NANOSCALE MODELLING TECHNIQUES (RPV)

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Outline

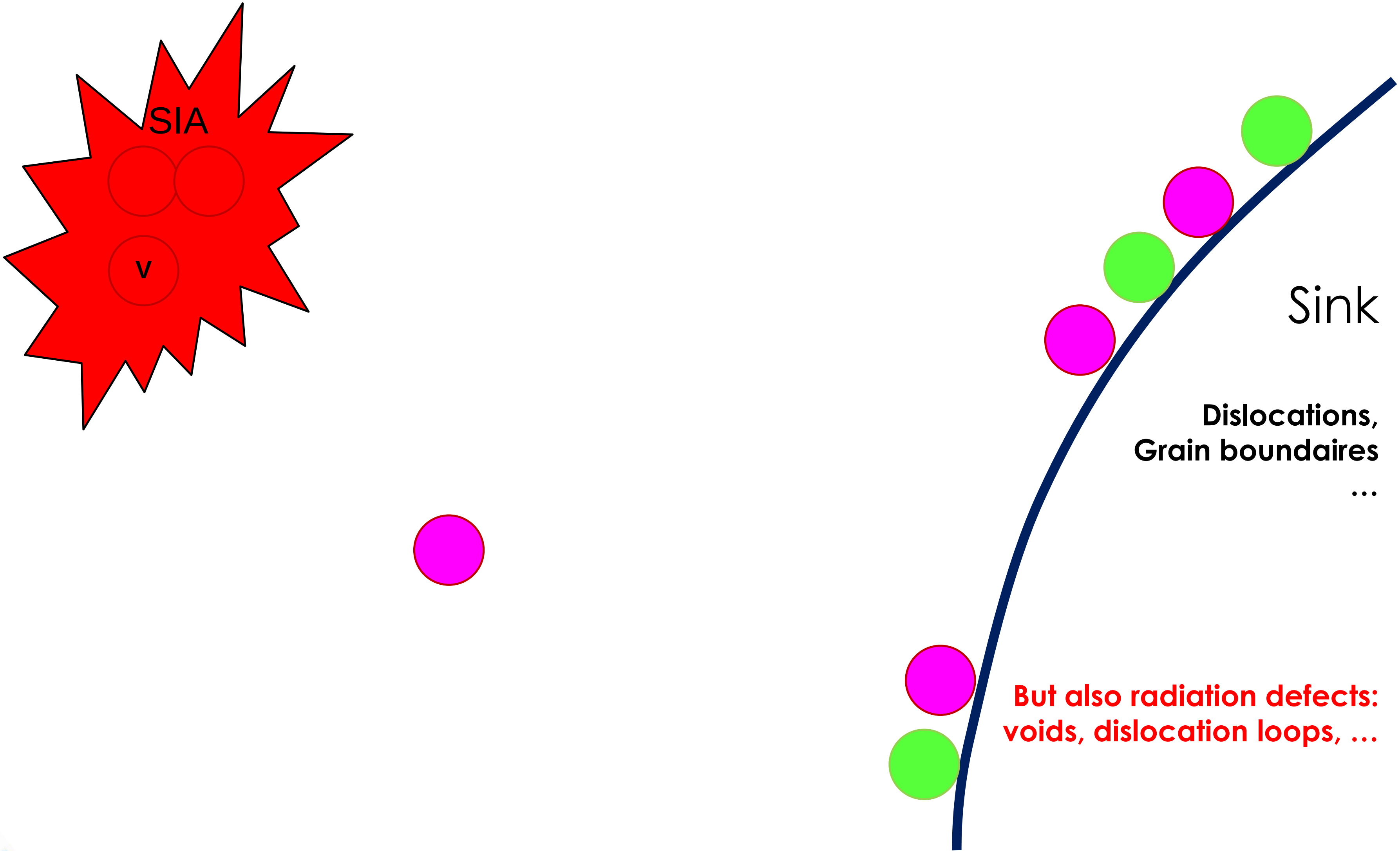
- ❑ Introduction: multiscale modelling

- ❑ "Deterministic" atomic-level modelling tools
- ✓ Density functional theory calculations
- ✓ Molecular Dynamics and interatomic potentials

- ❑ Stochastic atomistic modelling tools
- ✓ Metropolis Monte Carlo
- ✓ Kinetic Monte Carlo

