Cu Surface Diffusion Bias under Electric Field Gradient

Accelerated Molecular Dynamics, Finite Elements Method, and Density Functional Theory

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University of Helsinki

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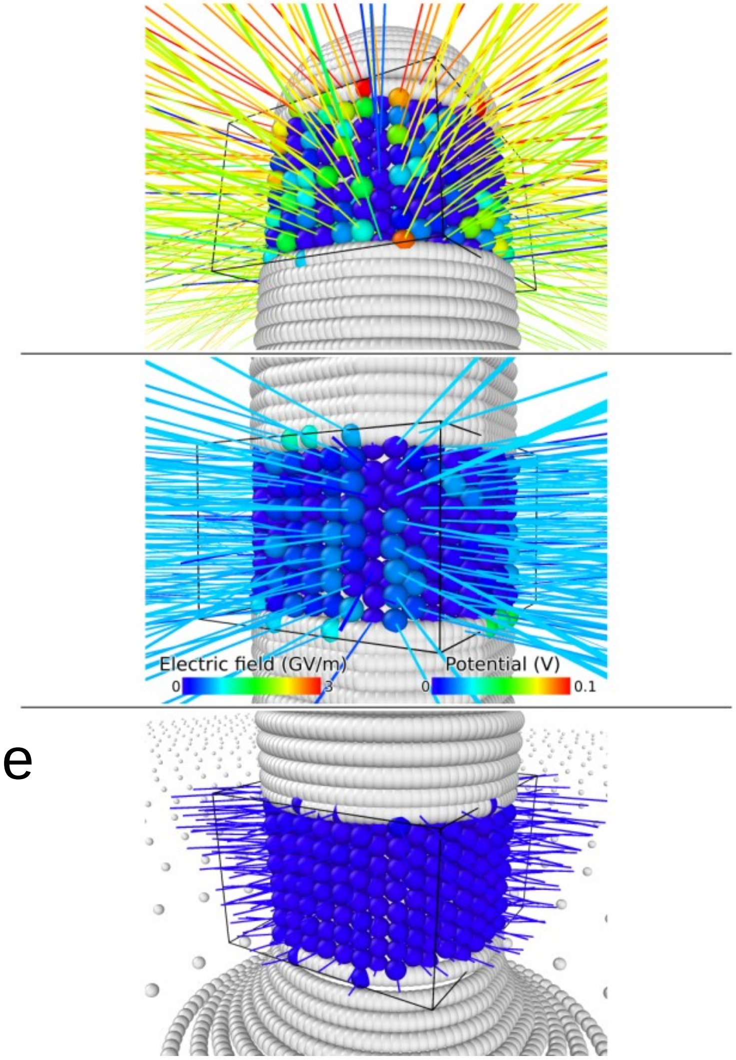
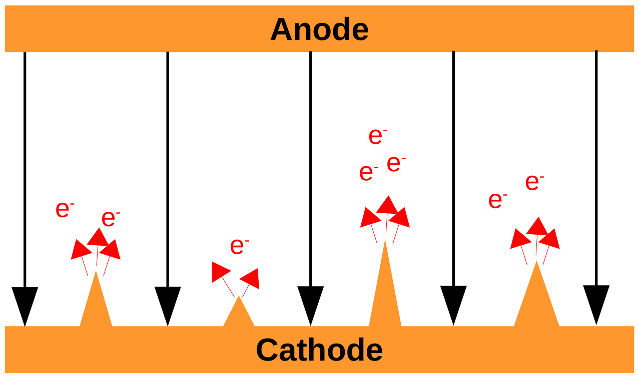
University of Tartu

Outline

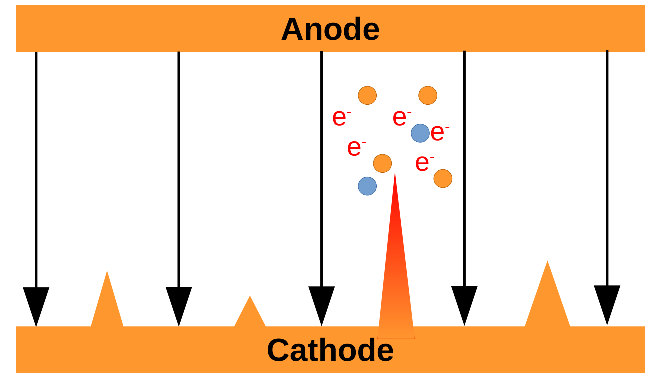
- Familar story of vacuum arc formation
- Atomistic view of mass transport by diffusion
- Molecular dynamics with extended time and length scale
- Comparison with density functional theory



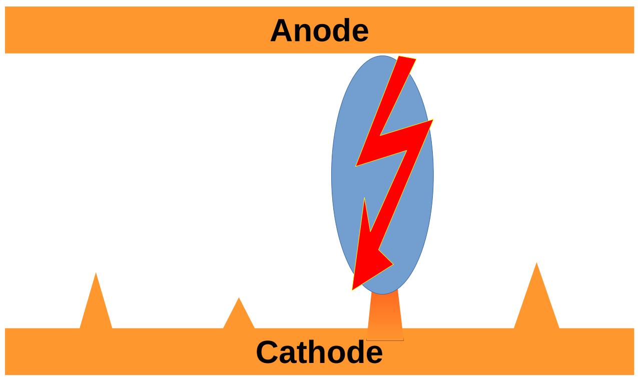
Familiar picture



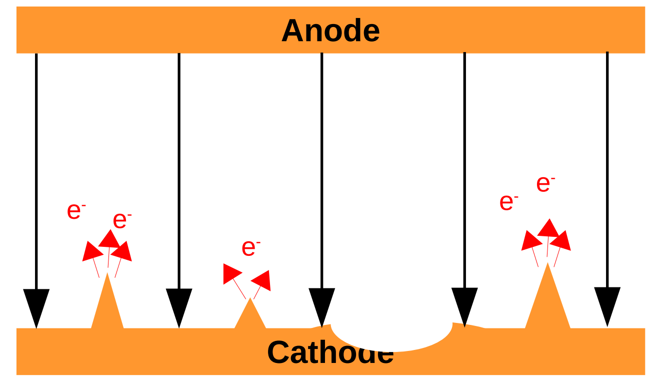
1. Field emission



2. Thermal runaway



3. Breakdown



4. Crater

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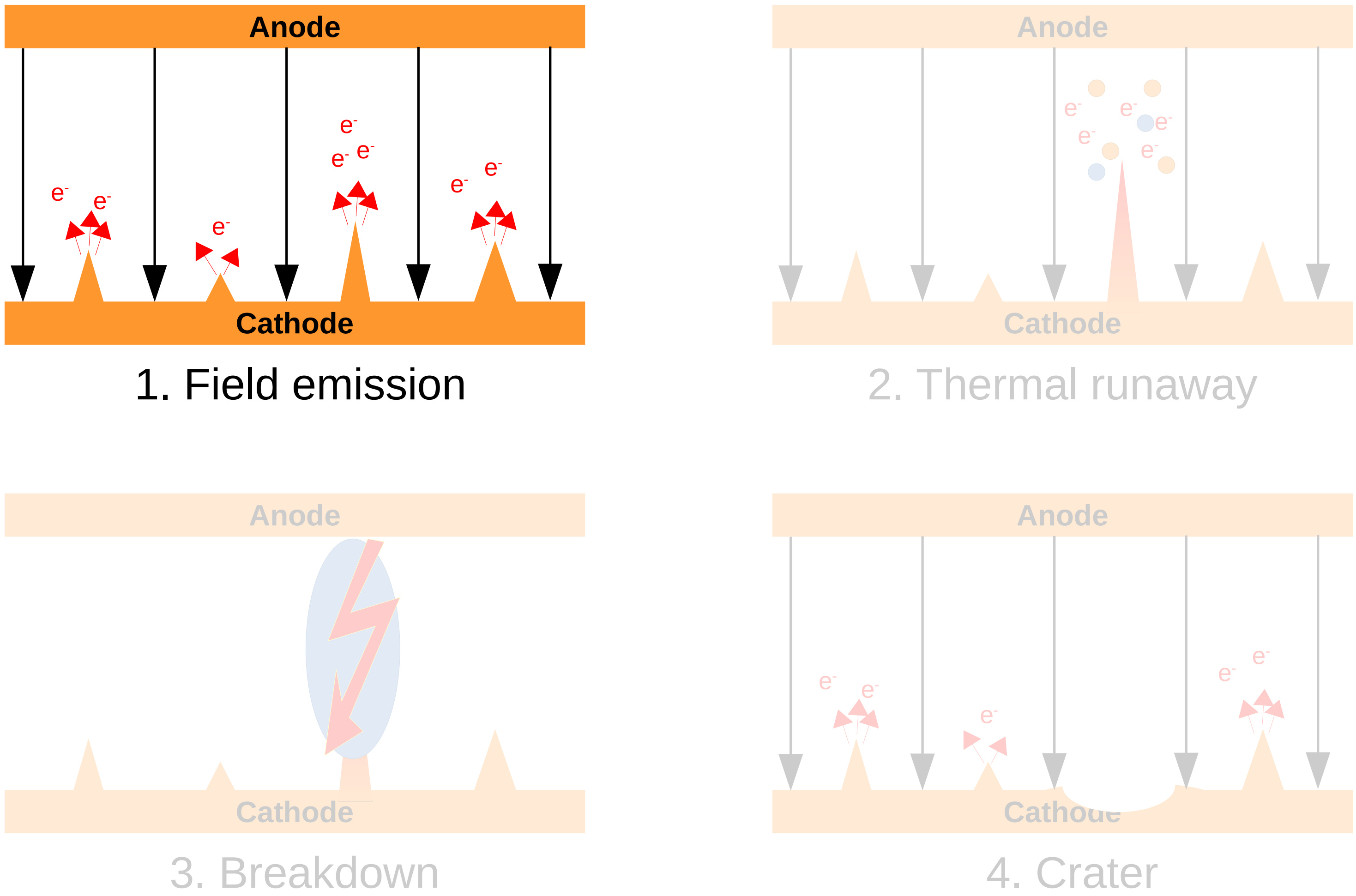
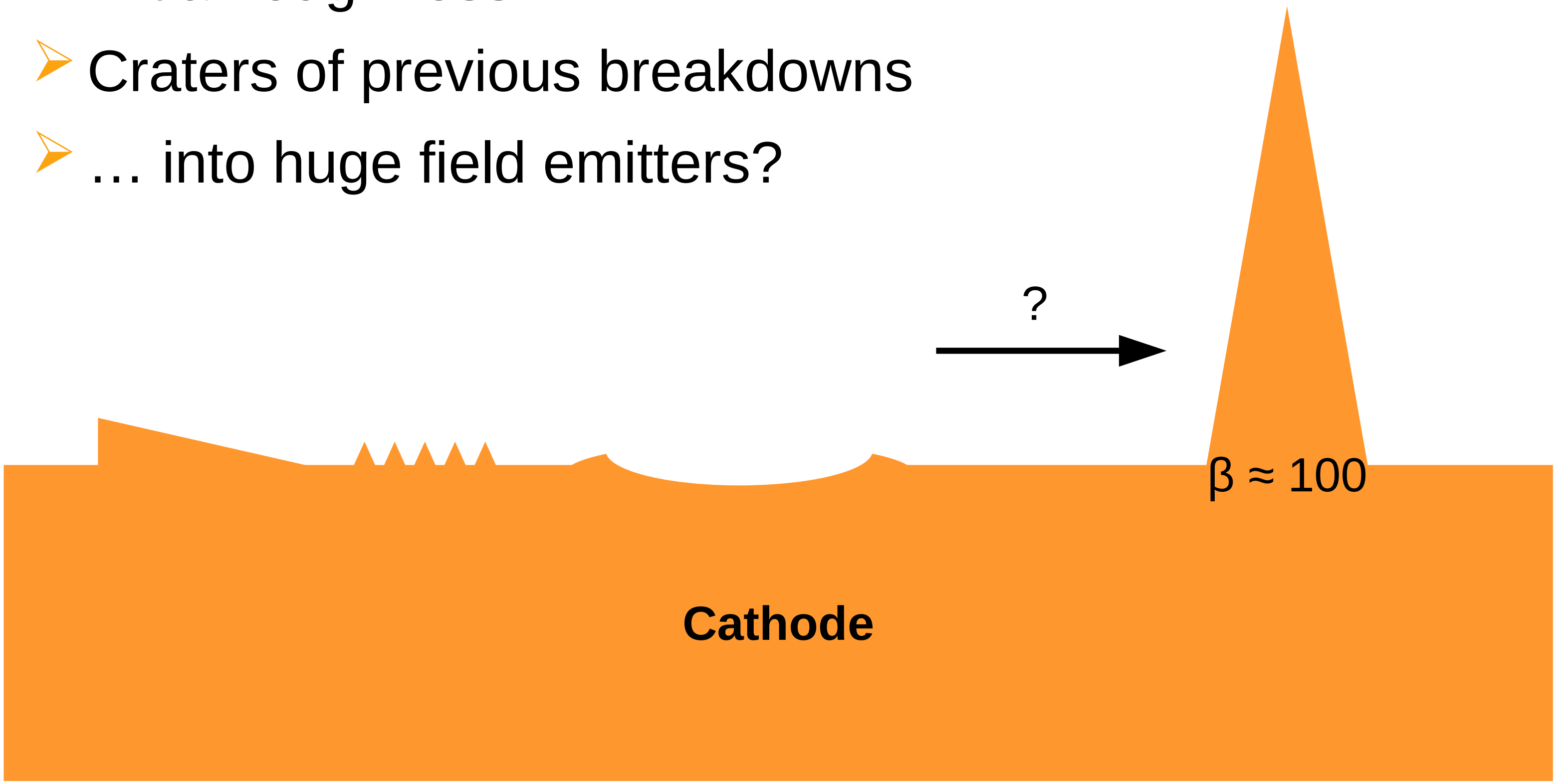


