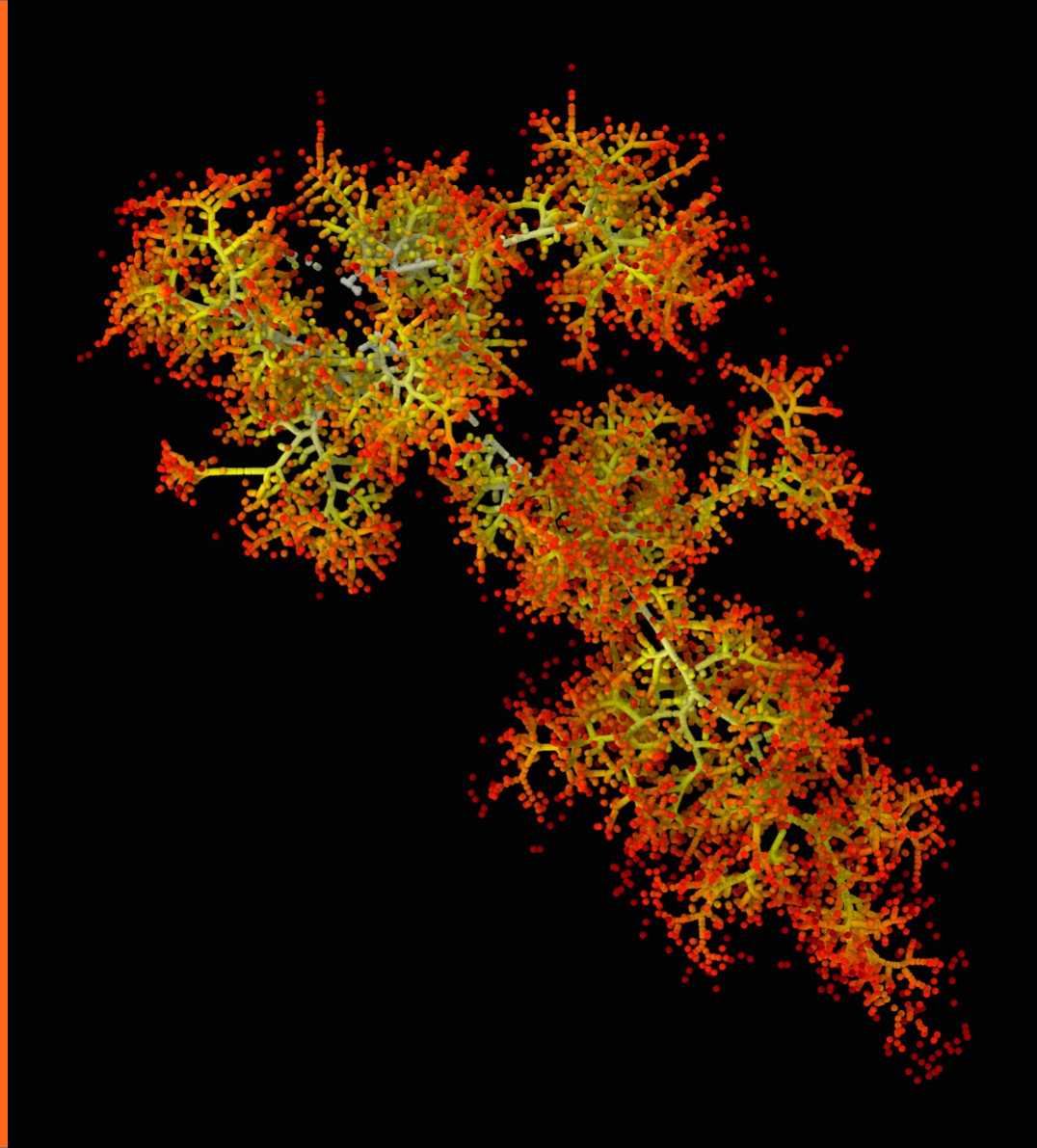
Atomistic modelling for radiation damage in space

Andrea E. Sand
Aalto University

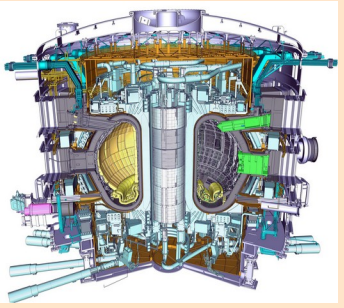
Aalto University
School of Science



My background

PhD in physics
University of Helsinki, 2015
Supervisor: Prof. Kai Nordlund

Eurofusion Research Fellow 2016 – 2017
Culham Centre for Fusion Energy (UK)
and University of Helsinki



Academy postdoctoral fellow 2017-2020
University of Helsinki,
Research visit to LLNL

Assistant professor at Aalto 2021

Aalto University
School of Science

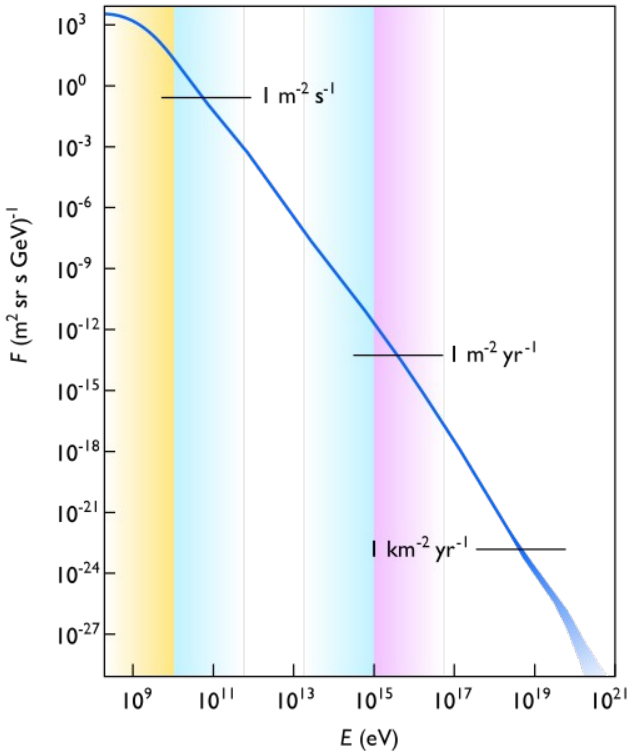
NuME

Contents

- Interactions of cosmic radiation with matter
- Modelling radiation damage with molecular dynamics
- Electronic effects in radiation damage beyond nonlocal stopping power
- Adding electronic effects to MD - parametrising energy loss with TDDFT
- Verification and application in materials

Cosmic radiation

- Primary cosmic rays
  - 99% atomic nuclei
    - 90% protons
    - 9% alpha particles (helium nuclei)
    - 1% heavier nuclei
  - 1% electrons
- Electromagnetic radiation of various energies (gamma rays, X-rays, UV,...)
- Causes damage to electronics and to biological organisms outside a protective atmosphere, ionizes molecules leading to chemical reactions



Cosmic flux versus particle energy at the top of Earth's atmosphere

Electron-matter interactions

- Damage from individual energetic electrons may be negligible for atomic displacements
  - Relevant for ionization effects
- Electron beams (e.g. in electron microscopes) can collectively affect atomic structure
  - May occasionally cause individual displaced atoms
  - A more pronounced effect is seen on the existing radiation damage
  - Heating and higher probability of large fluctuations affects disordered structures
  - Loss of defects observed under the electron beam compared to outside the electron-irradiated region
- Energy transfer in collisions can be calculated with classical kinematics including relativistic corrections, giving the energy of the (nonrelativistically) recoiling atom with mass M as

$$T = \frac{2E_\mathrm{i}}{Mc^2}\left(E_\mathrm{i} + 2m_0c^2\right)\sin^2\frac{\phi}{2}$$

where m_0 is the electron rest mass, E_i the electron energy, c the speed of light

Atom-atom interactions

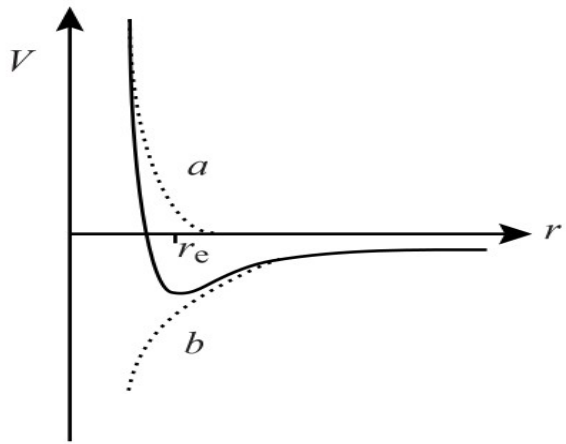
- Interaction of atomic projectiles with target atoms is governed by the interatomic potential
  - For close interactions, repulsive Coulomb interaction between charged particles

$$V(r) = \varepsilon^2 / r$$

  - At distances where the electron clouds screen the nuclei from each other, the repulsive potential can be described by multiplying the Coulombic repulsion between nuclei with a screening function φ(r/a)

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Z_1 Z_2 e^2}{r}\varphi(r/a)$$

    where φ(r/a) → 1 when r → 0
  - Attractive bonding at longer distances



Energy loss theory

- Particles lose energy as they travel through a material
- Average energy loss per unit distance travelled, -dE/dx, is called the **stopping power**

$$-dE/dx = NS(E); S = S_n + S_e$$

  where N is the atom number density and S is the stopping power in units of energy × distance squared (typically used especially in experimental papers)

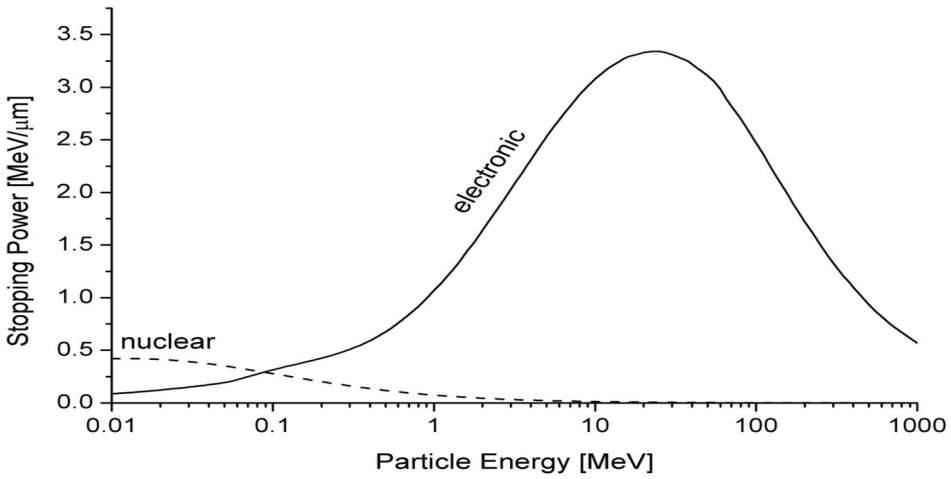
- The contributions to the stopping power are indexed according to

  n – nuclear interactions

  e – electronic interactions

Electronic stopping

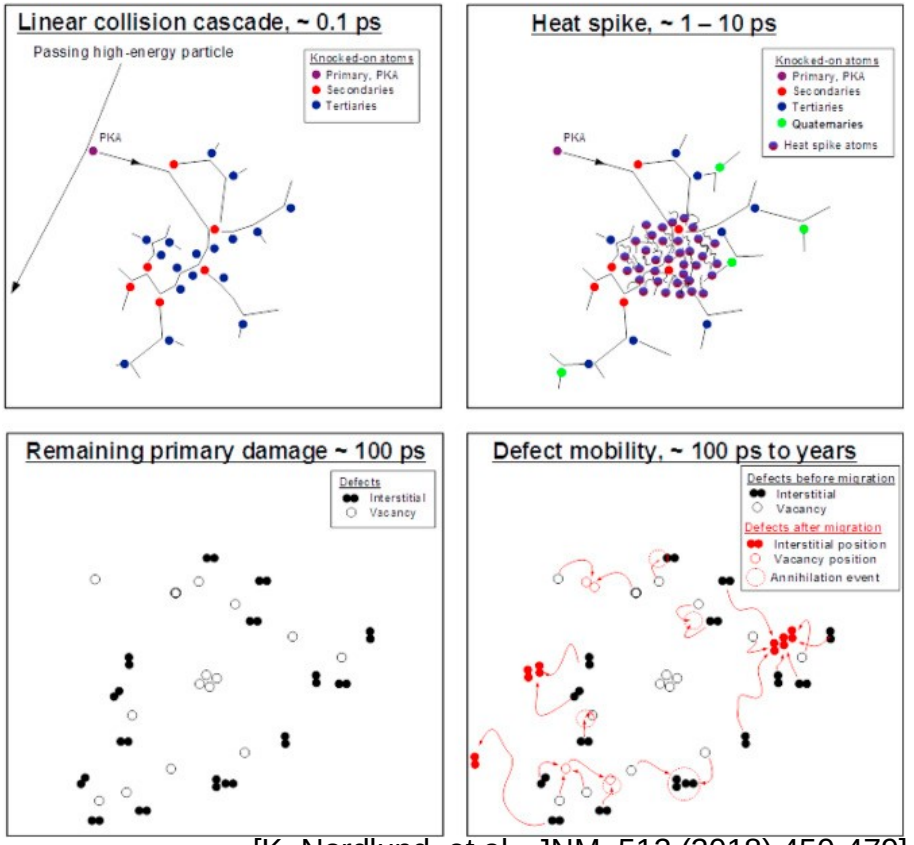
- Energy losses due to electrons, S_e, is called **electronic stopping**
  - Electronic excitation (electrons excited to higher energy states)
  - Ionization (electrons stripped from projectile or target atoms)
  - Brehmstrahlung at higher energies (emission of X-rays by electron passing through Coulomb field of a nucleus)



Electronic and nuclear stopping power for aluminum ions in aluminum, versus particle energy per nucleon.
By HPaul - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=1674656

