Surface diffusion in high electric fields

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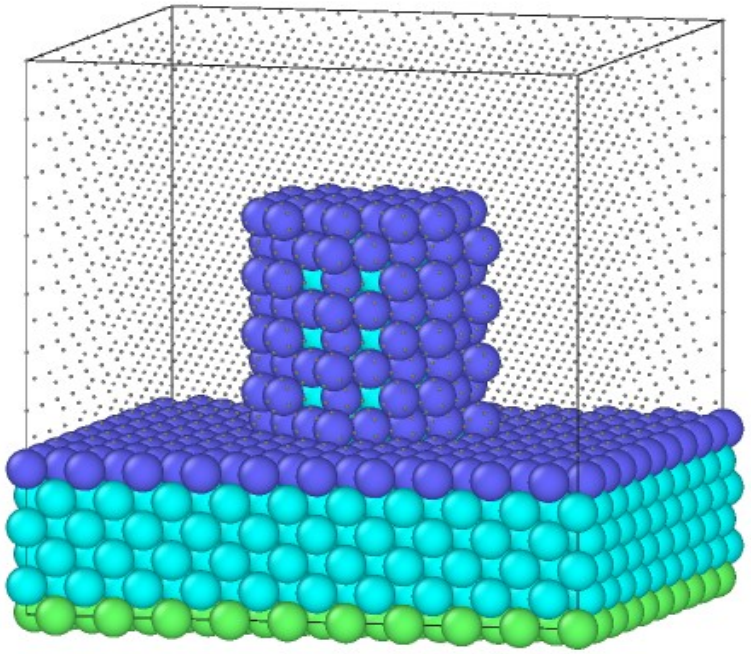
Kimocs

A Kinetic Monte Carlo (KMC) code for surfaces

- Designed to simulate the surface evolution on the atomic scale:
  - Arbitrarily rough surfaces
  - Clusters
  - Wires
  - Vacancy clusters in bulk
- The code uses a rigid atomic lattice
  - fcc or bcc
- Electric field effects are now implemented too



V. Jansson, E. Baibuz, F. Djurabekova
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http://arxiv.org/abs/1508.06870

Kinetic Monte Carlo (KMC)

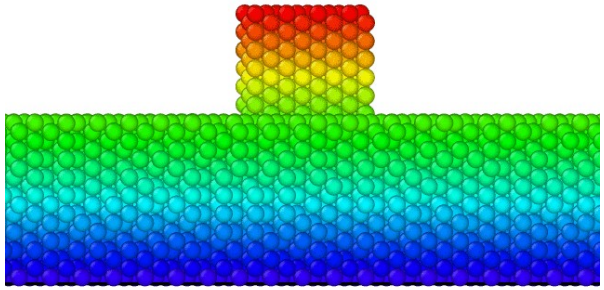
- Simulation method for slow physical processes (nanoseconds – seconds for atomic processes)
- Thermally activated processes, such as atom jumps, have probability rates of the form

$$\Gamma = \nu \exp\left(\frac{-E_m}{k_B T}\right)$$

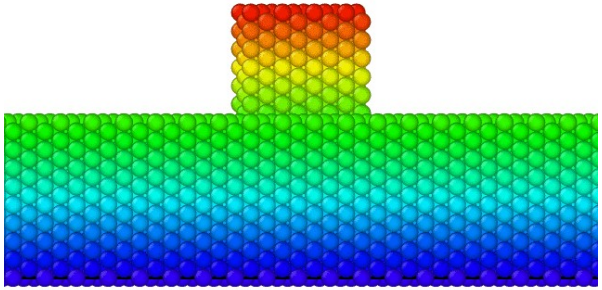
where

  - ν is the attempt frequency
  - E_m the migration (or activation) energy
- ν and E_m need to be known for all processes

MD

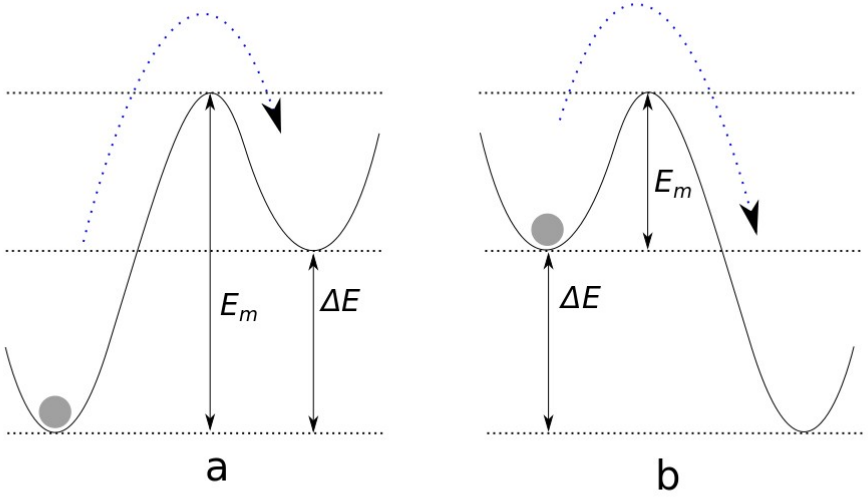


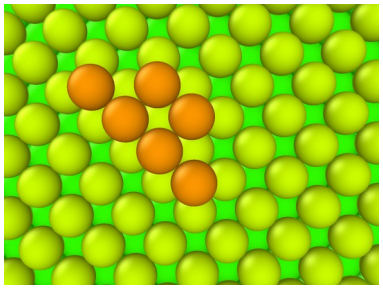
Kimocs



Kimocs is ~100 times faster than MD

The migration energy barriers E_m





(6,2)→(7,2)

