polarisability of the system:

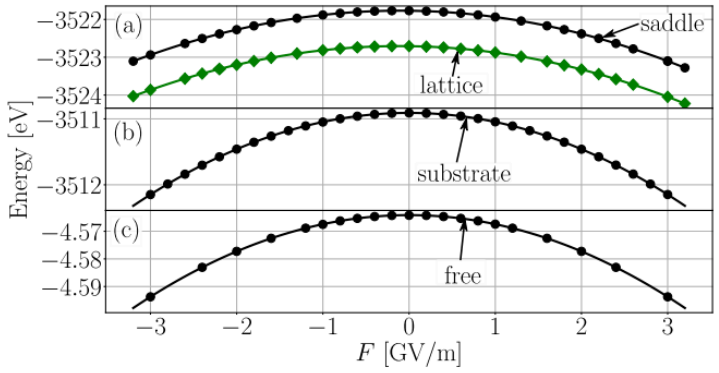
$$\mu(F) = \mu_0 + F\alpha$$

- We find that in

$$E(F) = E(0) - \mathcal{M}F - \frac{1}{2}\mathcal{A}F^2 + O(F^3)$$

  - *M* - permanent dipole moment of the whole system
  - *A* - polarisability of the atom in **its vicinity**





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- Started from energies
- Proved that change in energy depends on *M* and *A of the whole system*

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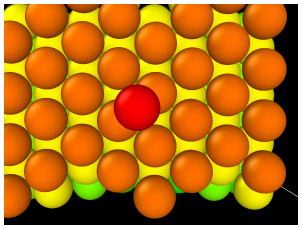
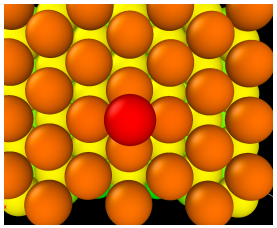
- Started from energies
- Proved that change in energy depends on *M* and *A of the whole system*
- Arrived to energy barriers vs electric field dependency
  - Non-gradient case $F_s = F_l$

E_m = E  − E 

Saddle Lattice

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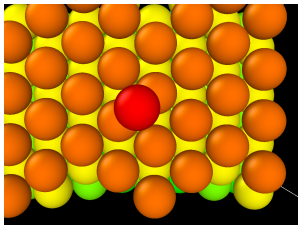
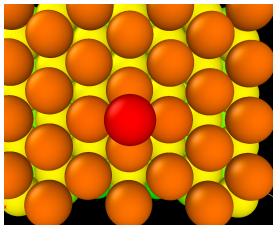
E_m = E  − E 

Saddle Lattice

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

Same form as Tsong et al.'s

Our theory

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- Started from energies
- Proved that change in energy depends on *M* and *A of the whole system*
- Arrived to energy barriers vs electric field dependency
  - Non-gradient case $F_s = F_l$
  - Field Gradient case $F_s \neq F_l$

Our theory

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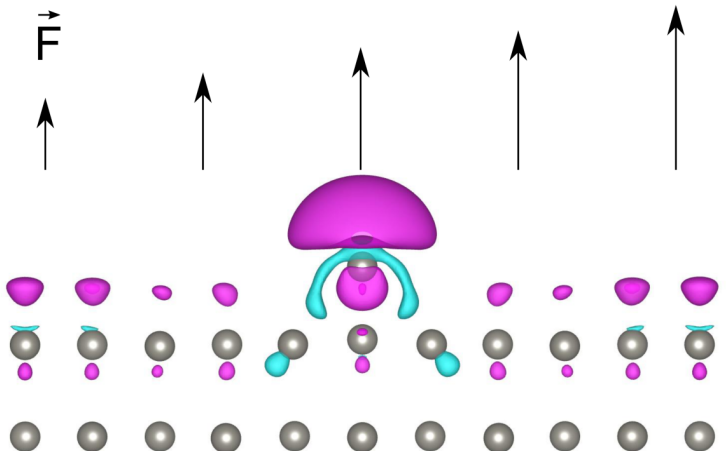
$$E(F) = E(0) - \int_0^F \mathcal{P}_z(F')dF'$$