INTRODUCTION: MULTISCALE MODELLING

Point defects and clusters are produced in cascades and migrate to sinks

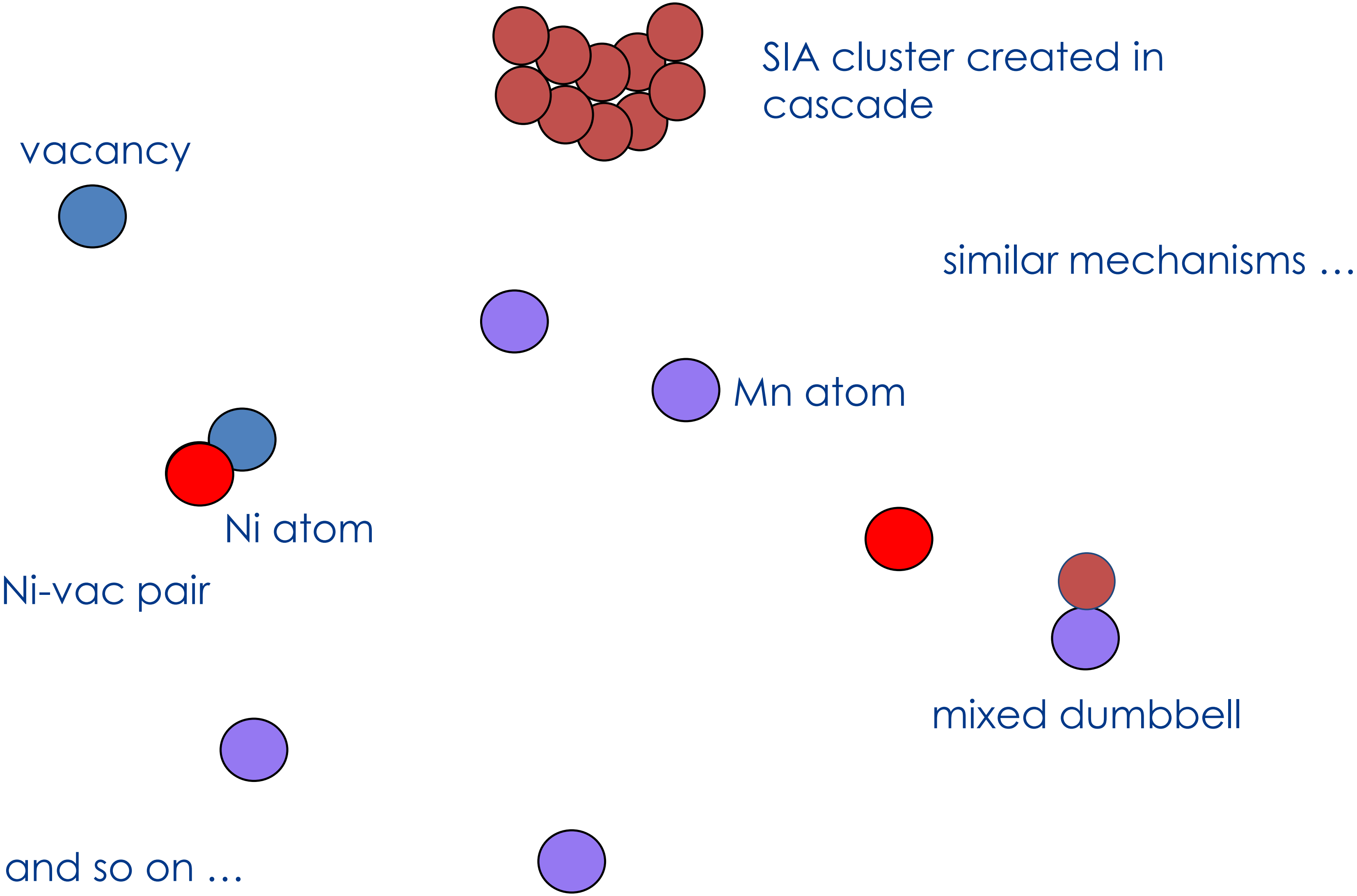


Sink

Dislocations,
Grain boundaires
…

But also radiation defects:
voids, dislocation loops, …

Solute rich clusters that harden RPV steels form via specific diffusion mechanisms



SIA cluster created in cascade

vacancy

similar mechanisms …

Mn atom

Ni atom

Ni-vac pair

mixed dumbbell

… and so on …

Questions

How can we model the atomic level mechanisms, whereby irradiation produces changes in the properties of RPV steels in particular, and materials in general?