- E_m for an atom jump depends on the local atomic configurations
- For calculating E_m, the Molecular Dynamics method Nudged Elastic Band (NEB) is used
- For a complete KMC model, a set of thousands of E_m barriers need to be calculated
- **We have developed an automated way to construct such sets for any fcc or bcc metal**
- Calculated sets: **Cu, Fe, Au, W, Ag**

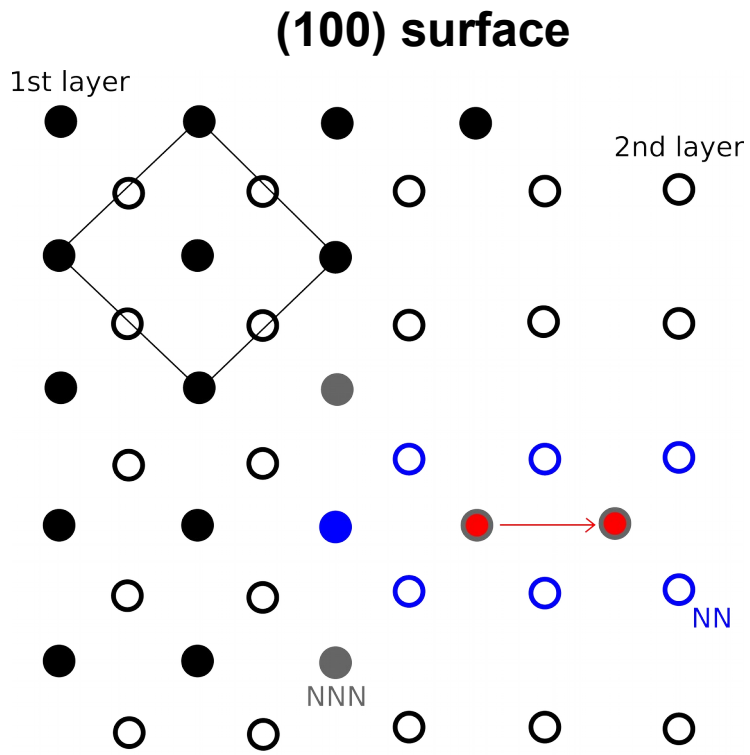
Barriers: E. Baibuz, S. Vigonski et al., https://arxiv.org/abs/1707.05765

Fe: J. Zhao et al: ACS nano, 2016

Au, Ag: S. Vigosnki et al: https://arxiv.org/abs/1709.09104

The migration energy barriers E_m

The Kimocs Parameterization



$E_m(5,3,5,1)$

Atom jumps are characterized by

- The number of nearest neighbour (1nn) atoms
- The 2nd nearest neighbour (2nn) atoms of the initial and final lattice sites

We are currently with J. Lahtinen trying to train artificial neural networks in order to replace the tables and increase the precision.

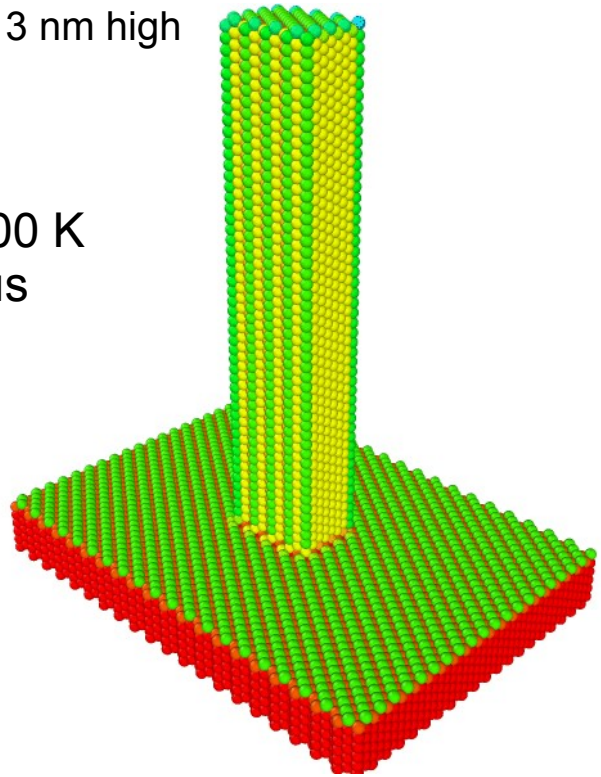
- In this case the relative positions of the 1nn and 2nn atoms are taken into account