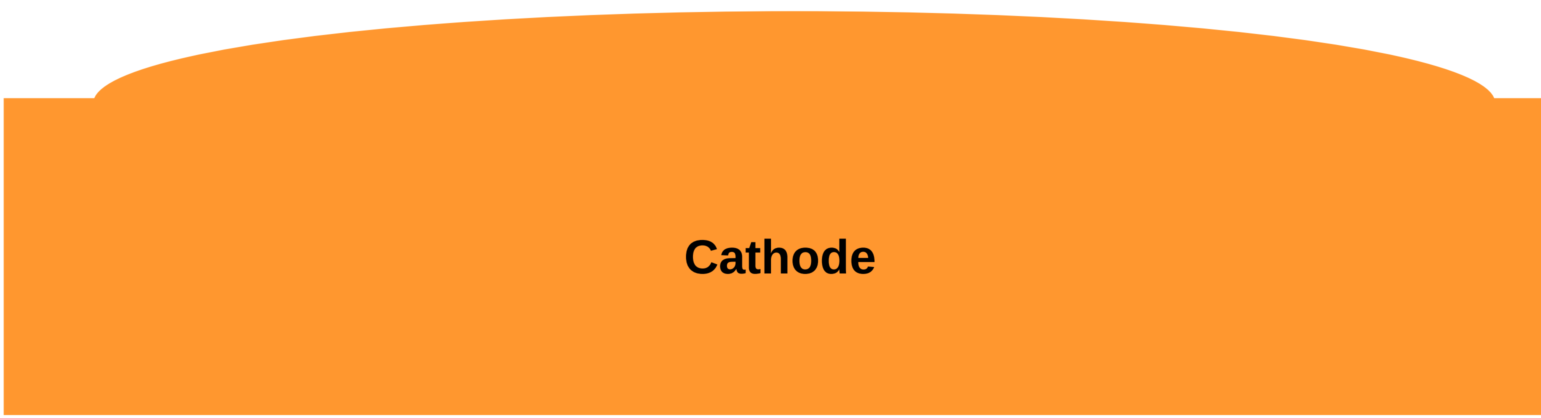
Growth and sharpening of field emitters

- Dislocation slips
- Initial roughness
- Craters of previous breakdowns
- … into huge field emitters?



Surface curvature driven mass transport

- Competition between minimizing surface energy and electric field energy



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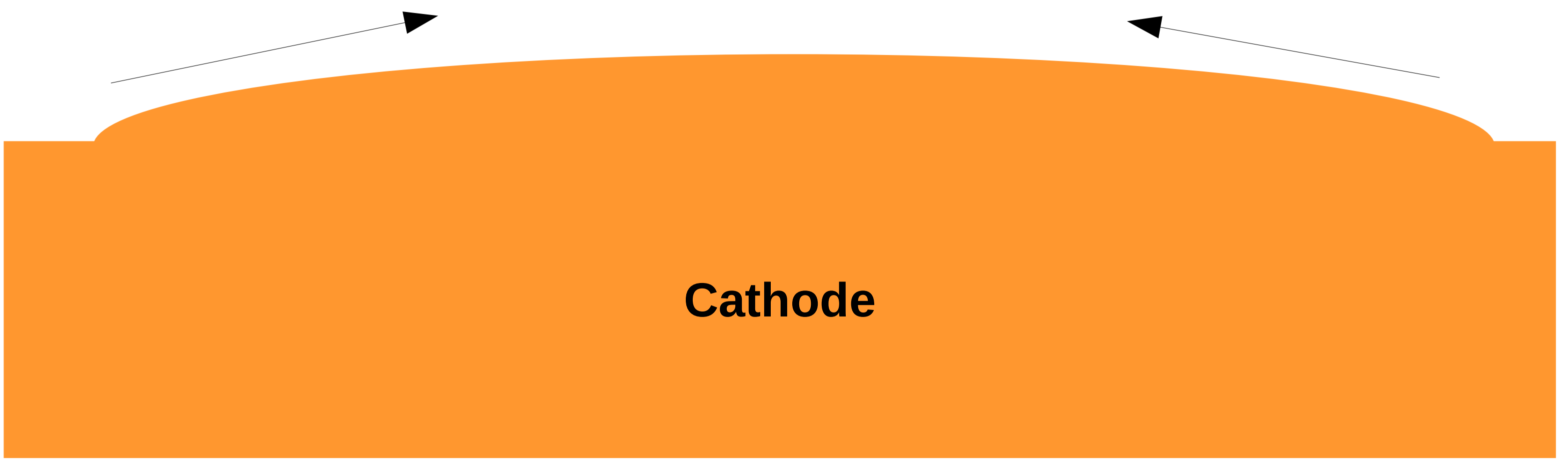

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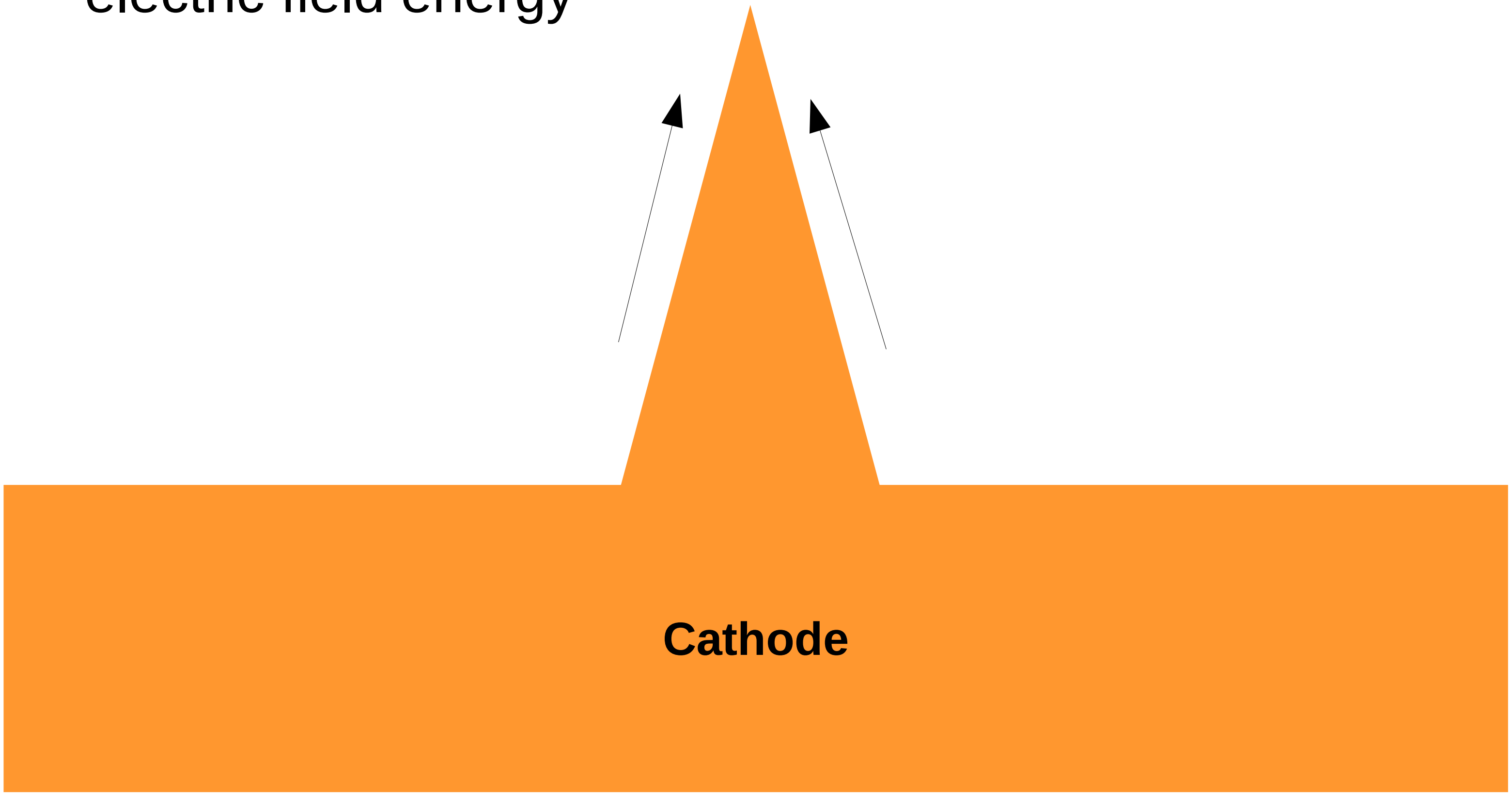

