Molecular dynamics simulations of collision cascades: method developments and results from 1993 on

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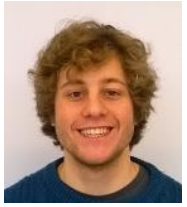

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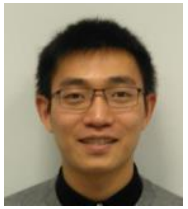
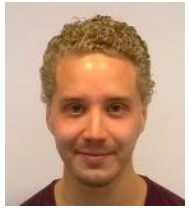
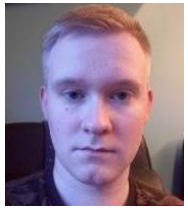


M. Sc. Jian Liu
Carbon nanomaterials



B.Sc Emil Levo
Fusion reactor mat'ls



B.Sc Ville Jantunen
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Machine learning

M.Sc. Anton Saressalo
Arcing experiments

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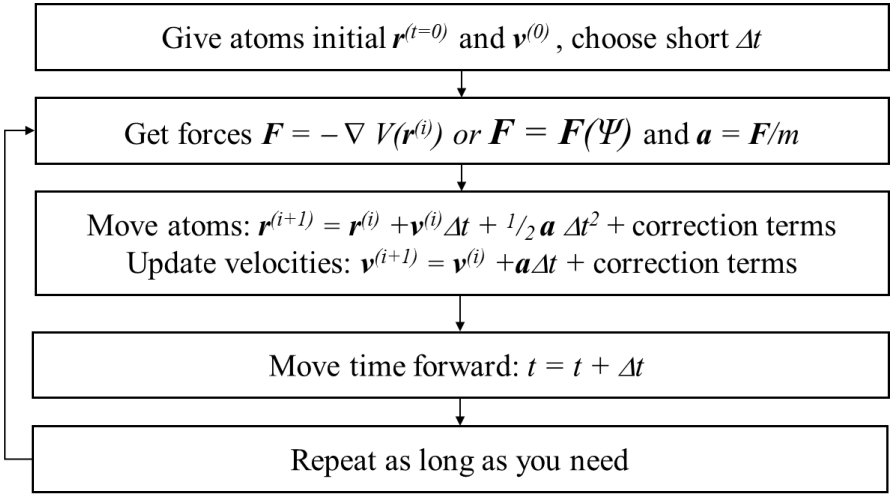
Contents

- Part 1: Crucial methods for handling irradiation effects
- Part 2: Results on overlapping damage cascades in metals
- Part 3: Comments on data formats and storage sizes

What is needed to model collision cascades beyong standard MD?

- We all know the basics of standard MD
- However, to model cascades one needs some special solutions



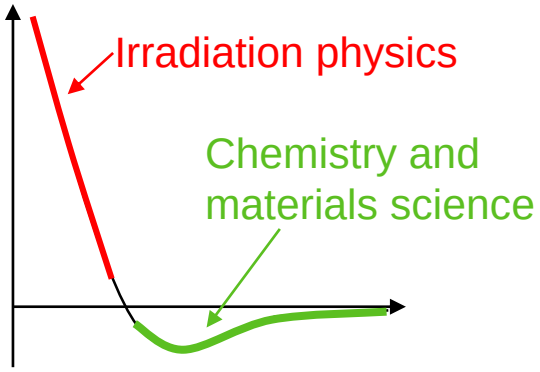
- Now with increasing amounts of LAMMPS black-box users, important to keep this in mind!
- We and others (Webb, Smith, Garrison, Averback, Diaz de la Rubia, Urbassek, Bacon, Caturla, Gao….) have developed the special solutions since about 1990

What is the special physics of irradiation effects?

- One needs to be able to handle:
  1) keV-energy collisions between nuclei
  2) Energy loss to electronic excitations
  3) Transition to high-pressure and high-T thermodynamics (E_{kin} ~ 1 eV)
  4) Realistic equilibrium interaction models
  5) Phase changes, segregation, sputtering, defect production…
  6) Long-term relaxation of defects
- Sounds daunting, but:
  - Steps 1 – 2 can be handled in a binary collision approximation simulation
  - Steps 1 – 5 can all be handled in the same molecular dynamics simulation
  - Step 6 requires kinetic Monte Carlo or rate theory

1) keV and MeV-energy collisions between nuclei

- To handle the high-E collisions, one needs to know the high-energy repulsive part of the interatomic potential
  - We have developed DFT methods to obtain it to within ~1% accuracy for all energies above 10 eV
    - New effort to get all potentials just started
  - So called “Universal ZBL” potential accurate to ~5% and very easy to implement



[K. Nordlund, N. Runeberg, and D. Sundholm, Nucl. Instr. Meth. Phys. Res. B 132, 45 (1997)].

1) keV and MeV-energy collisions between nuclei

- The equilibrium MD time step of 1 fs makes MD explode if used for keV or MeV ions
- Adaptive time step developed by us:

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

- Here 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 t_{max} is the time step for the equilibrated system.
- This relatively simple algorithm has been demonstrated to be able to handle collisions with energies up to 1 GeV accurately (by comparison with binary collision integral)

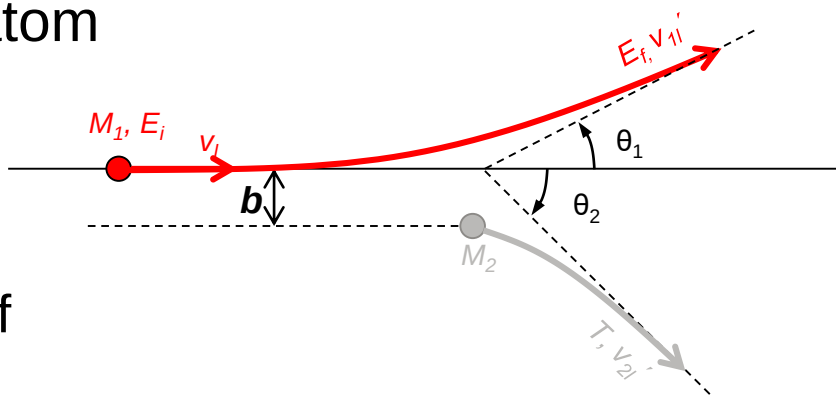
[K. Nordlund, Comput. Mater. Sci. 3, 448 (1995)].

Press-stop: how important is the ΔE_{max} term actually?

- We always use the ΔE_{max} term, but e.g. LAMMPS does not have it – how important is it?

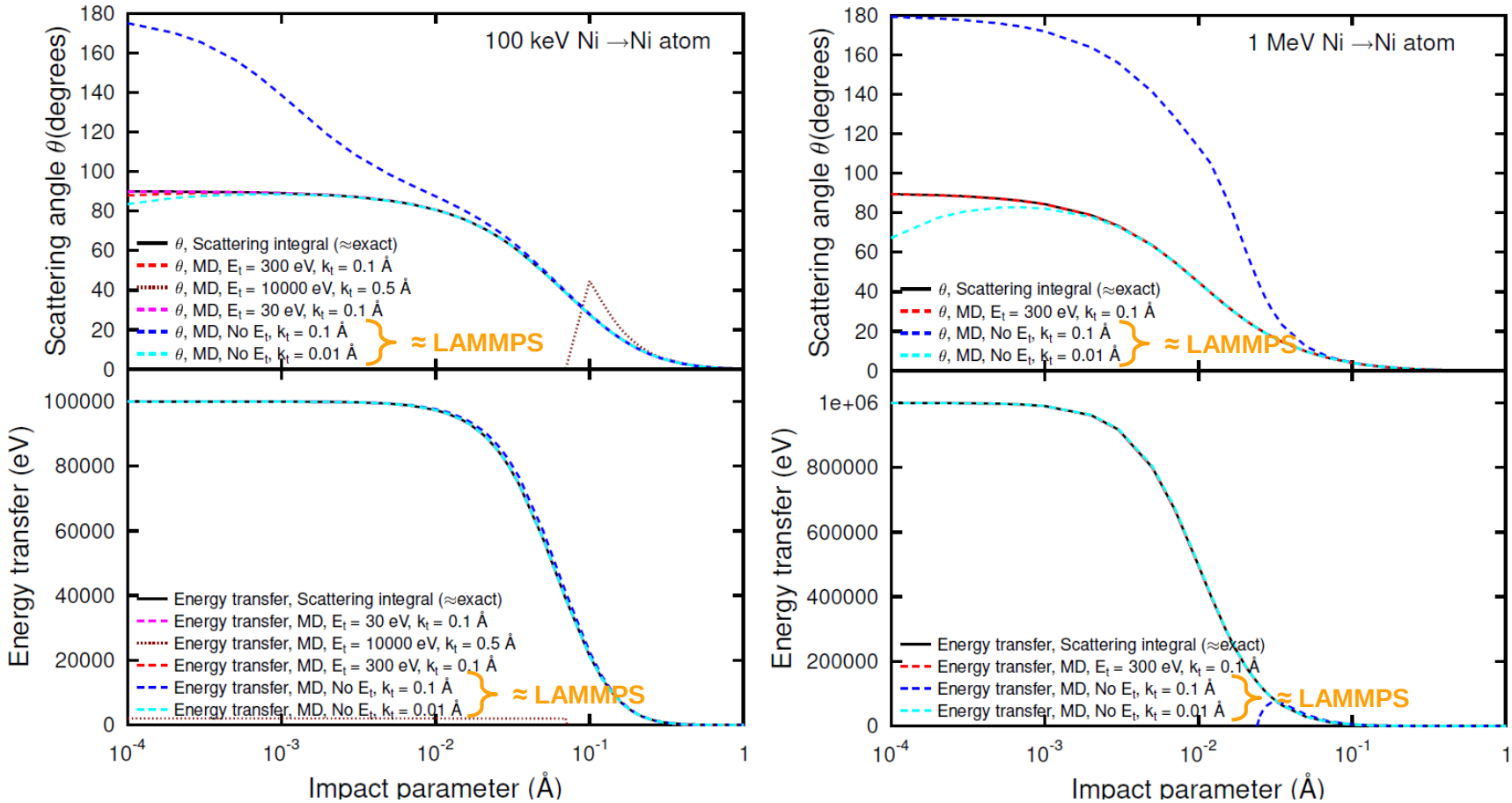
$$\Delta t_{n+1} = \min\left(\frac{\Delta x_{\max}}{v_{\max}} , \frac{\Delta E_{\max}}{F_{\max} v_{\max}} , \right.$$

- I ran today simulations of 100 keV and 1 MeV Ni collisions with a single Ni atom as function of impact parameter ***b***
  - One can compare with the essentially exact solution of the binary collision integral



- Monitor variation of dependence of scattering angle and energy transfer with Δx_{max} and ΔE_{max}