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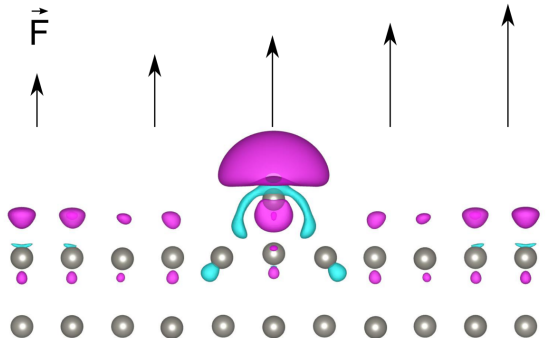

- Field Gradient case $F_s \neq F_l$

$$E(F) = E(0) - \int_0^F \mathcal{P}_z(F')dF'$$

$$E_m = \left(E_{\text{saddle}}^{F_s} - E_{\text{reference}} \right) - \left(E_{\text{lattice}}^{F_l} - E_{\text{reference}} \right)$$

$$E_m \approx E_m(0) - \mathcal{M}_{\text{sl}} F_l - \frac{\mathcal{A}_{\text{sl}}}{2} F_l^2 - \mathcal{M}_{\text{sr}} \Delta F - \mathcal{A}_{\text{sr}} F_l \Delta F$$

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- DFT can also be used to validate the theory

Our theory

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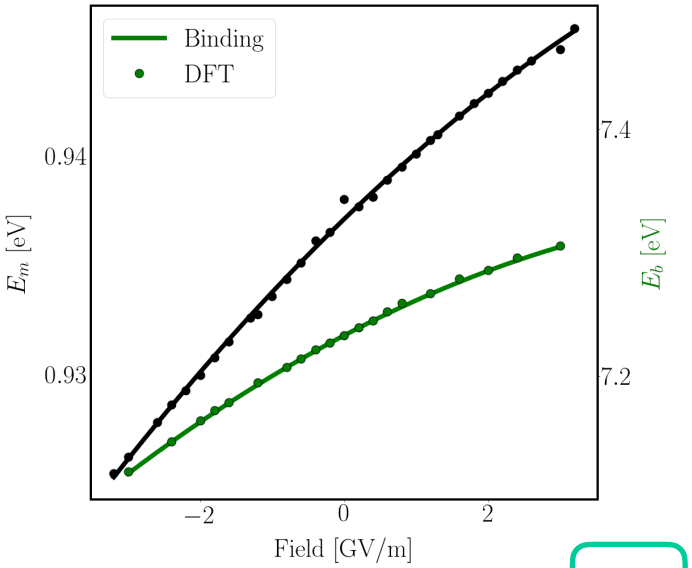
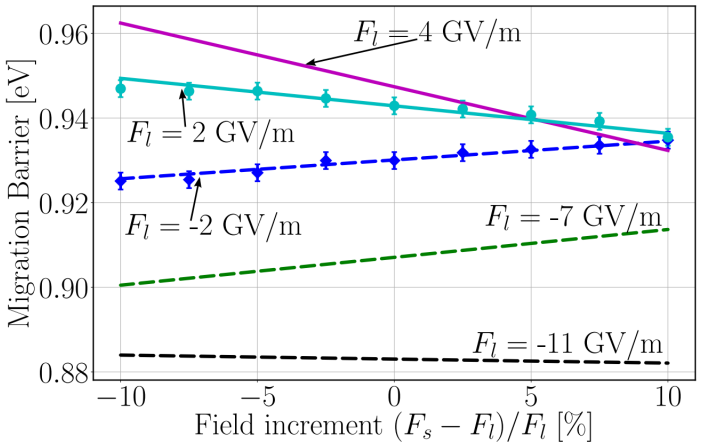
- Validation of the theory with DFT

- Non-gradient case



- Field gradient case



Theory

DFT

Theory: $$E_m \approx E_m(0) - \mathcal{M}_{\mathrm{sl}} F_l - \frac{\mathcal{A}_{\mathrm{sl}}}{2} F_l^2 - \mathcal{M}_{\mathrm{sr}} \Delta F - \mathcal{A}_{\mathrm{sr}} F_l \Delta F$$

DFT: $$E_m = \left(E_{\text{saddle}} - E_{\text{reference}} \right)_{F_s} - \left(E_{\text{lattice}} - E_{\text{reference}} \right)_{F_l}$$

Our theory

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- Validation of the theory with DFT
- We also got a good comparison with Tsong et al. ‘s experiment