Atomistic view of mass transport

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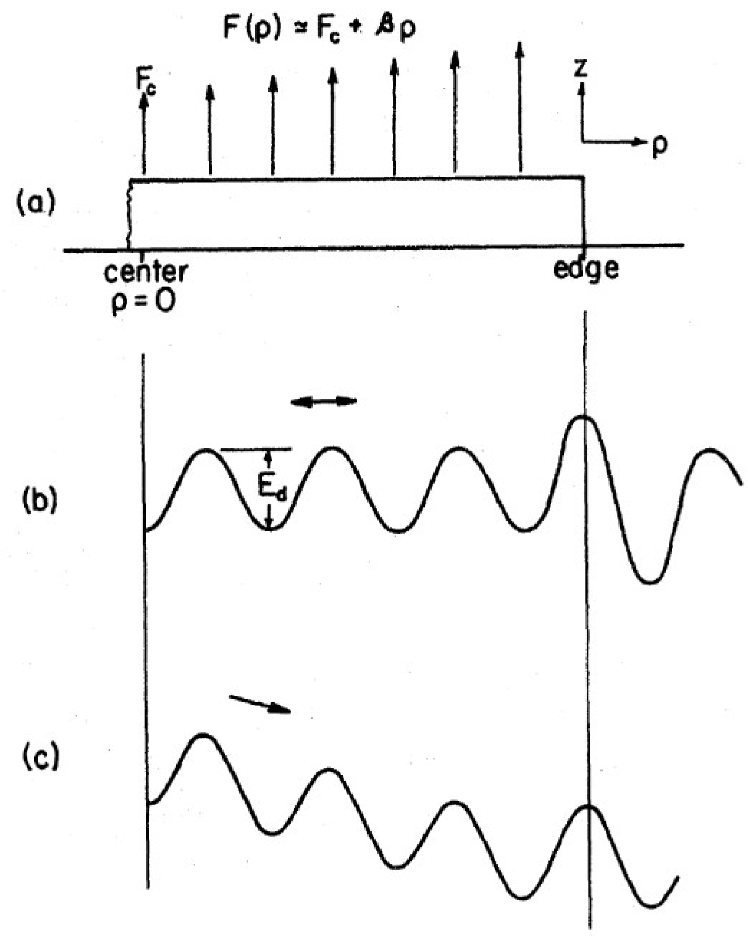

T. T. Tsong, P. Cowan, and G. Kellogg, *Thin Solid Films* **25**, 97 (1975).

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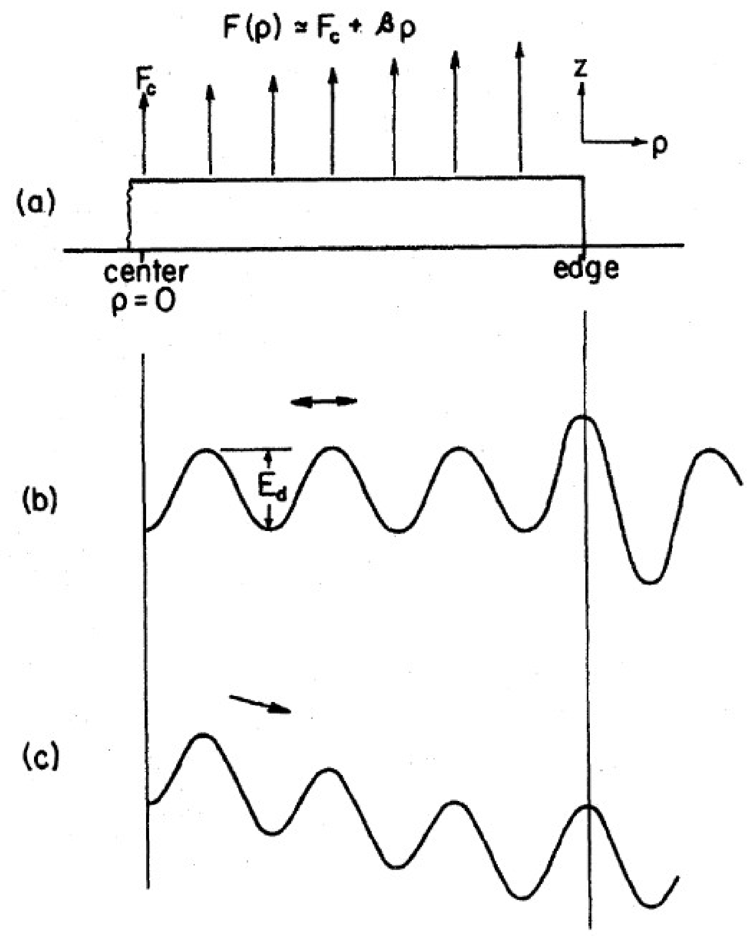

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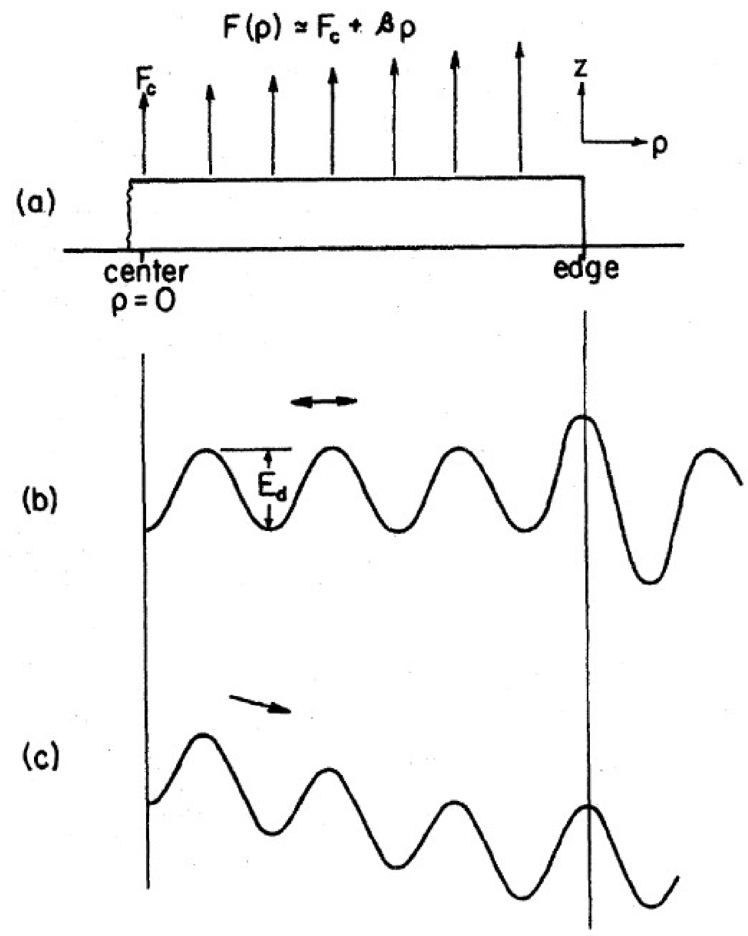

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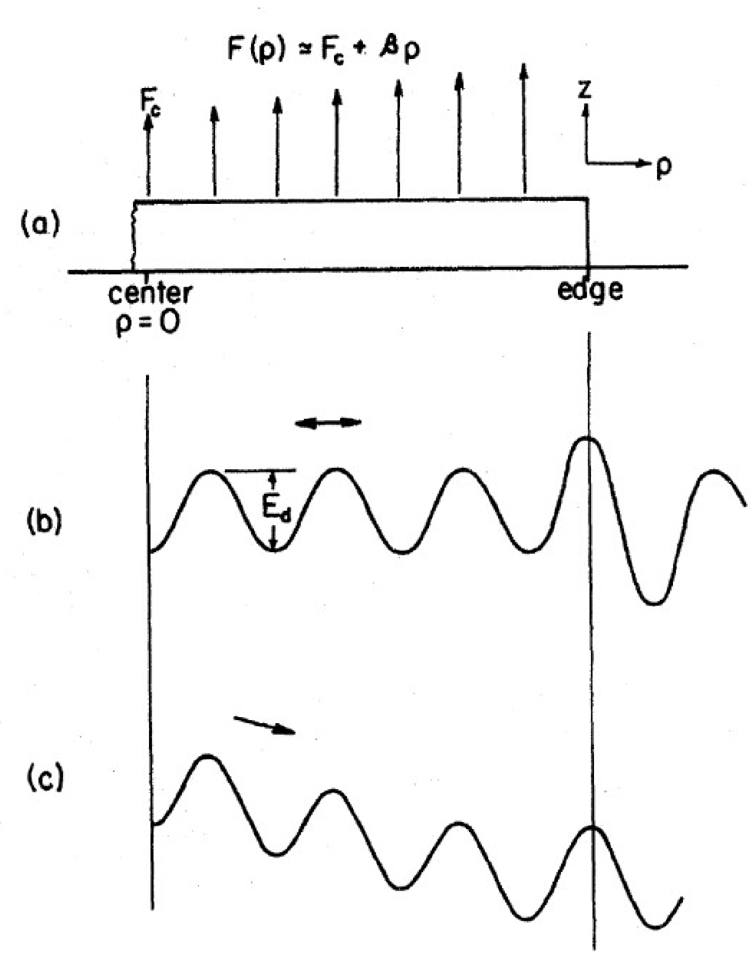