Radiation damage in materials

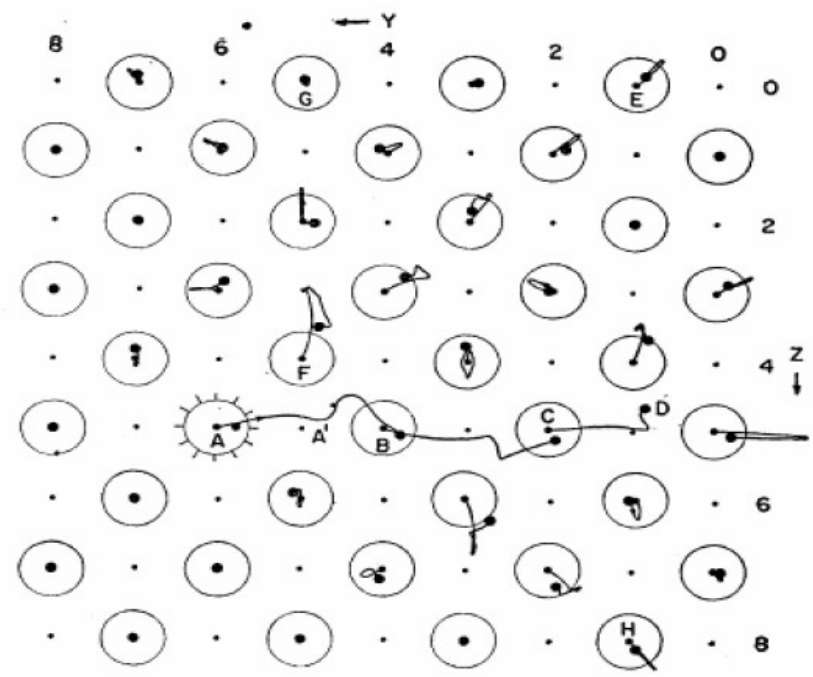
- The radiation damage event
  - A particle collides with an atom in the target material
    - **Primary knock-on atom (PKA**)
  - The atom is displaced
  - This (potentially) causes further collisions
    - Secondary, tertiary (and so on) recoils
    - This stage is called the collision cascade
  - Eventually all atoms come to rest
  - The surviving damage after the event is the **primary radiation damage**
- Time scale of the radiation damage event
  - First atomic displacement ~ ***femtoseconds***
  - Collision sequence comes to an end ~ ***picoseconds***
  - Thermal relaxation and possible annealing of damage ~ ***nanoseconds to years***



[K. Nordlund, et al., JNM, 512 (2018) 450-479]

Modelling radiation effects

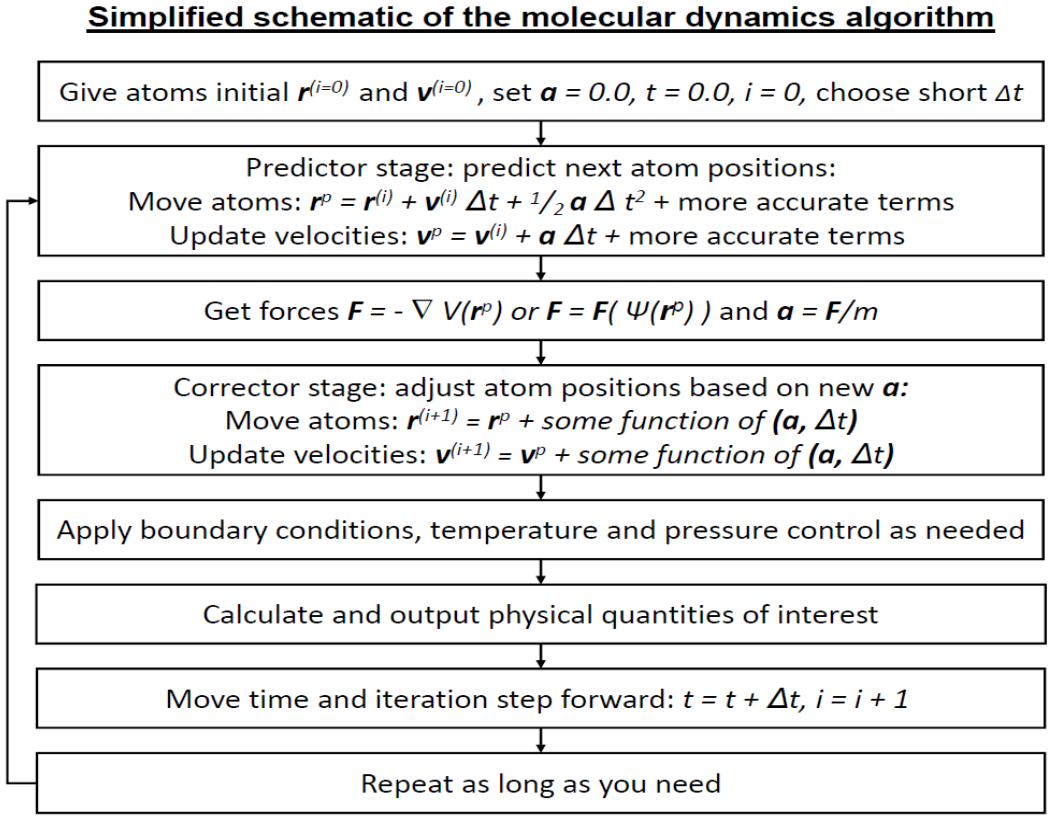
- The primary damage formation involves processes occurring on nanometer length scales and nanosecond timescales
  - Cannot be directly observed in experiment
- Molecular dynamics (MD) can be used to can be used to model directly all atoms involved in the radiation damage process
- Provides insight into the processes and final damage state
  - First MD simulation of radiation effects by Gibson in 1960 – found the replacement collision sequence (RCS)
  - RCS is a key formation process of a defect pair involving an atom hitting its neighbor, which hits its neighbor, and so on...



[Gibson, J B; Goland, A N; Milgram, M; Vineyard, G H (1960). "Dynamics of Radiation Damage". Phys. Rev. 120 (4): 1229–1253]

Molecular dynamics basics

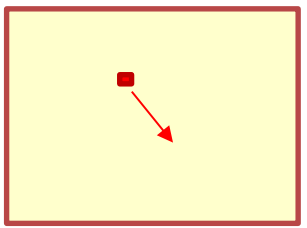
- Molecular dynamics (MD) involves numerically solving the equations of motion for all interacting particles
- Input consists of atomic positions (and velocities if desired), and the interatomic potential
- Evolution according to interaction model (interatomic potential or force field)



By Knordlun - With powerpoint, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=41419953

Non-equilibrium extensions to MD

- The basic MD algorithm is not suitable for high-energy interactions, and does not describe electronic stopping at all
- But over the last ~25 years augmentations of MD to be able to handle this have been developed
  - Variable integration time step
  - Handling short range interactions
  - Accounting for energy dissipation to surrounding material (thermostats)
  - Addition of electronic energy losses as a friction term
  - Still under development: electron-phonon coupling and electronic heat conduction
- Simulation idea: initiate primary knock-on atom, follow until near-equilibrium conditions

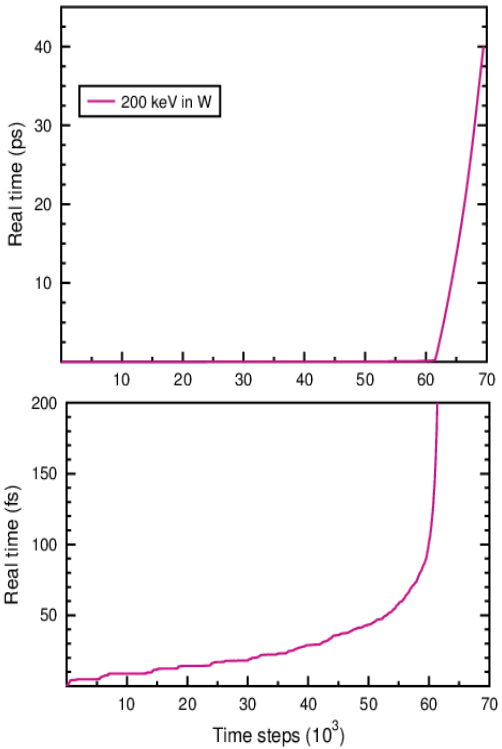


Variable time step

- Longer time step in integration gives faster simulations
- *BUT*: ions with initially very high kinetic energy travel fast and experience strong interactions
  - Time step needs to be exceedingly small for energy conservation and correct trajectories in early stage of damage event
- Solution: variable time step
- The following form for the time step has been demonstrated to be able to handle collisions with energies up to 1 GeV

$$\Delta t_{n+1} = \min\left(\frac{\Delta x_{\max}}{v_{\max}}\ ,\ \frac{\Delta E_{\max}}{F_{\max} v_{\max}}\ ,\ c_{\Delta t}\Delta t_n\ ,\ \Delta t_{\max}\right)$$

[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].



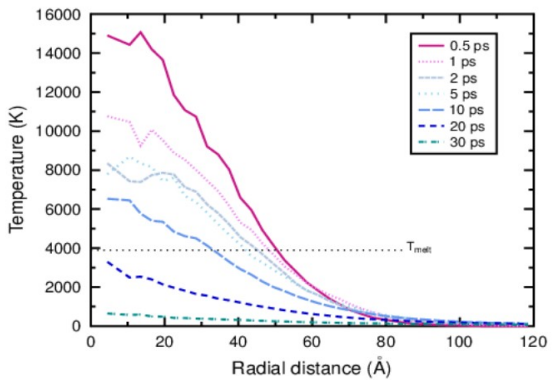
- Δx_{max} *is the maximum allowed distance moved* during any *t (e.g. 0.1 Å)*
- ΔE_{max} *is the maximum allowed* change in energy (e.g. 300 eV)
- v_{max} *and* F_{max} *are the* highest speed and maximum force acting on any particle at *t*, respectively
- $c_{\Delta t}$ prevents sudden large changes (e.g. 1.1), and Δt_{max} is the time step for the equilibrated system

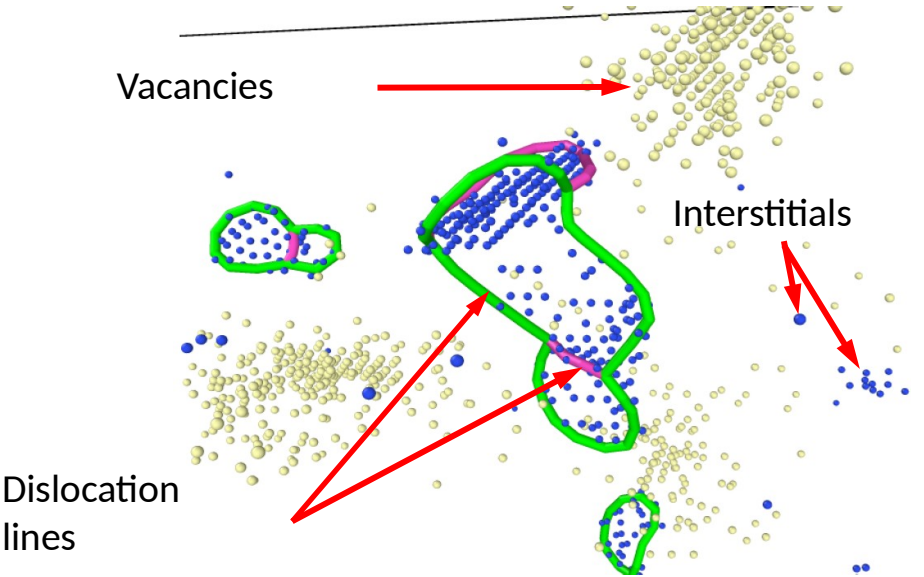
Interatomic potentials

- MD requires as input a description of the interaction between particles, i.e. the potential energy function *V(r)*
  - In chemistry and biology: force field; in physics: interatomic potential
- Different formalisms have different levels of physical accuracy
  - In semi-empirical potentials, quantum mechanical properties are approximated by a function, with free parameters fitted to empirical data such as elastic constants, cohesive energy, lattice parameter, vacancy formation energy, …
    - “empirical “ data can nowadays also be e.g. DFT calculations
    - May or may not be able to capture bonding (and bond breaking)
  - Quantum mechanical accuracy can be obtained with *ab initio* MD (AIMD)
    - Computationally heavy
  - ML potentials are increasingly being used for radiation damage simulations, but many challenges remain, particularly potential validation and computational cost

Interatomic potentials for radiation damage

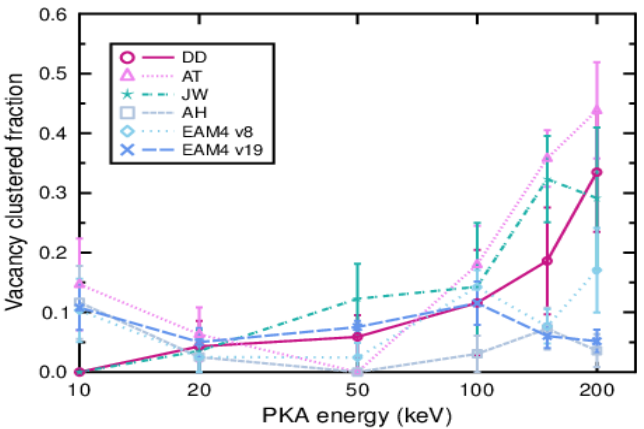
- For simulations of radiation damage formation, the material in a cascade region experiences a wide range of states
  - Molten heat spike region
  - Underdense core
  - Large pressure and temperature gradients
  - Crystal phase in surrounding material
  - Final defects in the crystal
- Sets strong requirements on the interatomic potential