J. Lahtinen et al., Artificial neural networks for Cu surface Migration barrier prediction. To be submitted.

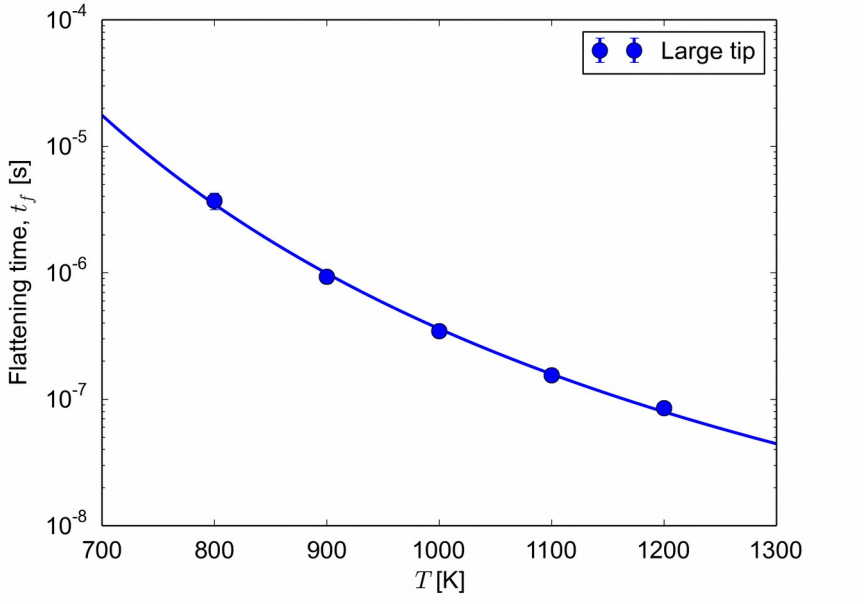
Stability of Cu nanotips (no field)

13 nm high

[110], 800 K
6.3 μs



V. Jansson (2015)



- Without field, tips flattens down
- <110> tips are the most stable ones
- At 300 K, no change was seen after 10 μs
- Extrapolation gives a flattening time of 3.1 h at 300 K

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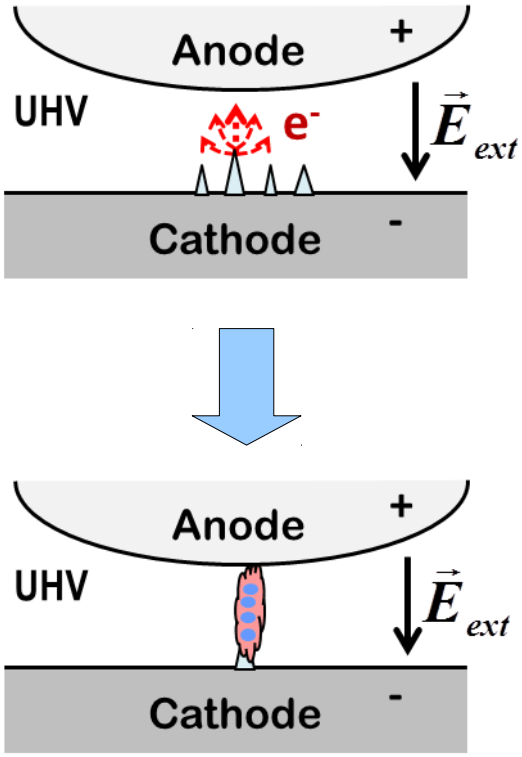
Nanotips (cause of the arcs?)

Field emission measurements suggests the existences of sharp nano-tips that would explain the β factor in the Fowler-Nordheim equation for field emission.

Observations of nanotips with aspect ratios of ~10 are however rare

Are there any mechanisms for forming such tips?



Field-emitting tips appears and a plasma is formed

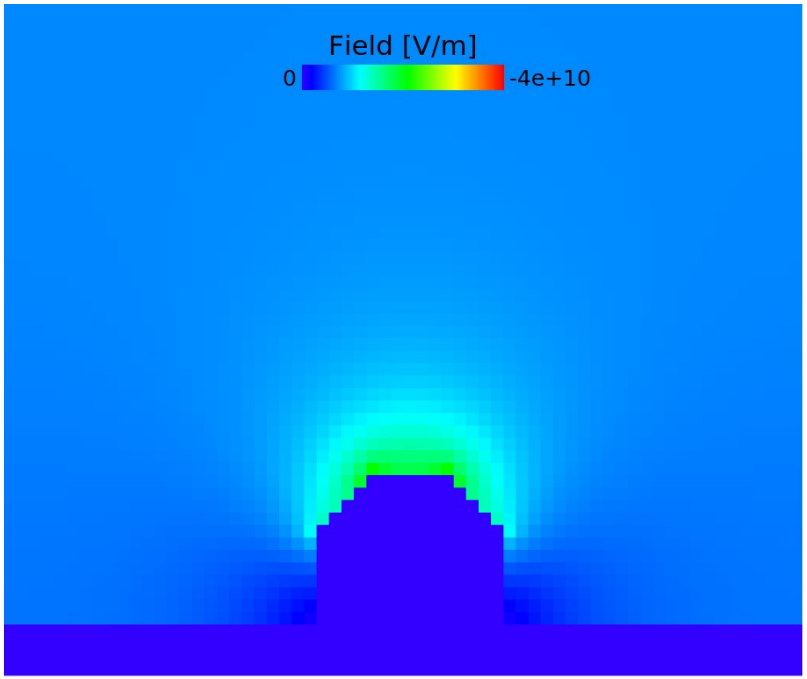
The plasma burns (breakdown) and the tips are destroyed

KMC + field

- Two field solvers have been implemented into Kimocs
  - HELMOD, finite difference

    [F. Djurabekova et al., PRE 2011]
  - FEMOCS, finite elements

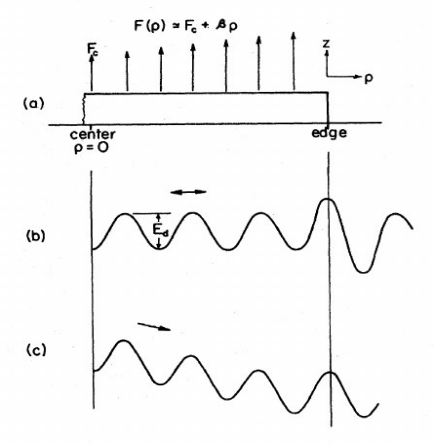
    [M. Veske et al. https://arxiv.org/abs/1706.09661]
- The field is obtained by solving Laplace's equation