Results on scattering dependence on Δx_{max} and ΔE_{max}



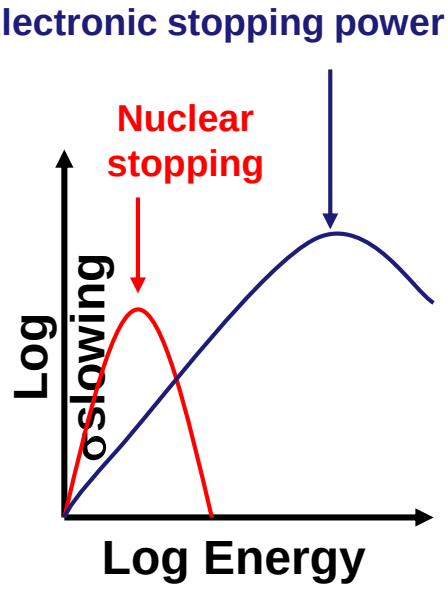
- Conclusion: ΔE_{max} is important for energies >~100 keV

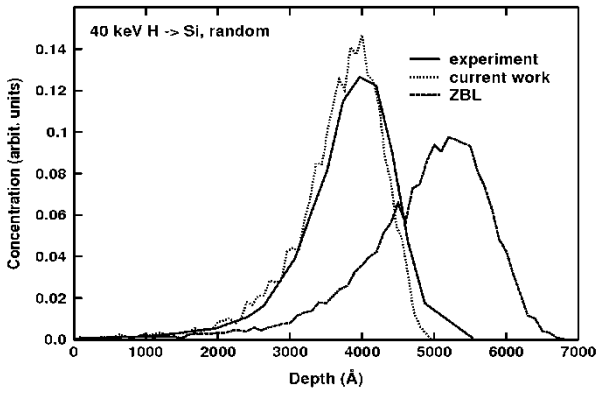
2) Energy loss to electronic excitations

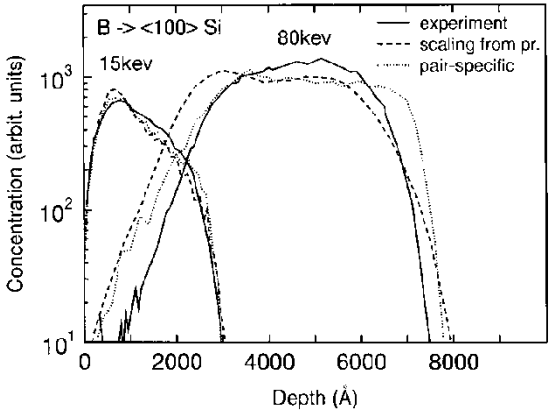
- The energy loss to electronic excitations = electronic stopping S can be included as a frictional force in MD simply as:

$$v^{(i+1)} = v^{(i)} - S(v)/m\Delta t$$

- The nice thing about this is that this can be compared directly to experiments via BCA or MD range or ion transmission calculations. Examples of agreement:



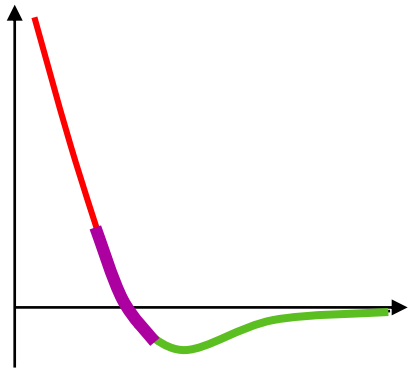




[J. Sillanpää, K. Nordlund, and J. Keinonen, Phys. Rev. B 62, 3109 (2000); J. Sillanpää J. Peltola, K. Nordlund, J. Keinonen, and M. J. Puska, Phys. Rev. B 63, 134113 (2000); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 217, 25 (2003); J. Peltola, K. Nordlund, and J. Keinonen, Nucl. Instr. Meth. Phys. Res. B 212, 118 (2003);); J. Peltola, K. Nordlund, and J. Keinonen,, Rad. Eff. & Def. in Sol. 161, 511 (2006).]

3) Transition to high-pressure and high-T thermodynamics

- Requires realistic **intermediate part** in potential

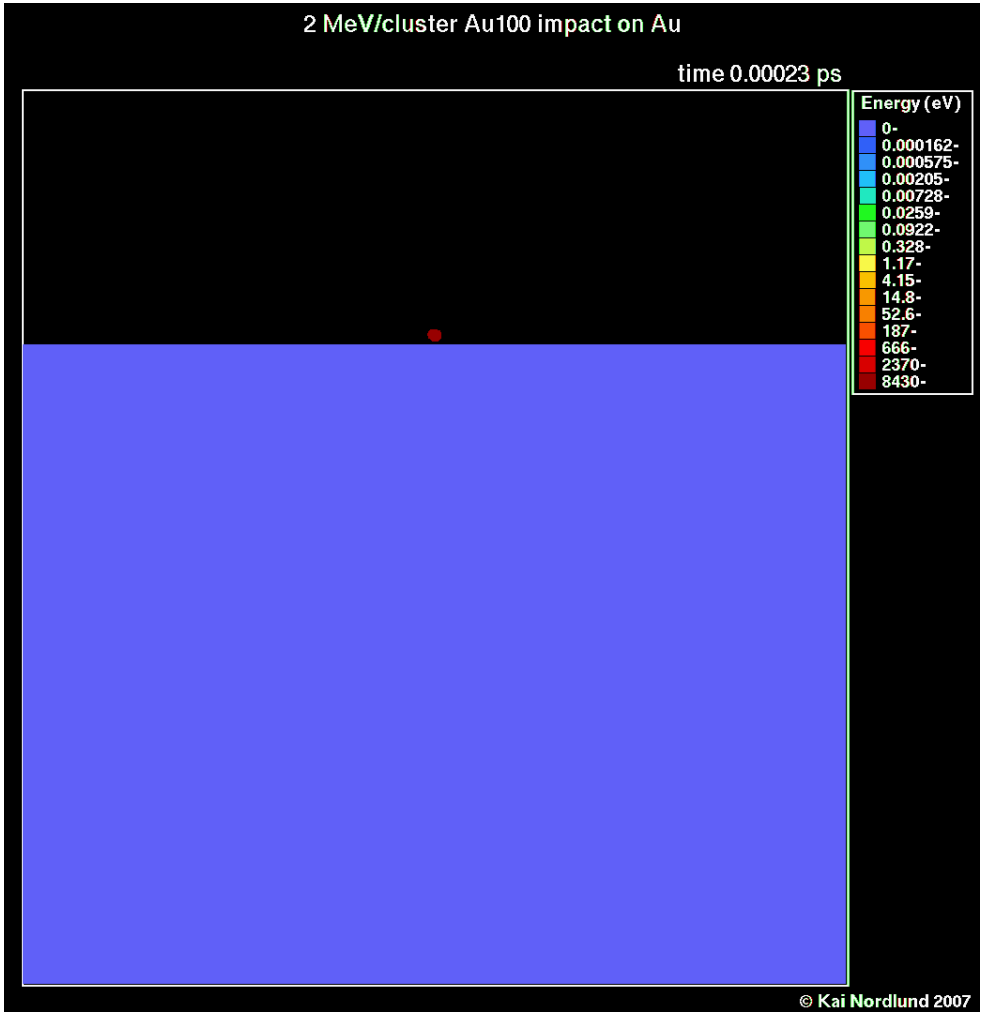


- Can be adjusted to experimental high-pressure data and threshold displacement energies
  - Somewhat tedious ‘manual’ fitting but doable
- Could also be fit to DFT database in this length range, done recently e.g. by Tamm, Stoller et al.

[K. Nordlund, L. Wei, Y. Zhong, and R. S. Averback, Phys. Rev. B (Rapid Comm.) 57, 13965 (1998); K. Nordlund, J. Wallenius, and L. Malerba. Instr. Meth. Phys. Res. B 246, 322 (2005); C. Björkas and K. Nordlund, Nucl. Instr. Meth. Phys. Res. B 259, 853 (2007); C. Björkas, K. Nordlund, and S. Dudarev, Nucl. Instr. Meth. Phys. Res. B 267, 3204 (2008)]

3) Transition to high-pressure and high-T thermodynamics

- The transition to thermodynamics occurs naturally in MD
- But boundary conditions a challenge due to heat and pressure wave emanating from a cascade

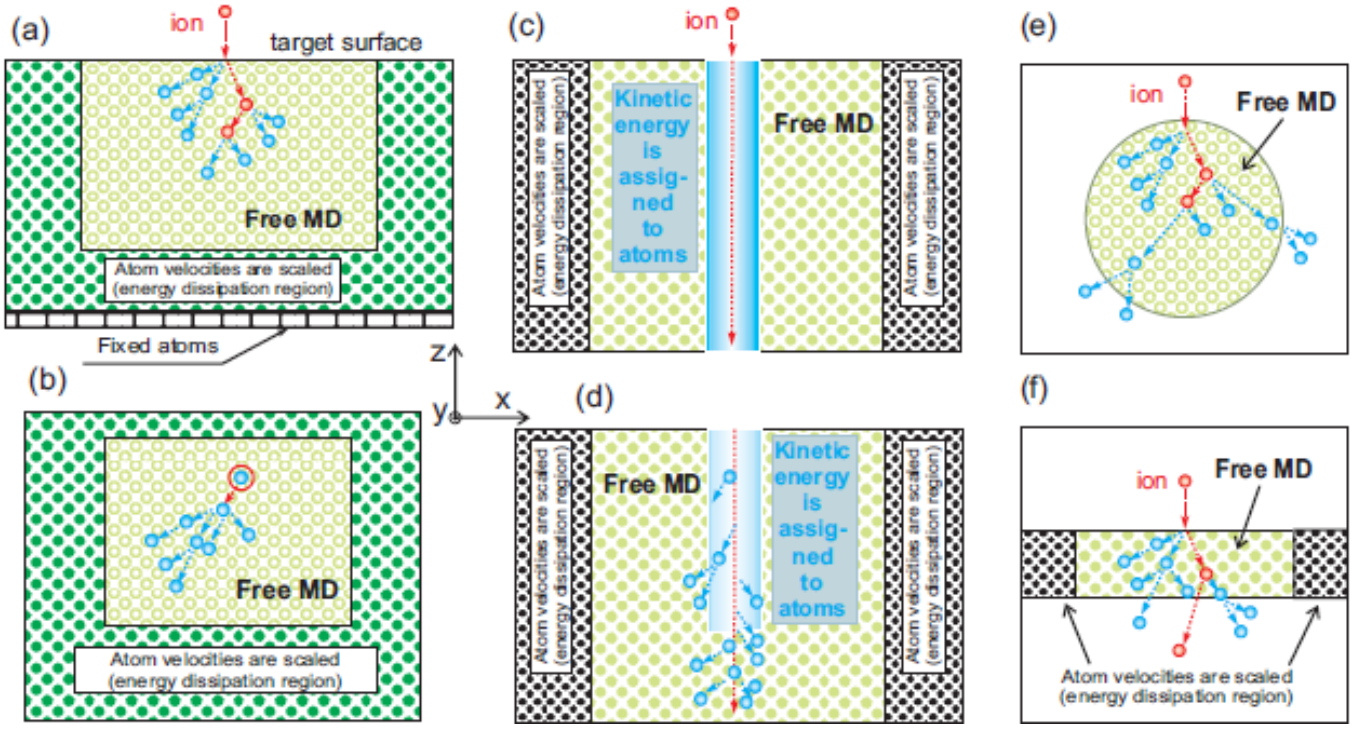


3) Transition to high-pressure and high-T thermodynamics:

MD irradiation temperature control

- Central part 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:

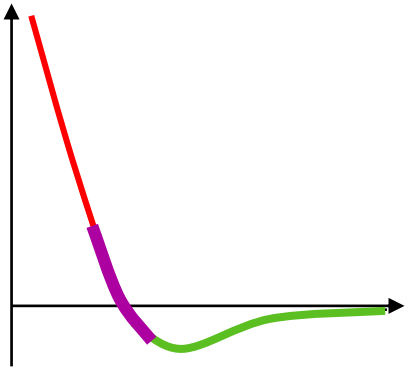
a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire



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

4) Realistic equilibrium interaction models

- Finally one also needs the **normal equilibrium part** of the interaction model



- Since we start out with the extremely non-equilibrium collisional part, all chemical bonds in system can break and reform and atoms switch places
  - **Conventional Molecular Mechanics force fields are no good at all!**

Results: overlapping cascades

- Our collision cascade simulations have produced results published in about 400 scientific publications since 1994.
  - Materials covered: metals, semiconductors, ionic materials, organic materials, nanotubes, nanowires, nanoclusters, amorphous materials, quasicrystals
- Focus of rest of this presentation: damage overlap effects

Molecular dynamics of primary damage event

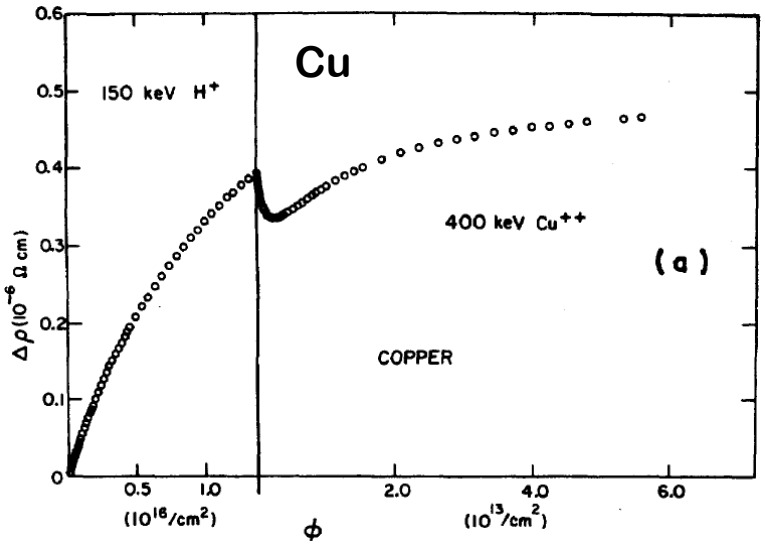
- The primary damage (ns timescale) produced by neutron irradiation can be readily simulated by molecular dynamics (=simulation of atom motion)
- Simple example: 10 keV recoil cascade in FeCr, cross-sectional view

Overlapping damage effects?

- It is well established that overall damage levels in metals saturate on long-term irradiation
- Basic explanation: new cascades recombine some of old damage
  - Saturation at ~ 1% defect concentration

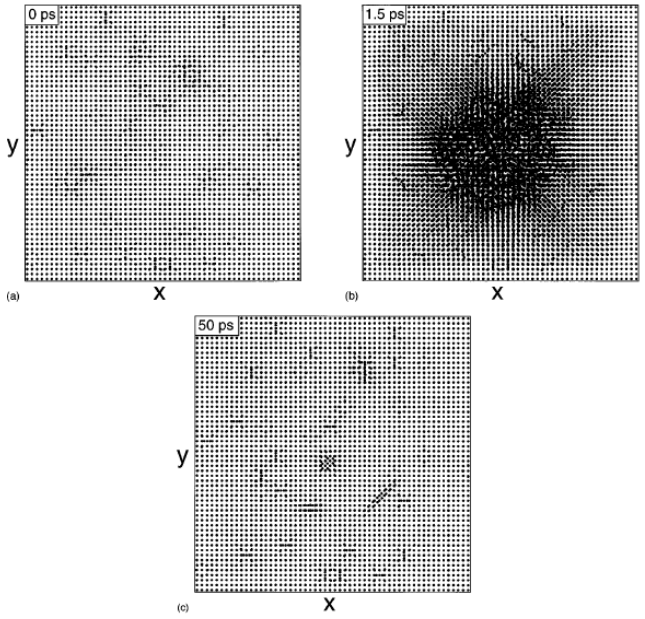
[Gao, Bacon et al, J. Nucl. Mater. 230 (1996) 47; Nordlund and Averback, Phys. Rev. B 56, 2421 (1997)]

Experiment



[Averback et al,. Phys. Rev. B 16 (1977) 3860]

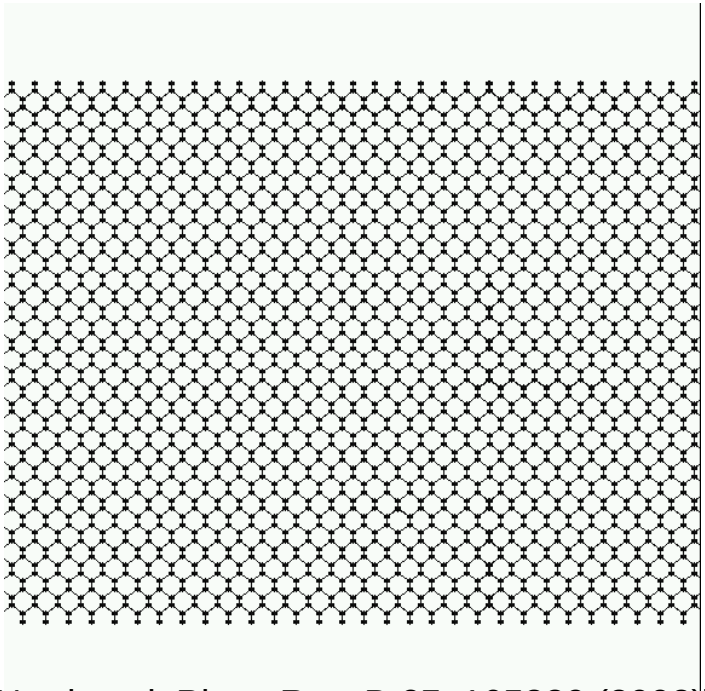
Simulation



[Nordlund and Averback, Phys. Rev. B 56, 2421 (1997)]

Simulations of high-dose damage in semiconductors

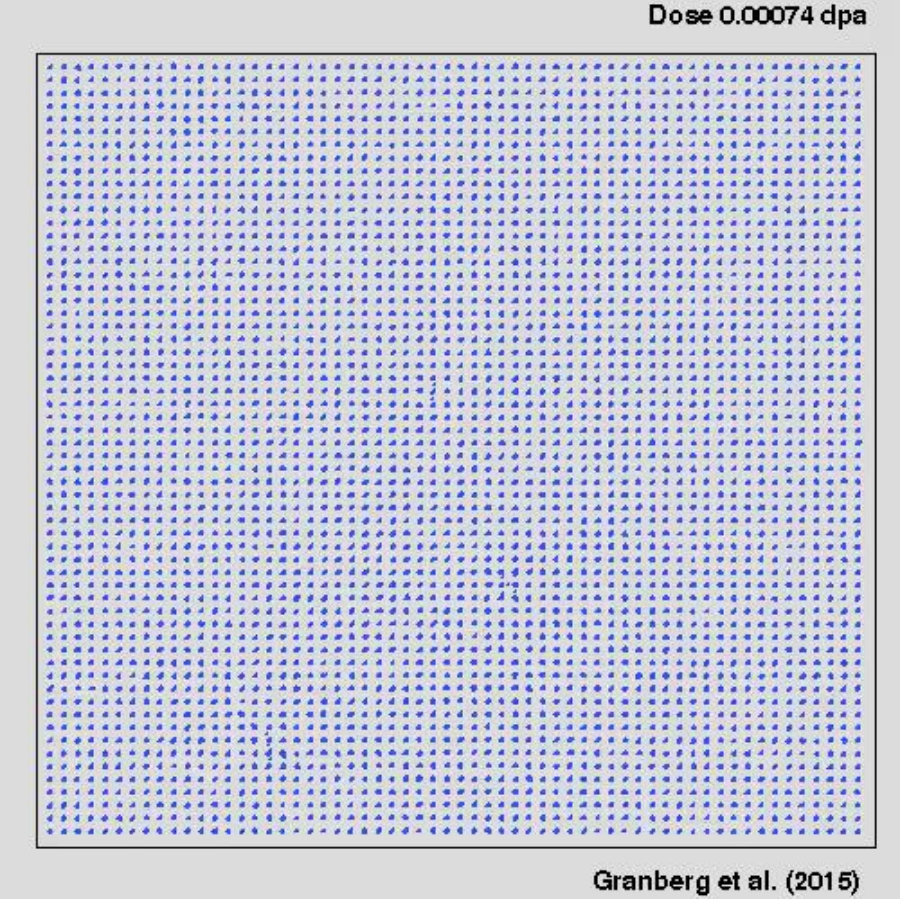
- High-dose damage can be simulated by molecular dynamics by running repetitive cascades in same cell
  - If there is no thermally assisted defect migration, this corresponds directly to high-dose radiation experiments
- For semiconductors such simulations have been done already long ago, and gave good agreement with experiments
- E.g. amorphization of silicon
  - Dose about 14 eV/atom in MD, about 12 eV/atom in expt.



