Applications of Accelerated Molecular Dynamics in Materials Science

Blas Pedro Uberuaga

Los Alamos National Laboratory

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LA-UR-12-20928

NNSA

Acknowledgements

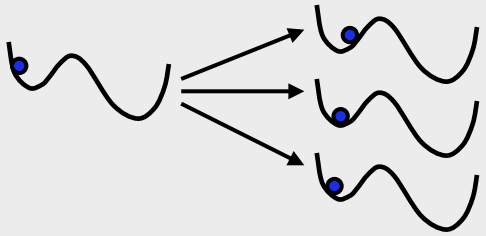
- **Art Voter** (LANL)
- **Radiation damage in MgO:**
  - Kurt Sickafus (*now at University of Tennessee*)
  - Robin Grimes and Antony Cleave (*Imperial*)
  - Roger Smith and Pravesh Bacorisen (*Loughborough*)
  - Francesco Montalenti (*now at University of Milano*)
  - Graeme Henkelman (*now at University of Texas, Austin*)
- **Void evolution:**
  - Steve Valone and Richard Hoagland (*LANL*)
- **Stretched nanostructures**
  - Steve Stuart (*Clemson*)
  - Chun-Wei Pao (*now at Academia Sinica*)
  - Danny Perez and Sriram Swaminarayan (*LANL*)

Funding: BES, CMIME EFRC, LANL LDRD, Enhanced Surveillance

Brief Introduction to Accelerated Molecular Dynamics

- Many processes occur on much longer timescales than accessible via MD (ps-ns-μs)
  - e.g. surface growth
  - radiation damage annealing
  - mass transport
  - etc.
- Need method to reach experimentally relevant timescales
- Three accelerated dynamics methods developed at LANL (Art Voter's team)
  - Parallel-Replica Dynamics
  - Hyperdynamics
  - Temperature Accelerated Dynamics (TAD)

Accelerated Molecular Dynamics Methods

Parallel Replica Dynamics (1998) 	Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps

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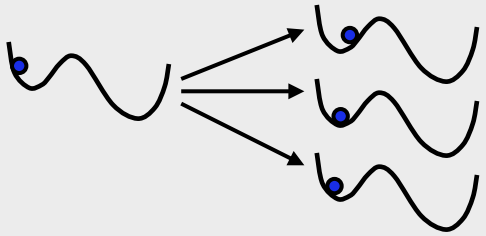
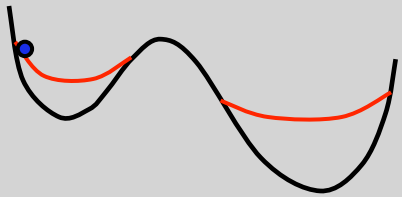
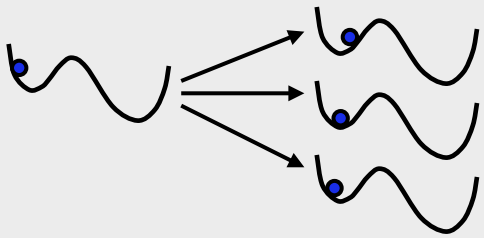
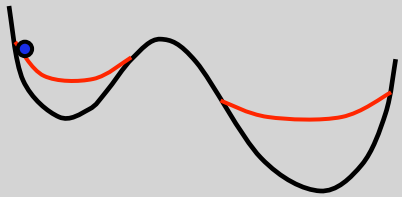
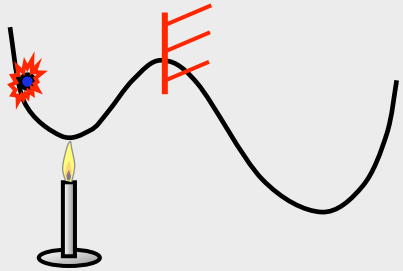
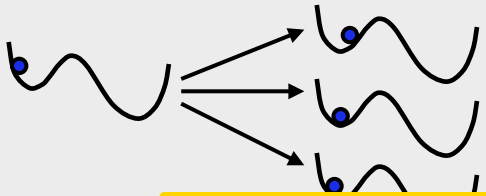
Parallel Replica Dynamics (1998) 	Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps
Hyperdynamics (1997) 	Increase rate by reducing effective barriers

Accelerated Molecular Dynamics Methods

Parallel Replica Dynamics (1998) 	Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps
Hyperdynamics (1997) 	Increase rate by reducing effective barriers
Temperature Accelerated Dynamics (2000) 	Increase rate by raising temperature

Accelerated Molecular Dynamics Methods

Parallel Replica Dynamics (1998) 	Explore basin with many processors *M* such that $M \sim \tau_{rxn}/1$ ps
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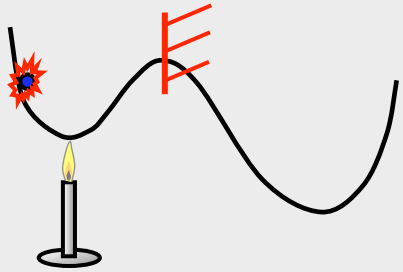
Temperature Ac… 	…ng temperature

Common Themes:

- ***reduce waiting time for a transition to order of picoseconds***
- ***let the trajectory find an appropriate way out of state, but coax it into doing so more quickly***

Demonstrations of AMD methods

- Vacancy Void Annealing in Cu
- Defect Dynamics in MgO
- Strain-rate dependent behavior in wires and nanotubes

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Common Theme:
Examples where achieving long times in atomistic simulations provided critical insight

A Parallel-Replica Study

VACANCY VOID ANNEALING IN CU

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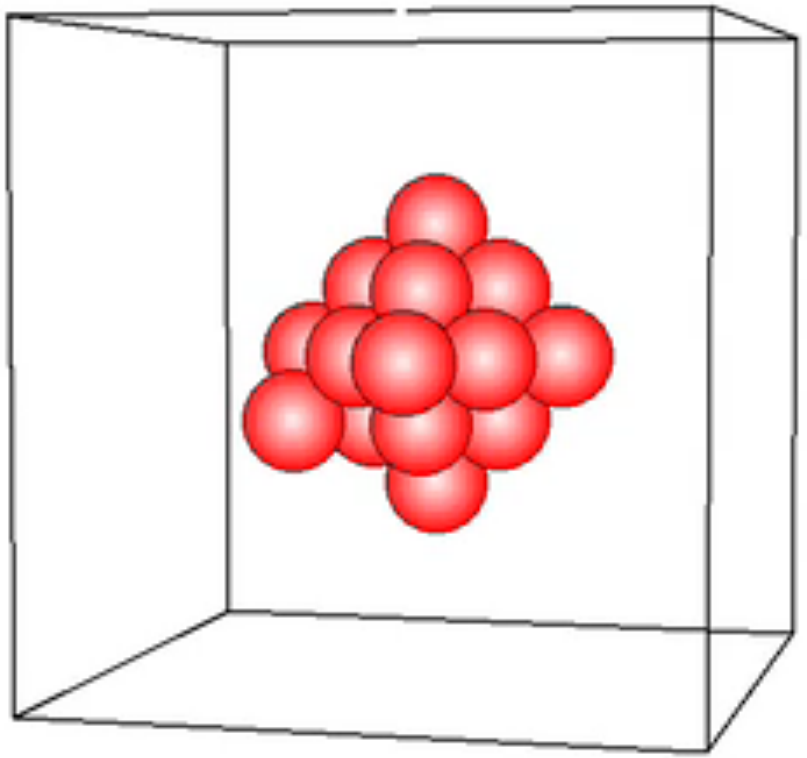
Vacancy void annealing in Cu

- Goal:
  - Understand vacancy aggregation/void formation
  - Probe kinetics of vacancy voids
- Method:
  - Parallel-replica dynamics: explore long-time behavior of voids
  - Molecular dynamics: obtain statistics on possible pathways
  - Nudged elastic band (molecular statics): characterize pathways
- Reference:
  - Uberuaga, Voter, Hoagland, and Valone, PRL **99**, 135501 (2007).