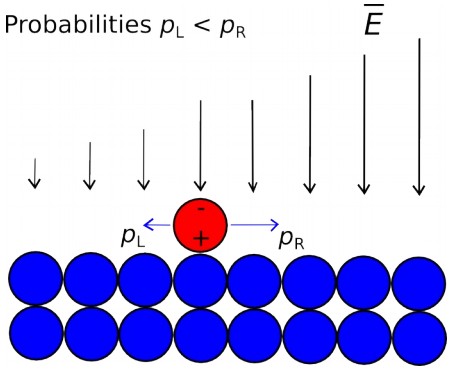


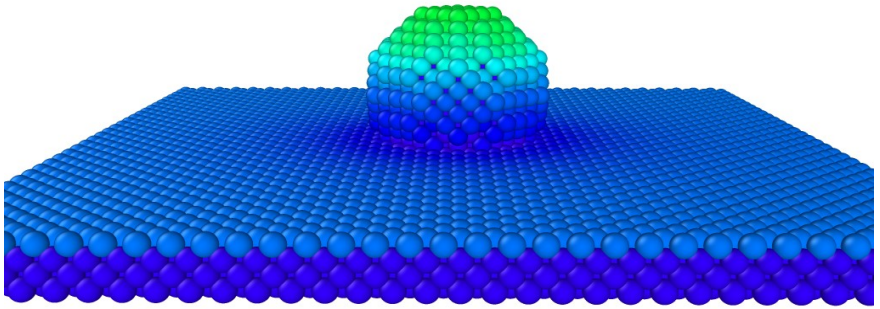
Surface diffusion in electric fields

- Adatoms in electric fields become polarized
- This introduces a dipole force, perpendicular to the field, that will bias the adatom's migration towards stronger fields
- The bias of the adatom migration is achieved by using migration barriers modified by the field at the lattice point (0) and the saddle point (s):

$$E_m = E - (\mu_s F_s - \mu_0 F_0) - \frac{1}{2}(\alpha_s F_s^2 - \alpha_0 F_0^2)$$





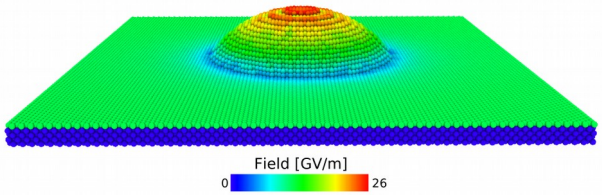


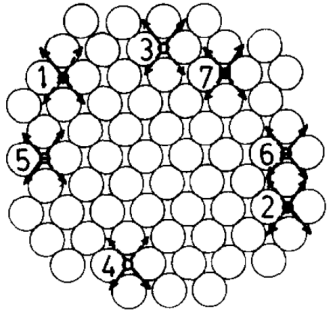
Tsong & Kellogg PRB 1975

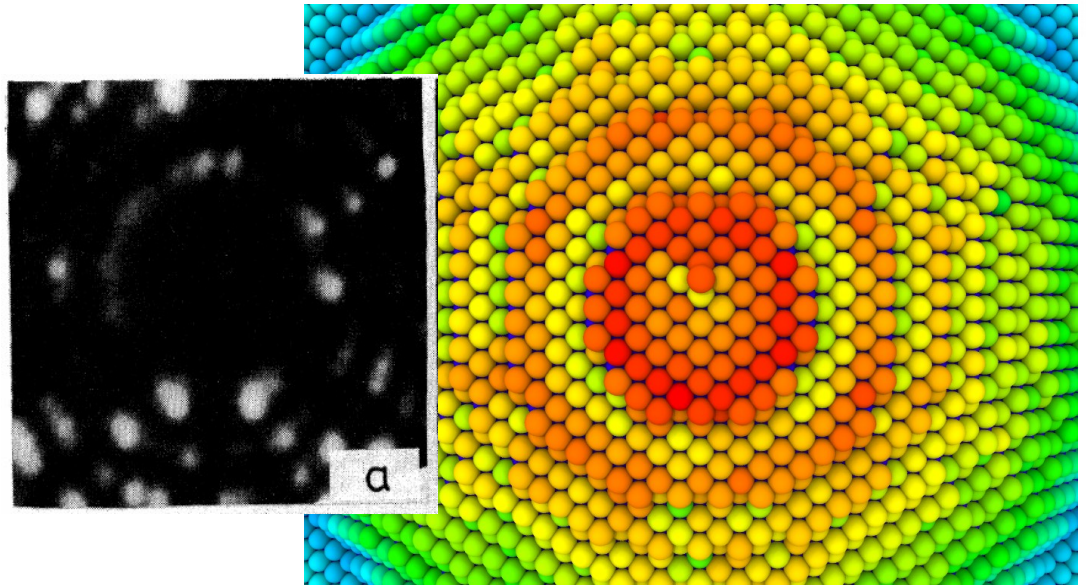
Surface diffusion in electric fields

Comparison with experiment

We can compare the drift velocity of a single W atom on a W{110} surface in a field gradient with experiments [Wang & Tsong PRB 1982]