[Nord et al, Phys. Rev. B **65**, 165329 (2002)]

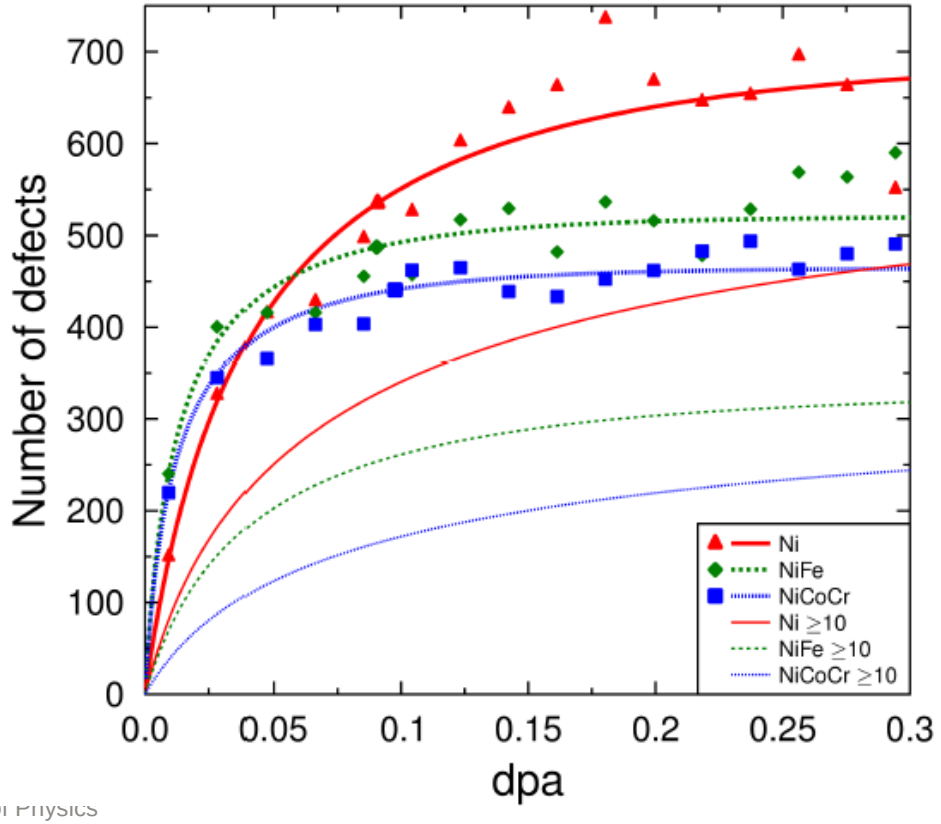
Simulations of high-dose damage in metals

- Until recently, there were no corresponding simulations in metals
- We have now carried out numerous such series in Fe, FeCr, Ni and Ni-related high entropy alloys
- Example: 1500 overlapping 5 keV cascades in Ni
  - 108000 atom cell, all atoms plotted in projection



Damage saturation

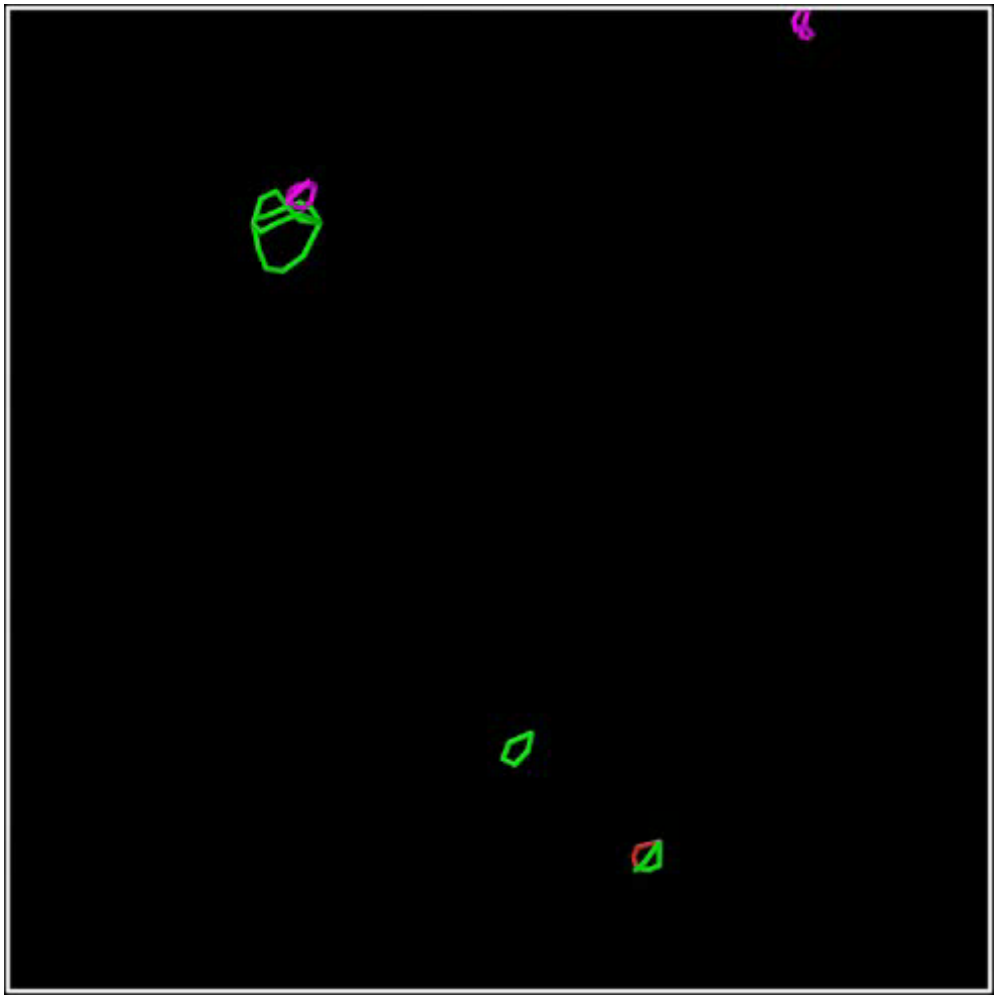
- Damage saturates around defect concentration ~ 0.7%
  - Very nice agreement with experimental value around roughly 1%...



Damage buildup by dislocation view

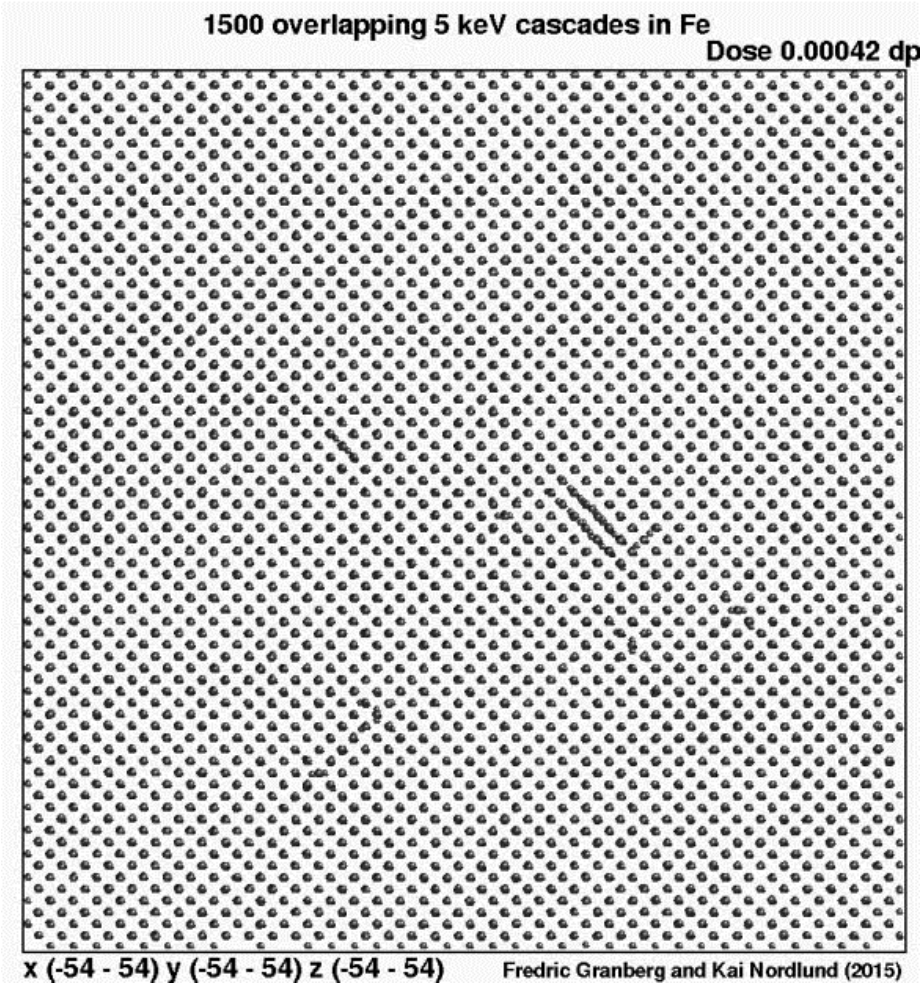
Stair-rod dislocation
Shockley partial
Frank loop

- DXA analysis in ovito software enables automated analysis of the dislocation structure
- Example: damage buildup by 3500 recoils in Ni
  - Note: disordered vacancy clusters not shown

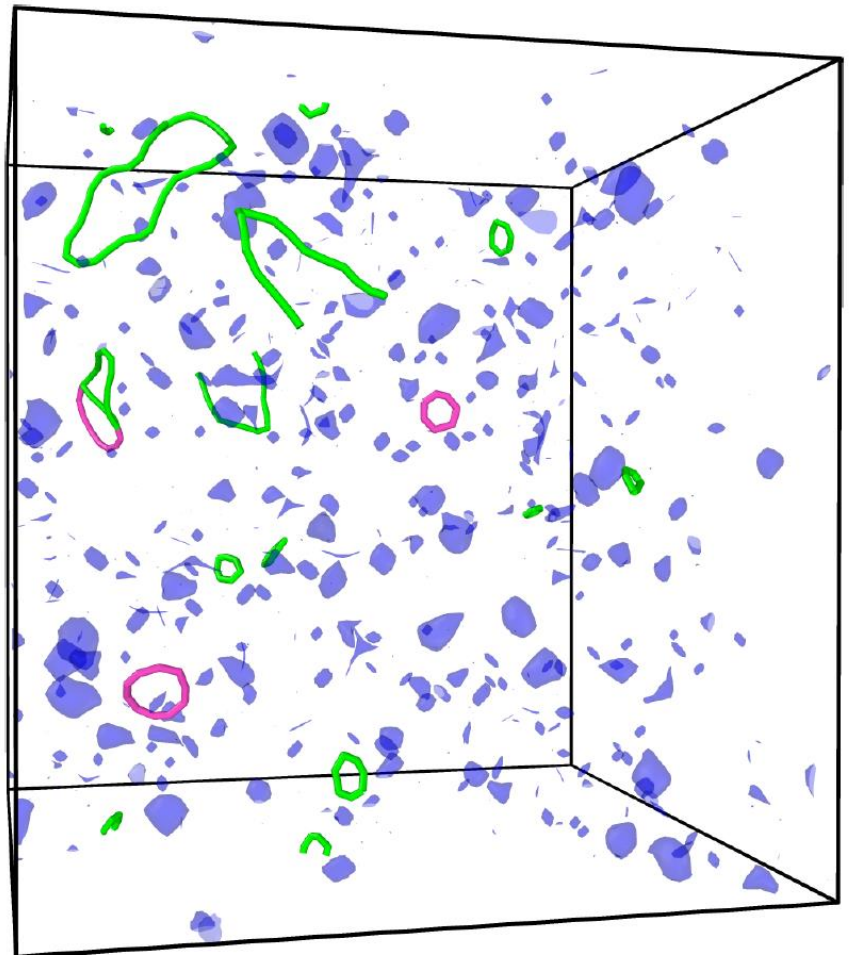


High-dose radiation damage in Fe and FeCr

- We have also carried out corresponding series in Fe
- Key question addressed in these simulations: what is the mechanism of 100 loop formation?