Long time annealing of 20 vacancy void in Cu

- EAM Cu
- Parallel-replica simulation of 20-vacancy void annealing at 400 K
  - 20 vacancies is one too many for "perfect" void
- Total simulation is 7.82 μs
- At 1.69 μs, void transforms to SFT
- Run on 39 processors for 15 days
- Efficiency = 79%
- *Equivalent single processor time: 1.3 years*



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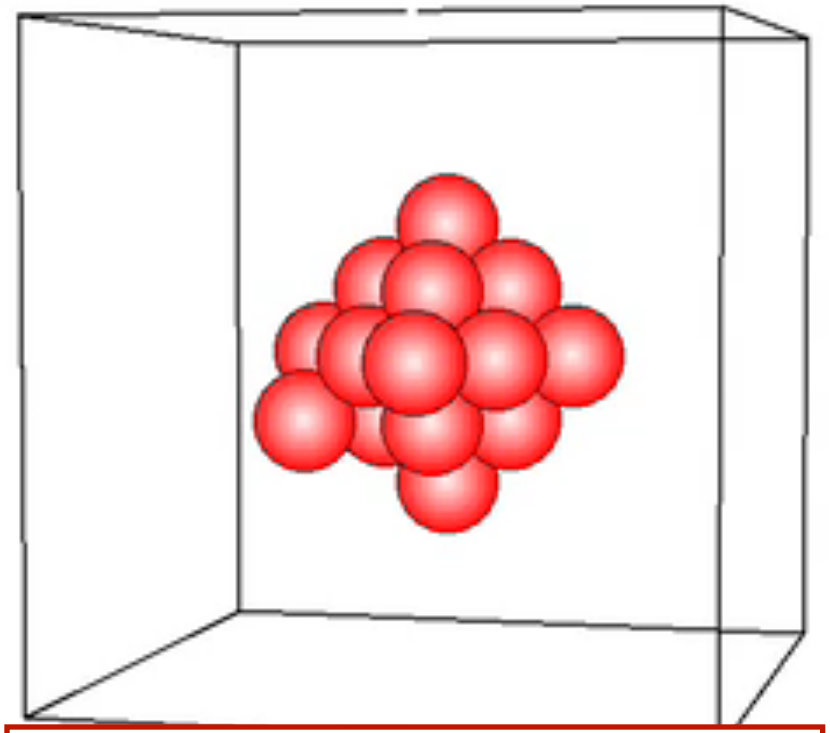
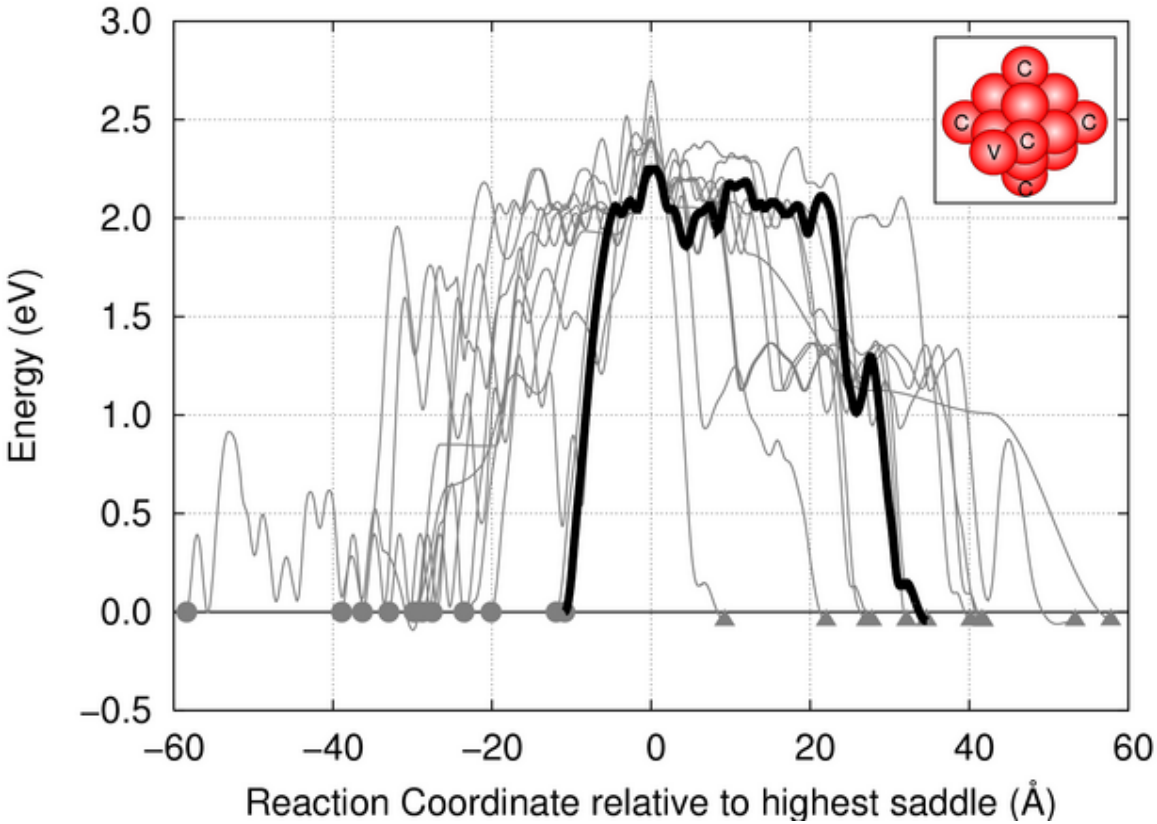


New transformation pathway for the formation of stacking fault tetrahedra (SFTs)

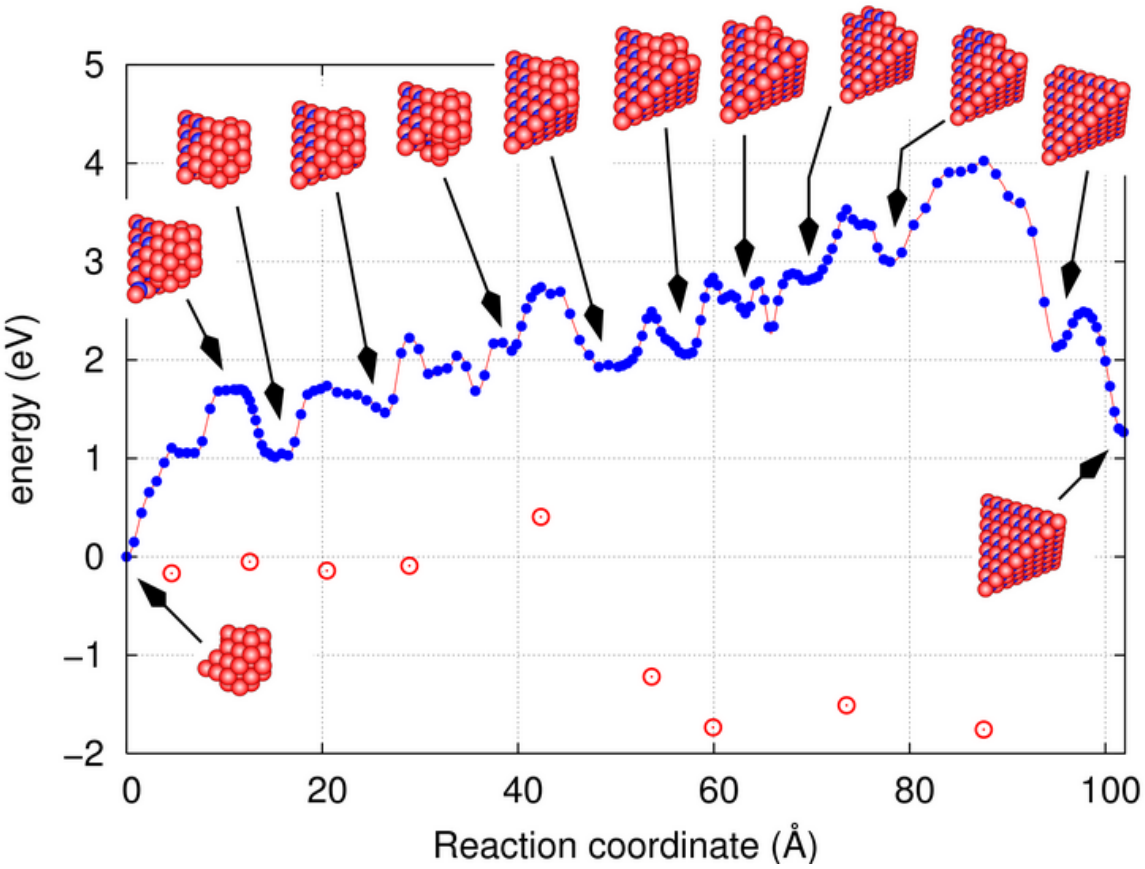
Transformation pathway for 20 vacancy void