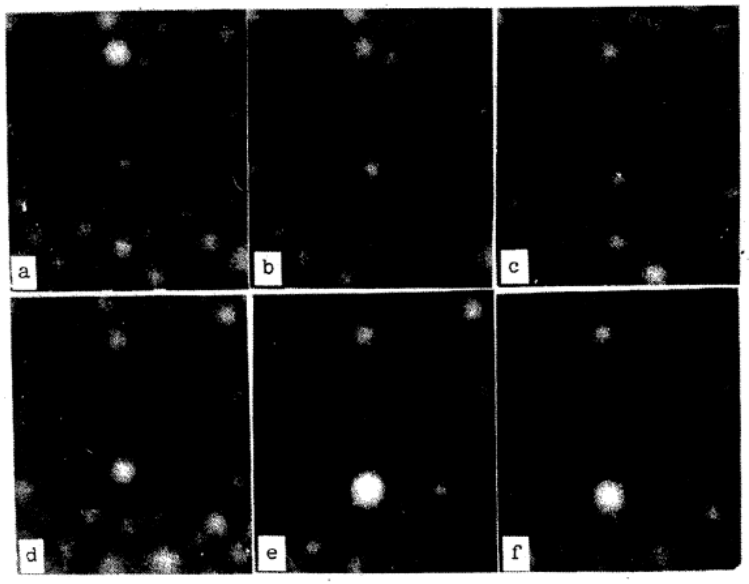
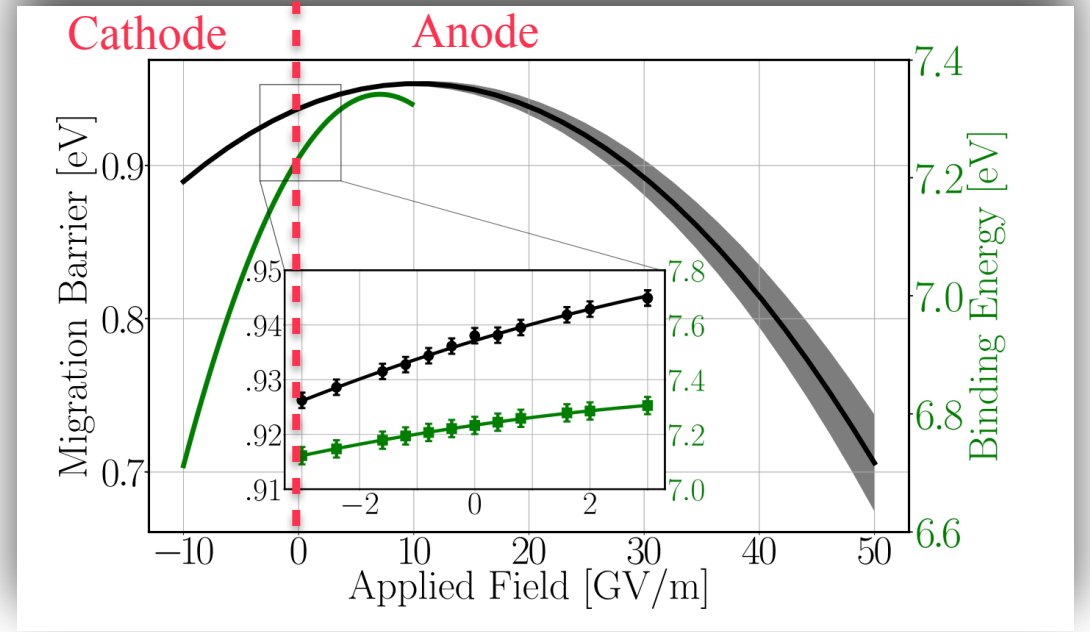
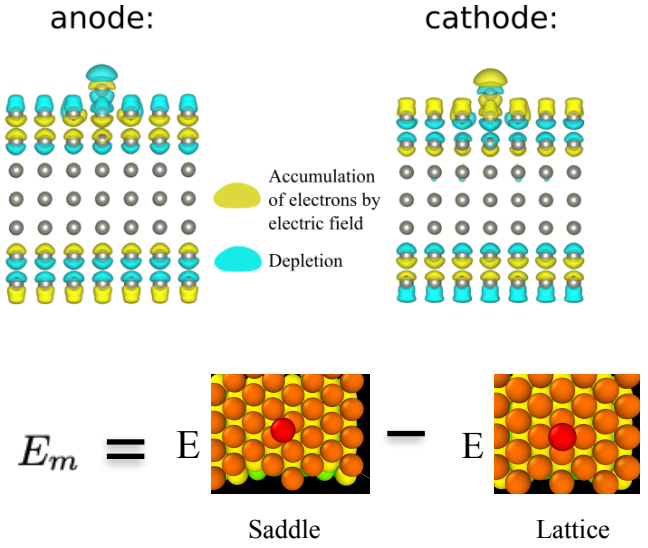


FIG. 4. Continuous observation of the directional walk of a W adatom on a W (110) plane at ~3.8 V/Å and ~295°K.