Dislocation structure after 1000 5 keV cascades

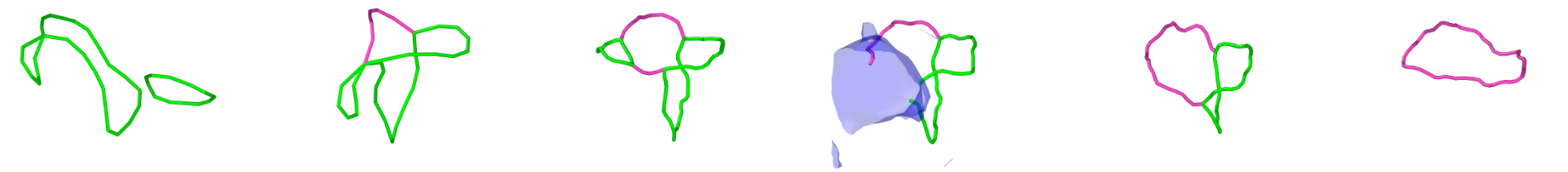


½ <111> dislocation
<100> dislocation
Unidentified; mainly vacancy clusters

100 loop formation mechanism

- From the simulations, we analyzed the dislocation structure [with Ovito DXA analysis) and sought 100 loops
- We found that they can form spontaneously by transformation from 111 loops by cascade overlap
- Example:

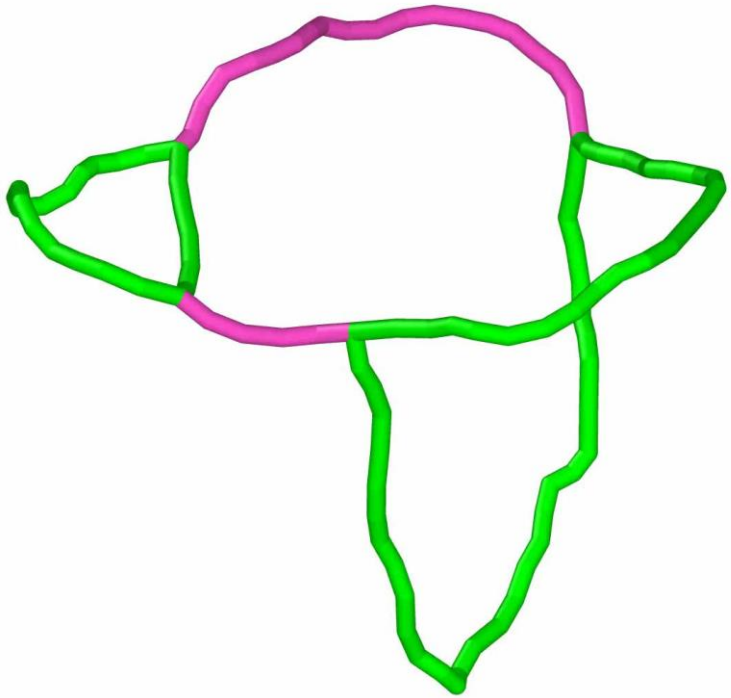
½ <111> dislocation
<100> dislocation



(a) Before cascade 1026 (b) After cascade 1026 (c) Before cascade 1288 (d) During cooldown (e) During cooldown (f) After cascade 1288

[Granberg et al, EPL (2017) accepted for publication]

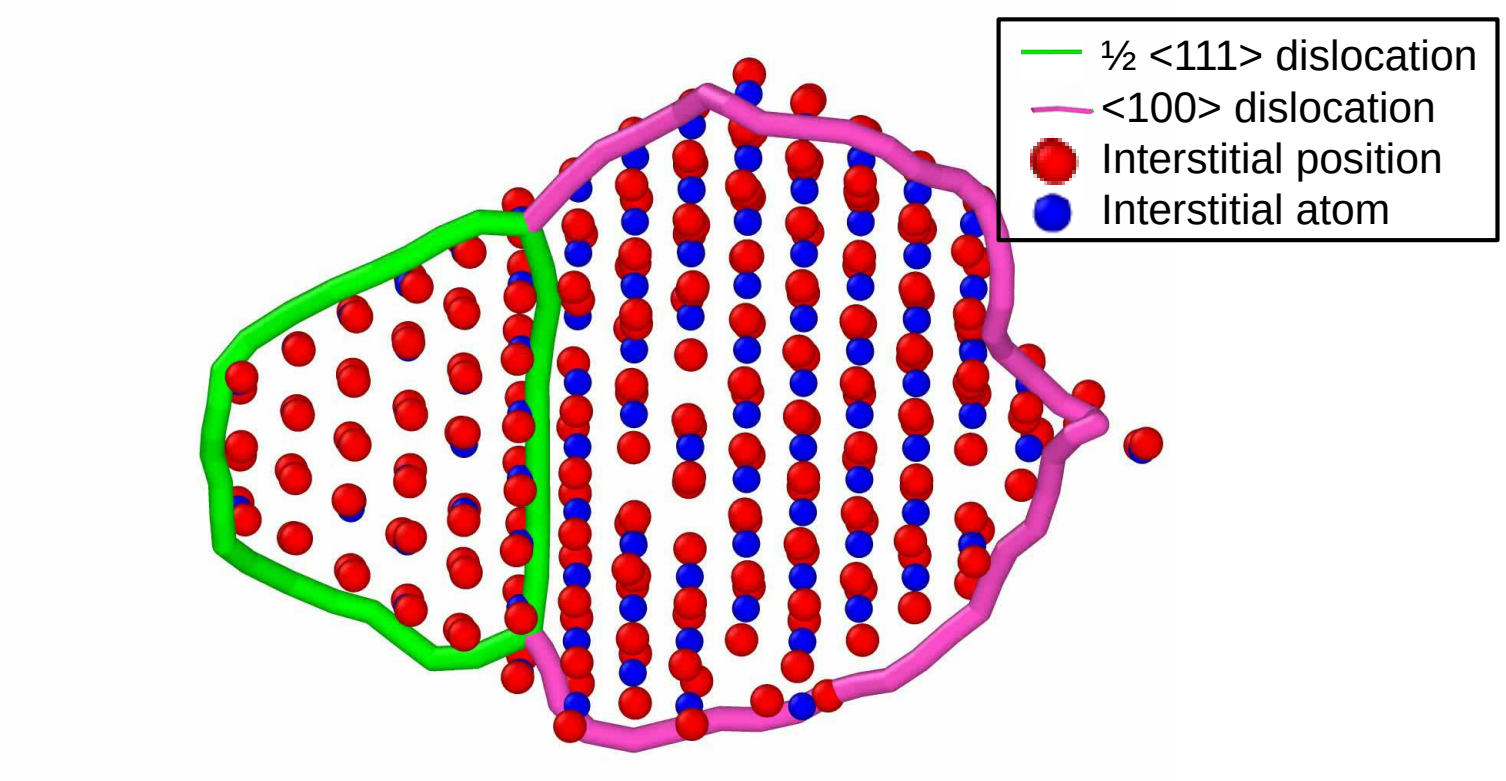
Video of final transformation



- Note time scale: final loop transformation occurs after heat spike: spike ‘activates’ a locked-in dislocation configuration

Another case…

- Transformation of final <111> segment to <100>



- Note time scale: final loop transformation occurs after heat spike: spike ‘activates’ a locked-in dislocation configuration

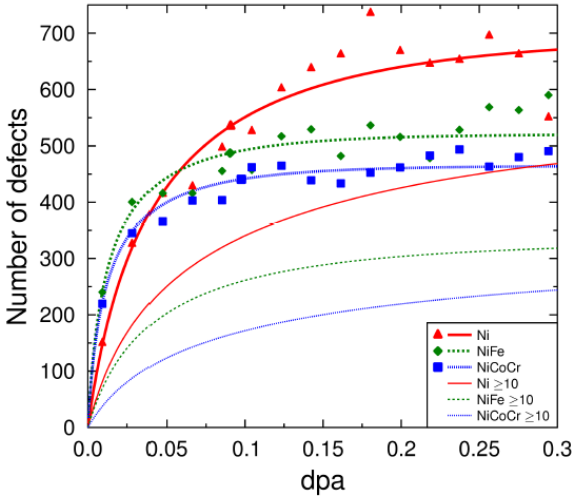
Data format for atom coordinates

- Simple asci, chemistry standard XYZ file format, PARCAS's own comment line

```
 1048577
 Frame number 12167 60000. fs boxsize  261.12000 261.12000 261.12000
Au -129.50471    98.95047  -129.48866  1    14337
Au -129.49184   100.96440  -127.60044  1    14338
Au -127.40943    98.98577  -127.59976  1    14339
Au -127.39278   100.97281  -129.52580  1    14340
Au -129.50714    98.96373  -125.52203  1    14341
Au -129.51006   101.00097  -123.48265  1    14342
Au -127.46703    98.96598  -123.47671  1    14343
Au -127.44661   100.98751  -125.51329  1    14344
Au -129.52190    98.96834  -121.45099  1    14345
Au -129.52920   101.01742  -119.41268  1    14346
Au -127.49000    98.96988  -119.41059  1    14347
Au -127.47555   101.01135  -121.44197  1    14348
Au -129.53004    98.97553  -117.37141  1    14349
Au -129.54058   101.01434  -115.32237  1    14350
Au -127.49979    98.98058  -115.33032  1    14351
Au -127.49655   101.01412  -117.36185  1    14352
...
```

Data needs

- **All** atom coordinates for 108 000 atom cell for all time steps for a single cascade would be: ~ 40 Gb
- **Final** atom coordinates of 108 000 atom cell: ~ 4 Mb
  - Not much at all
- But a cascade series of 3500 cascades:
  - All stored: 14 Gb
  - Every 10'th frame stored: 1.4 Gb
  - Every 100'th frame stored: 140 Mb



- Gzipping: about factor 2 down..

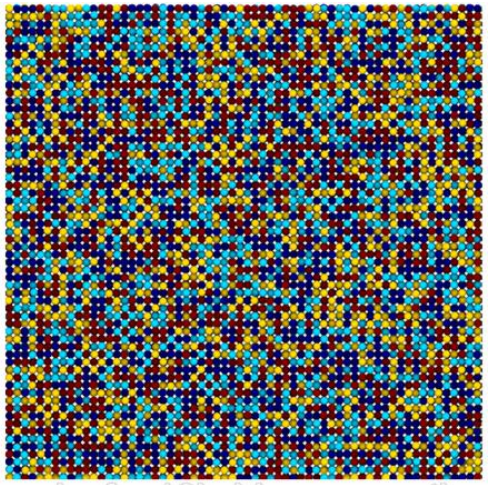
Conclusions

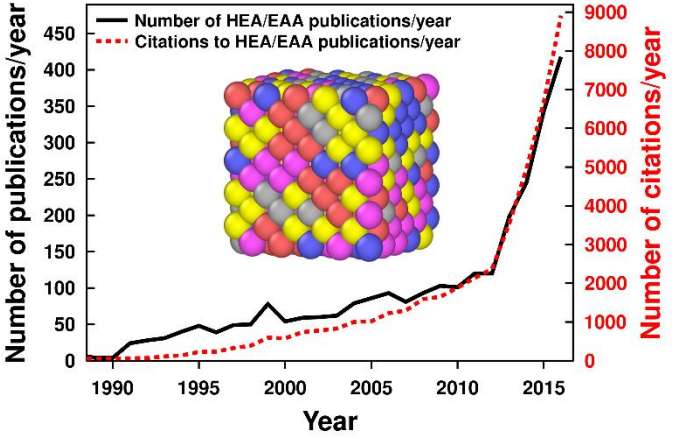
- MD simulations of radiation effects need special solutions
  - Some of which are not found by default in LAMMPS!
- Damage overlap simulations can reproduce the experimental observation of damage saturation in metals
- In Fe, <100> loops can form stepwise by cascade-induced activation of <111> dislocation segments

Thank you for you attention!