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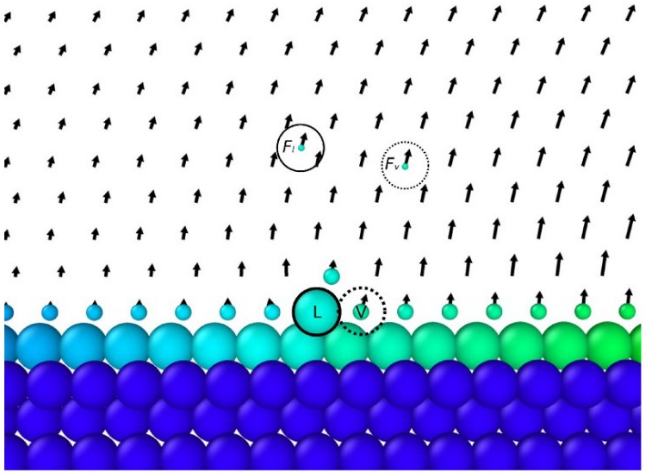

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V. Jansson et al., *Nanotechnology* **31**, 355301 (2020).

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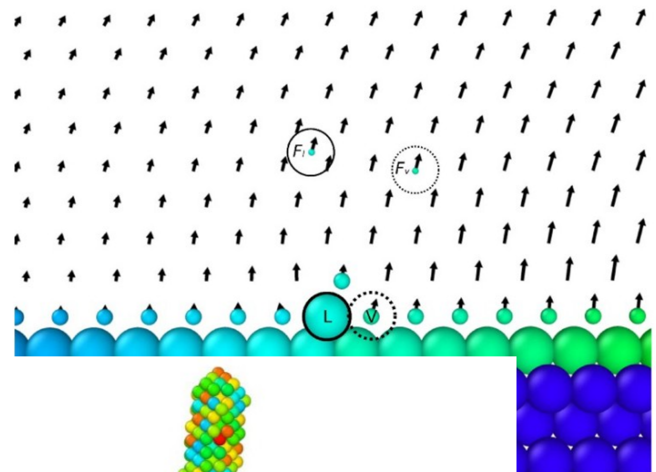

tungsten

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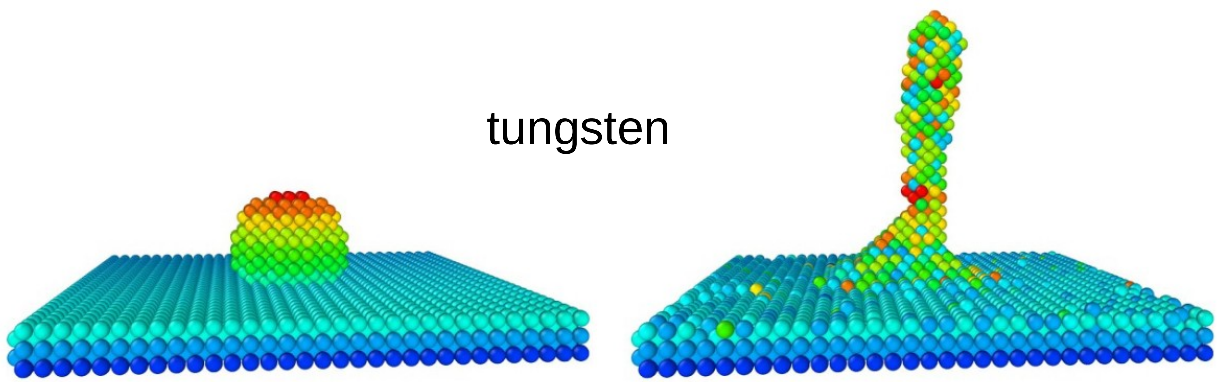

(a) $t = 0$ (b) $t = 7.6$ ns

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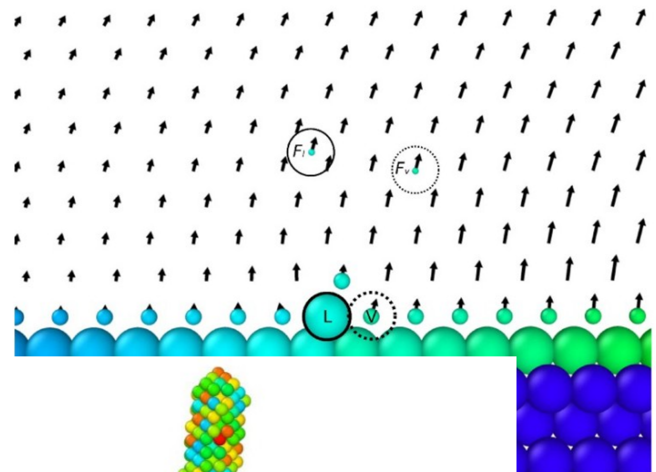
- Still a lot of uncertainty with estimating dipole parameters!



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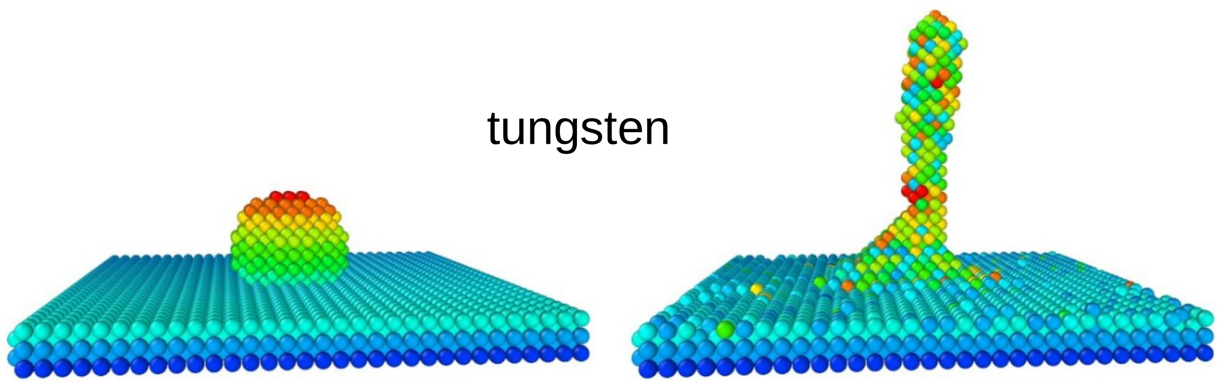

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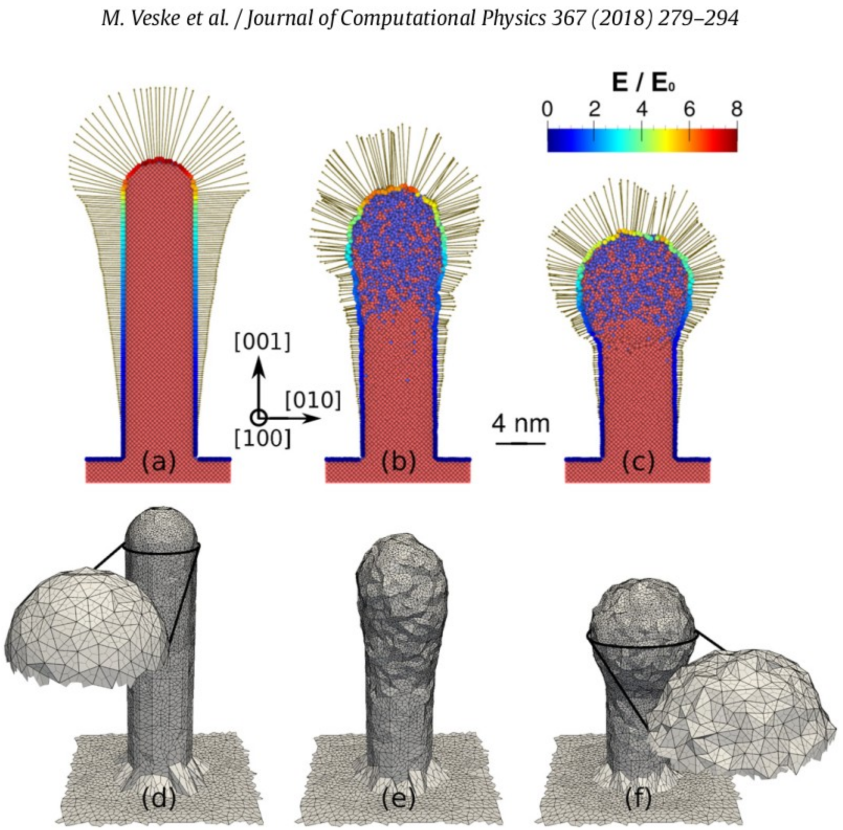

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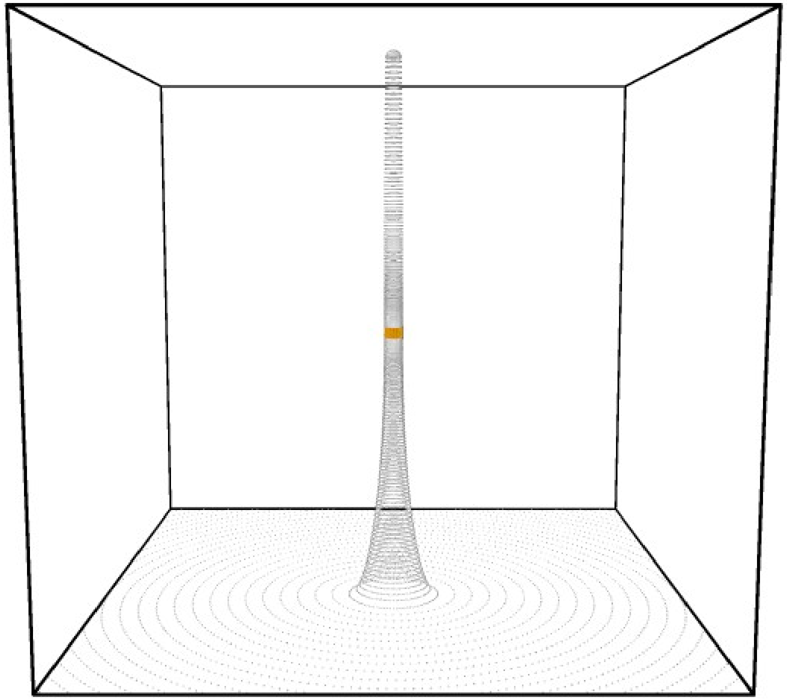
  - Cu {100} surface has relatively high migration energy barriers, ~0.5 eV
  - **Accelerated dynamics**