- Full path for transformation to SFT calculated with NEB
- Initial barrier is > 2 eV
  - Should have taken >10^5 years at 400K to occur (assuming standard prefactor)
- Vineyard prefactor for first step between 10^{36} and 10^{43} Hz



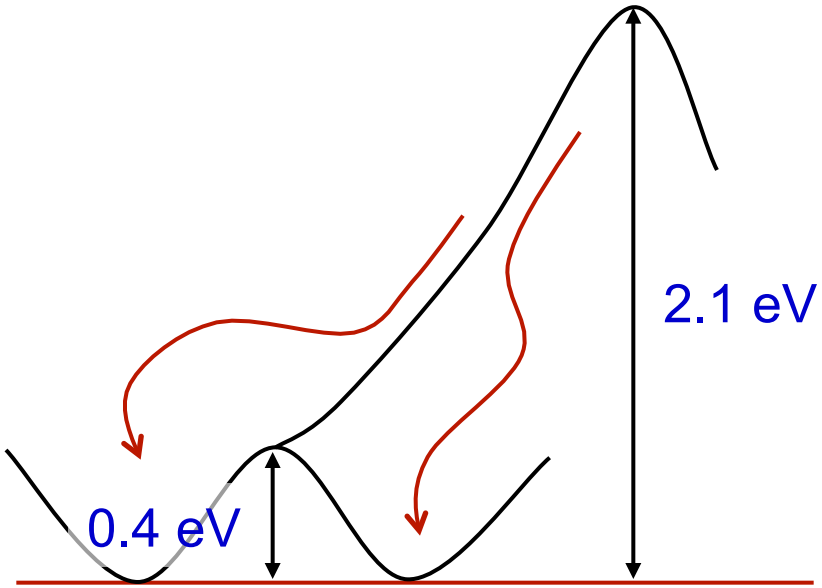
Void to SFT transformation: 45 vacancy void in Cu

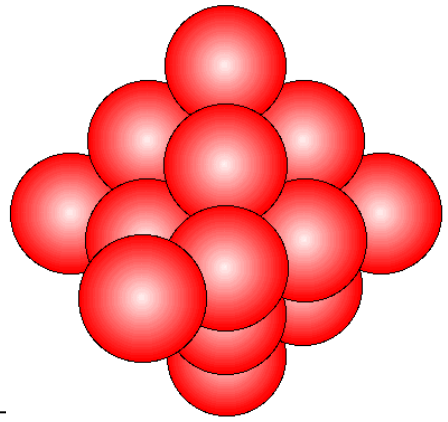
- Par-rep of 45 vacancy void at 475 K
  - 39 processors
  - 39% efficiency
  - 5.6 days
    - Effective 1 CPU time: 85 days
  - 0.24 μs
- Figure is minimum energy path at constant volume
- Overcomes a very large internal energy barrier (~4 eV) at 475 K
- Free energy barrier is much lower, as estimated by open symbols



Initial step in void to SFT transformation

- Barrier to initiate transformation accessible from a number of states
- Part of path is a ridge, minimizing along it can land to either lower energy state
  - Problem for ensuring connectivity of saddles
- Vineyard rate for 2.1 eV process very fast
  - 144 ns at 400 K
  - *About 1 fs at 500 K*
  - Harmonic TST valid?
  - TAD valid?

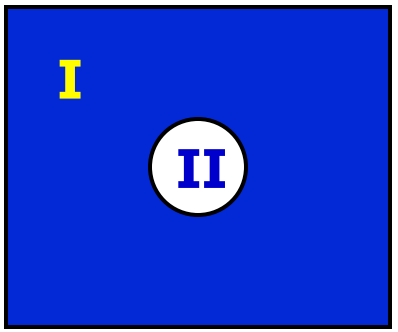




Prefactor for Transformation

- Barrier for 20-vacancy void is between 2.3 and 2.7 eV
  - Assuming a standard prefactor (~10^{13} Hz), would take 10^6 years to occur at T=400 K
  - Observed waiting times are 1-15 ns
  - Prefactor observed from dynamics: 10^{38} Hz; calculated with Vineyard: 10^{43} Hz
  - *Prefactor is anything but standard!*

- Origin of Prefactor
  - View material containing void as partitioned into two regions
    - Region I: Cu
    - Region II: void
  - Before transition, volume of Cu is Region I volume
  - After, volume of Cu is Region I + Region II
  - Entropy change ΔS due to volume change ΔV: $\Delta S=\alpha B \Delta V$
    - α=coefficient of thermal expansion, B=bulk modulus
  - Assuming ΔV=10 atomic volumes ⇨ $\Delta S=67.5/k_B$ ⇨ prefactor enhanced by factor of 10^{29}
  - Consistent with observed/calculated prefactor



Why long time simulations were needed?

- Once system is in corner state, time scale for void → SFT transformation very quick, ns
- However, time to reach corner state can be very long, 1.7 μs at 400 K
- Parallel-replica was critical for reaching time scales for surface vacancy to sample surface configurations and discover corner state
- HTST-based methods may have failed to predict mechanism

A Temperature Accelerated Dynamics Study

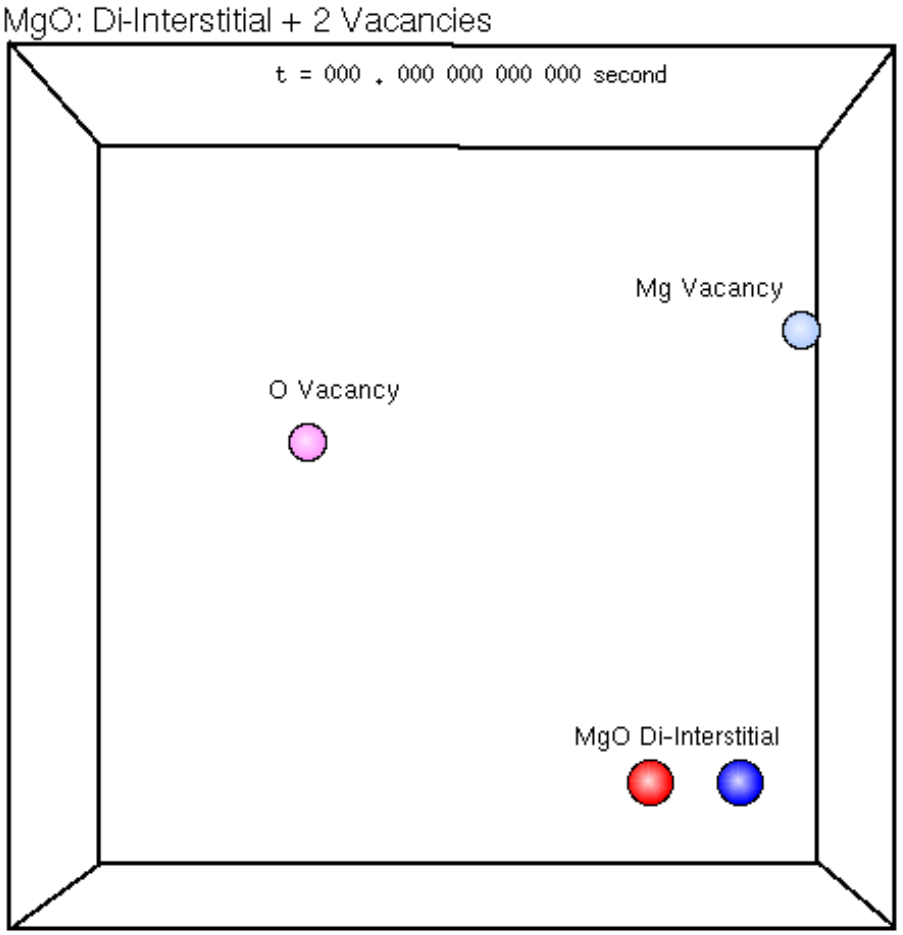
DEFECT DYNAMICS IN MgO

Defect Dynamics in MgO

- Goal:
  - Understand origin of radiation tolerance in complex oxides
  - Determine the relevance of metastable defects
- Methods:
  - Buckingham potential with long range electrostatics
  - MD: non-equilibrium production of damage due to irradiation
  - TAD: evolution of defects produced under irradiation
  - Rate theory: impact of atomistic defect properties on experimental observables
- References:
  - Uberuaga, Smith, Cleave, Henkelman, Grimes, Voter, and Sickafus, PRL **92**, 115505 (2004); PRB **71**, 104102 (2005); NIMB **28**, 260 (2005).