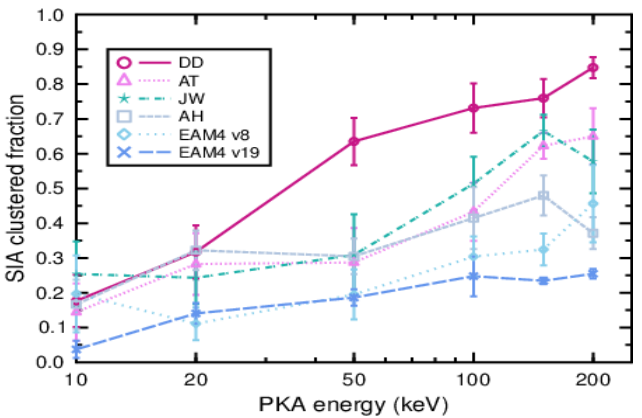




Uncertainty of potentials

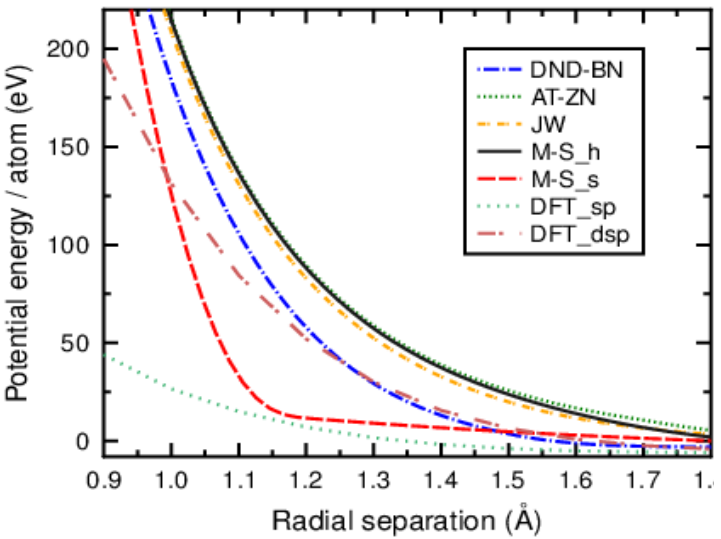
- Potentials with largely similar point defect formation and migration energies disagree regarding clustered fraction of defects for high PKA energies
  - This is an important aspect of the damage affecting subsequent evolution
- Potentials are being continuously developed and improved





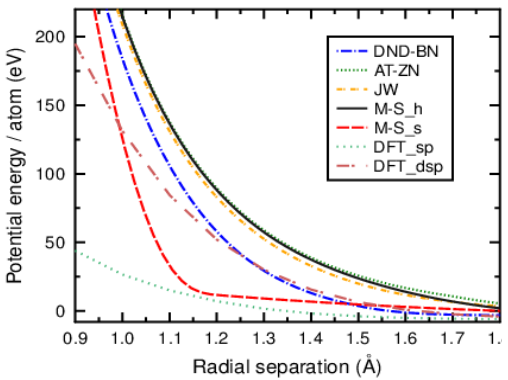
Stiffening of the potential

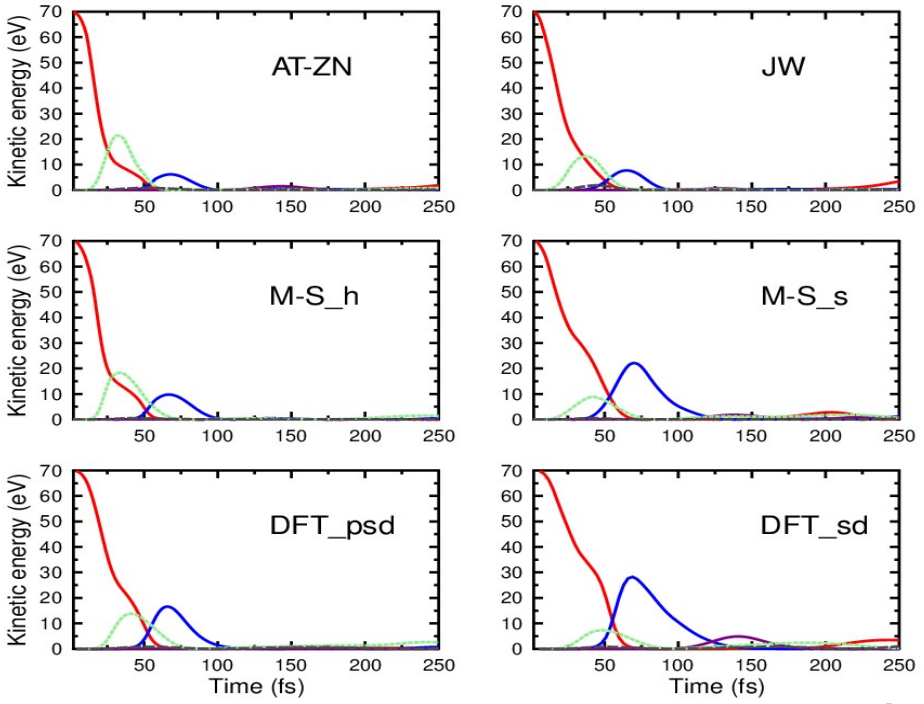
- Potentials fitted to equilibrium properties do not normally yield physical behaviour at short distances
- Close interactions well described by, e.g., the universal Ziegler-Biersack-Littmark (ZBL) potential
  - The two potentials must be smoothly joined
  - “smooth” can be done in many ways!
- Affects threshold displacement energy (TDE)
- Picture shows the intermediate range of a number of potentials for W dimer
  - All versions are smooth (continuous first and second derivatives)
  - All versions yield reasonable TDE
  - All versions **DO NOT** yield damage predictions in agreement with experiment

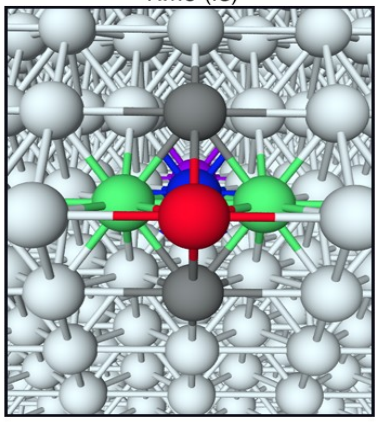


Impact of intermediate range

- Harder potential → more energy transferred to neighboring atoms; less to head-on atom
  - In general, DFT results including semi-core electrons agree with harder potentials







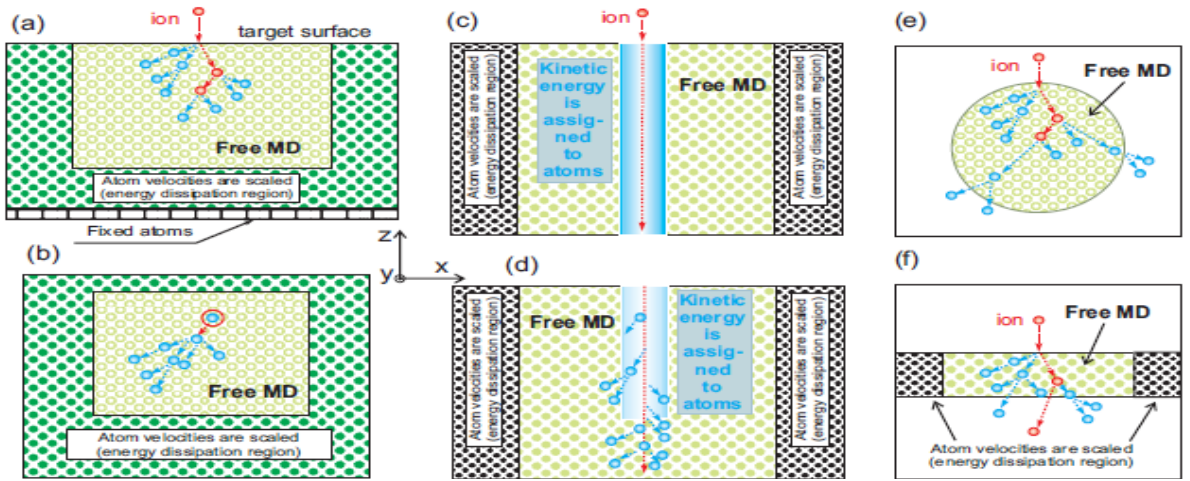
<101> recoil direction

[A. E. Sand et al., JNM **470** (2016)]

Use of thermostats

- Central part of the cell has to be in NVE ensemble, but on the other hand extra energy/pressure wave introduced by the ion or recoil needs to be dissipated somehow
- Exact approach to take depends on physical question:

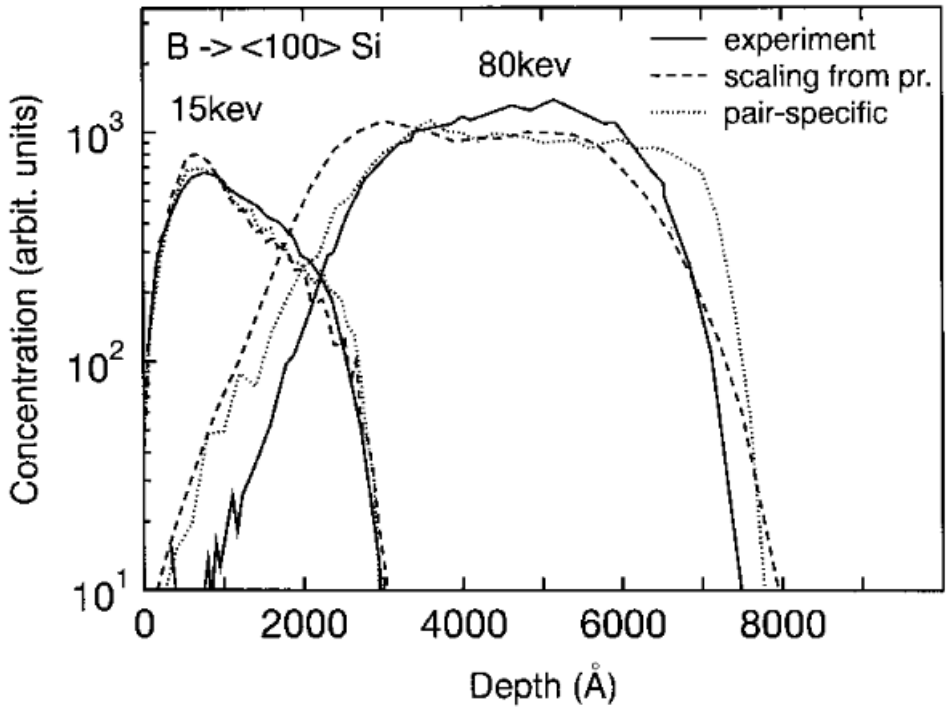
a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster or molecule, f) nanowire



[A. V. Krasheninnikov and K. Nordlund, J. Appl. Phys. (Applied Physics Reviews) 107, 071301 (2010)]

Electronic stopping in MD

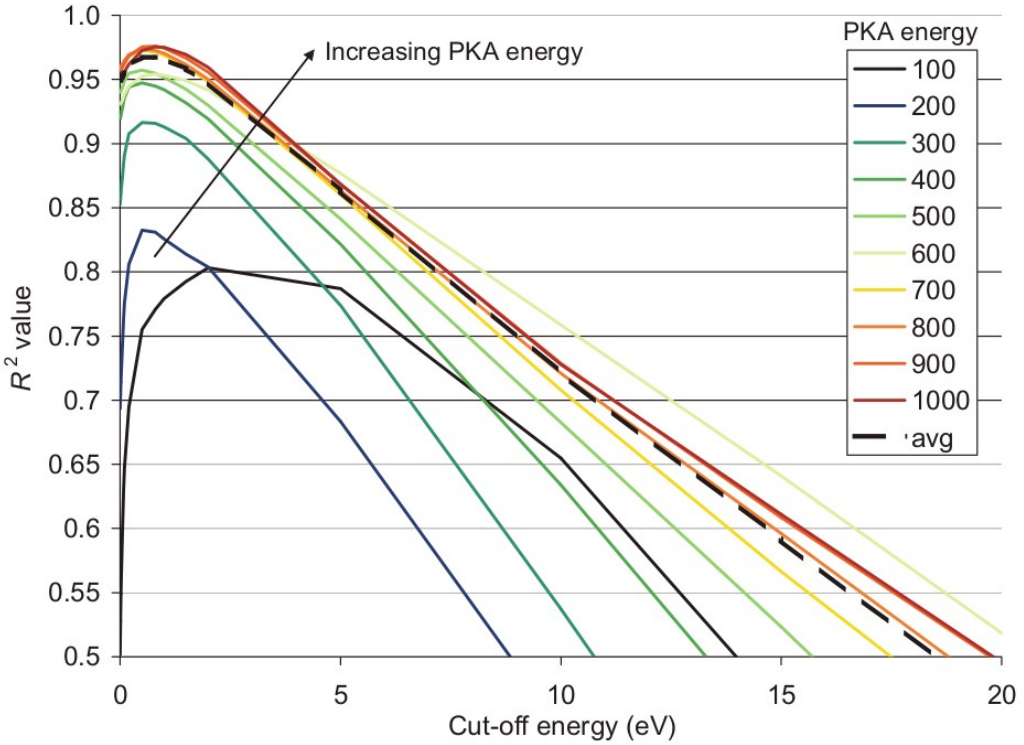
- Electronic stopping can be included as a frictional force applied to energetic atoms in MD
- Obtained e.g. from SRIM semi-empirical model (theories and corrections with free parameters fitted to experimental data)
  - No theoretical lower velocity/energy limit
- Comparison with atomistic simulations directly to ion range experiments shows good agreement
  - The ion is moving at > eV energies through a “perfect” crystal
- A **cut-off energy**, below which stopping is not applied, is necessary in standard MD simulations (else all thermal modes are quenched)
  - Usually chosen to be above thermal/cohesive energies
  - 10 eV or 2*E_{coh}



[J. Sillanpää, et al., Phys. Rev. B 63, 134113 (2000)]