Extending the electrostatic system



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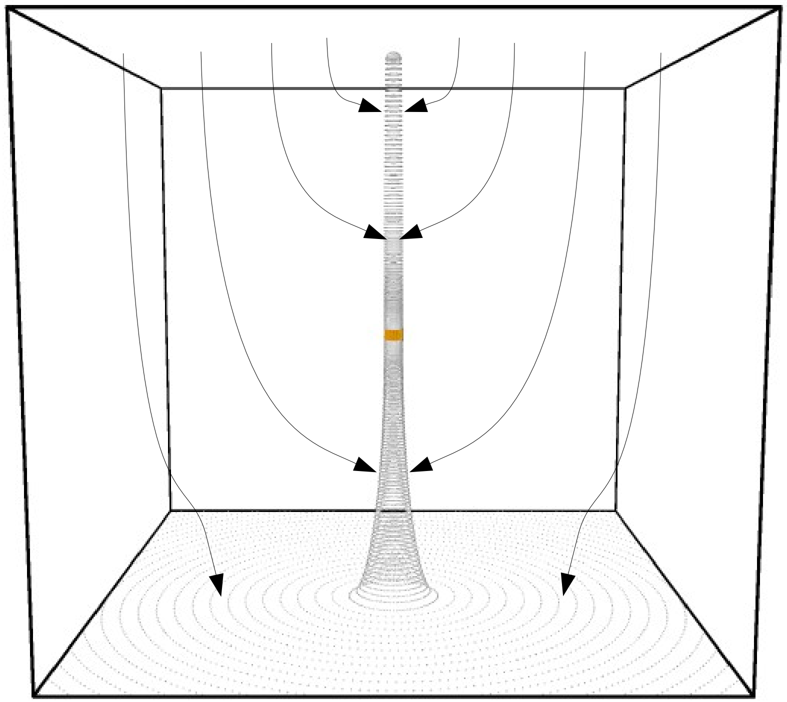

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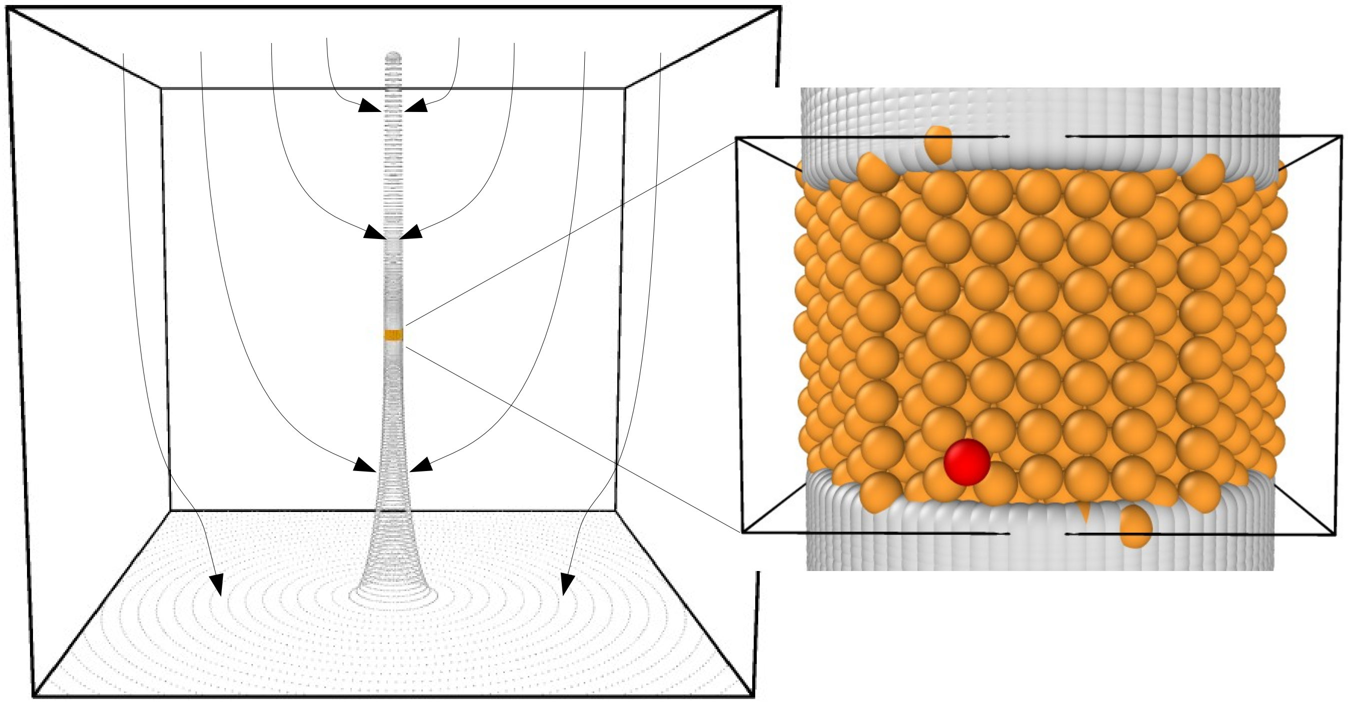

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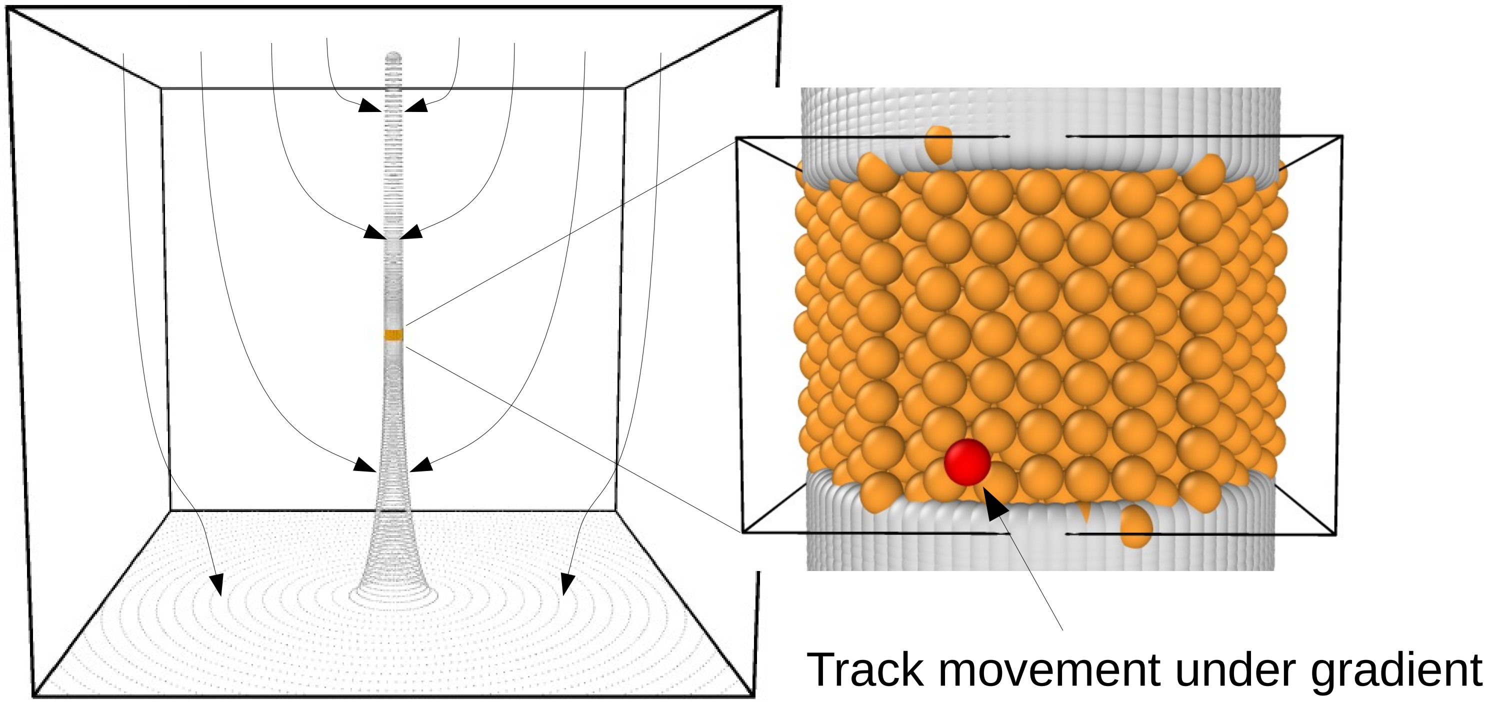

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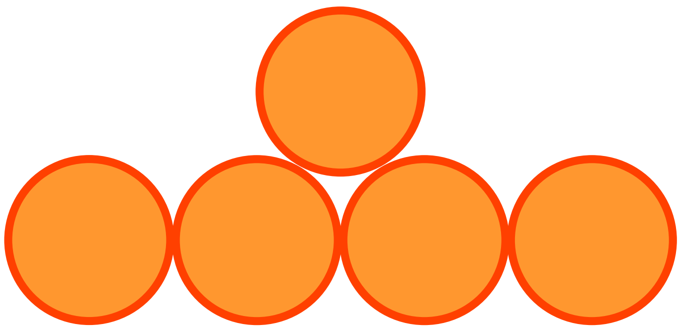