2. High-Entropy and Equiatomic multicomponent Alloys

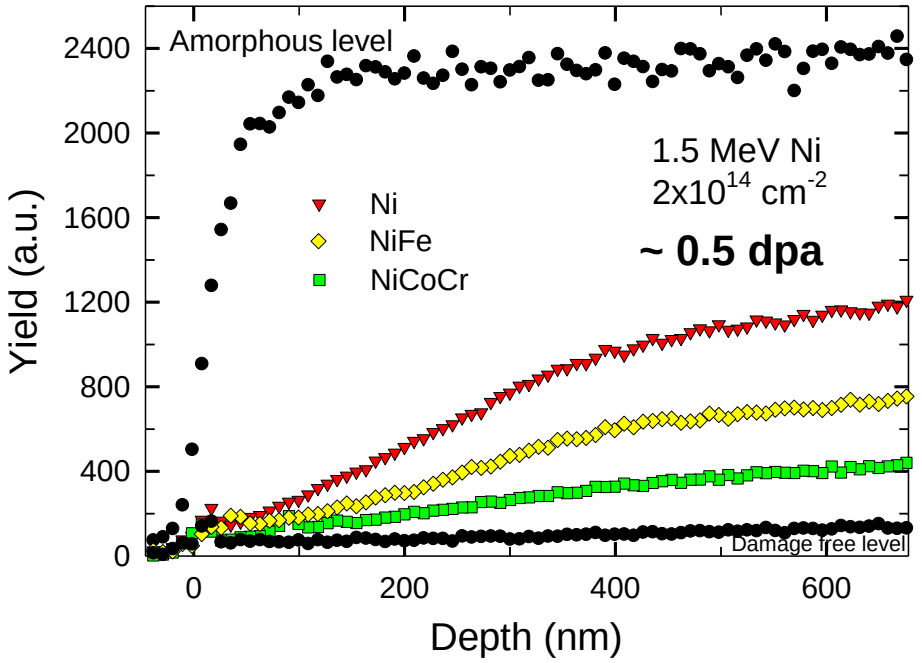
- High-entropy (HEA) and Equiatomic MultiComponent (EAMC) alloys are metal mixtures with multiple elements at equal or roughly equal concentrations, homogeneously distributed, in a single simple crystal
  - Definitions:
    - HEA: 5 or more elements
    - EAMC: 2 or more elements
- Rapidly rising interest to them due to promising mechanical, corrosion-resistant and radiation hardness properties





Damage in high-entropy alloys?

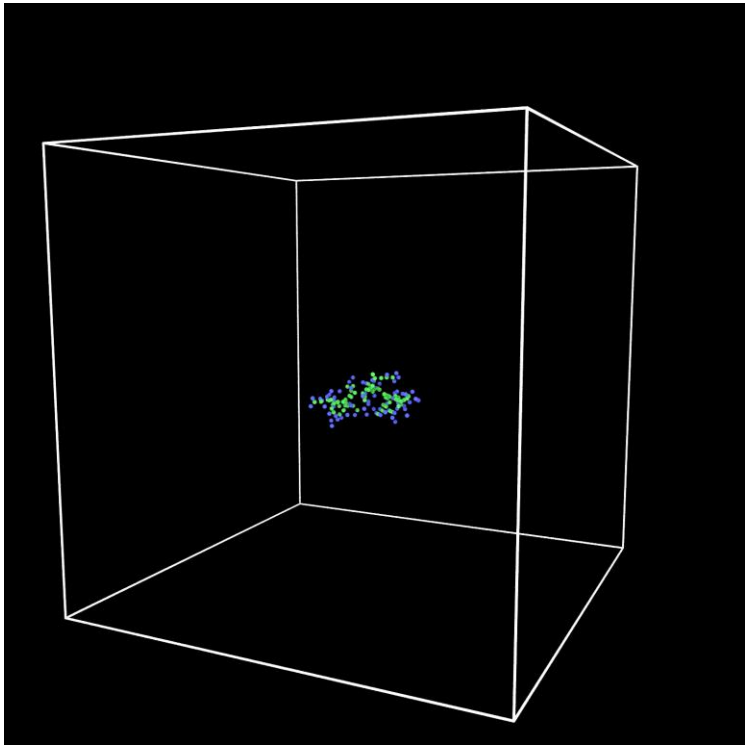
- Experiments by Yanwen Zhang *et al* (ORNL) show that damage in some FCC high-entropy alloys can be clearly lower than in the corresponding pure elements
  - Standard point of comparison: Ni, which is already quite radiation-hard



[Granberg, Nordlund, Zhang, Djurabekova et al, Phys. Rev. Lett. 116, 135504 (2016).

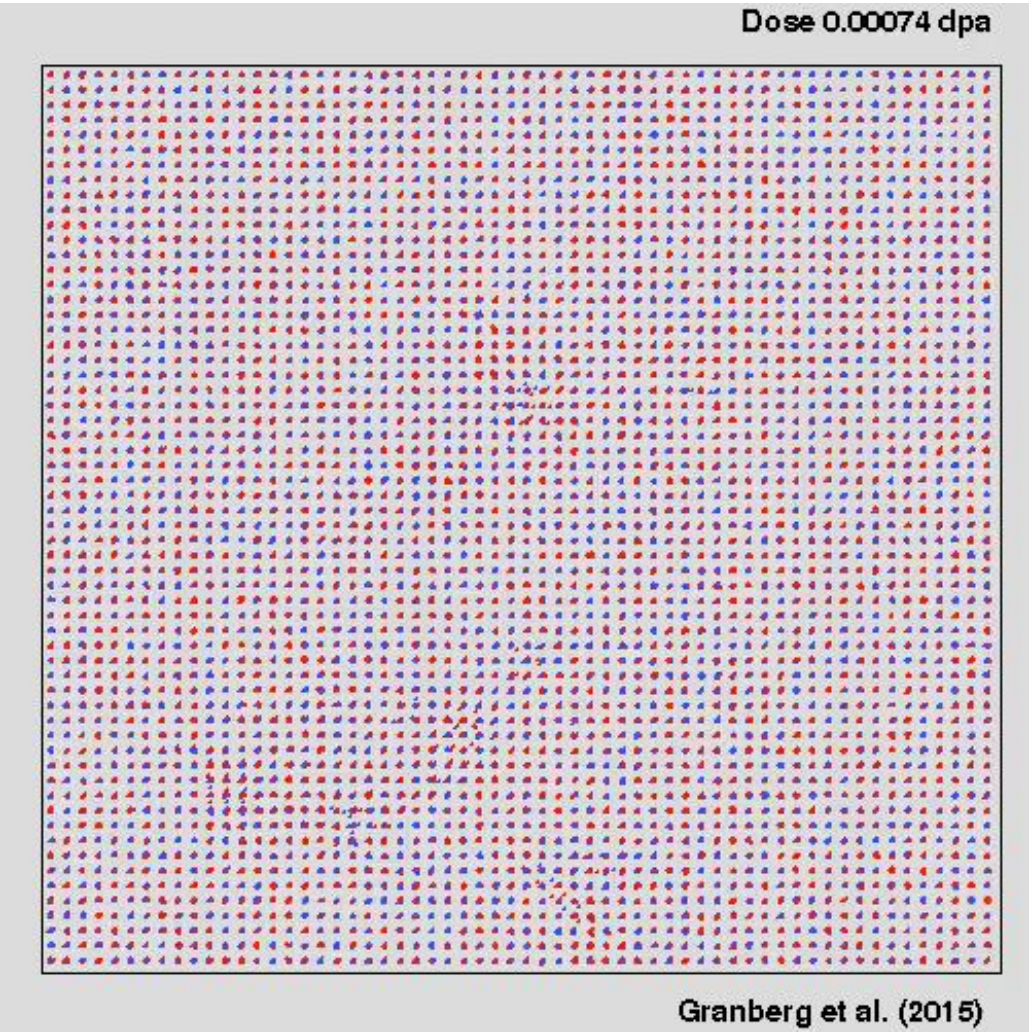
Single cascades in HEA's

- It is not *a priori* clear why damage should be lower in high-entropy alloys
- Some alloys, such as NiAl, amorphize on irradiation!
- Single cascades in HEA's do not really show a difference to pure elements
- Example: 5 keV cascade in model CoNiFeCr HEA:
  - Recombination as usual, very similar to pure Ni
  - Damage slightly **higher** than in Ni
- Cannot explain experiments – something else is needed



Damage overlap effects in HEA's

- To try to understand the damage saturation effects in HEA's, we ran > 1500 overlapping cascades in them
- Key observation: after about 0.05 dpa, almost all damage is in clusters – and this evolves!
- Example: FeNi



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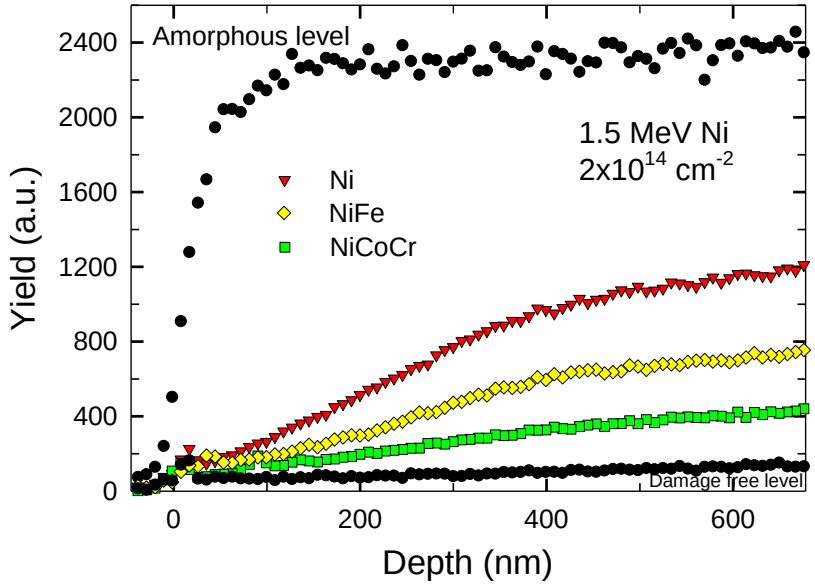
[Granberg, Nordlund, Zhang, Djurabekova et al, Phys. Rev. Lett. 116, 135504 (2016).