Electronic stopping threshold

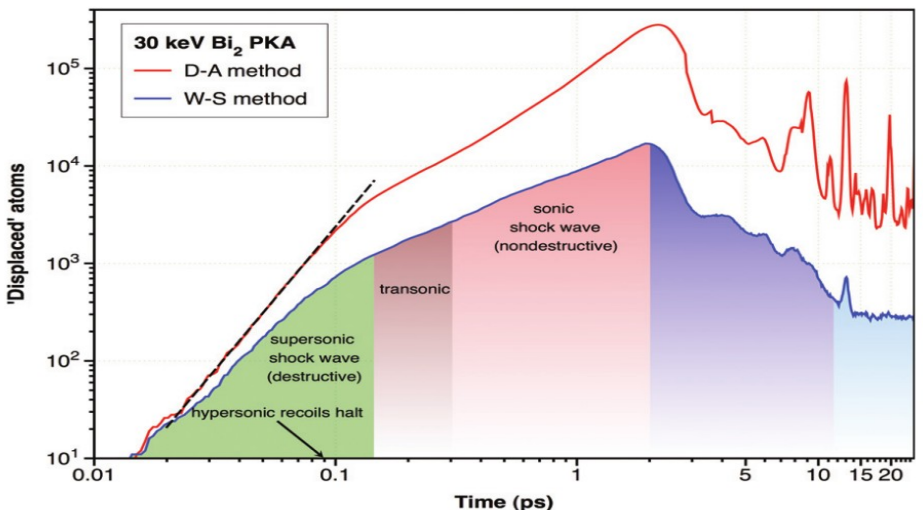
- Comparison of non-adiabatic energy losses between classical MD with friction term and quantum-classical Ehrenfest calculation
  - constant electronic stopping with a cut-off is not entirely satisfactory
  - best agreement found for a cut-off slightly below 1 eV



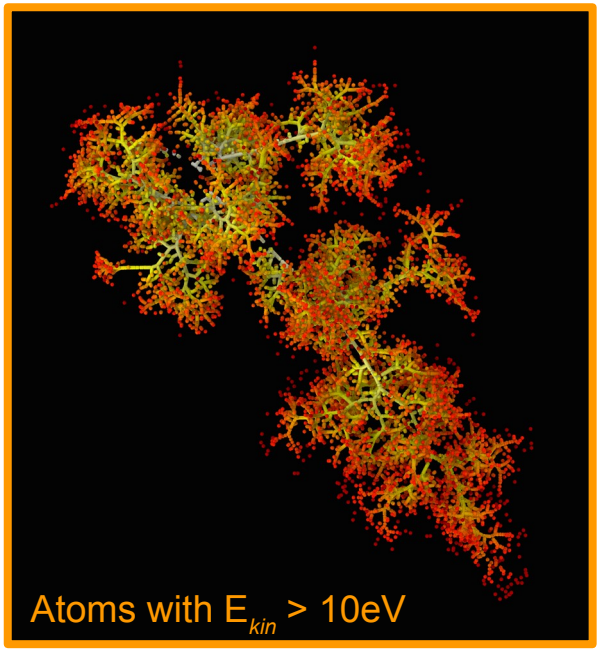
[Page et al. New Journal of Physics 11 (2009) 013004]

Stages of cascade development

1) Initial “ballistic” stage, characterized by a few energetic recoils penetrating undisturbed regions of the material
   - Energetic atoms lose energy to electronic stopping
2) Heat spike phase is characterized by the development of a disordered “liquid-like” core
3) Cooling and recrystallization



[Calder, et al. Phil. Mag. 90 (2010) 863-884]



200 keV collision cascade in W, atoms colored according to time, from 0 fs to about 100 fs.

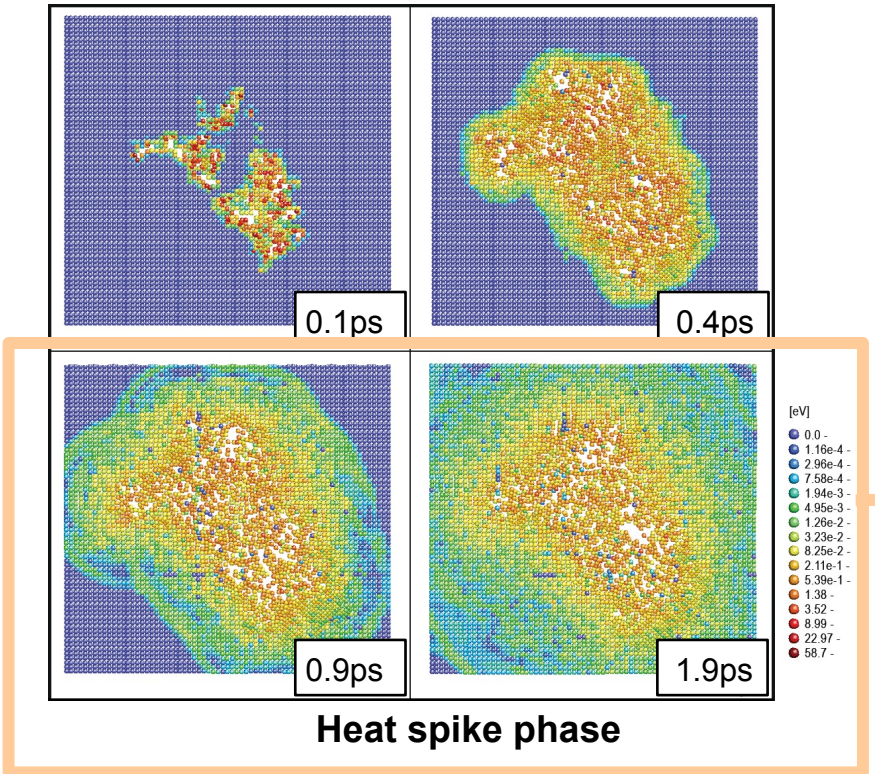
High energy cascade

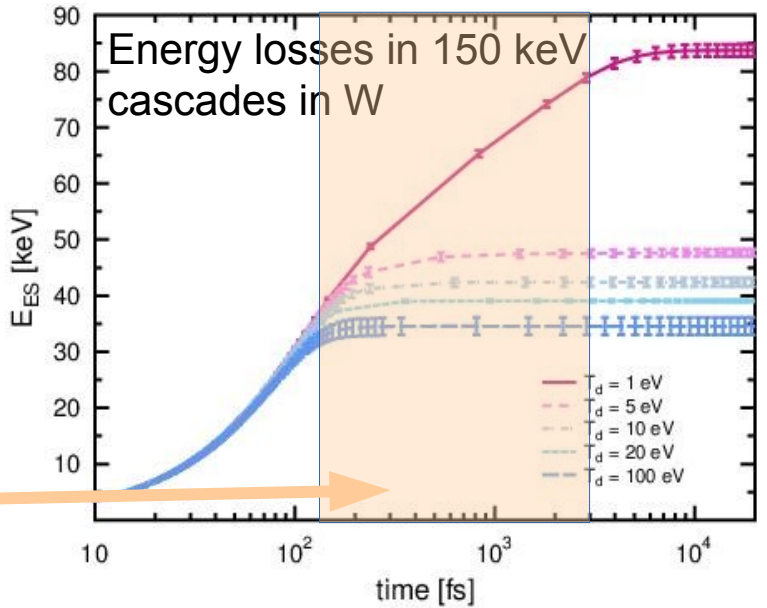


150 keV cascade in W



Energy losses during heat spike

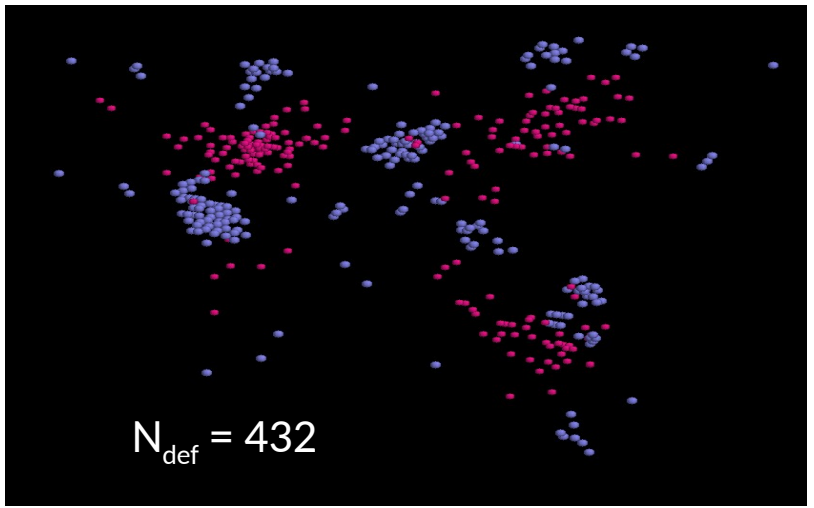


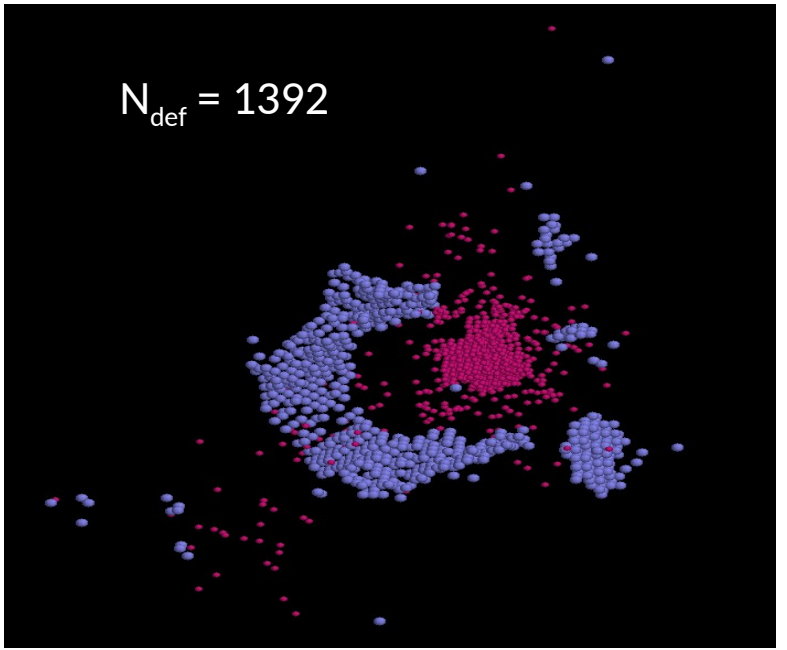


- Continuous transition from ballistic to near-equilibrium energy regime
- Many atoms can have energies > 1 eV even during the heat spike phase

Variation in cascade damage

- Cascades vary immensely!
- Illustrated: 200 keV cascades in W, identical initial conditions except for direction of recoil (no systematic dependence on direction)
- **We cannot look at single cascades for validation!**

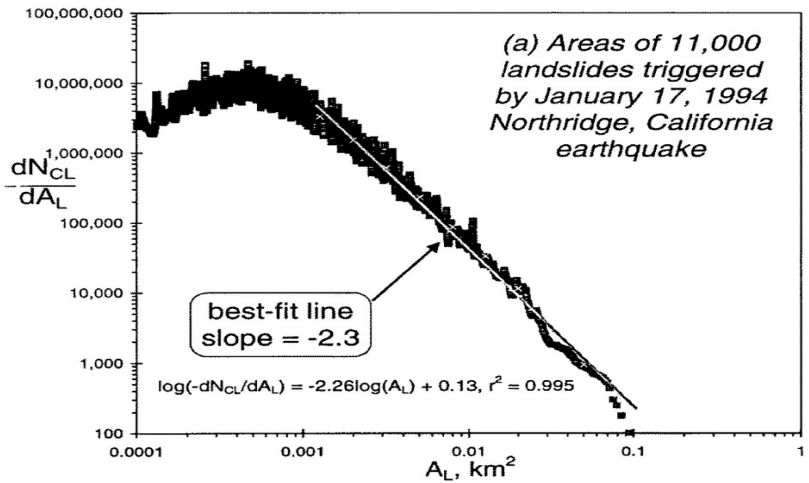




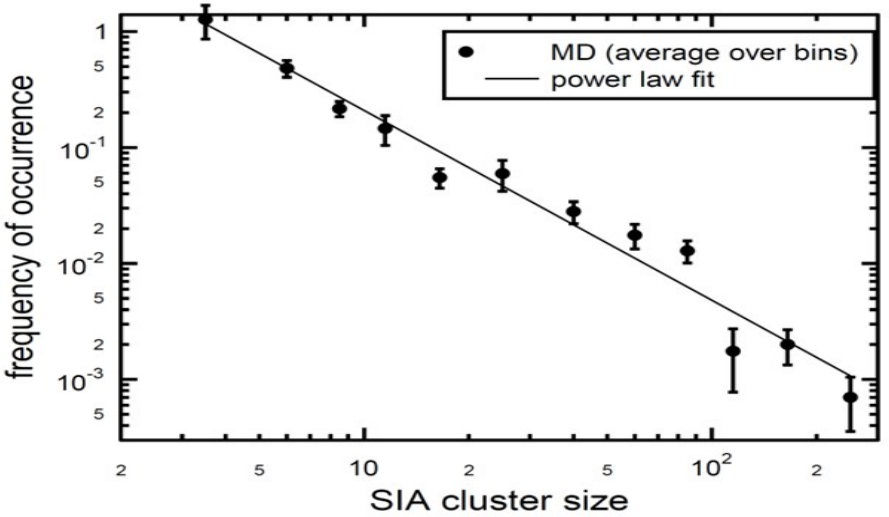
- In many cases, data is not normally distributed
  - Mean and variance not necessarily well defined!