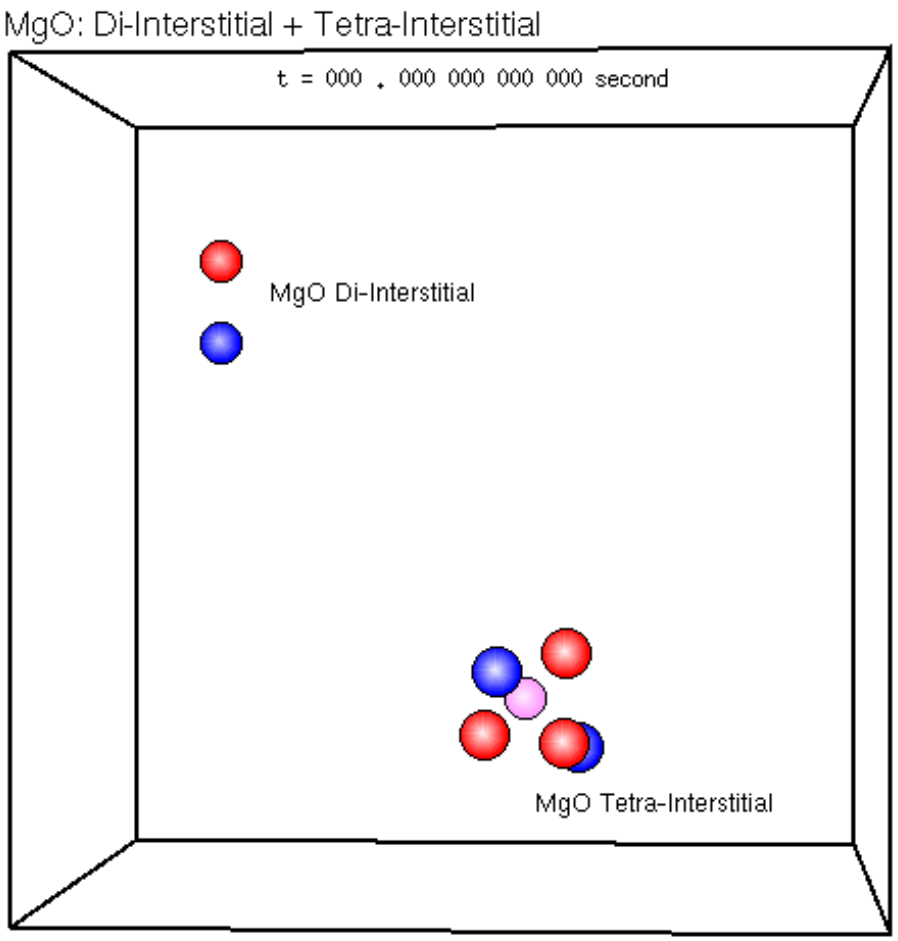
TAD Simulation: Long-range Annihilation

- Begin with I_2 and two vacancies
- I_2 attracted to charged vacancies, annihilating by 81 ms
- Annihilation via long range, concerted events involving many atoms
- Red=oxygen, Blue=magnesium
- Dark=interstitial, Light=vacancy



Defect aggregation in MgO

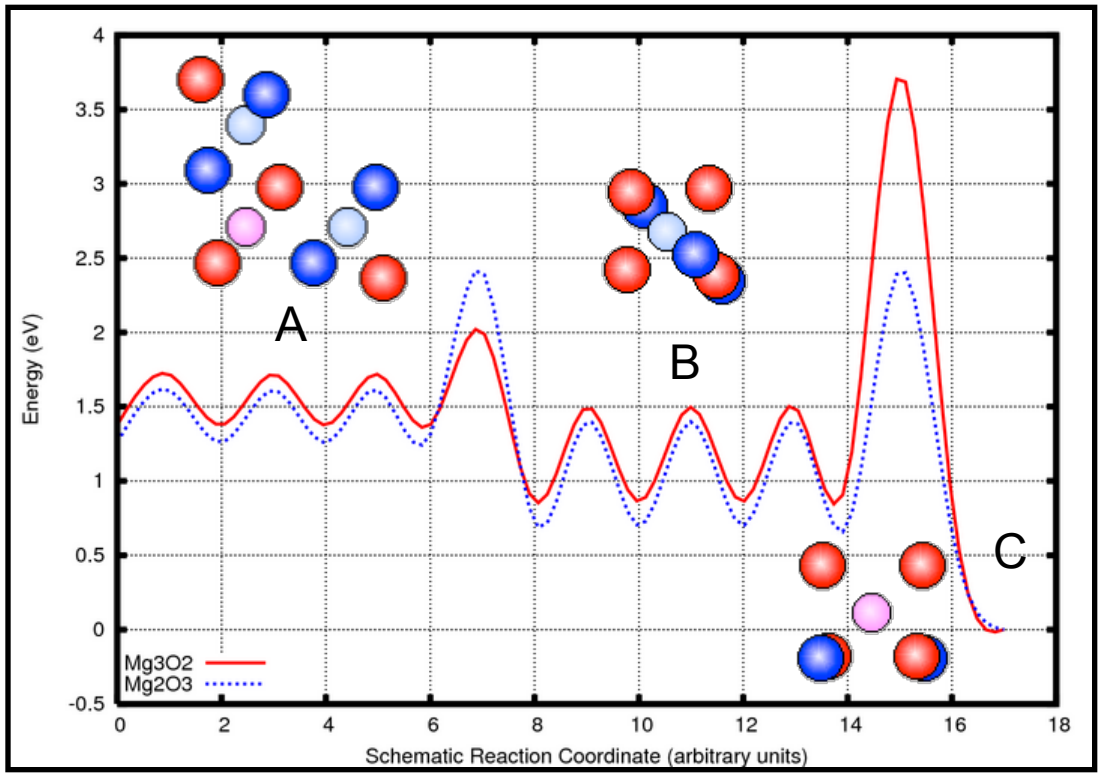
- Begin with I_2 and I_4
  - Defects found at end of collision cascade
- I_2 attracted to I_4, binds forming I_6
- Metastable I_6 diffuses very quickly
  - ns timescale at 300 K
  - diffusion is 1D along <110>
  - decay to ground state takes years
- Red=oxygen, Blue=magnesium
- Dark=interstitial, Light=vacancy



TAD simulation, Uberuaga et al, 2003

Cluster dynamics: Kinetics of the pentamer cluster in MgO

- Two versions of pentamer:
  - Mg_2O_3
  - Mg_3O_2
- Both can exist in 3 forms
- Each has unique diffusive characteristics
  - A: diffuses quickly in <110> direction
  - B: diffuses more slowly, again in <110> direction
  - C: immobile at 300K
- A, B and C behave similarly for both pentamers
- But decay between forms is different