Anode vs cathode diffusion

- Non-gradient case $F_s = F_l$

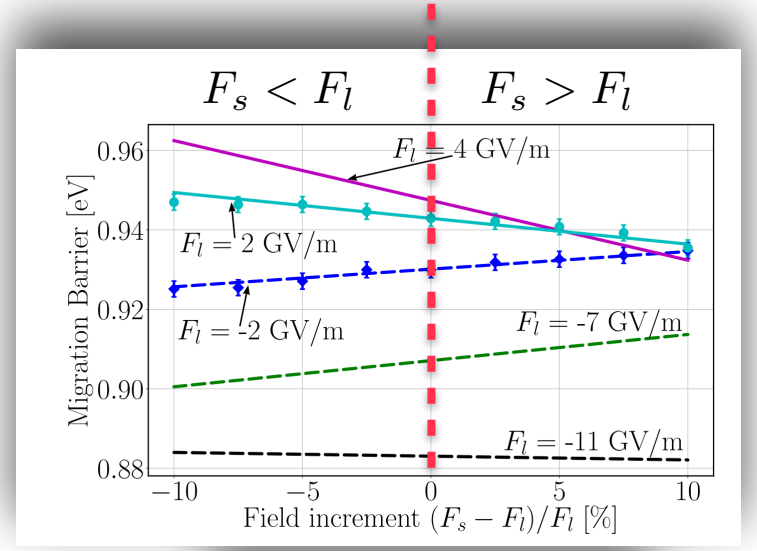


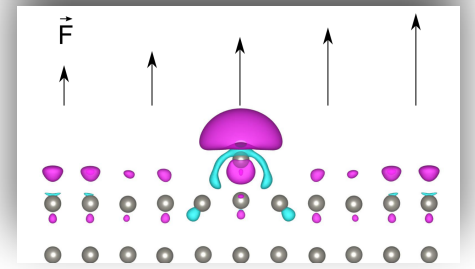


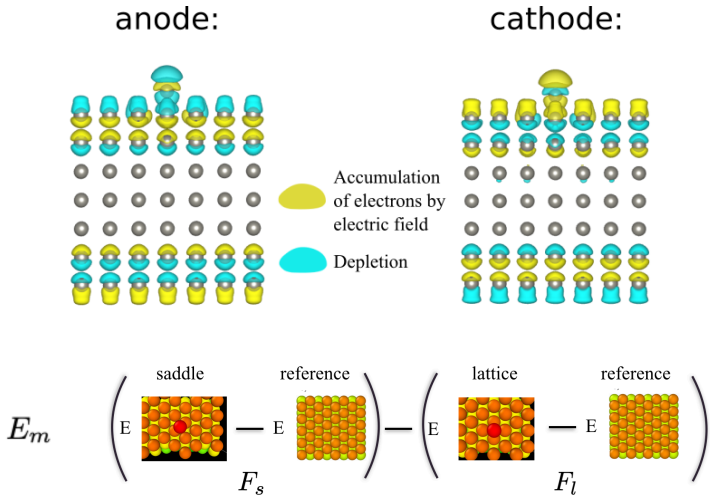
$$E_m \equiv E_s - E_l = E_m(0) - \mathcal{M}_{sl} F - \frac{1}{2}\mathcal{A}_{sl} F^2$$

Anode vs cathode diffusion

- Field gradient case $F_s \neq F_l$







What we've learnt from our theory

- Physics behind diffusion under field

$$E_m \approx E_m(0) - \mathcal{M}_{\mathrm{sl}} F_l - \frac{\mathcal{A}_{\mathrm{sl}}}{2} F_l^2 - \mathcal{M}_{\mathrm{sr}} \Delta F - \mathcal{A}_{\mathrm{sr}} F_l \Delta F$$

- 1st order terms correspond the permanent dipole moment due to the adatom-induced charge redistribution

- 2nd order terms depend on how the field induced charge redistribution is modified in different configurations.