Power law distributions

- We find a power law distribution of defect cluster sizes
  - Typical of self-organized critical phenomena
  - Other examples: earthquakes, landslides, forest fires
  - Rare events statistically significant



[Turcotte, Rep. Prog. Phys. **62** (1999) 1377–1429]

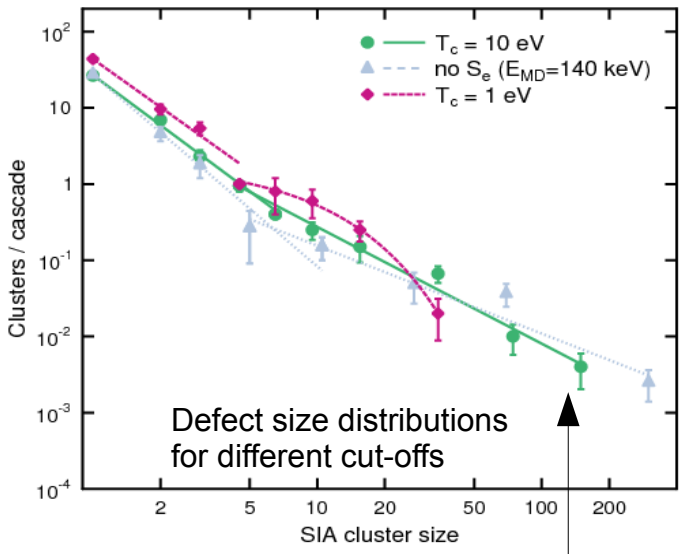


[A. E. Sand, S. L. Dudarev, and K. Nordlund, EPL **103**, 46003 (2013)]

- Although large clusters form rarely, they contain most of the defects
- Significant impact on defect evolution
- Exponent < 2 : no well defined average size

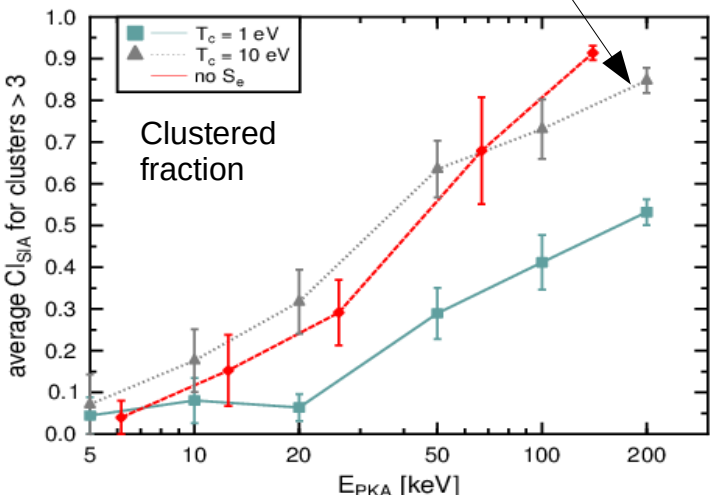
Effects of energy losses

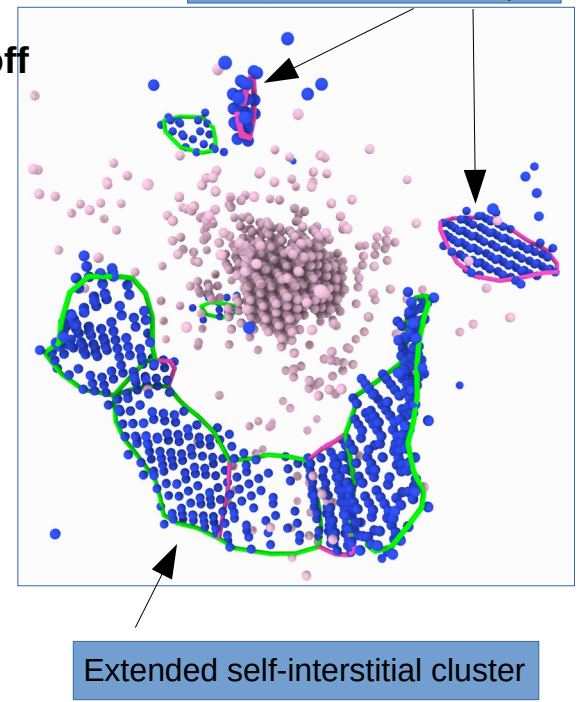
- Different thresholds for electronic stopping give completely different predictions of damage morphology



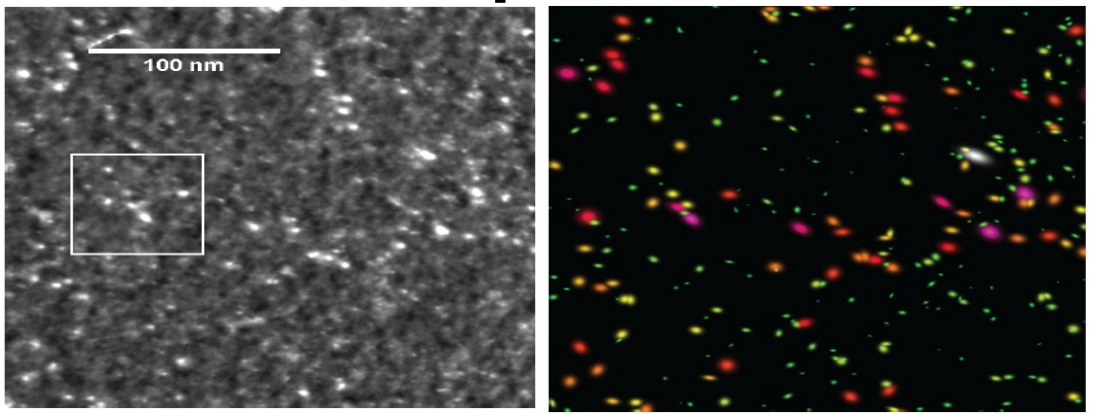
Larger defects with 10 eV cut-off

More clustering with 10 eV cut-off

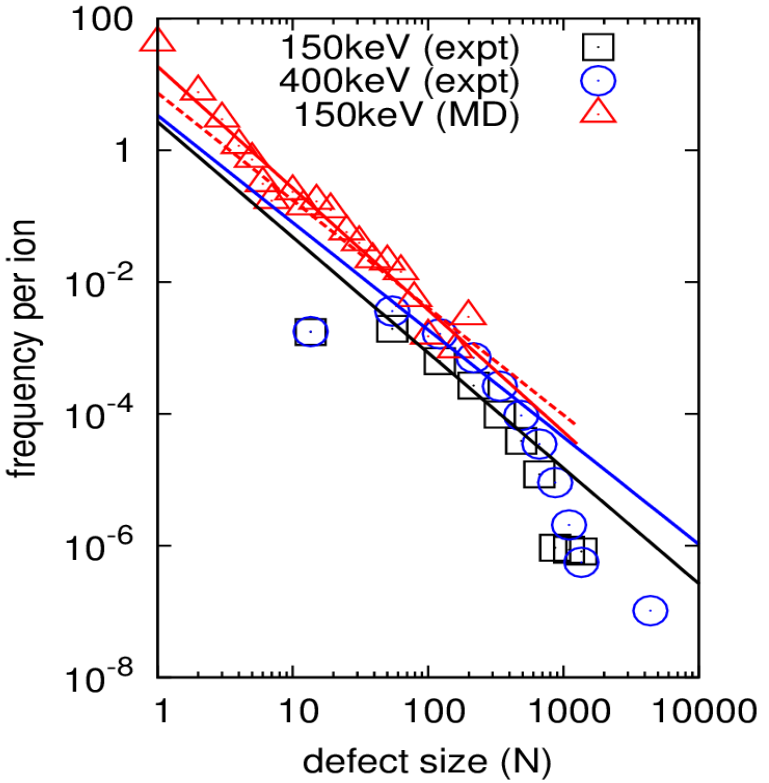




Experimental validation



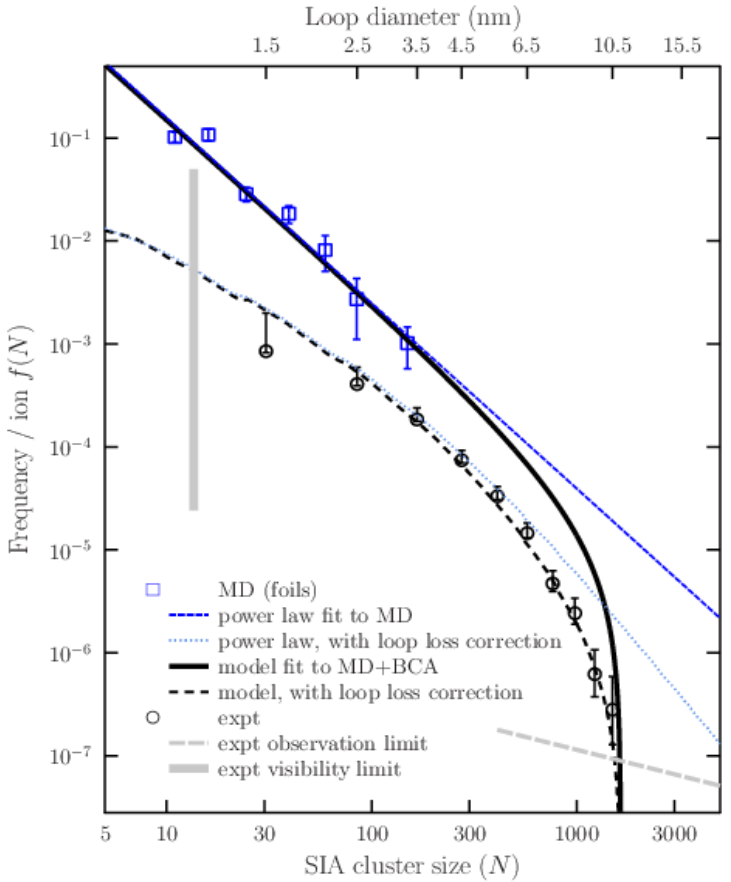
[X. Yi, A.E. Sand, D.R. Mason, M.A. Kirk, S.G. Roberts, K. Nordlund and S.L. Dudarev, EPL **110** (2015) 36001]



- Automated analysis of in-situ TEM
- Experiments performed at 30 K
  - Reduced defect mobility
  - Some loop loss
  - No visible growth of defects
- Good agreement over several orders of magnitude in size
  - But experiment shows deviation in tail of distribution, below MD ”visibility”

Defect size distribution

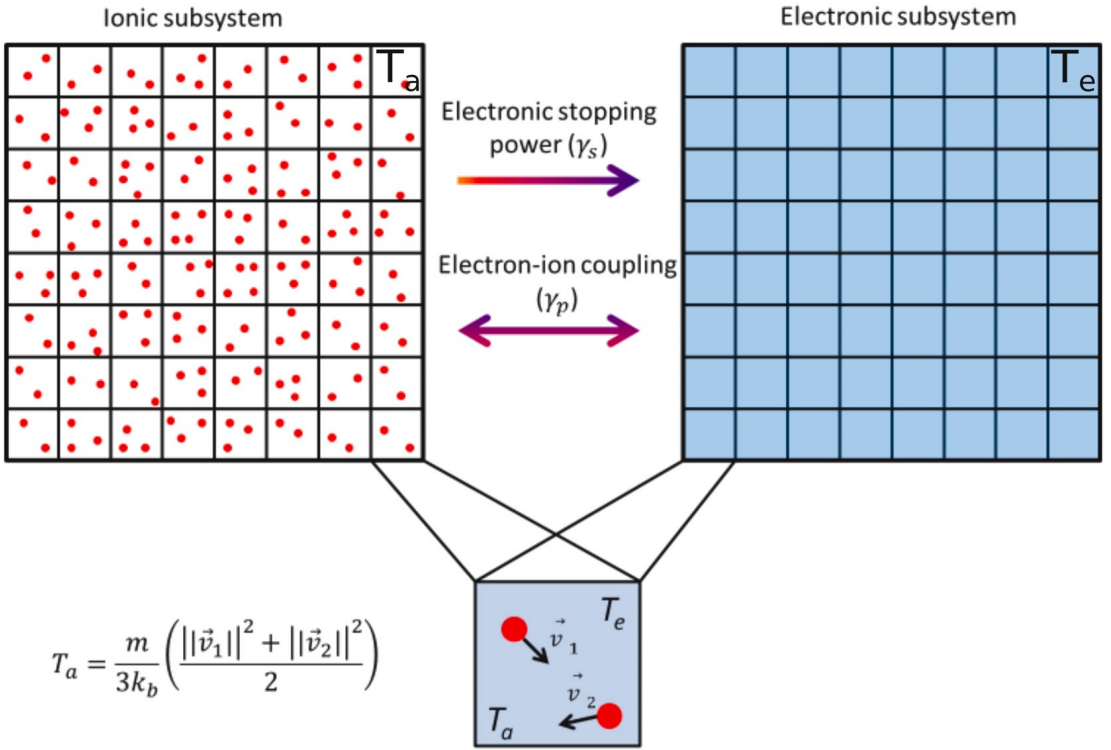
- Combining MD + BCA with probabilistic treatment of loop loss gives near perfect agreement with experiment
  - Error bars for experiment derived from estimate of ”invisible” loops
  - Correction for loop loss (observed even at 30 K) gives dotted black line
- Describes the full defect size distribution
  - Below visible range in TEM
  - Beyond direct accessibility by MD
- Can be used as input in evolution models
- Well defined upper size limit
  - Computationally expedient



[A. E. Sand, et al. MRL (2017)]

Two-temperature MD

- We can extend MD with a heat bath representing the electronic system
- The bath can be divided into cells, and a heat diffusion equation implemented to emulate electronic heat conductivity
  - Realistic local response to cascade heating
- Electron-ion coupling determined by electron-phonon coupling strength
- For cascade simulations, electronic stopping also needed
- Energy lost from electrons can be fed back to the atomic system
  - *No quenching even without a cut-off on the electronic stopping*



[T. Jarrin, et al., NIMB 485(2020) 1-9]