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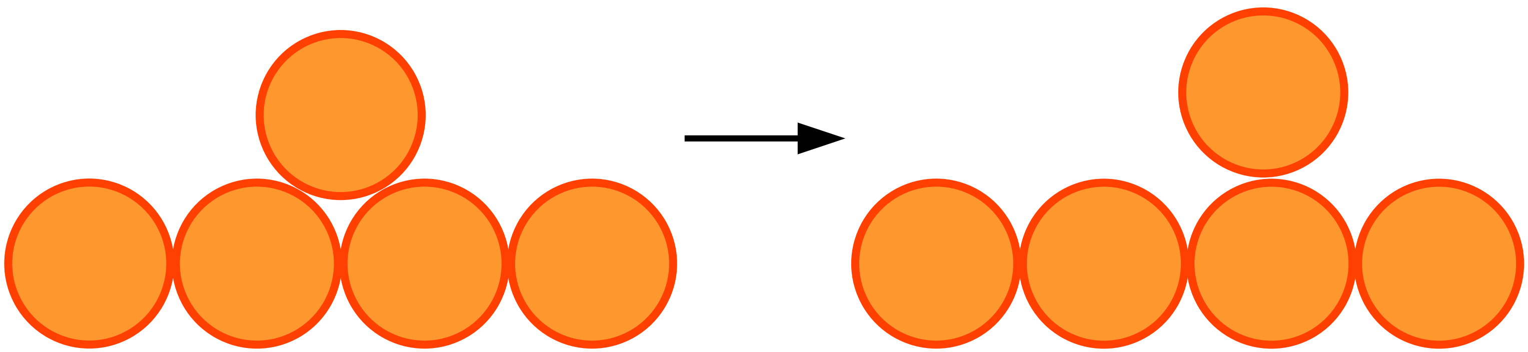

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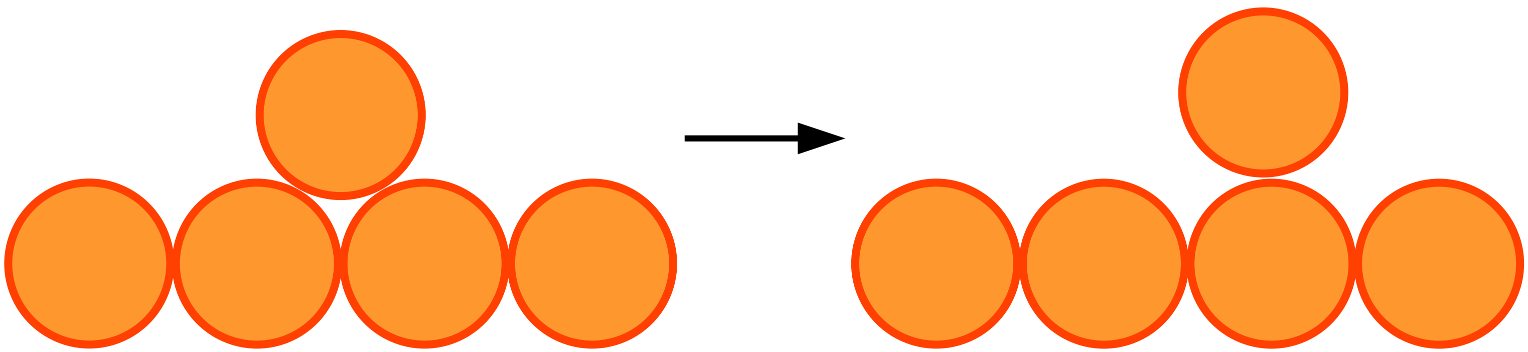

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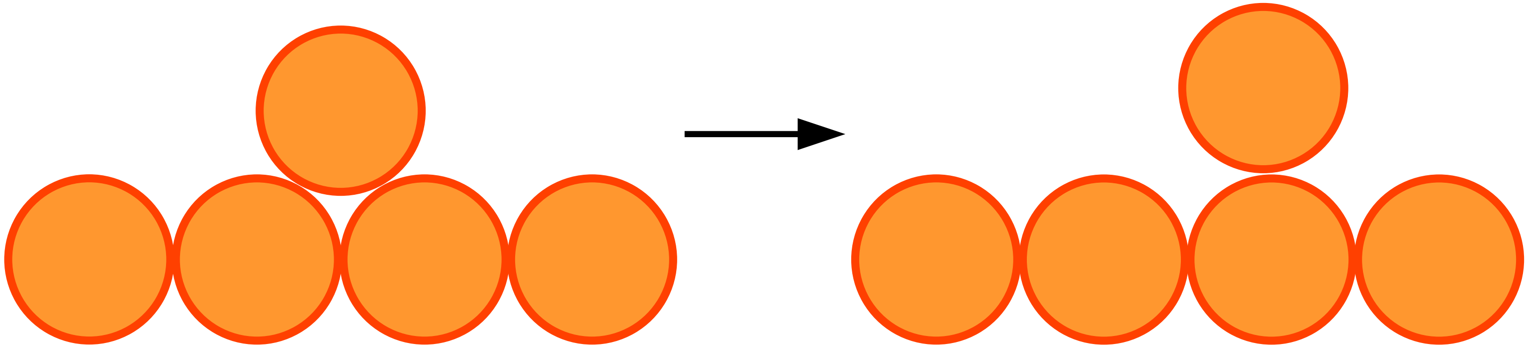

At equilibrium, $\eta \approx 0$

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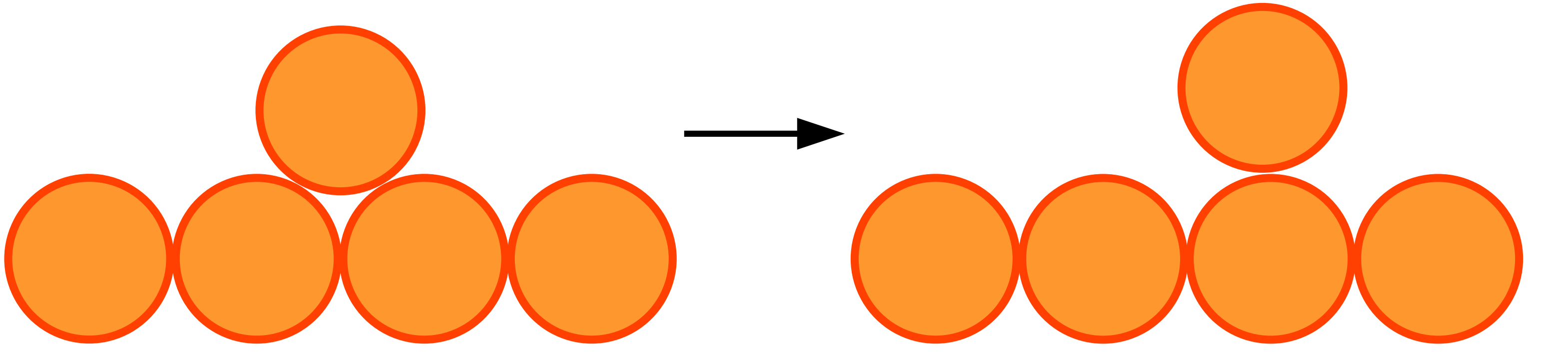

At equilibrium, $\eta \approx 0$

Almost at saddle point, $\eta \approx 1$

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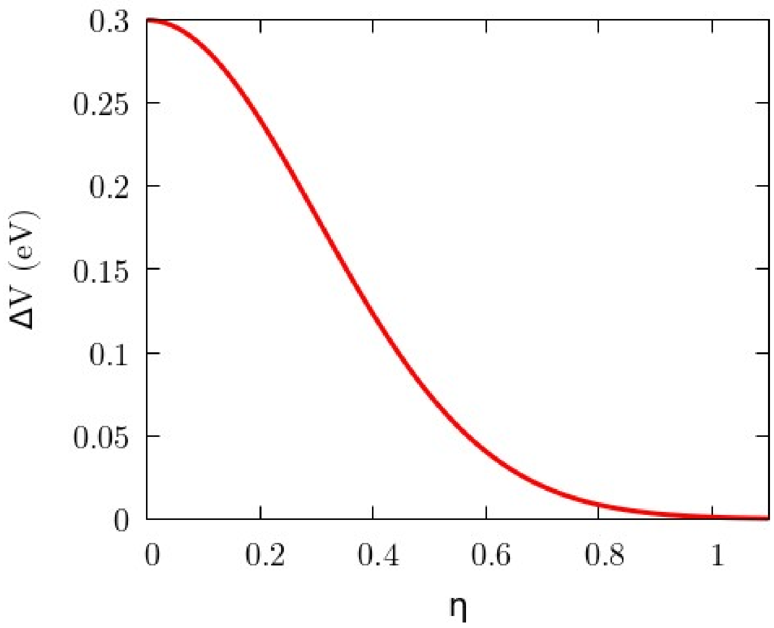
Yanking the system toward events



K. M. Bal and E. C. Neyts, *J. Chem. Theory Comput.* **11**, 4545 (2015).

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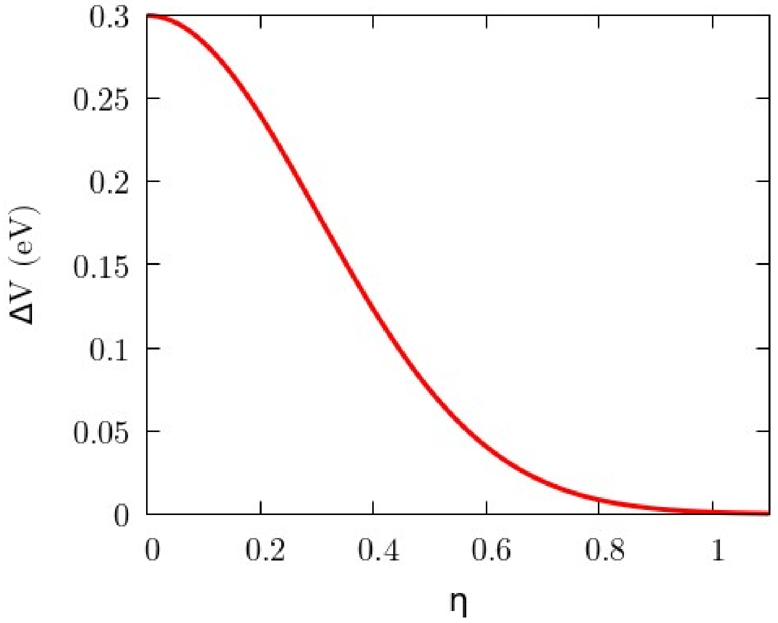