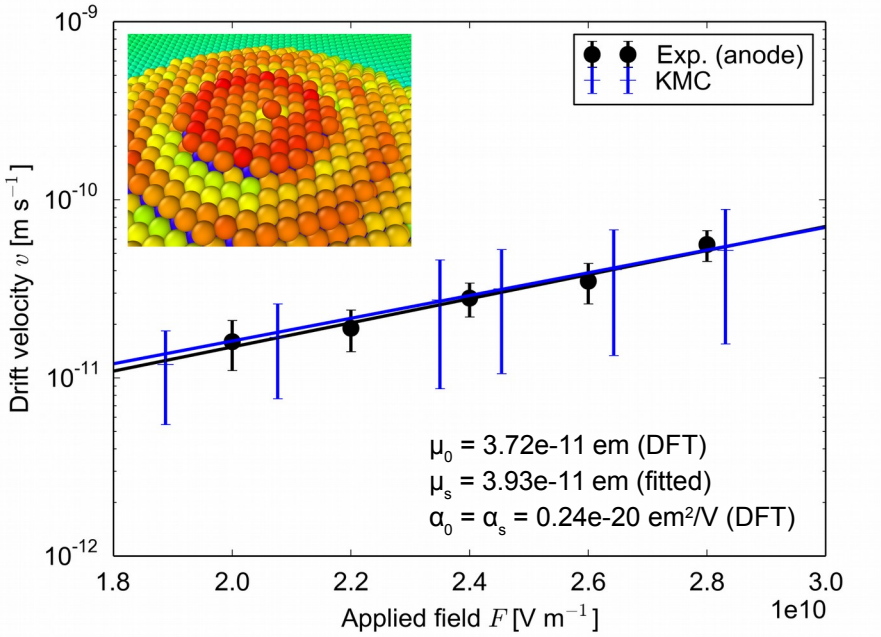


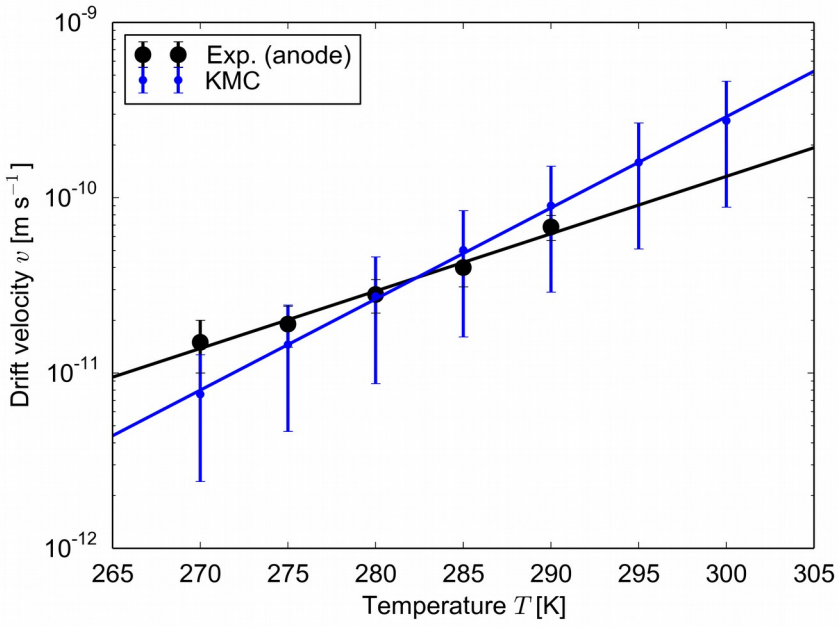




Surface diffusion in electric fields

Comparison with experiment



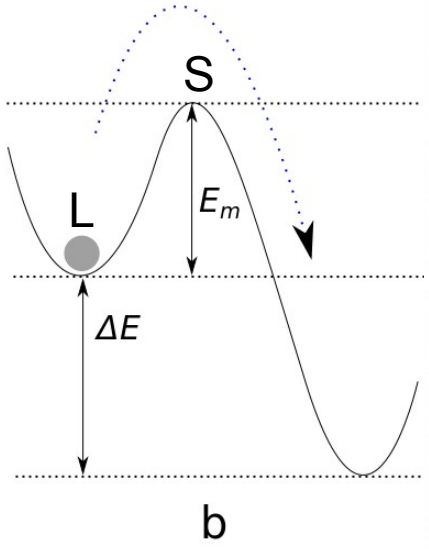


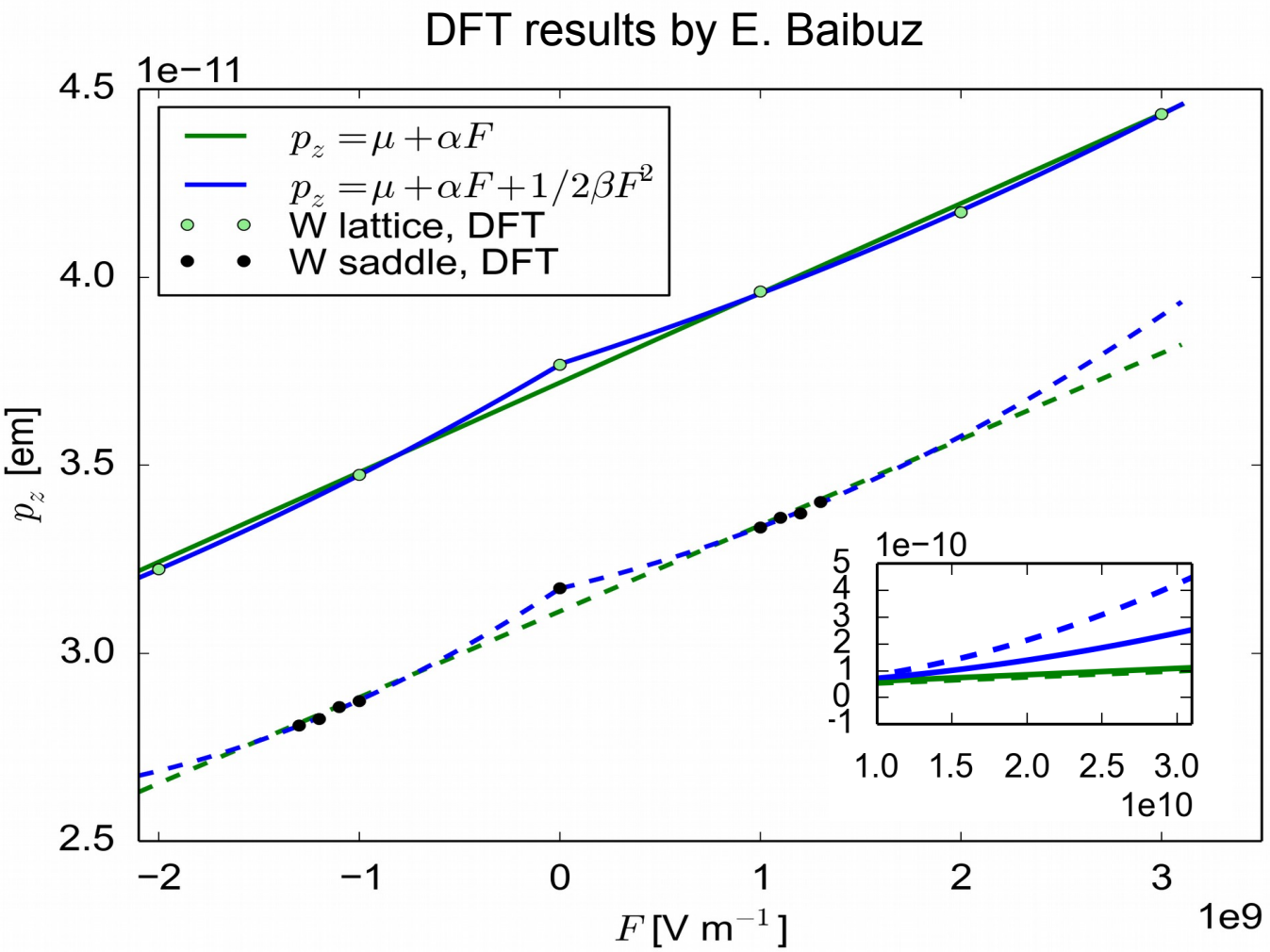
Excellent agreement so far. However, using newer DFT values also for the saddle point μ_s and α_0 gives a disagreement of two orders of magnitude (see Ekaterina's talk). We still have too little DFT data to explain this disagreement.

V. Jansson et al. https://arxiv.org/abs/1709.04694.

Dipole moment and polarizability

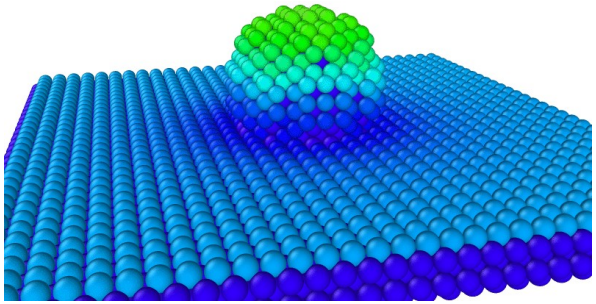