Unified two-temperature model

- Strength of coupling between ions and electrons in **electronic stopping** and **electron-phonon coupling** models can differ by an order of magnitude
- Caro and Victoria [PRA **40** (1989)] proposed a model incorporating effects of both electronic stopping and e-ph coupling in an empirical expression suitable for large scale atomistic simulations
  - Ion-electron coupling as function of local electron density
  - Further developed to the current form [A. Tamm, et al. PRL **120** (2018) 185501]

damping term

stochastic force

$$m_i \mathbf{a}_i = \mathbf{F}_i - \boldsymbol{\sigma}_i + \boldsymbol{\eta}_i$$

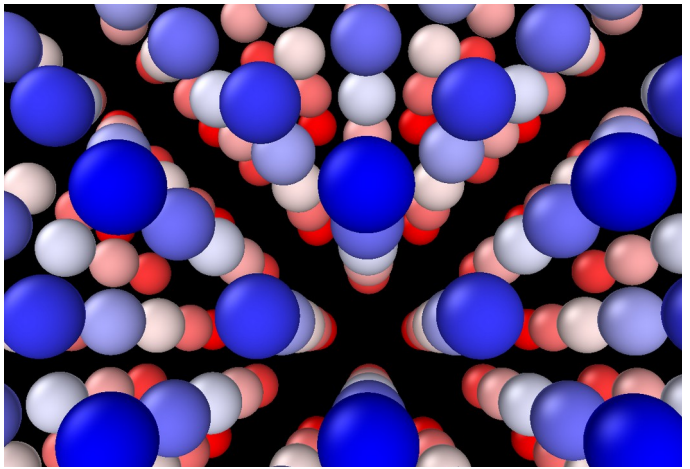
$$\boldsymbol{\sigma}_i = \sum_j \mathbf{B}_{ij}\mathbf{v}_j \quad \text{where} \quad \mathbf{B}_{ij} = \sum_k \mathbf{W}_{ik}\mathbf{W}^{\mathrm{T}}_{jk}$$

$$\mathbf{W}_{ij} = \begin{cases} -\alpha_j \frac{\rho_i(r_{ij})}{\bar{\rho}_j}\mathbf{e}_{ij}\mathbf{e}_{ij}, & (i \neq j) \\ \alpha_i \sum_{k\neq i} \frac{\rho_k(r_{ik})}{\bar{\rho}_i}\mathbf{e}_{ik}\mathbf{e}_{ik}, & (i = j) \end{cases}$$

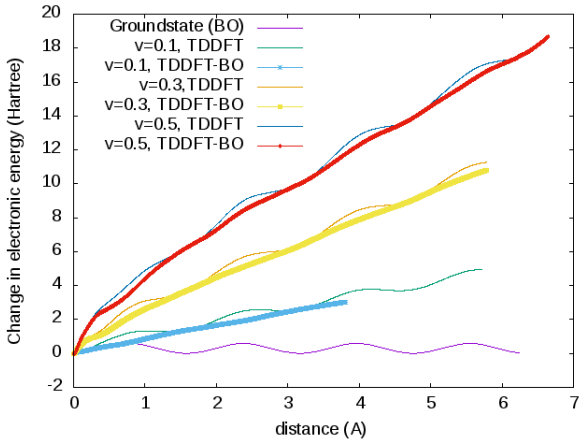
$$\alpha_i = \alpha(\bar{\rho}_i)$$

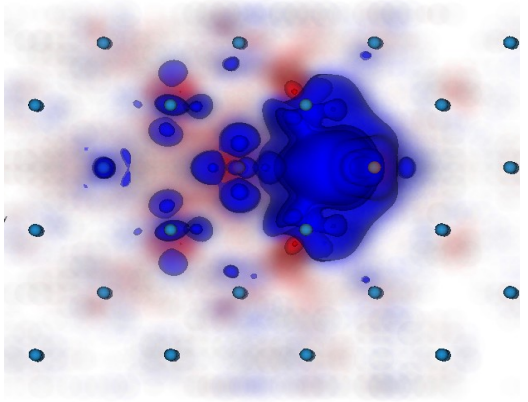
Stopping power with rt-TDDFT

- TD-DFT can predict the instantaneous stopping power in any local environment
  - Could be used to predict also other time-dependent effects, excitation etc.
- For stopping power predictions we obtian non-adiabatic energy losses as the difference between the non-adiabatic and adiabatic energies along trajectories



<100> channel in bcc lattice

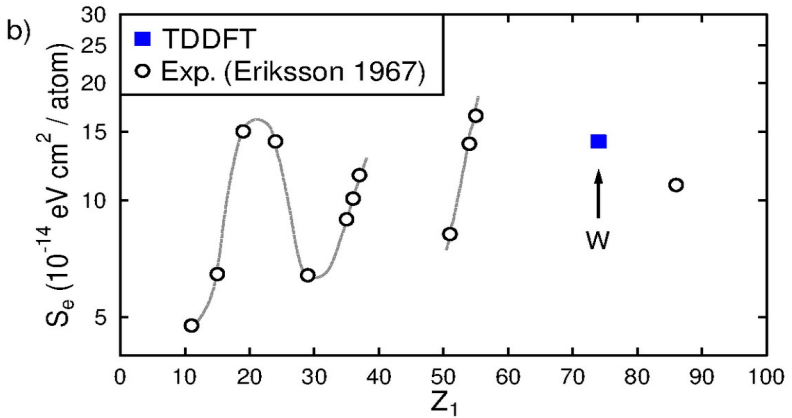


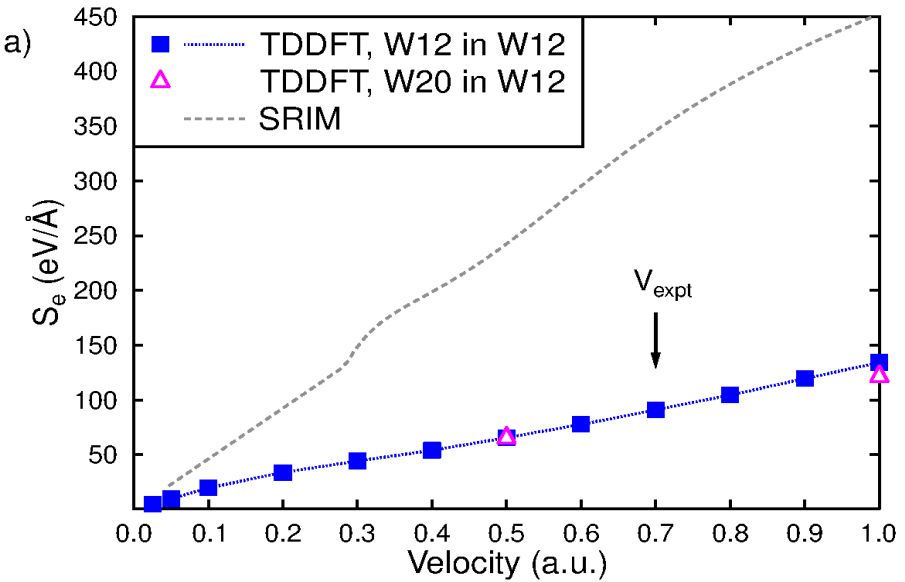


W projectile in <100> channel in W

Stopping power with rt-TDDFT

- Computational predictions always require validation from experimental observations
- Computed value of stopping power for W ions lies in the same range as experimental values for other ions in the <100> channel in W (no data point for W ions)

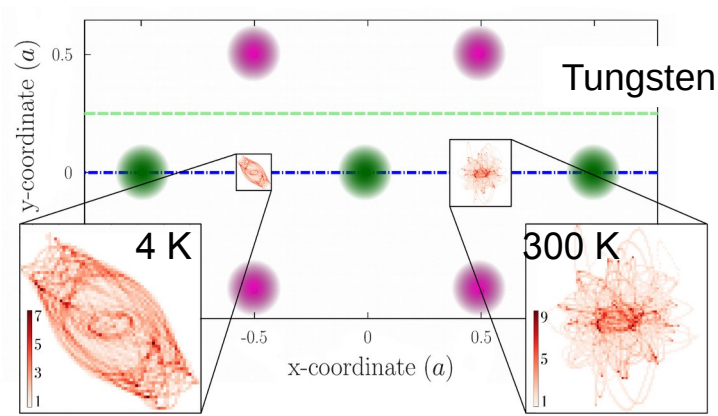




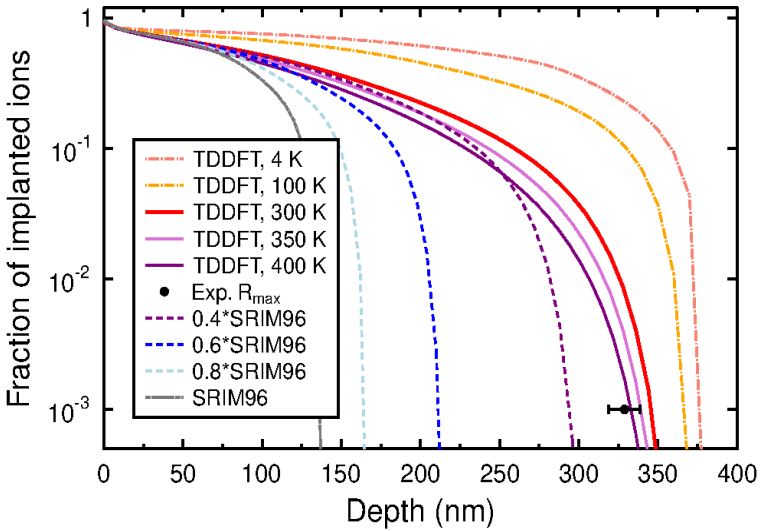
[A. E. Sand, et al., npj Comp. Mat. **5** (2019) 43]

Comparison to ion ranges

- Multiscale simulations show excellent agreement with the experimental ion ranges in [Eriksson et al., Phys.Rev. 161, 219 (1967)]
  - Statistics from 1 million trajectories for each curve



Strongly channelled trajectories

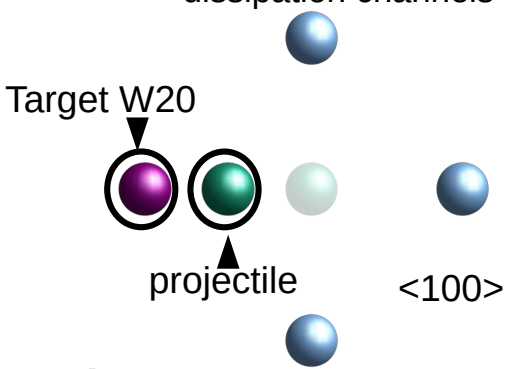


- ***No free parameters!***
  - For example, the charge state of the ion is not a parameter, but a product of the calculation

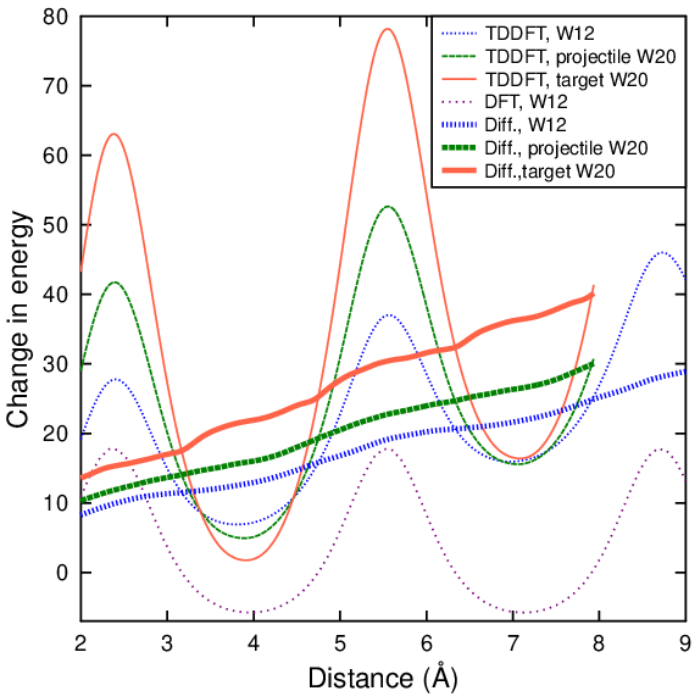
[A. E. Sand, et al., npj Comp. Mat. **5** (2019) 43]

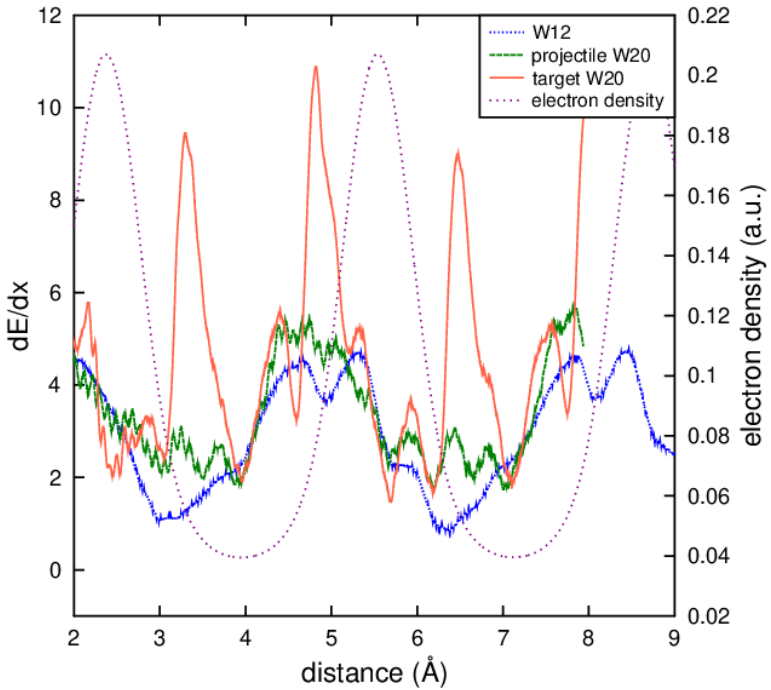
Close collisions

- Pseudopotential with more core states in off-channeling trajectories (small impact parameters) increases prediction of energy dissipation
- Both projectile and target states provide dissipation channels