- How do we know about the different phases of displacement cascades?
- How do we know about the mobility of point defect clusters?
- How do we know about the way dislocations interact with defects?
- How can we describe nucleation and growth of precipitates, voids, loops, … simultaneously?
- How can we use the physics of dislocations and radiation defects to describe hardening and embrittlement?

The application of multiscale modelling tools dedicated to the smaller scales helps to answer some of these questions

Irradiation effects are inherently a multiscale problem

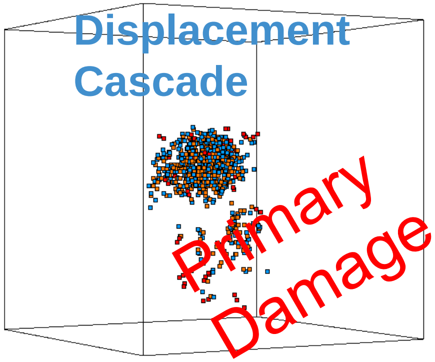
1 fs = 10^{-15} s   1-100 ps = 10^{-12}- 10^{-10} s   ns = 10^{-9} s ….. ms = 10^{-3} s ….. 1 s …… 10^{3} s

Time scale

Incident particles

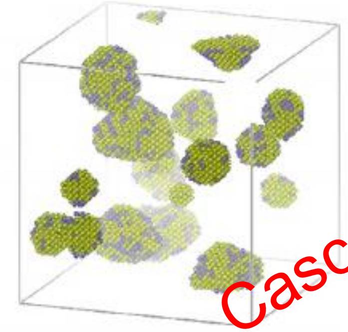
From n spectrum to PKA & Displacement Cascade Spectrum

Displacement Cascade

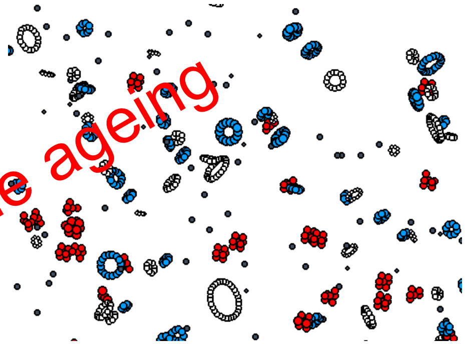


Primary Damage State

Precipitates



Loops & Cavities



Cascade ageing

Collisions

Thermal spike

Relaxation

Defect Migration

Clustering

Nucleation of Precipitates & Large Clusters

Length scale

10s of nm = 10^{-8} m   100s of nm = 10^{-7} m

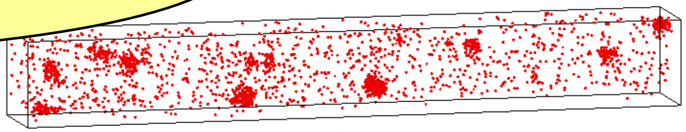
Irradiation effects are inherently a multiscale problem

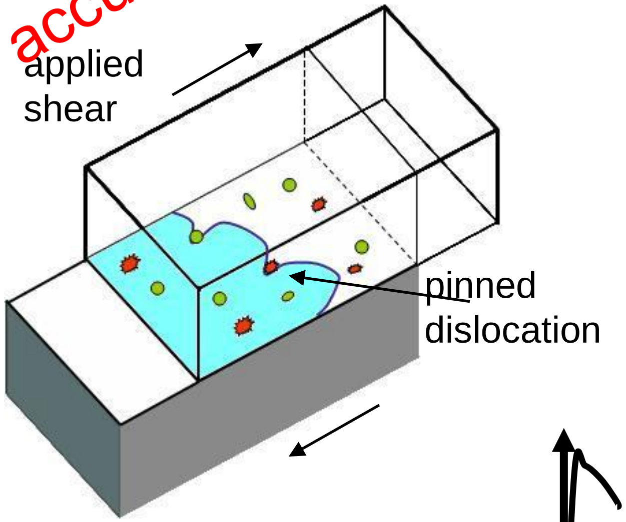
$\mu s = 10^{-3}$ s……………………………………… Years = $10^{7} - 10^{9}$ s