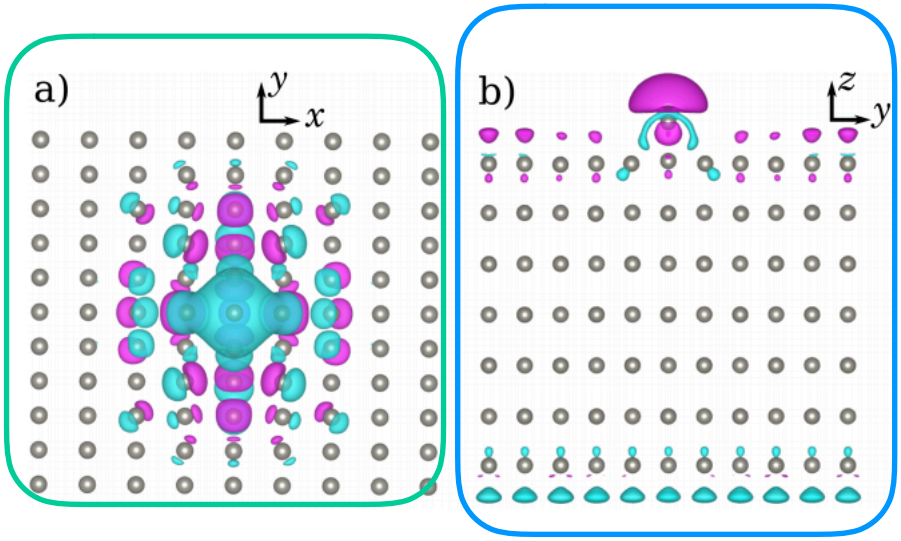


FIG. 1. Charge redistribution induced by (a) the presence of an adatom, (b) a positive 1 GV/m applied field (anode) on a system with adatom (the atoms are fixed to their original zero–field positions for illustration purposes). The open surface of the W slab is of the {110} kind. Cyan and magenta colored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

Diffusion on W under electric field: a KMC study

- Experiment from

Fujita, Shin, and Hiroshi Shimoyama. "Mechanism of surface-tension reduction by electric-field application: Shape changes in single-crystal field emitters under thermal-field treatment." *Physical Review B* 75.23 (2007): 235431.

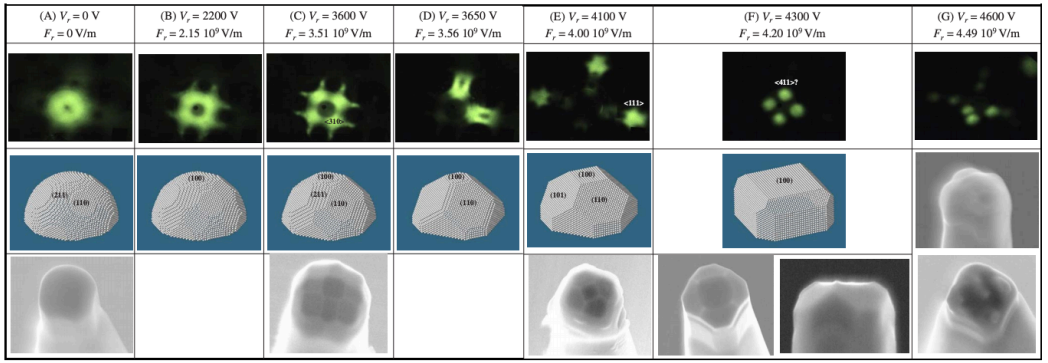


FIG. 5. (Color online) Summary of the evolution of the tip shape in the remolding process at the temperature T_r=2300 K. The FE patterns (second row), the emitter tip shape models (third row), and the SEM images of the tips at selected stages (fourth row) are given in the order of the increasing remolding voltage.