The surface-induced dipole moment μ and polarizability α are dependent on the material and the placement of the adatom:
- lattice point L
- saddle point S



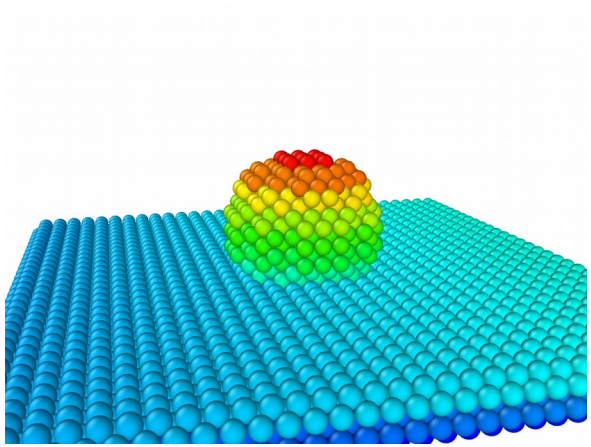


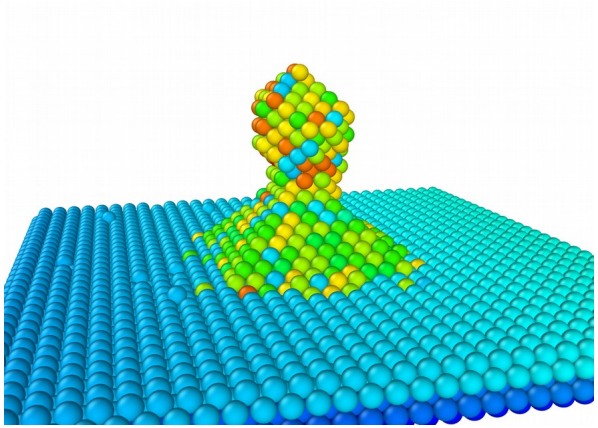
Growth of W nanotips

W nanotip at 3000 K in 1 GV/m applied field



Colours: field





Colours according to the initial atom positions to show the diffusion

The bias diffusion in fields causes formation of nanotips

V. Jansson et al. To be submitted.

Faceting of W nanotips

- Experiment by Fujita & Shioyama show faceting of W tips in fields at 2400 K
- In particular a peculiar growth of a {100} facet