Total potential energy:

$$V'(\boldsymbol{R}) = V(\boldsymbol{R}) + \Delta V(\eta)$$

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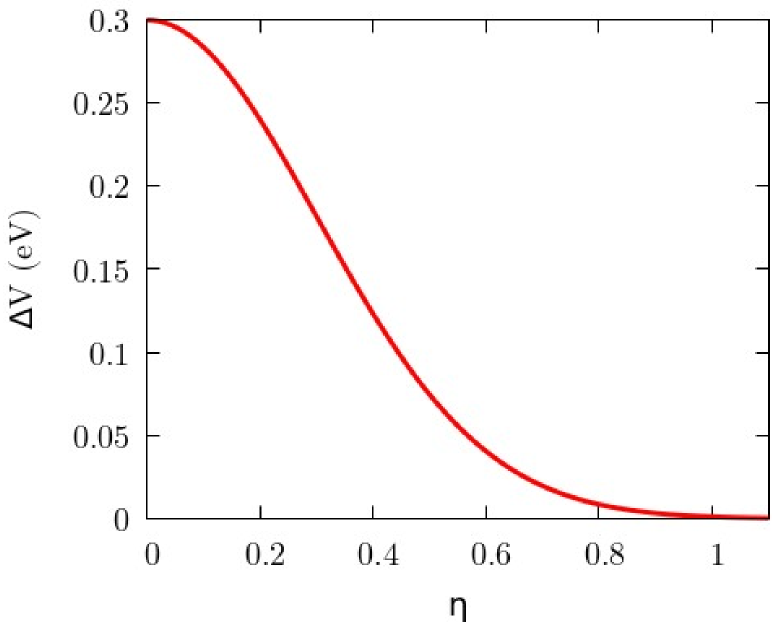

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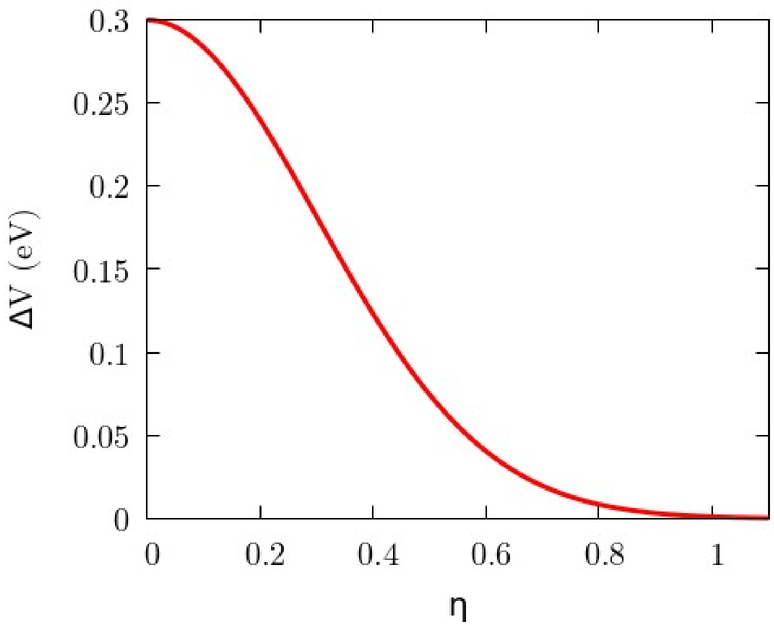

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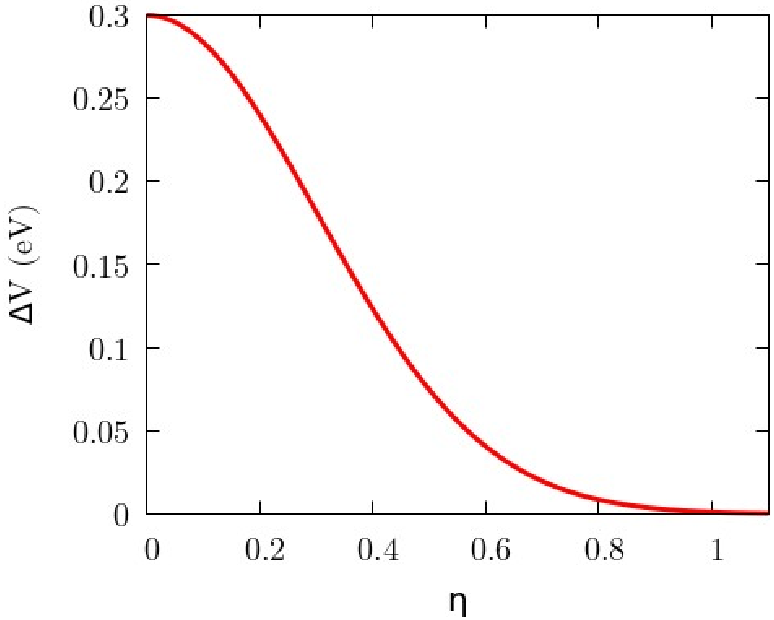

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Timestep stretch:

$$\Delta t_{\mathrm{CVHD}} = \Delta t_{\mathrm{MD}} \left\langle \exp\left(\frac{\Delta V}{k_{\mathrm{B}} T} \right) \right\rangle$$

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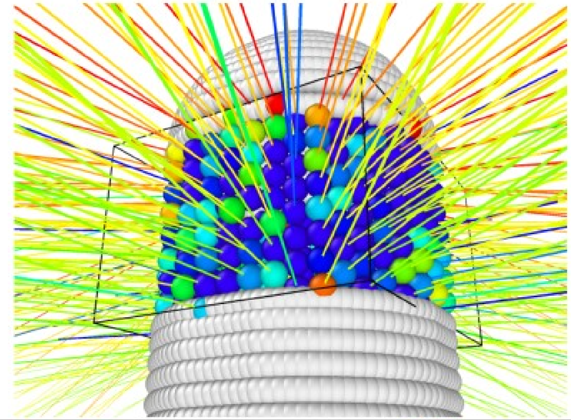
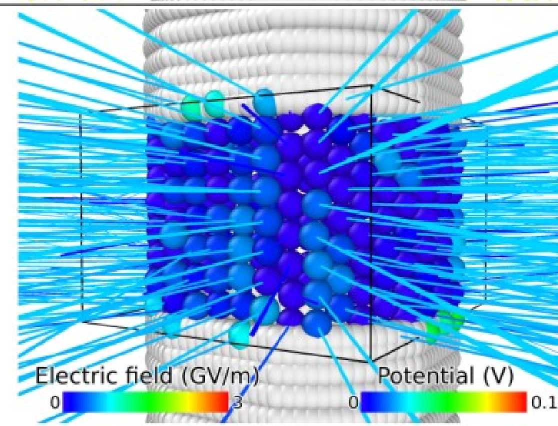
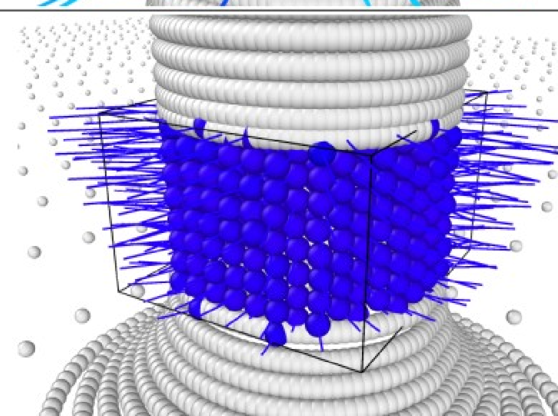
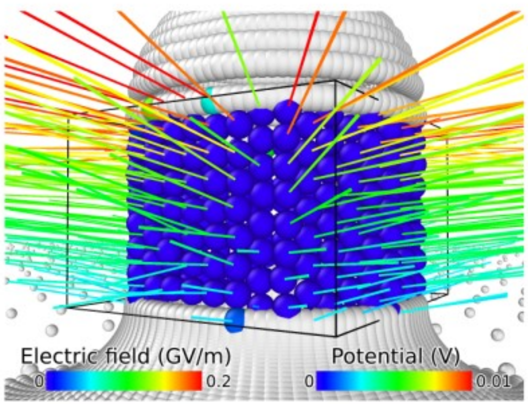
Field solutions