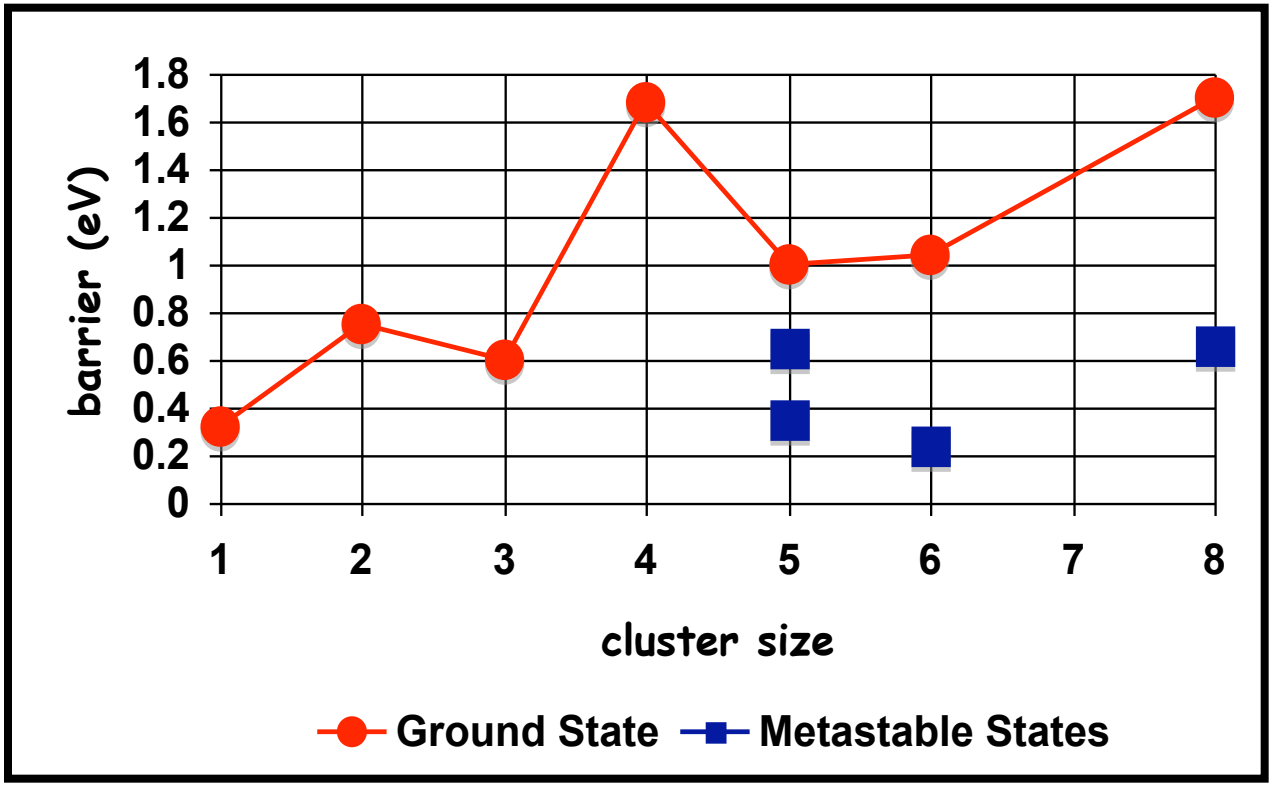


- Encounters of $MgO+MgO_2$ can form any type of Mg_2O_3
  - 10 simulations: 1 forms A, 7 form B, 2 form C

Uberuaga, et. al., *PRL* **92**, 115505 (2004); *PRB* **72**, (2005); *NIMB* **28**, 260 (2005)

Interstitial cluster kinetics in MgO

- Diffusion barrier of ground state structures follow no clear pattern
- For clusters of size 5 and greater, there are metastable structures that diffuse faster than the ground state



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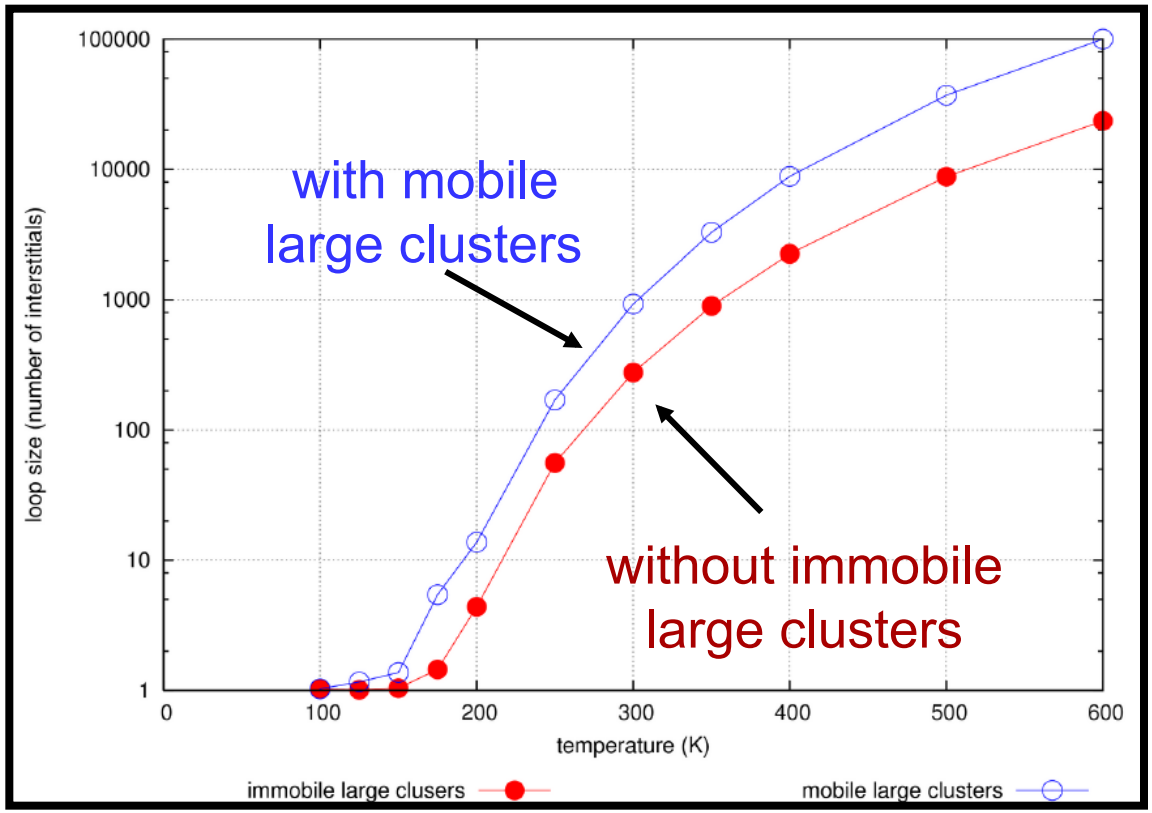
Effects of cluster mobility on observables

- 1-D reaction rate theory
  - Mobilities from TAD
  - Steady-state conditions
- Size of loops increases by more than 3 times when large clusters are mobile
  - "large" clusters contain more than 1 interstitial
- Enhanced defect mobility results in fewer, larger loops



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Why long time simulations were needed?

- TAD simulations revealed that aggregation of interstitials leads to metastable interstitial cluster structures with high mobilities
- Critical that evolution observed at low temperature as lifetime of metastable clusters at high temperature would be short and possibly missed if simply performed high-temperature MD
  - Decay barriers 0.5 – 2 eV
  - Migration barriers 0.3 – 2 eV

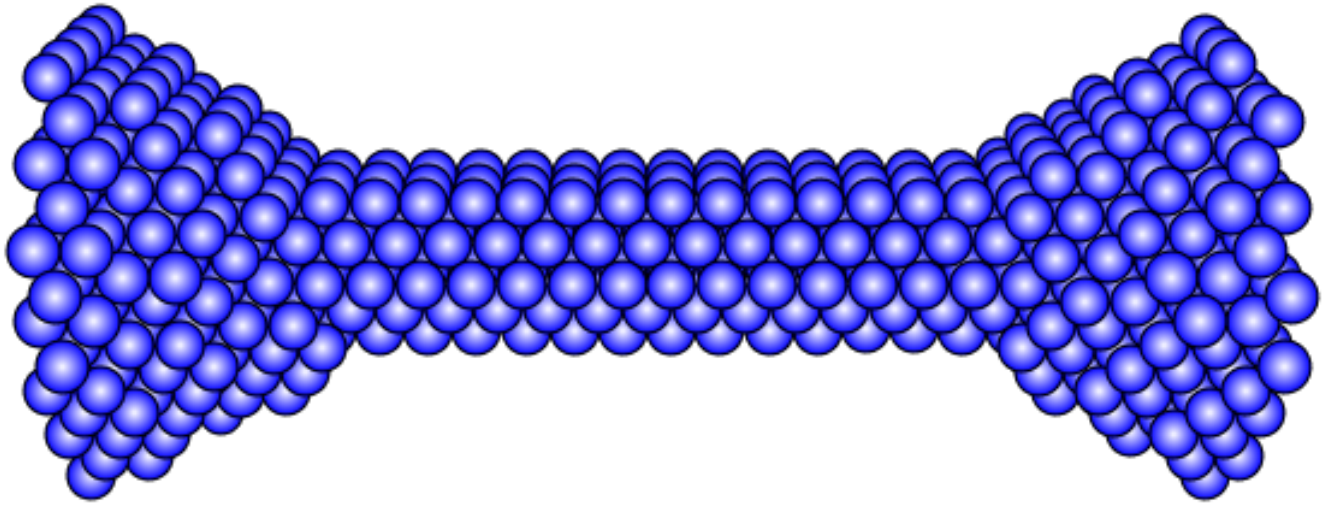
Two Parallel-Replica Studies

STRAIN-RATE DEPENDENT BEHAVIOR

ParRep of stretching Ag nanowire

- Run on LANL Roadrunner (1 PFLOPS if using all 12,240 cell processors)
- Boost good at first; drops as events become more frequent.
- Outer edge atoms clamped, advanced 0.01A at regular intervals