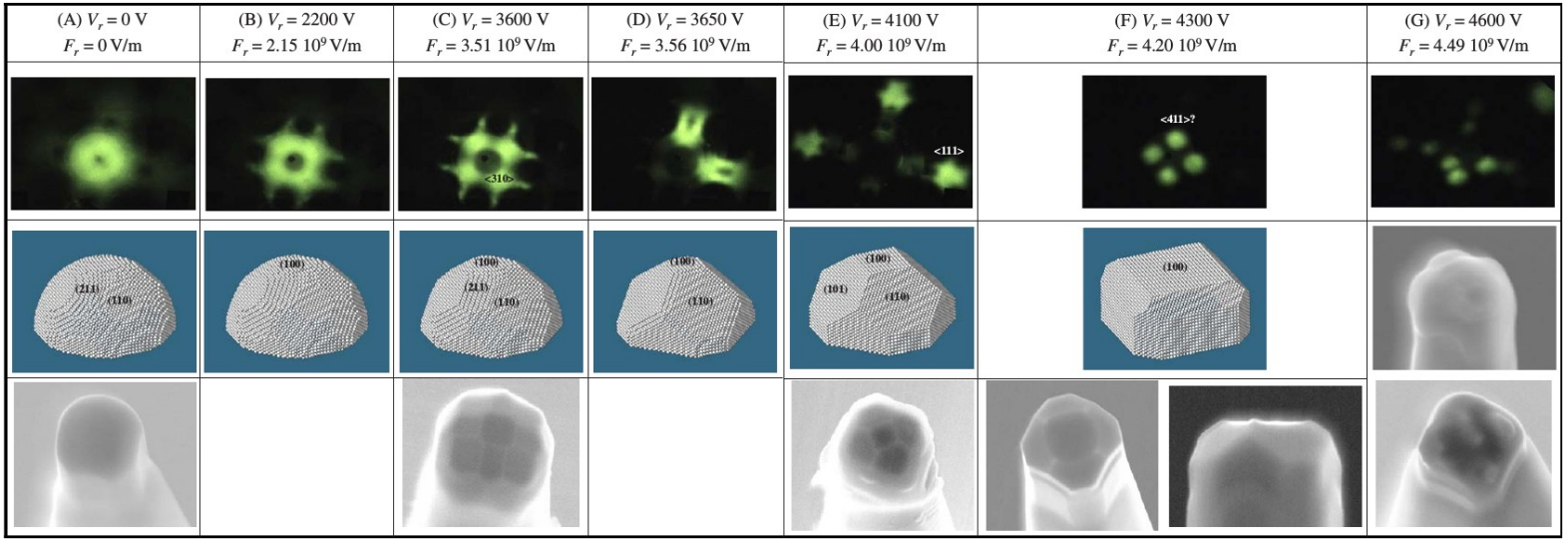


FIG. 5. (Color online) Summary of the evolution of the tip shape in the remolding process at the temperature T_r=2300 K. The FE patterns (second row), the emitter tip shape models (third row), and the SEM images of the tips at selected stages (fourth row) are given in the order of the increasing remolding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

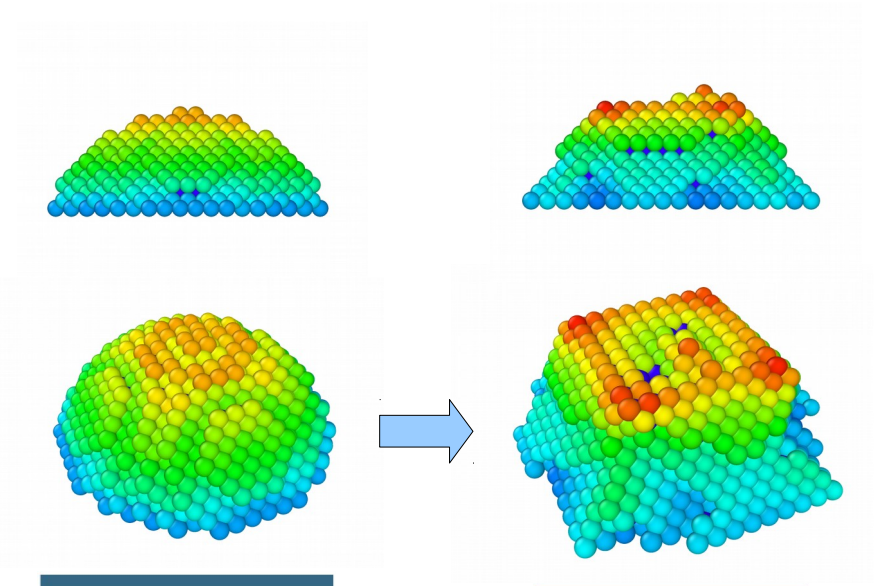
S. Fujita and H. Shioyama, PRB 75, 235431 (2007)