Time scale

Cascade accumulation

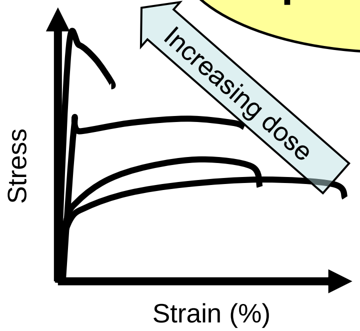
Growing Concentration of Radiation Induced Defects while the Irradiation Proceeds



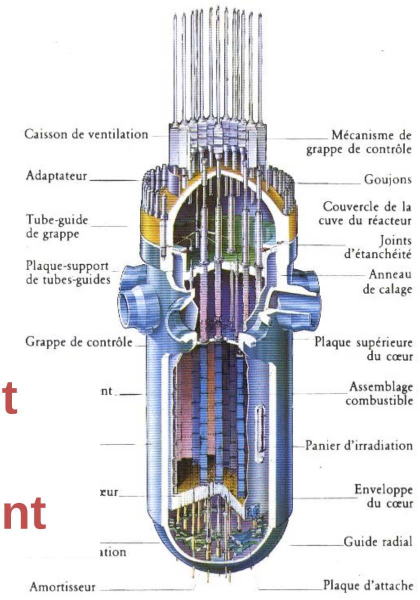


Mechanical Property Changes

Dislo/Defect Interaction
Yield Strength Increase
Loss of ductility



Component lifetime management



Length scale

10s of $\mu m = 10^{-5}$ m

cm = 10^{-2} m

What is multiscale modelling?

1. Use of the proper experimental examination and modelling technique to study each phenomenon of interest *at the correct scale*

2. Combination of experimental and modelling techniques to describe phenomena *at different scales*

3. Intensive and extensive use of not only advanced theory and experimental techniques, but also, and especially, computer simulation

Multiscale modelling tools

- ❑ Different computer simulation tools exist to study the different phases of radiation damage

- ❑ Each of them is the result of long algorithm development work, started already between the 1950s and 1970s

- ❑ The practical widespread implementation of these algorithms dates mainly from the late 1980s – early 1990s

- ❑ In what follows, a bird's eye view on some of these is given

<u>Two different classes of modelling tools exist</u>:

1. Those used to study phenomena not accessible to experiments → comparison with experiments is difficult

2. Those used to reproduce experiments / predict experimental outcomes → comparison with experiments is crucial

“DETERMINISTIC” ATOMIC-LEVEL MODELLING TOOLS

Density functional theory calculations

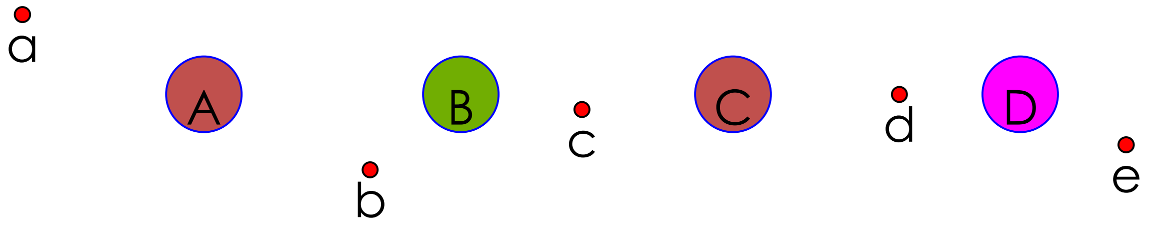
Molecular Dynamics and interatomic potentials

One single equation governs the whole physics of materials behaviour

$$i\frac{\partial}{\partial t}\Psi(\bar{r},t)=\hat{\mathrm{H}}\Psi(\bar{r},t)$$

Time-dependent Schrödinger equation
R_I is the position of ion I, r_j of electron j

$$\hat{\mathrm{H}}=-\tfrac{1}{2}\sum_{J}\frac{1}{M_J}\nabla_J^2-\tfrac{1}{2}\sum_{j}\frac{1}{M_j}\nabla_j^2+\tfrac{1}{2}\sum_{j\neq k}\frac{1}{\left|\bar{r}_j-\bar{r}_j\right|}-\sum_{j,J}\frac{Z_J}{\left|\bar{r}_j-\bar{R}_j\right|}+\tfrac{1}{2}\sum_{J\neq K}\frac{Z_J Z_K}{\left|\bar{R}_J-\bar{R}_K\right|}$$



Good news: By solving this equation for (at least) $N_{AV} = 6.023 \cdot 10^{23}$ ions and the corresponding number of electrons, all materials properties could be accordingly deduced exactly from the theory !