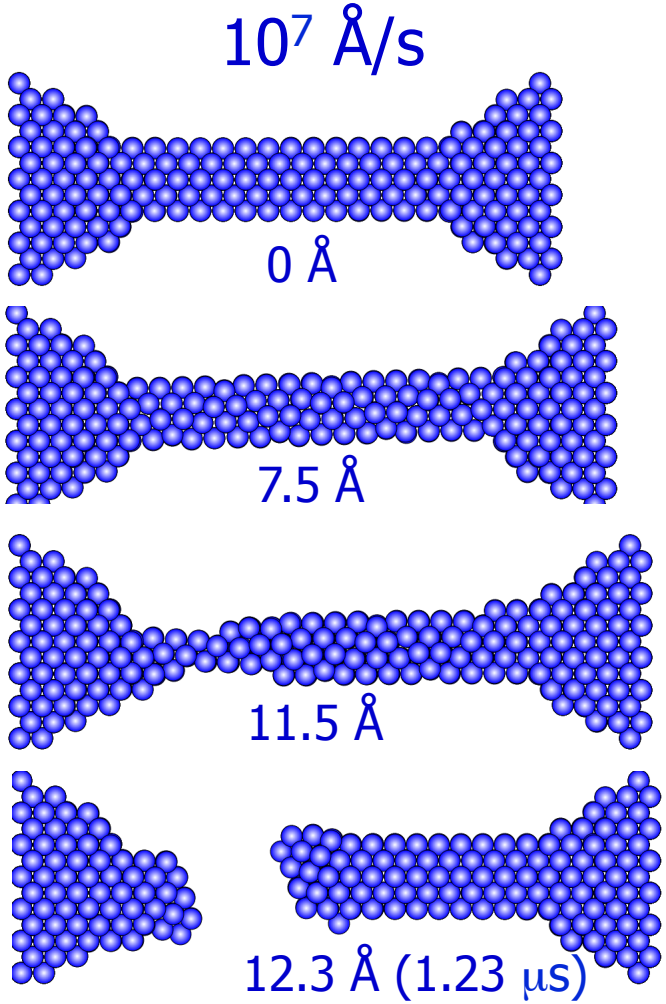
Ag[110] nanowire, 1.d5 A/s, 1 us per frame



Danny Perez, Chun-Wei Pao, Sriram Swaminarayan, AFV

Pulling slower changes behavior

At stretching speeds below ~10^6 Å/s, the system can thin down, coming back to perfect fcc. At higher speeds, it disorders or necks, never recovering perfect fcc.



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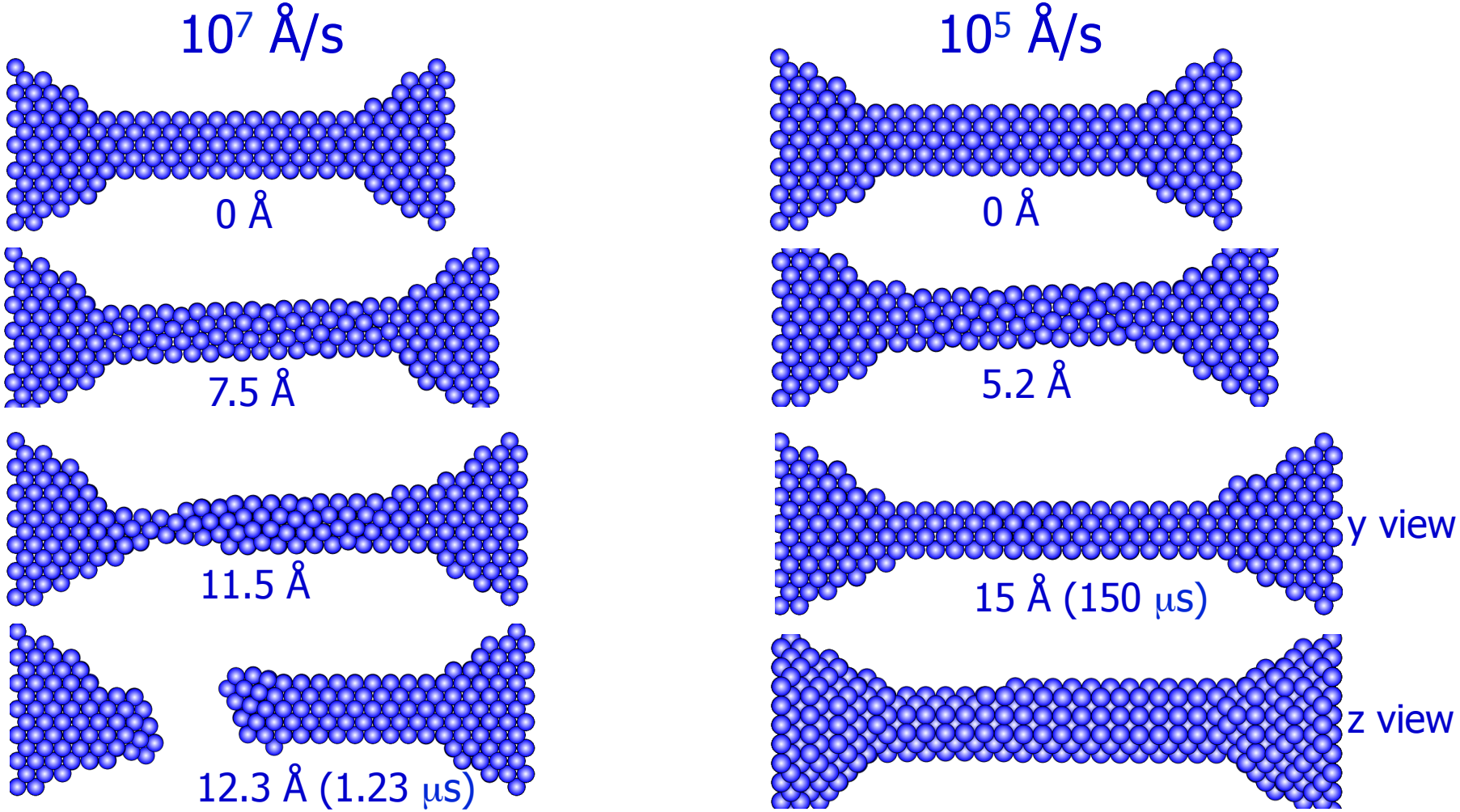
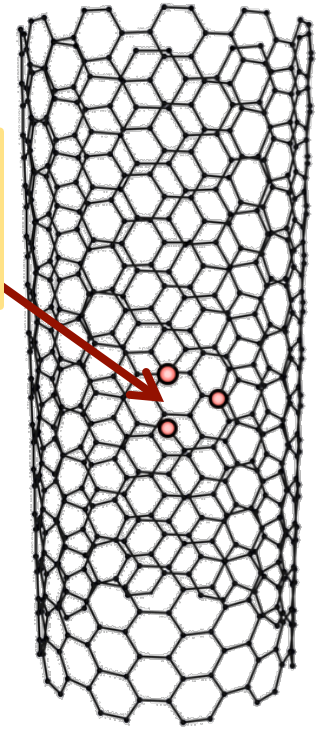


ParRep of stretched nanotubes

Vacancy to "seed" failure



unstretched

red=undercoordinated atoms
green=overcoordinated atoms

Uberuaga, Stuart and Voter, PRB **75**, 014301 (2007).