- Field solutions in different geometries at applied field 100 MV/m



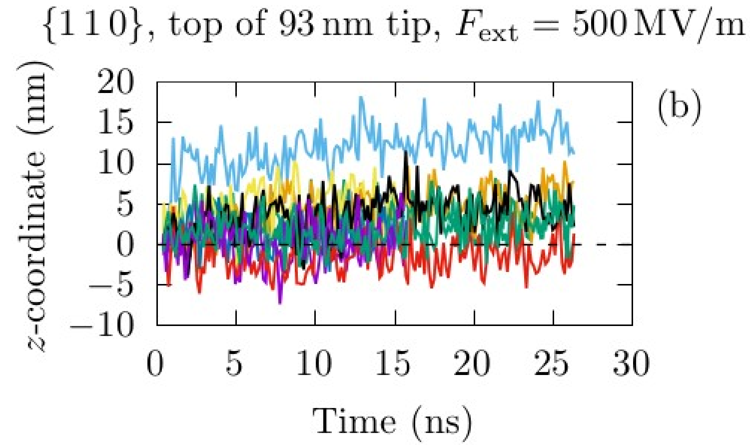


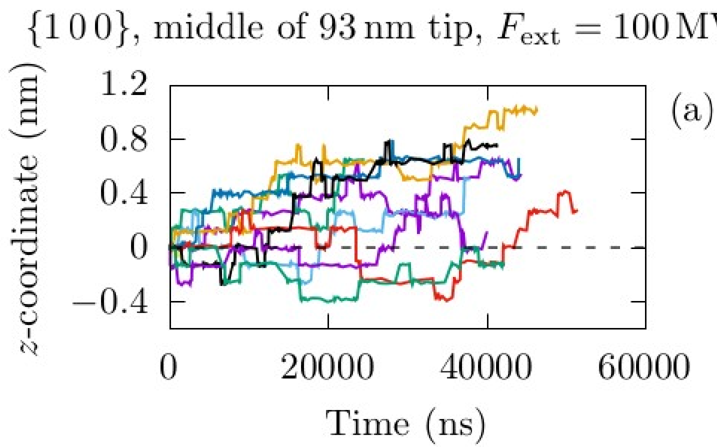


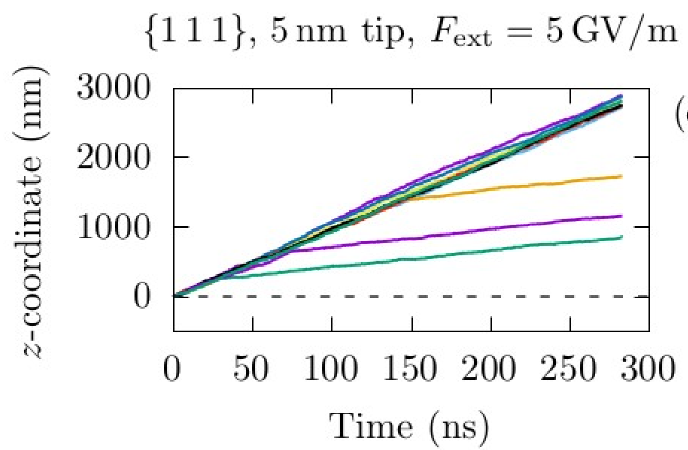


Trajectories of adatoms

- Ten repeats for each geometry, surface and applied field

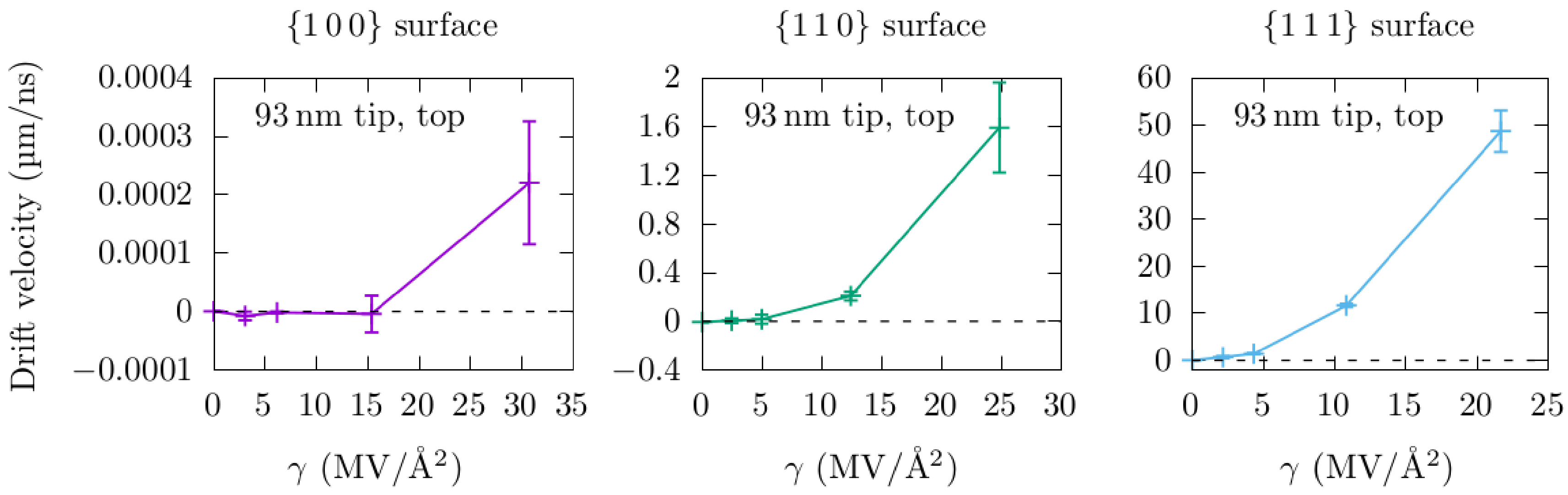






All surfaces display biased diffusion

- "Drift velocity" = final displacement divided by simulation time



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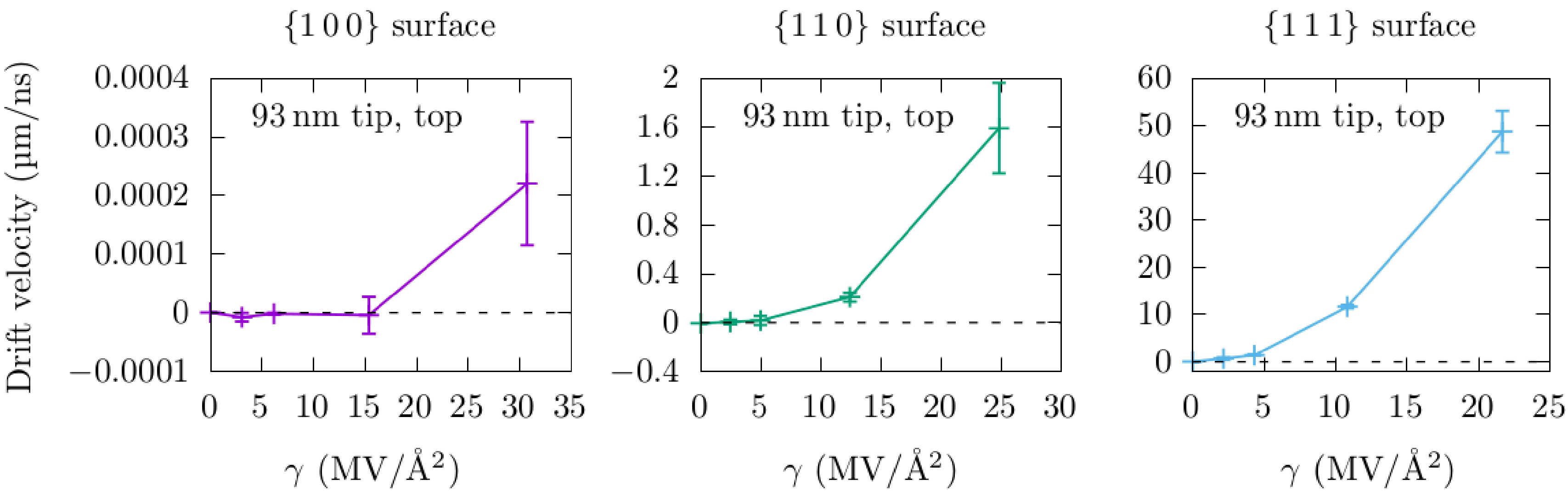

? $$E_m \approx E_m(0) - \mathcal{M}_{sl} F - \frac{\mathcal{A}_{sl}}{2} F^2 - \mathcal{M}_{sr} \Delta F - \mathcal{A}_{sr} F \Delta F$$?

dipole moment

polarizability

Fitting theoretical prediction

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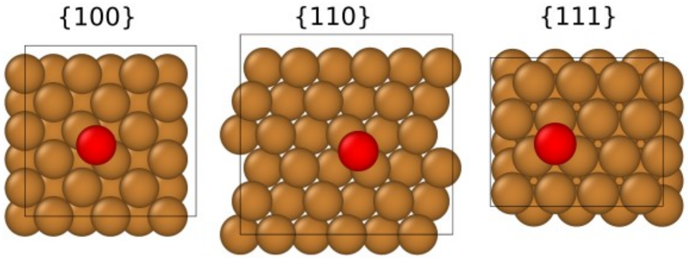
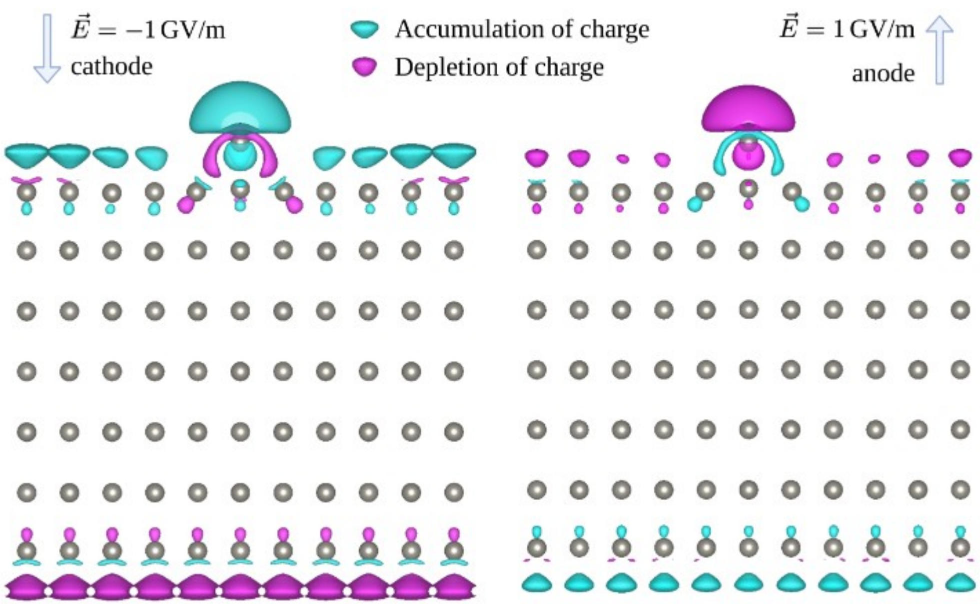
- Combining these, we can **fit $\mathcal{M}_{\mathrm{sr}}$ and $\mathcal{A}_{\mathrm{sr}}$ to the MD results**

Polarization parameters from density functional theory

- $\mathcal{M}_{\mathrm{sr}}$ and $\mathcal{A}_{\mathrm{sr}}$ directly *ab initio*





E. Baibuz et al., 10.48550/arXiv.2201.03460 (2022).

MD+electrostatics vs DFT

- Dipole moment $\mathcal{M}_{sr}$ error is expected
- Polarizability $\mathcal{A}_{sr}$ underestimated in MD, **possibly due to different geometry** (nanotip in MD, slab in DFT)

Surface	$\mathcal{M}_{sr}$ (eÅ)		$\mathcal{A}_{sr}$ (eÅ²/V)	
	MD	DFT	MD	DFT
{100}	0.0 ± 0.2	0.106 ± 0.003	0.1 ± 0.1	0.27 ± 0.02
{110}	–0.008 ± 0.005	0.094 ± 0.006	0.034 ± 0.008	0.30 ± 0.04
{111}	–0.016 ± 0.006	0.162 ± 0.003	0.02 ± 0.01	0.23 ± 0.02

Summary and outlook

- Biased diffusion captured in atomistic simulation
- Polarization physics can be directly compared to density functional theory
- Outlook:
  - Verify results on slab surface
  - Larger scale simulations – actual mass transport
  - Combine accelerated molecular dynamics with plasma formation dynamics in Femocs…?
- All details: J. Kimari et al., *J. Phys. D: Appl. Phys.* (in press). DOI: 10.1088/1361-6463/ac91dd