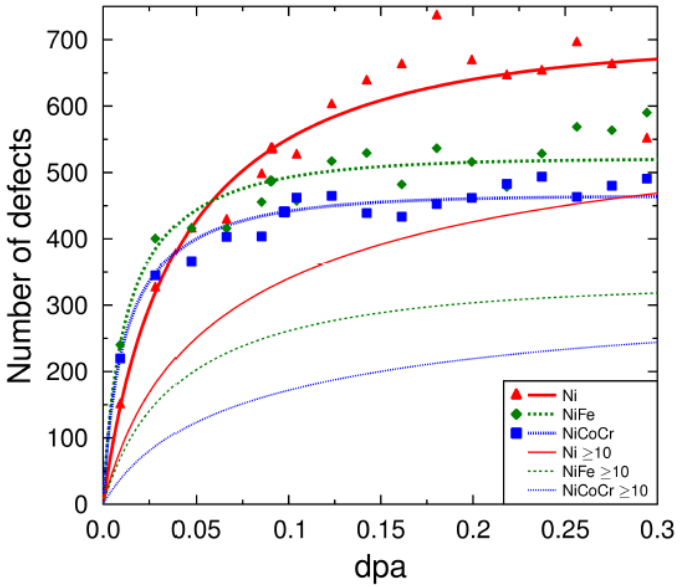
Damage in clusters in HEA's

- The clustered damage shows a similar damage reduction effect as the experiments!

Experiment (RBS)



Simulation (MD)



[Granberg, Nordlund, Zhang, Djurabekova et al, Phys. Rev. Lett. 116, 135504 (2016)]

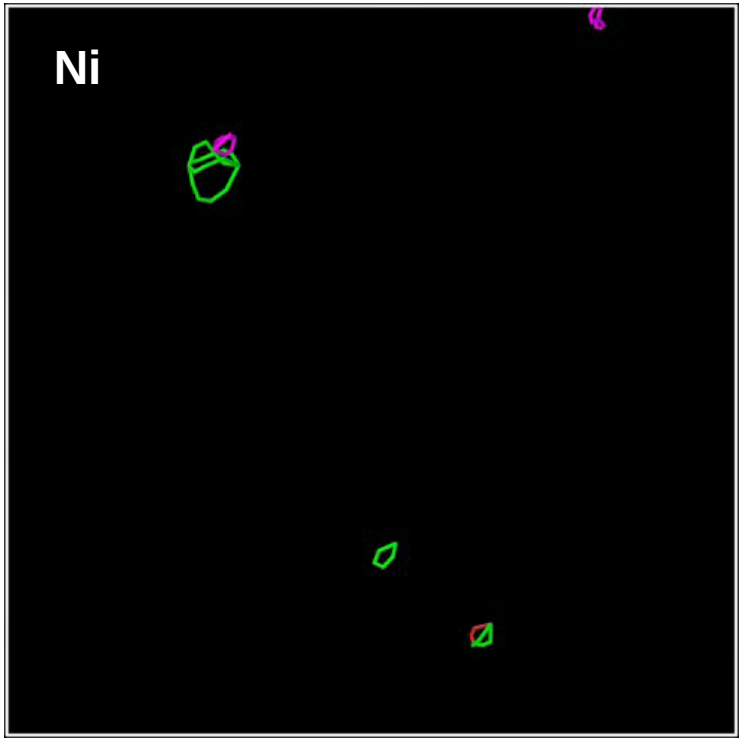
Analyses of dislocation structures

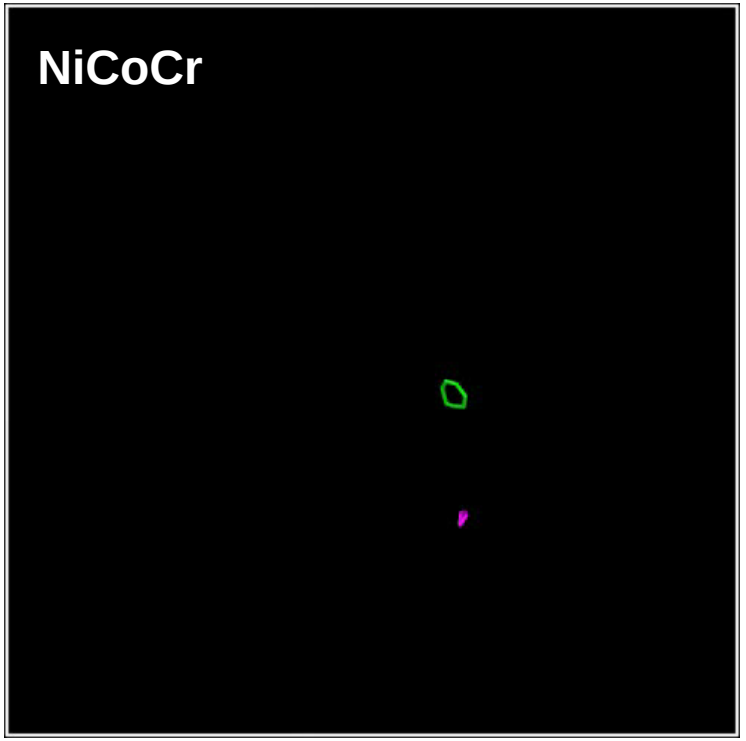
- We have analyzed all the frames for dislocations with the ovito DXA analysis (constructing Burgers vectors to detect dislocations)