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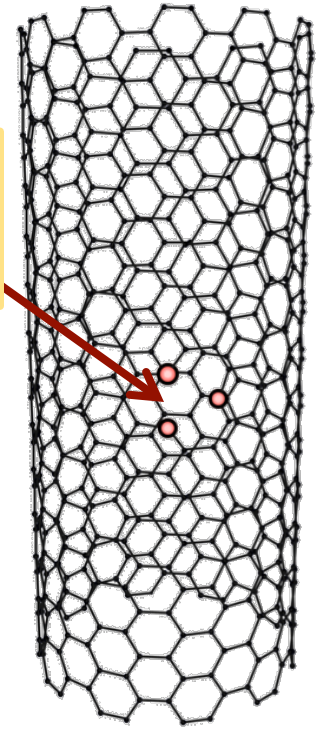

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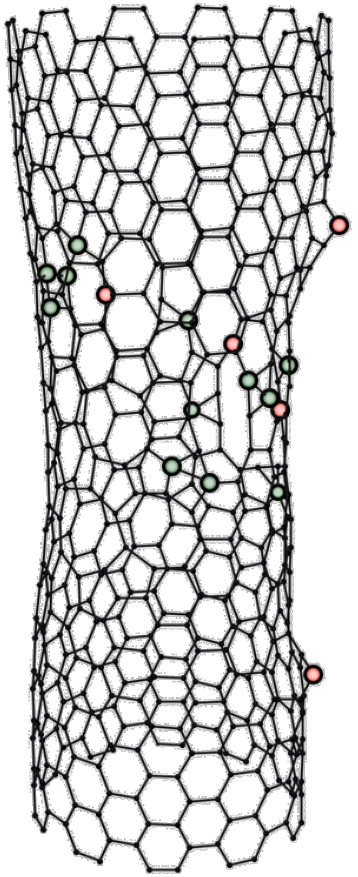

$\dot{\varepsilon}=5\text{x}10^{8}/\text{s}$, T=2000 K
yielded at 24%

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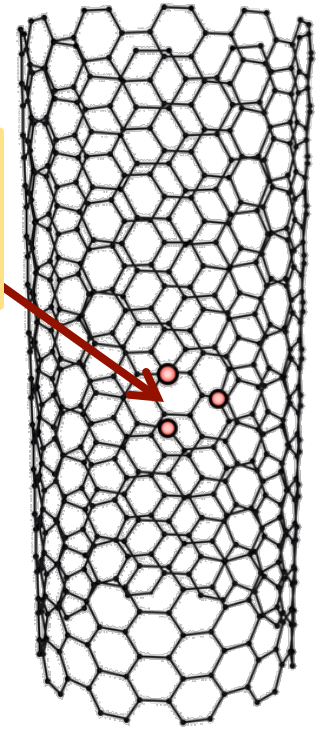

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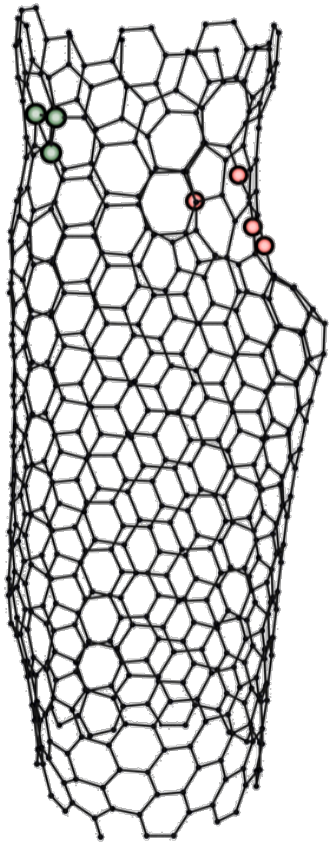
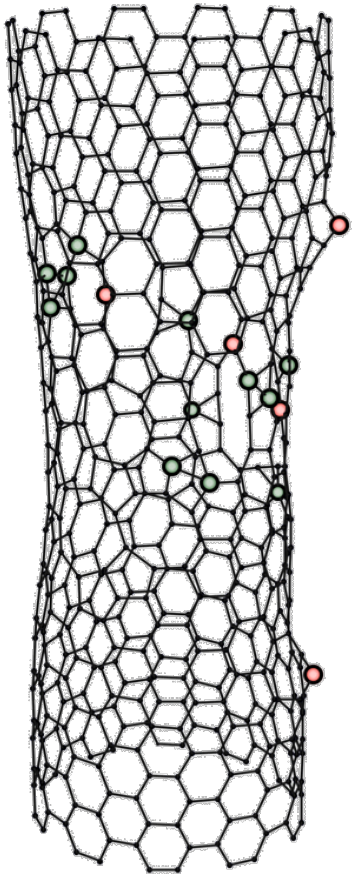


$\dot{\varepsilon}=10^{6}$/s, T=2000 K
yielded at 15%



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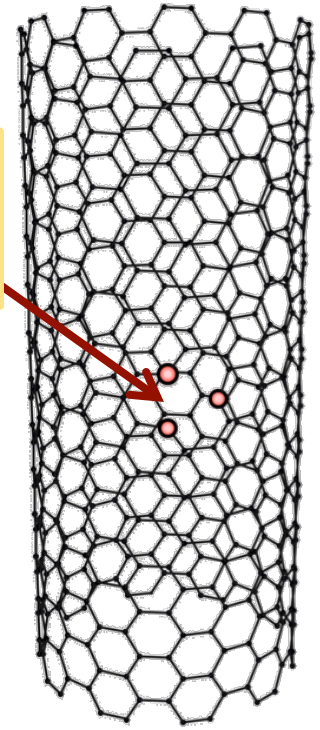

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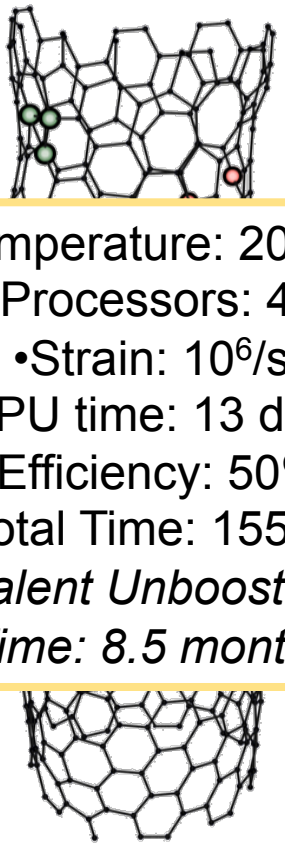
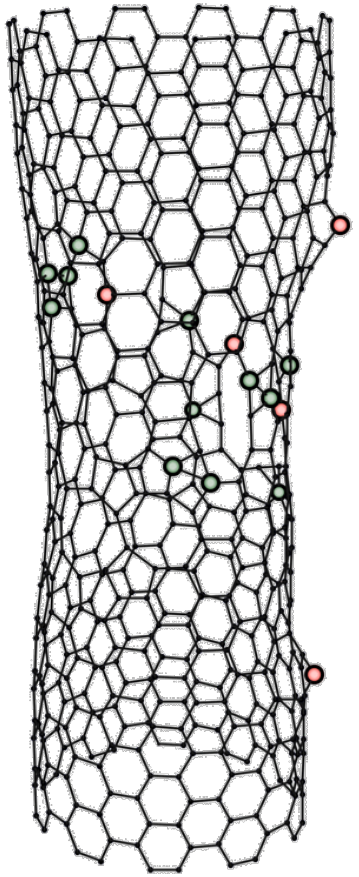


- Temperature: 2000K
- Processors: 40
- Strain: 10^6/s
- CPU time: 13 days
- Efficiency: 50%
- Total Time: 155 ns
- *Equivalent Unboosted CPU Time: 8.5 months*