Bad news: Unfortunately, this is impossible …

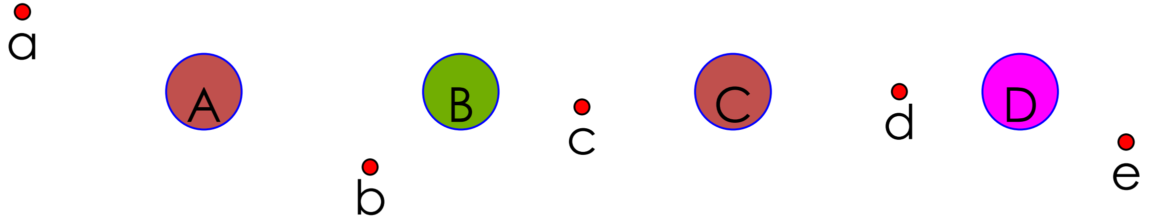
Theory → Models

One single equation governs the whole physics of materials behaviour

Even the time-*in*dependent Schrödinger eq., in Born-Oppenheimer approximation (= electrons respond instantaneously to changes in nuclear configurations; ions only provide the external potential)

$$\hat{\mathrm{H}}\psi(\bar{r}) = E\psi(\bar{r})$$

$$\hat{\mathrm{H}} = -\tfrac{1}{2}\sum_{j}\left(\nabla_J^2 + 2\sum_{J}\frac{Z_J}{\left|\bar{r}_j - \bar{R}_j\right|} - \sum_{k\neq j}\frac{1}{\left|\bar{r}_j - \bar{r}_k\right|}\right)$$



cannot be solved, except for few electrons

→ Density Functional Theory

- The DFT is a reformulation of the Schrödinger eq., based on the Hohenberg-Kohn theorem:
  - The **ground-state energy** of a set of interacting electrons in an external potential is a unique functional of their density

Potential

$$E\left[n(\bar{r})\right] = \int V(\bar{r})\, n(\bar{r})\, d^3 r + F\left[n(\bar{r})\right]$$

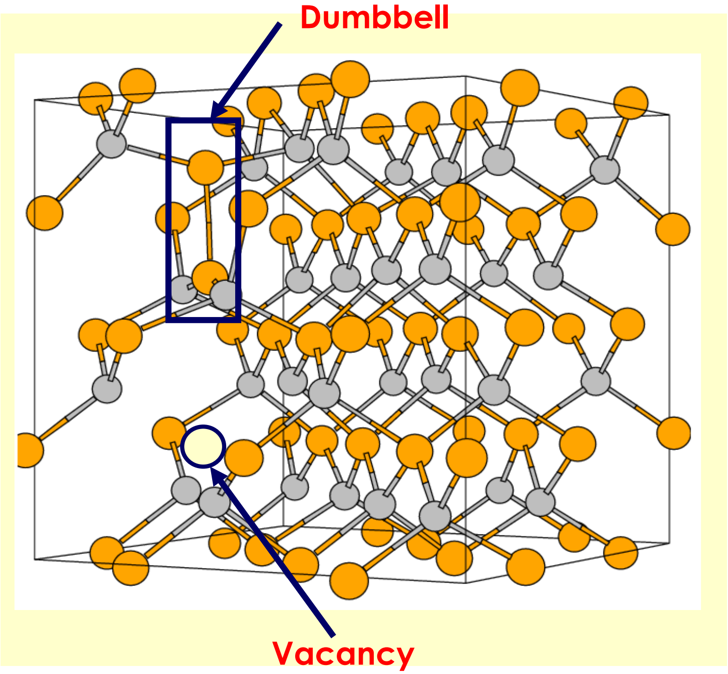
Functional

- The trouble is that **nobody knows the exact form of the functional**
- So, different DFT approximations exist that consist in
  - **Approximate expressions for the functional**, generally reducing the problem of interacting electrons to that of non-interacting single-particles
  - **Basis sets of functions** to express the wavefunctions of the single-particles
  - **Approximation of the electron-nucleus interaction with pseudopotentials** that, like interatomic potentials, contain a degree of empiricism