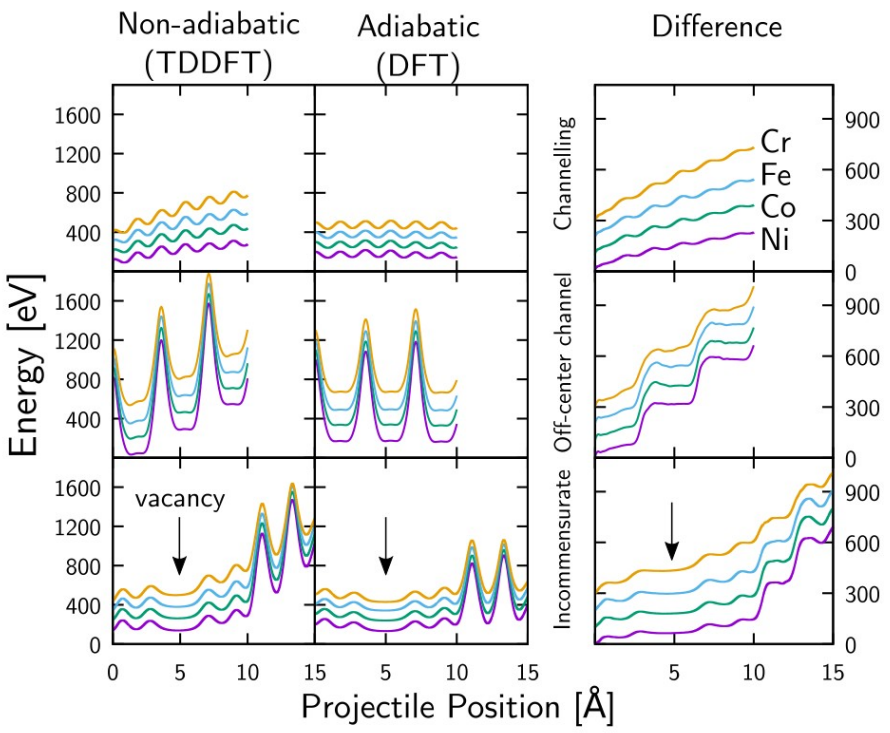


<100> channel in bcc

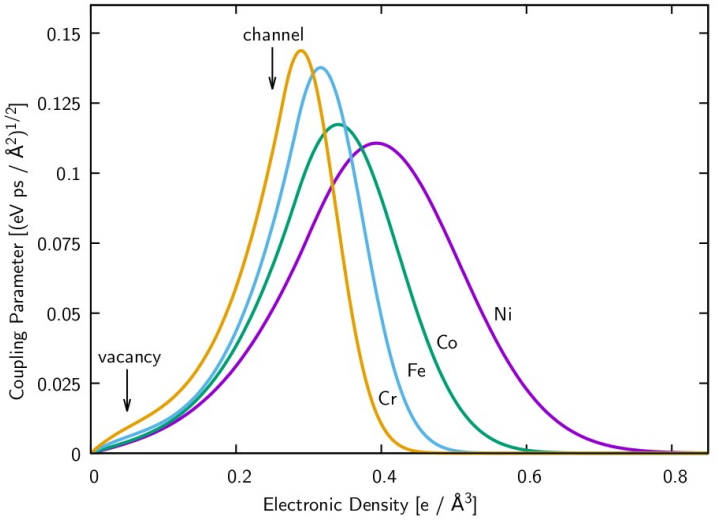




Coupling strength from TDDFT



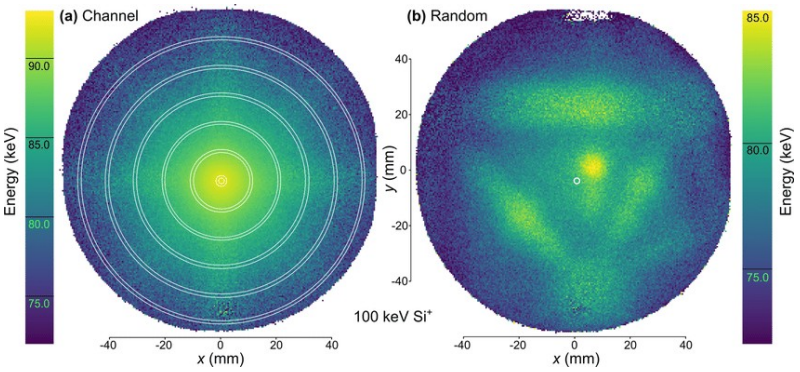
Coupling between atoms and electron bath expressed as function of local electron density



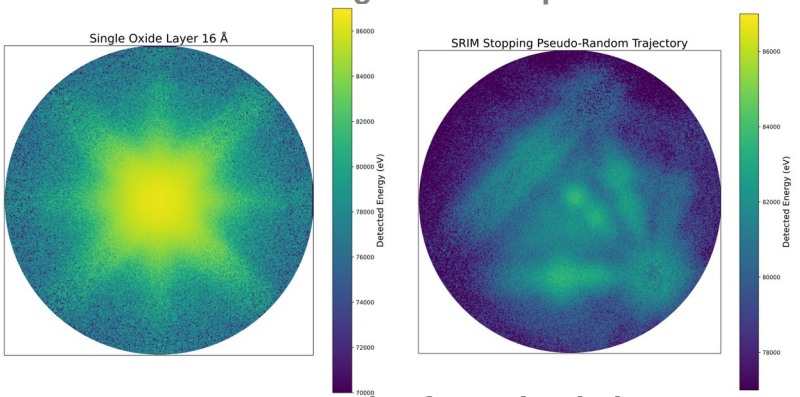
[A. Tamm, et al., Phys. Rev. B 99, 174302]

Si ion energy losses in Si

- Experiments of low energy Si ions in Si show clear trajectory dependence
- By combining electronic energy loss model with efficient atomistic calculations, we can directly simulate the experimental setup and measurements
- Used to validate the electron energy loss model



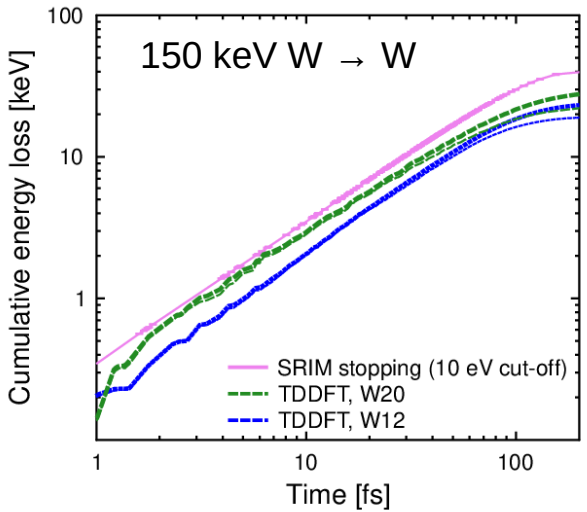
Ion energies from experiment

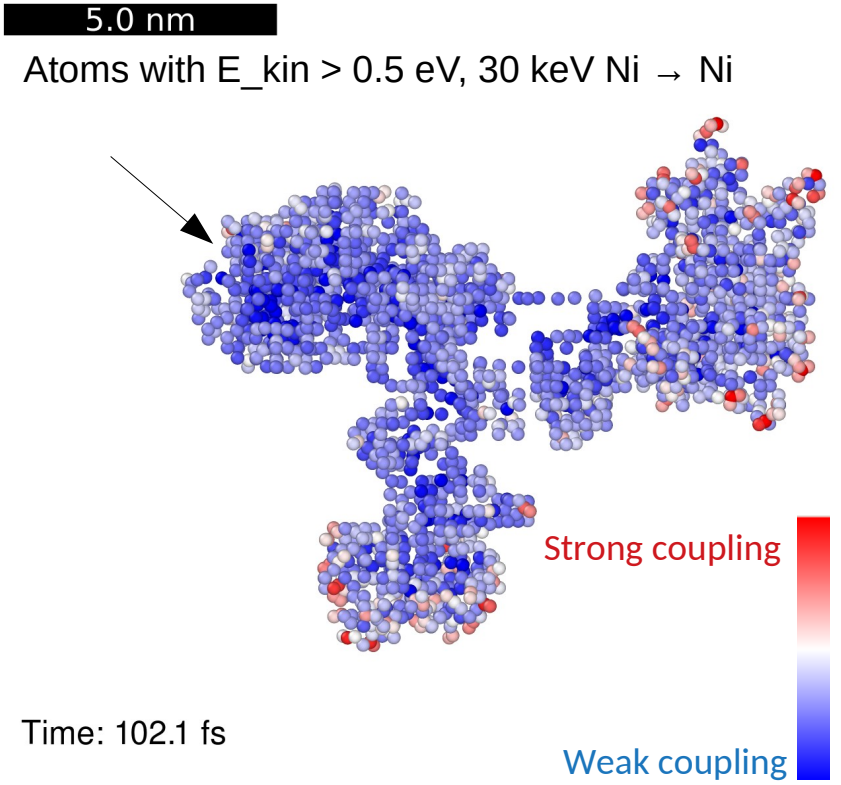


Ion energies from simulation

Coupling during cascade

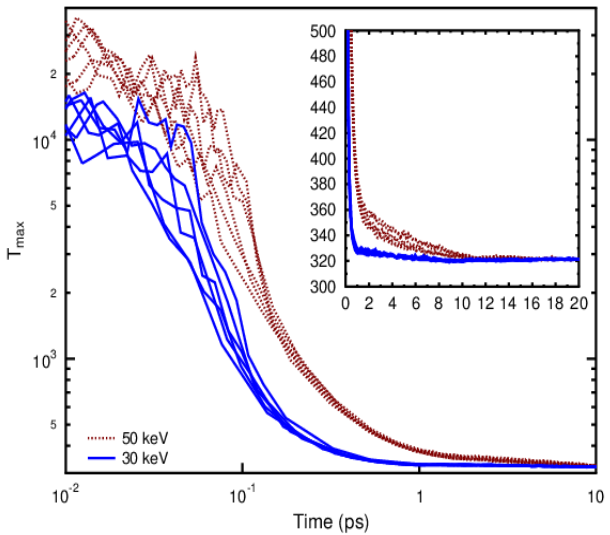
- Leading, ballistic ions have strong coupling
  - Overall energy losses during ballistic phase closer to SRIM using W20
- Ions in the developing core have low coupling due to low density





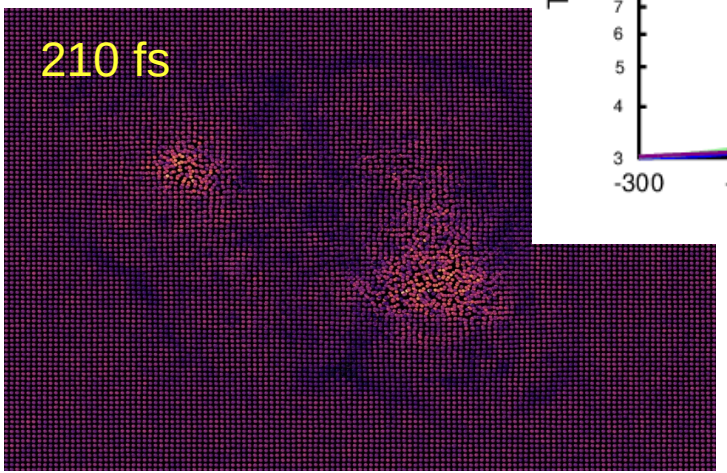
Subsystem temperatures

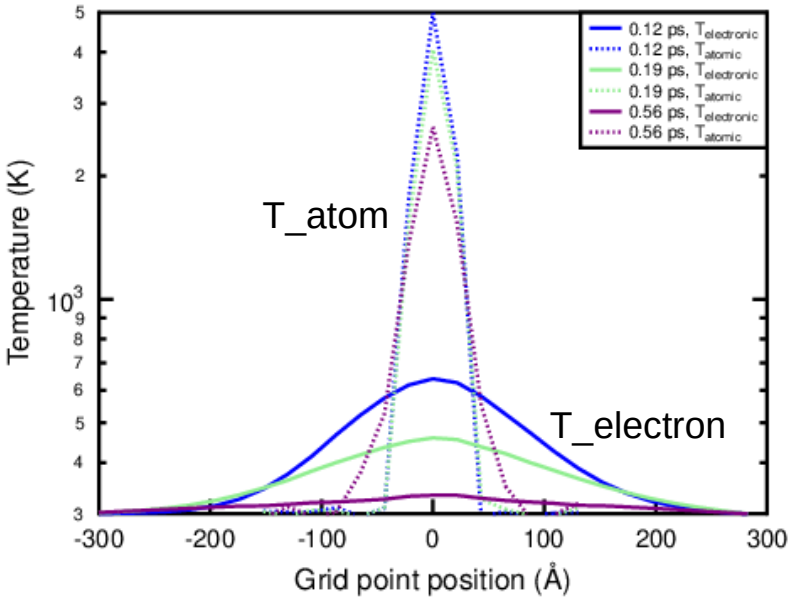
- Electronic system cools rapidly after initial impact



Maximum electronic temperature.