Stair-rod dislocation => Stacking fault tetrahedron

Shockley partial

Frank loop



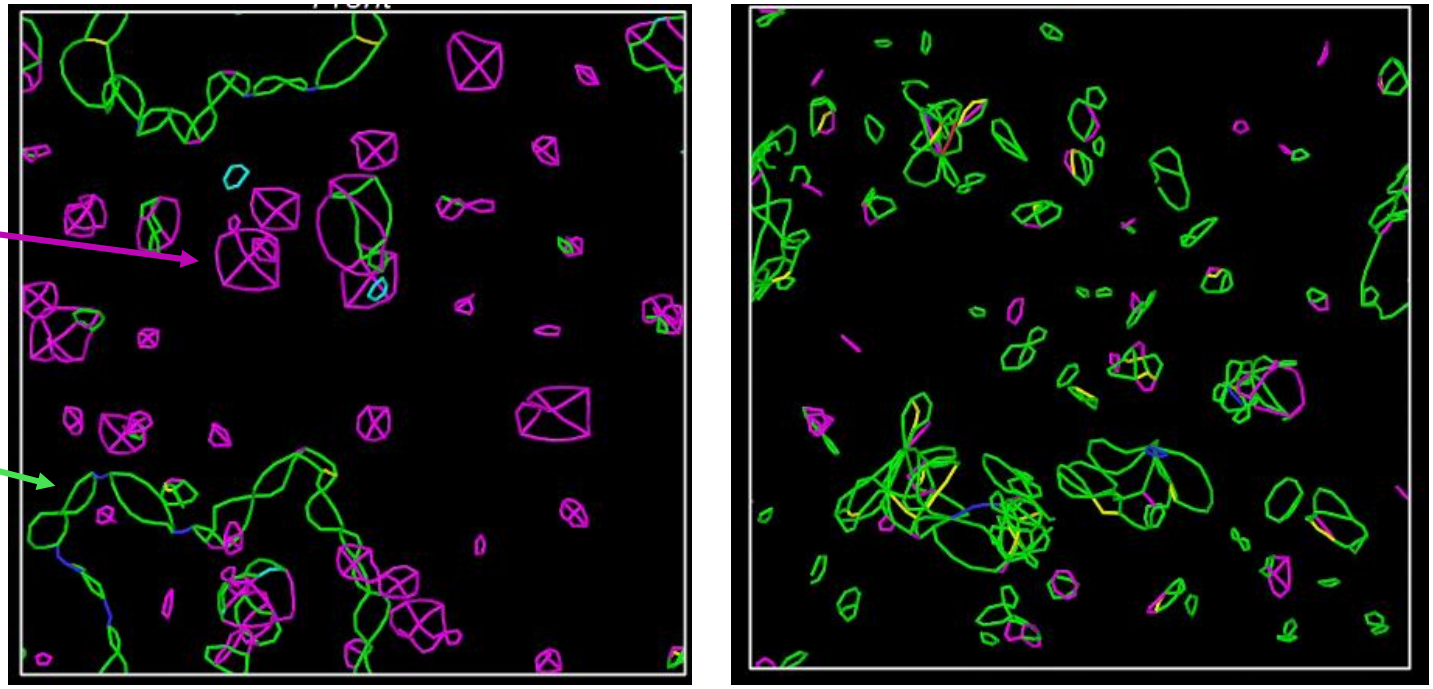


Final dislocation state Ni vs. NiCoCr

- Ni has larger dislocation loops and much more SFT's than NiCoCr

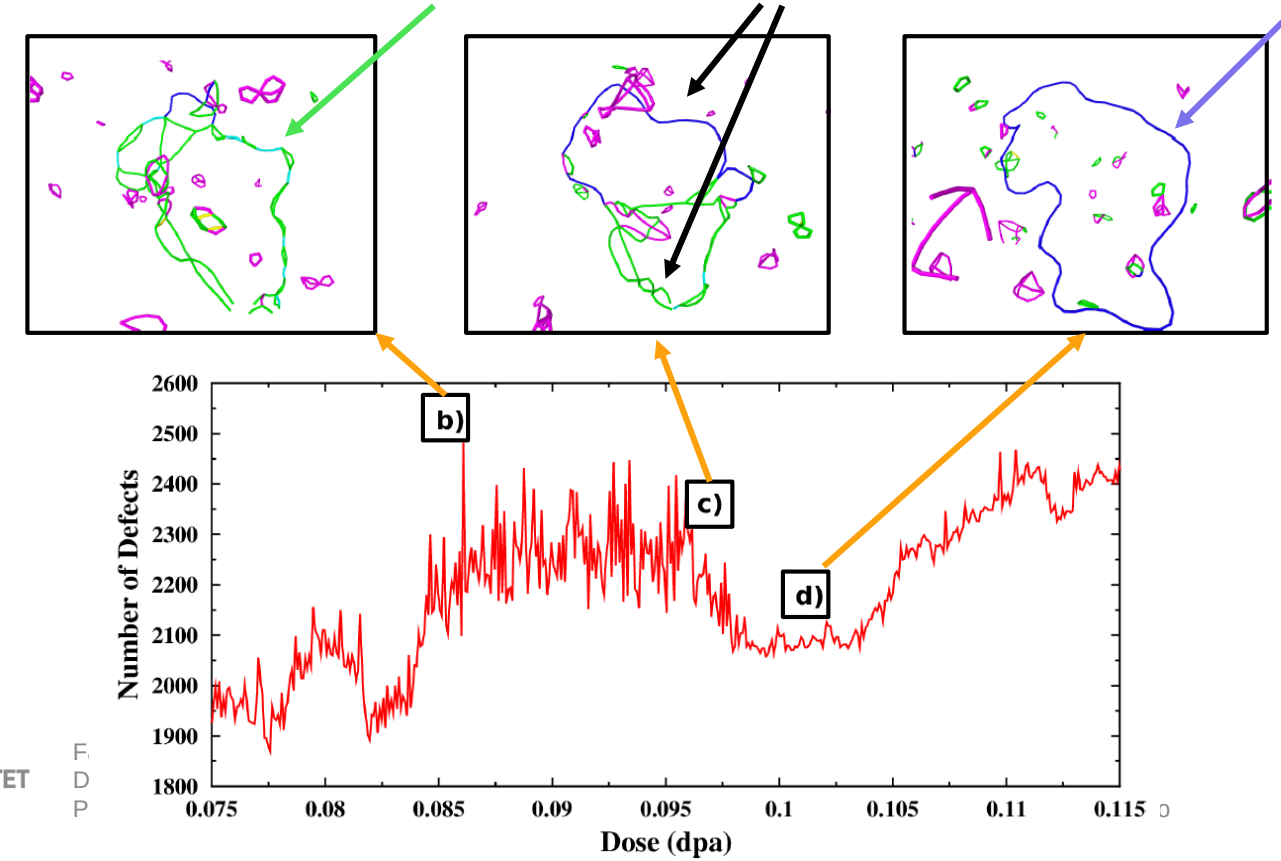
Ni ~ 0.3 dpa

NiCoCr ~ 0.3 dpa



Dislocation reactions affecting overall damage level

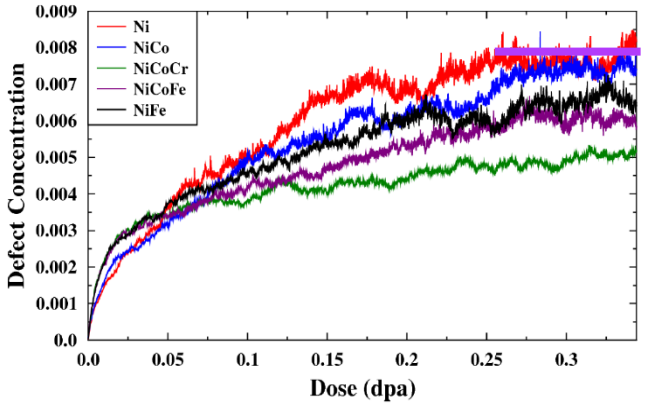
- The dislocations dominate the overall damage level
- Numerous dislocation reactions occur driven by the irradiation
- Example: Shockley partial stepwise becoming a Frank loop

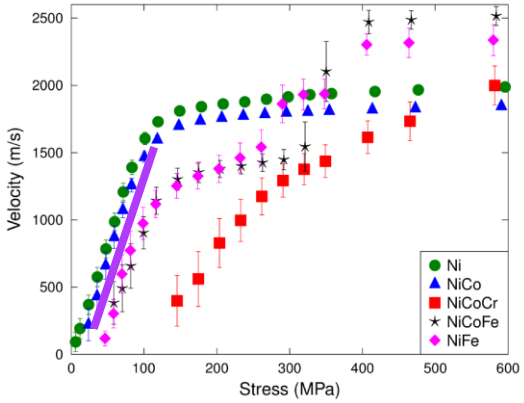


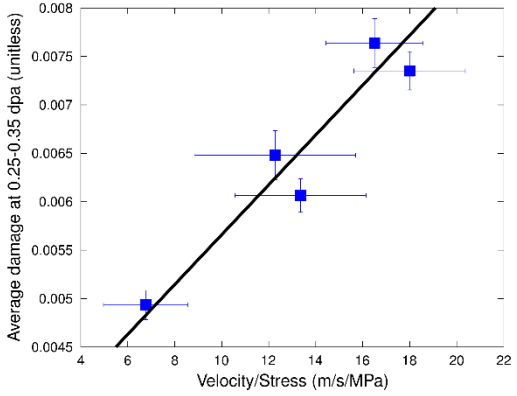
Reason to damage reduction: reduced dislocation mobility

- The reduction in damage level correlates clearly with dislocation mobility
  - In the alloys, each atom has a local strain field, and this reduce dislocation mobility
  - Lower dislocation mobility keeps dislocations from growing, and the smaller dislocations can recombine easier during cascade overlap

Final damage level vs. Slope of dislocation mobility => Clear correlation



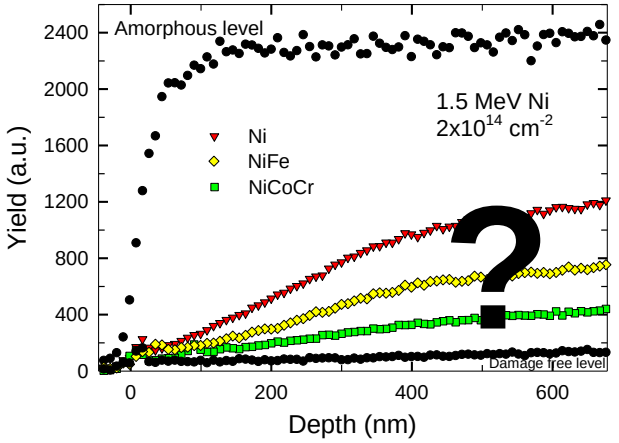


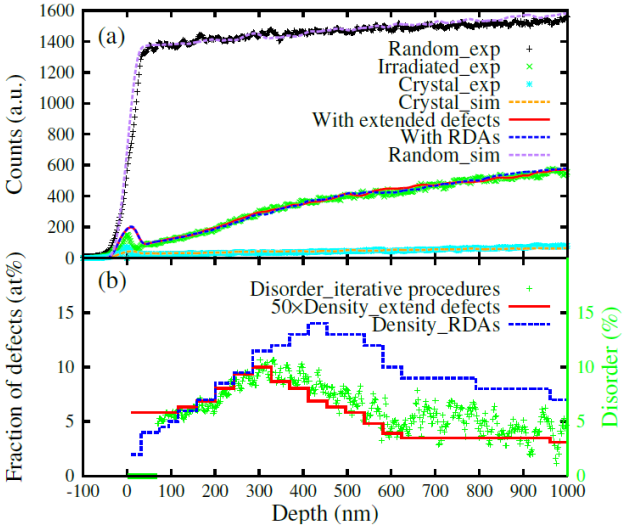


[Granberg et al, Nucl. Instr. Meth. B (2017), accepted]

Why is RBS signal so high?

- In the experiments, the RBS/channeling signal appears very high, about ”1/2 randomly displaced atoms”
- 50% damage does not at all correspond to TEM, resistivity or MD results, which show <1% defective atom fraction
- Explanation just determined by us: dislocations give a very high RBS signal due to strain effects
  - New code RBSADEC to simulate RBS/channeling from arbitrary atom coordinates shows that signal from loop ~50x higher than for same number of randomly displaced interstitial atoms!





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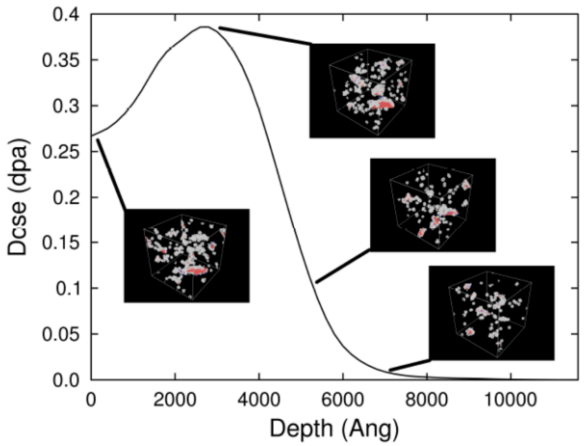
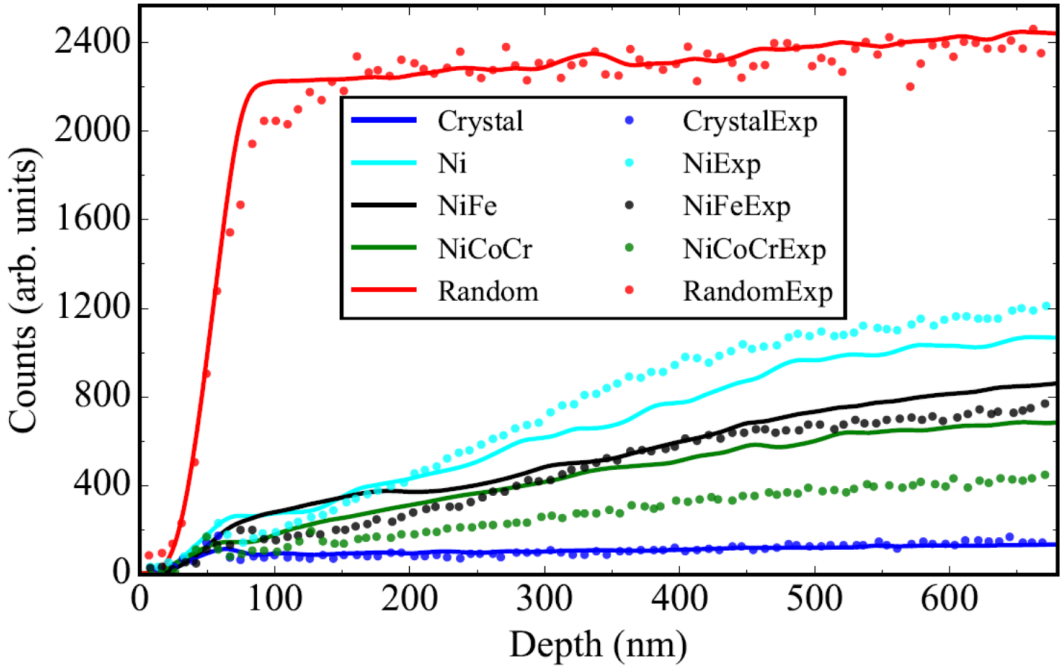
[S. Zhang, K. Nordlund, F. Djurabekova, Y. Zhang, G. Velisa, and T. S. Wang, Phys. Rev. E 94 (2016) 043319]

Direct comparison of damage structure with experiments

- Using the RBSADEC code we can compare our structures directly with experiments (with no fitting!)
- Agreement is very good considering defect migration is not included in MD simulations and we use a single ion energy





[S. Zhang, K. Nordlund, F. Djurabekova, F. Granberg, Y. Zhang, and T. S. Wang, Mater. Res. Lett. (2017) accepted]

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Potentials developed: one-slide overview of thousands of publications…

- In general, potentials suitable for irradiation effects exist:
  - For almost all pure elements
  - For the stoichiometric state of a wide range of ionic materials
    - But these do not always treat the constituent elements sensibly, e.g. in many oxide potentials O-O interactions purely repulsive => predicts O_2 cannot exist => segregation cannot be modelled
  - For a big range of metal alloys
- Not so many potentials for mixed metal – covalent compounds, e.g. carbides, nitrides, oxides in non-ionic state
- Extremely few charge transfer potentials
- For organics only ReaxFF for CNOH, extended Brenner for COH systems
- NIST maintains a potential database, but pretty narrow coverage – one often really needs to dig deep in literature to find them

Origin of molecular dynamics for radiation effects

- MD is solving the Newton's (or Lagrange or Hamilton) equations of motion to find the motion of a group of atoms
- Originally developed by Alder and Wainwright in 1957 to simulate atom vibrations in molecules
  - Hence the name "molecular"
  - Name unfortunate, as much of MD done nowadays does not include molecules at all
- Already in 1960 used by Gibson to simulate radiation effects in solids [Phys. Rev. 120 (1960) 1229)]
  - A few hundred atoms, very primitive pair potentials
    - But discovered replacement collision sequences!