Faceting of W nanotips

Similar growth of a W{100} facet is seen in our model

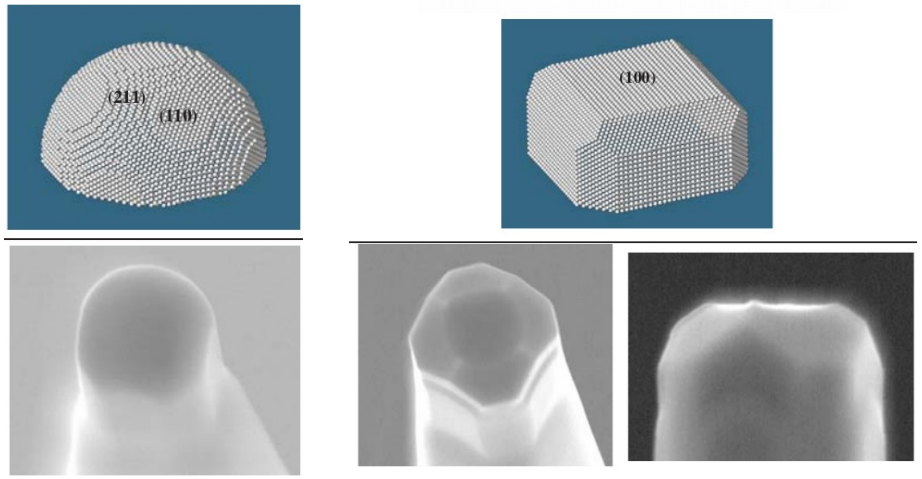
T = 2300 K
F = 1e10 V/m
time = 400 ns
radius = 3 nm

KMC

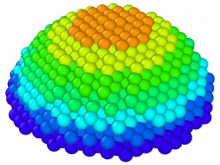


Fujita & Shimoyama

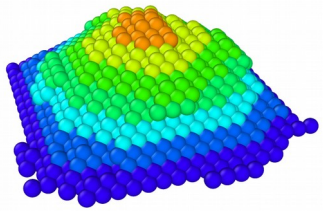
T = 2400 K
F = 4.2e9 V/m
radius = 200 nm



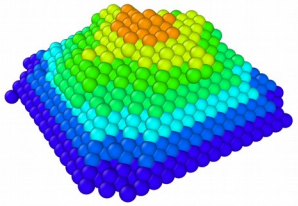
Faceting of W nanotips



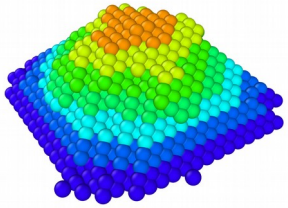
Initial



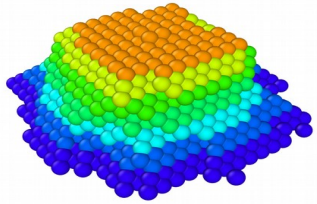
0.0 V/m
t = 4e-7 s
T = 2300 K



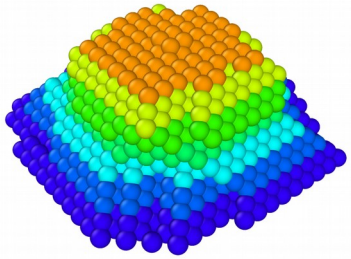
2.0 GV/m



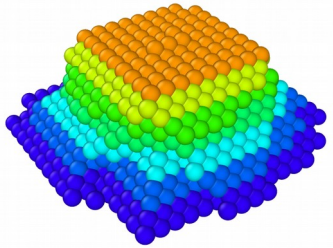
4.0 GV/m



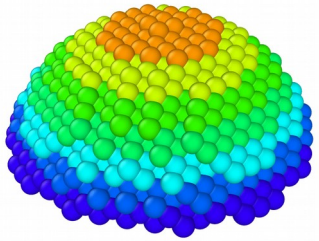
6.0 GV/m



8.0 GV/m



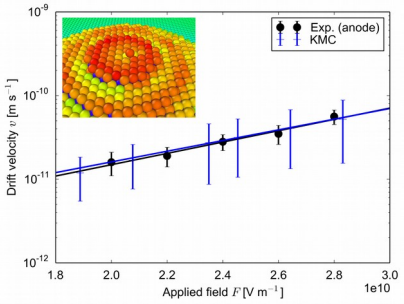
10.0 GV/m

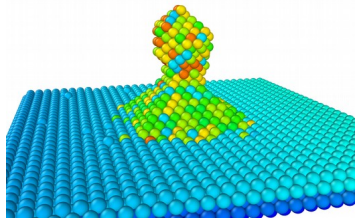


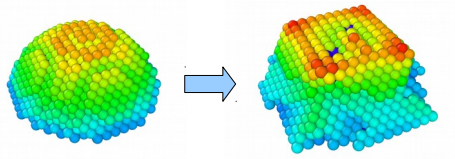
10.0 GV/m

Summary & conclusions

- Kimocs now can be used with Cu, Fe, W, Au and Ag systems
- The effect of electric field on the adatom diffusion is also implemented
  - We can fit parameters to get excellent agreement with experiments
  - However, the fitted parameters do not currently agree with DFT
  - Hemispherical asperities in strong fields are observed to start growing into tips
  - We can reproduce faceting observed in experiments







Acknowledgement

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