$\dot{\varepsilon}=10^6$/s, T=2000 K
yielded at 15%



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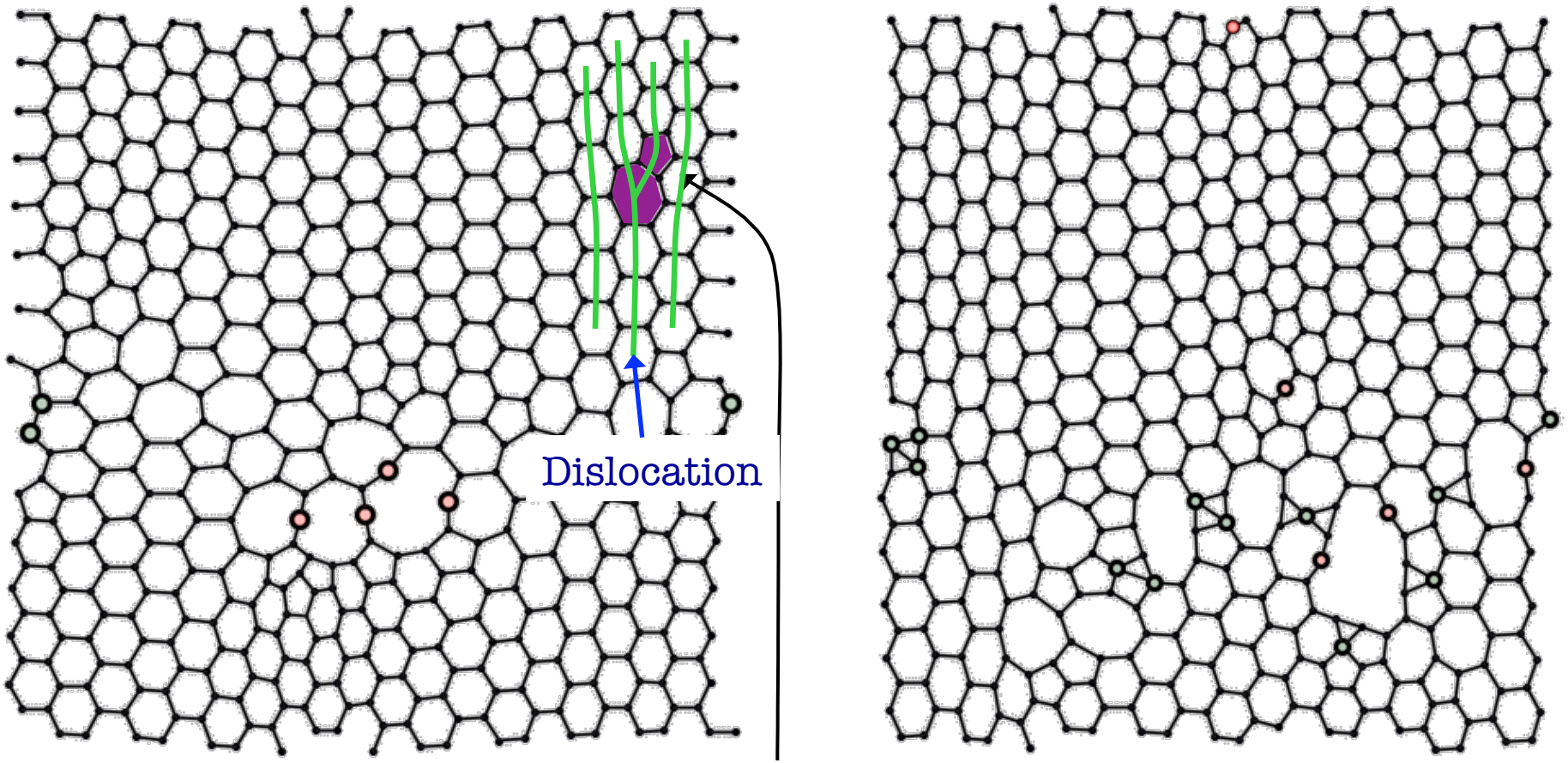
Structure of Nanotubes after Yield



Strain rate: 10^6/s

Strain rate: $5x10^8$/s

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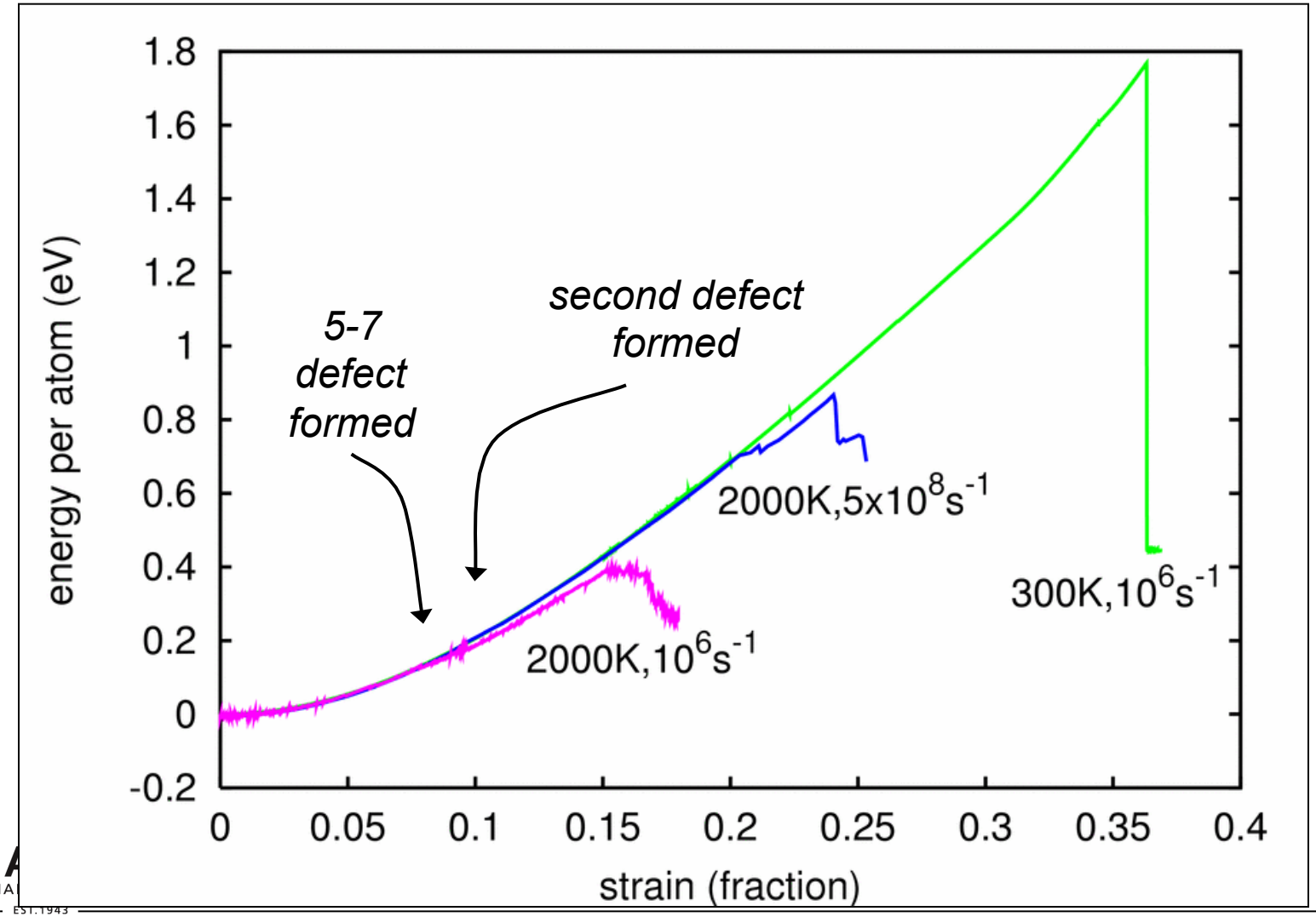
Energy vs Strain for Nanotube with a Vacancy



Why long time simulations were needed?

- In both nanowire and nanotube, new processes occur as strain rate is decreased
- These processes relieve strain in a qualitatively differently manner than in over-driven cases
- Observation of these processes depends on reducing strain rates by reaching longer time scales

Summary

- AMD methods allow the study of processes not accessible to MD
- Often, results are very surprising
  - Many mechanisms that would be left out of e.g. KMC if intuition alone is used
  - New insights into kinetic processes, even in the simplest of materials

➔Probing long-time kinetics is crucial for understanding material evolution in complex environments