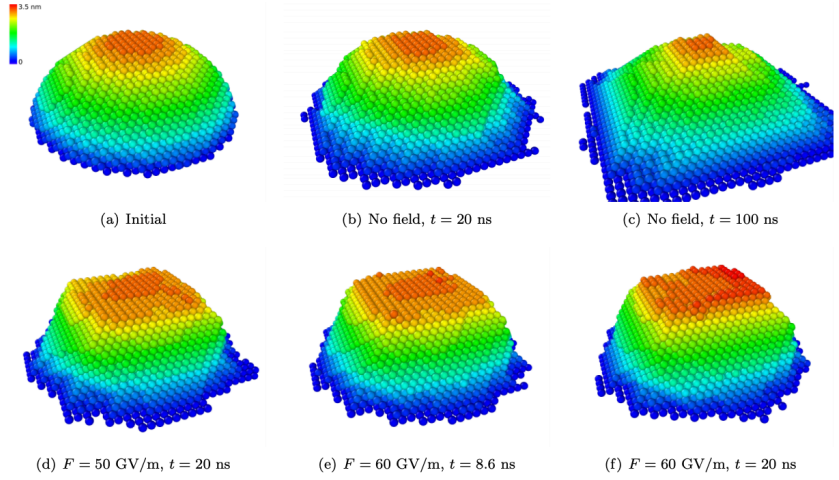
- Our simulations from

arXiv.org > cond-mat > arXiv:1909.05825

Condensed Matter > Materials Science

Growth mechanism for nanotips in high electric fields

Ville Jansson, Ekaterina Baibuz, Andreas Kyritsakis, Simon Vigonski, Vahur Zadin, Stefan Parviainen, Alvo Aabloo, Flyura Djurabekova



(a) Initial (b) No field, $t = 20$ ns (c) No field, $t = 100$ ns

(d) $F = 50$ GV/m, $t = 20$ ns (e) $F = 60$ GV/m, $t = 8.6$ ns (f) $F = 60$ GV/m, $t = 20$ ns

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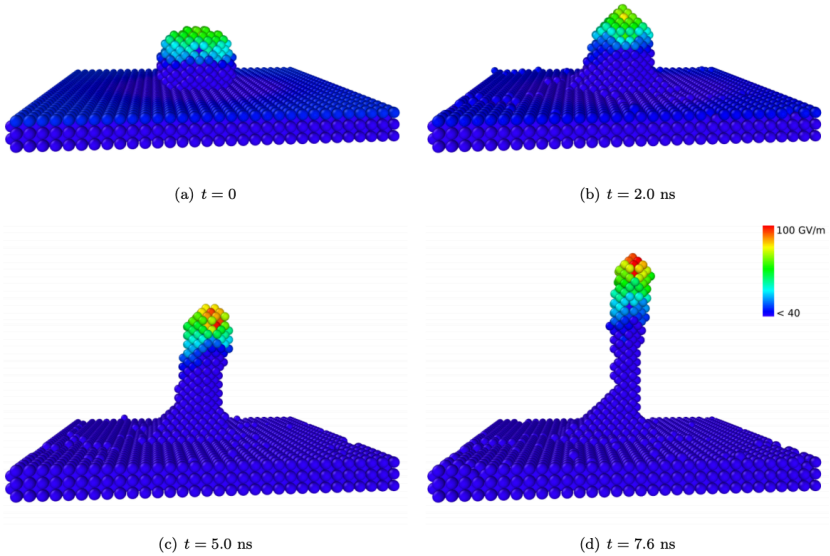
(Submitted on 12 Sep 2019)



(a) $t = 0$ (b) $t = 2.0$ ns

(c) $t = 5.0$ ns (d) $t = 7.6$ ns

Figure 5. Time frames showing the growth process of a W nanotip at different stages in an applied electric field of 50 GV/m (initial local field 72 GV/m) at 3000 K, starting from a hemispherical asperity (a). The initial asperity (a) is 2.0 nm high and the final nanotip (d) is 6.3 nm high. The atoms are coloured according to the local surface field strength. For an animation, see the Supplementary Materials.

Conclusion

- We can now have a fundamental theory of surface diffusion under electric field gradient
- We can now simulate long-term evolution of W on W surfaces under applied electric field
  - Surface diffusion under electric field leads to the formation of nano-tip if surface is rough under certain applied fields
- Our methods can be used for other materials
  - Copper studies are in progress

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Doctoral Programme in Materials Research and Nanosciences

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V. Jansson thanks
Waldemar von Frenckells Stiftelse
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for research funding

Science Outreach

https://www.thesciencebasement.org/
Science Outreach group
based in UH and Aalto

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Cu(100), 5.5 ps, 700 K by V. Jansson

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