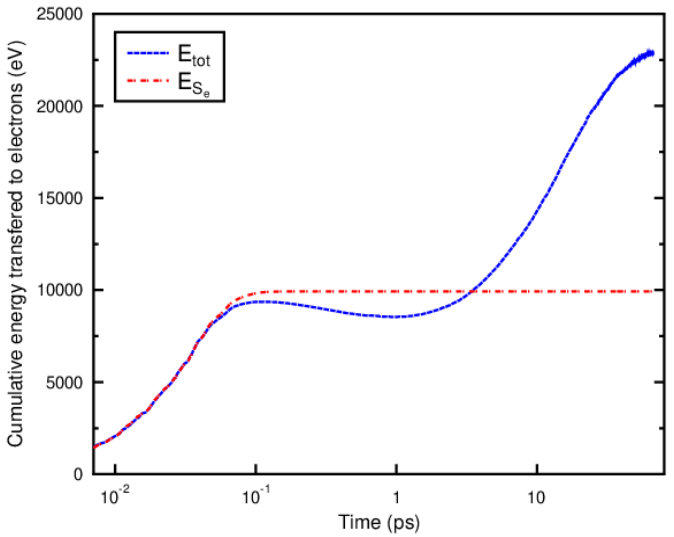
- Energetic atoms the in heat spike phase no longer heat the electronic system, due to low coupling because of low density

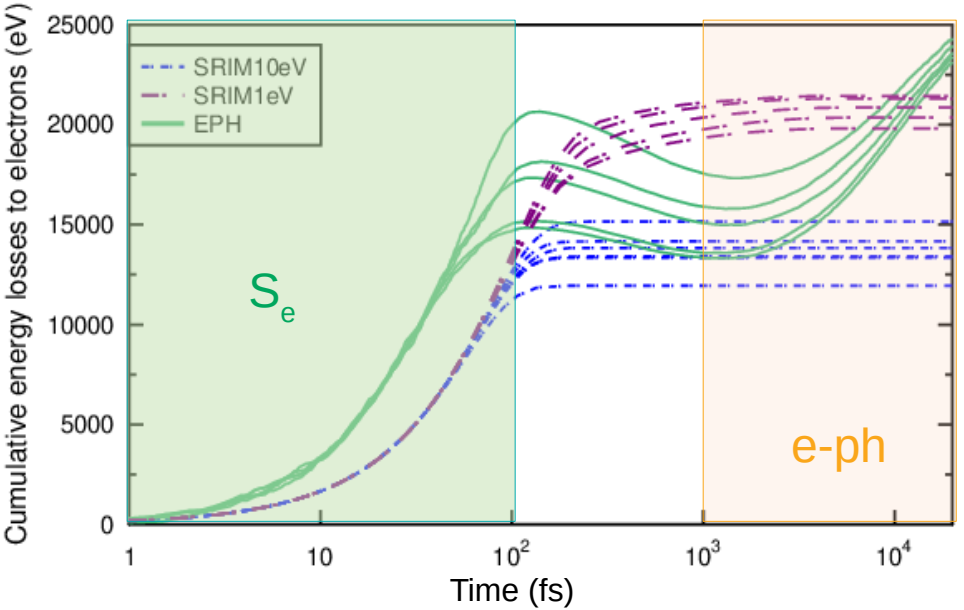




Total energy losses

- **Two different energy loss regimes emerge naturally**
- Plateau region from 0.1 – 1 ps, this is the heat spike phase

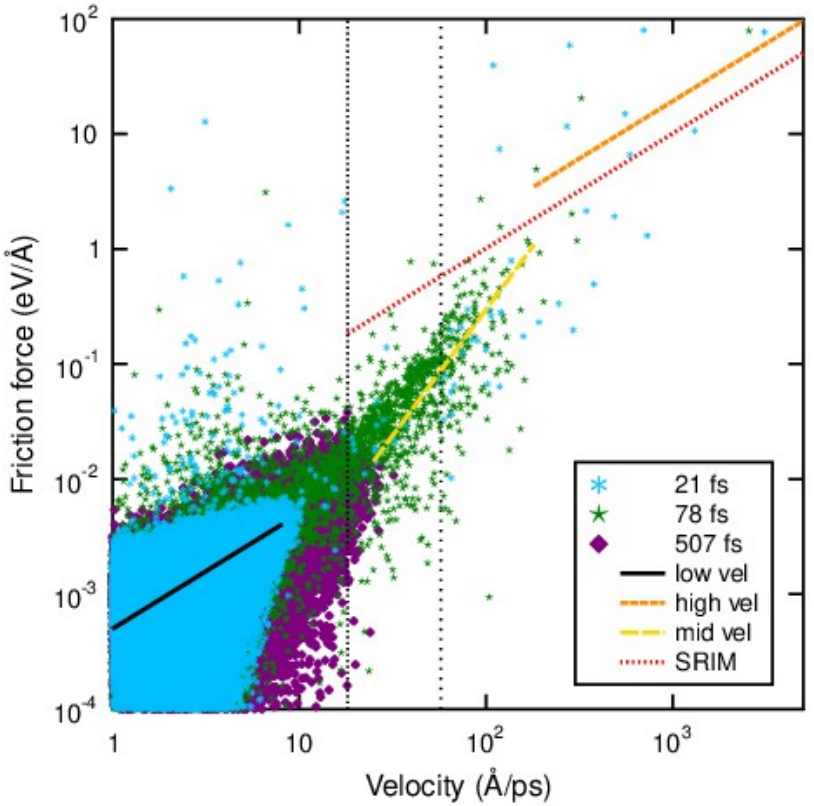




Ballistic energy losses level off at similar total magnitude as with electronic stopping with 10 eV cut-off → comparable ”damage energy”

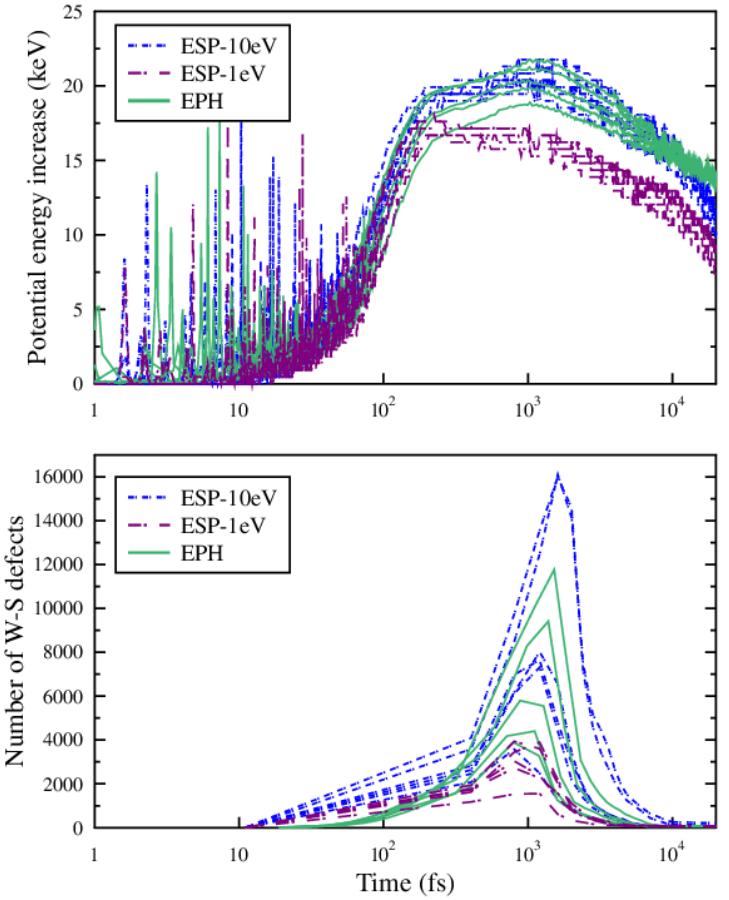
Effective friction

- The coupling model predicts a constant friction coefficient for atoms with velocities in the low and high limits, of 0.0005 eV ps / Å^2 and 0.0193 eV ps / Å^2 , respectively
  - The high velocity limit can be compared to the effective SRIM friction coefficient 0.0101 eV ps / Å^2
  - These coefficients yield characteristic time scales of 12 ps for the electron-phonon coupling regime and 0.3 ps for the ballistic regime
- For intermediate velocities, the effective friction force better fits to a power law



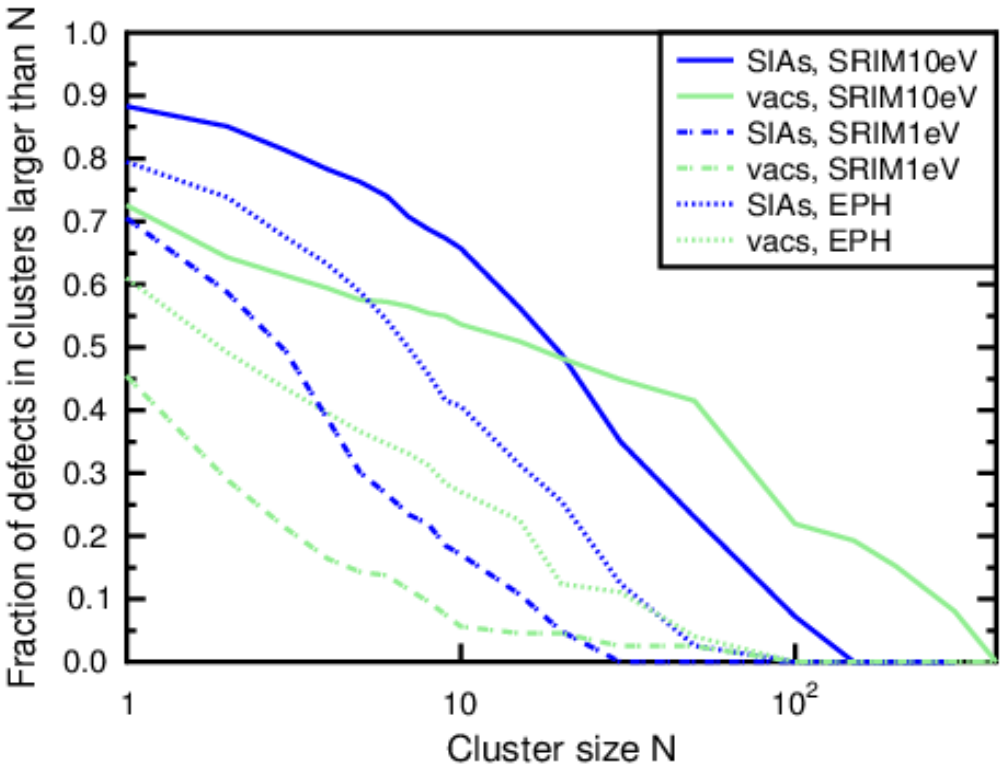
Cascade evolution in Ni

- Excessive energy losses (employing dissipation at the strength of electronic stopping to atoms in the heat spike) leads to diminished heat spike effect
- TTMD model gives on average fewer displaced atoms during heat spike, compared to electronic stopping with 10 eV cut-off



Defect clustering in Ni

- Available energy during the heat spike phase directly impacts athermal in-cascade defect cluster formation
- Larger energy losses leads to smaller clusters of both SIA and vacancy type
- Threshold-free coupling leads to predictions of clustering that lie between the predictions using SRIM friction with 1 and 10 eV cut-off

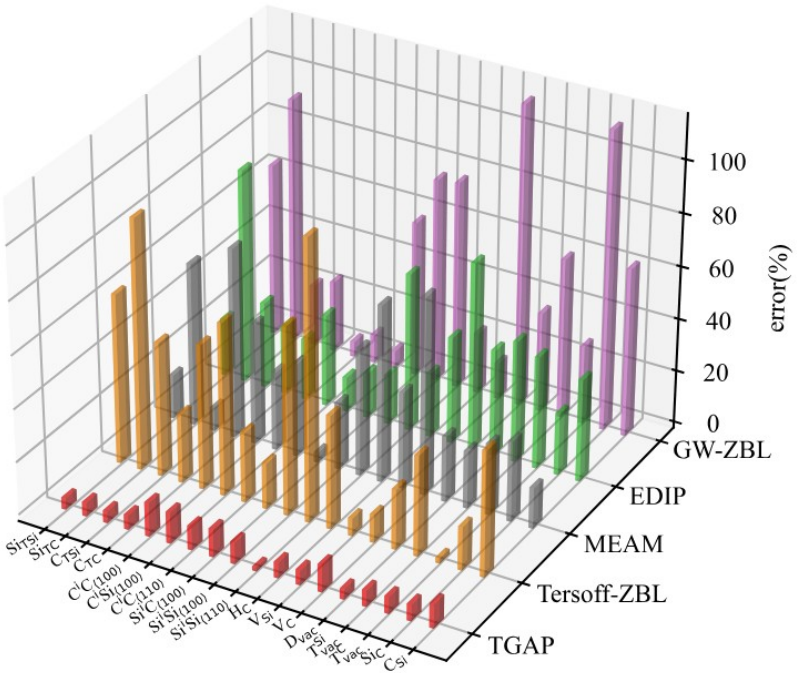


Cluster sizes from 50 keV cascades in Ni

Implementation in TurboGAP

- An electronic subsystem, the UTTM coupling, variable time step and border thermostats have been implemented in TurboGAP
- Recent **SiC potential** trained for radiation damage simulations (currently only for 3C-SiC)
- UTTM coupling for Si, C, under development for SiC

TurboGAP
Data-driven atomistic simulation



Relative error in prediction of the stable point defects and vacancy clusters with respect to DFT

Conclusions

- Radiation by charged particles can both displace atoms and excited electronic system
- Electronic effects can be directly modelled only on very small scale
- Large scale atomistic simulations can incorporate effects of electronic excitation via parametrized models
- Careful validation of different stages of the multiscale approach lends confidence in extrapolation

Acknowledgements



LLNL

Alfredo A. Correa

Artur Tamm (currently at *University of Tartu, Estonia)*



EMIL AALTOSEN SÄÄTIÖ



Culham Centre for Fusion Energy

Daniel Mason





Aalto University

Glen Kiely, Rafael Nuñez, Ali Hamedani, Uttioyarnab Saha



Thank you!

Acknowledgements

Funded by the European Union

• This presentation is given under the auspices of COST Action CA21126 - Carbon molecular nanostructures in space (NanoSpace), supported by COST (European Cooperation in Science & Technology).

• COST (European Cooperation in Science & Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.

• www.cost.eu
• https://www.cost.eu/actions/CA21126/
• https://research.iac.es/proyecto/nanospace/