- Despite these approximations, DFT is a powerful tool for atomic-level calculations, extremely reliable to **give access to quantities experimentally inaccessible**

DFT is most commonly used to calculate characteristic energies of small defective systems

- ❑ Systems of 102-103 atoms are created assigning initial positions
- ❑ Defects are introduced
- ❑ Formation, binding, or migration energy are calculated
- ❑ The reliabilty of the result calculation is generally high



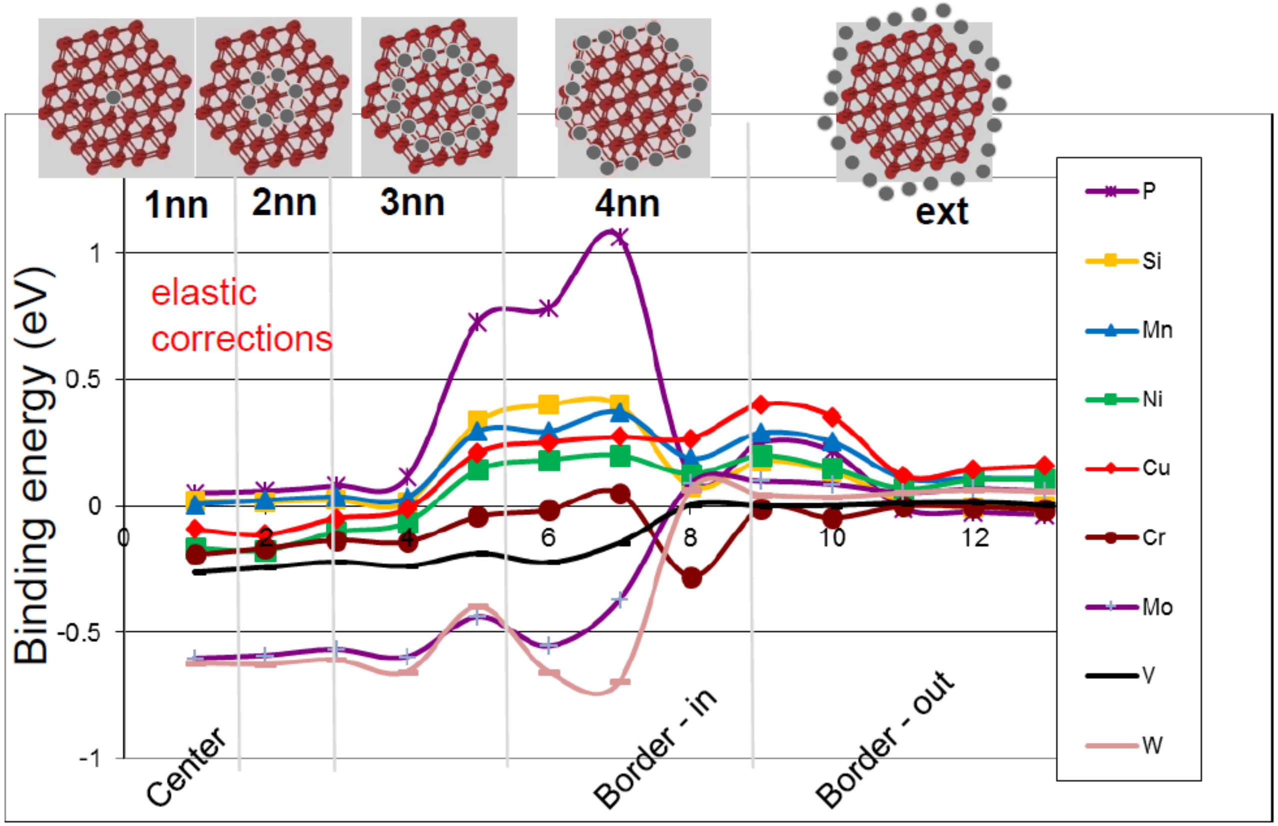
Typical size of system studied by DFT

These values, **generally inaccessible to experiments**, provide fundamental hints and allow qualitative predictions to be made or conceptual models to be developed

Importantly, DFT data can be used to fit interatomic potentials or parameterise nanostructure evolution models

Impressive examples of large scale DFT calculations for RPV steels

C. Domain, C.S. Becquart, JNM 499 (2018) 582



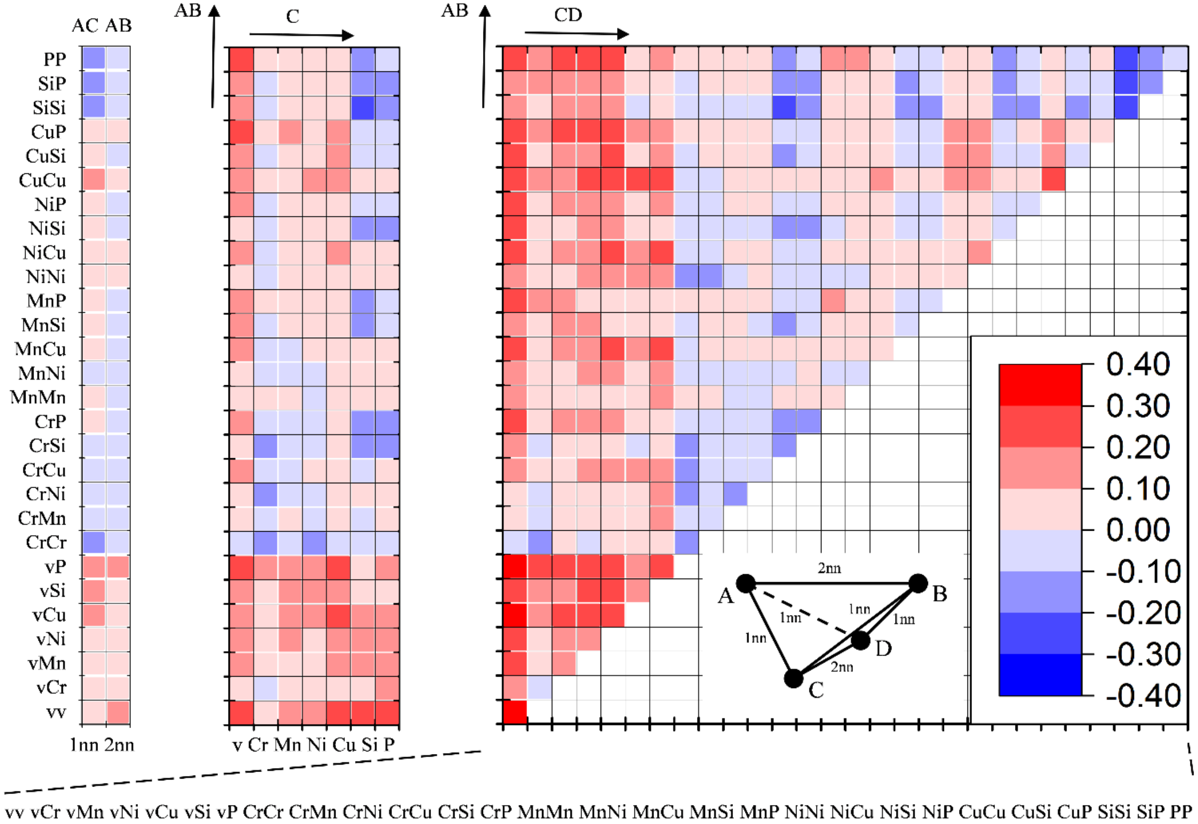
P (in) >> Si (in), Mn (in), Cu (out) > Ni

DFT 1458 atoms Fe
bcc - magnetism

This study provides key data for the development of models that describe microstructural evolution in irradiated RPV steels

Impressive examples of large scale DFT calculations for RPV steels

C. Domain et al., to be published



> 700 data points of binding energies up to triplets and quadruplets of solutes and vacancies

This study provides key data for the development of models that describe microstructural evolution in irradiated RPV steels

Pros & Cons of DFT calculation methods

Advantages

- ☐ Can give the most reliable estimate currently available for quantities not accessible through experiments:
  - Defect formation energies, binding energies, saddle point energies, …
- ☐ Nowadays hardly any materials modelling activity is thinkable without contribution from DFT

Drawbacks

- ☐ Numerically very demanding:
  - Size of the system limited to max. ~10^3 atoms
  - Essentially used only for static calculations (although dynamic calculations start to become frequent → **molecular dynamics**)

Molecular Dynamics

Principle: The (classical) equations of motion for a set of N atoms are solved timestepwise, using finite difference integration algorithms, so as to **know atomic positions and velocities at each timestep**:

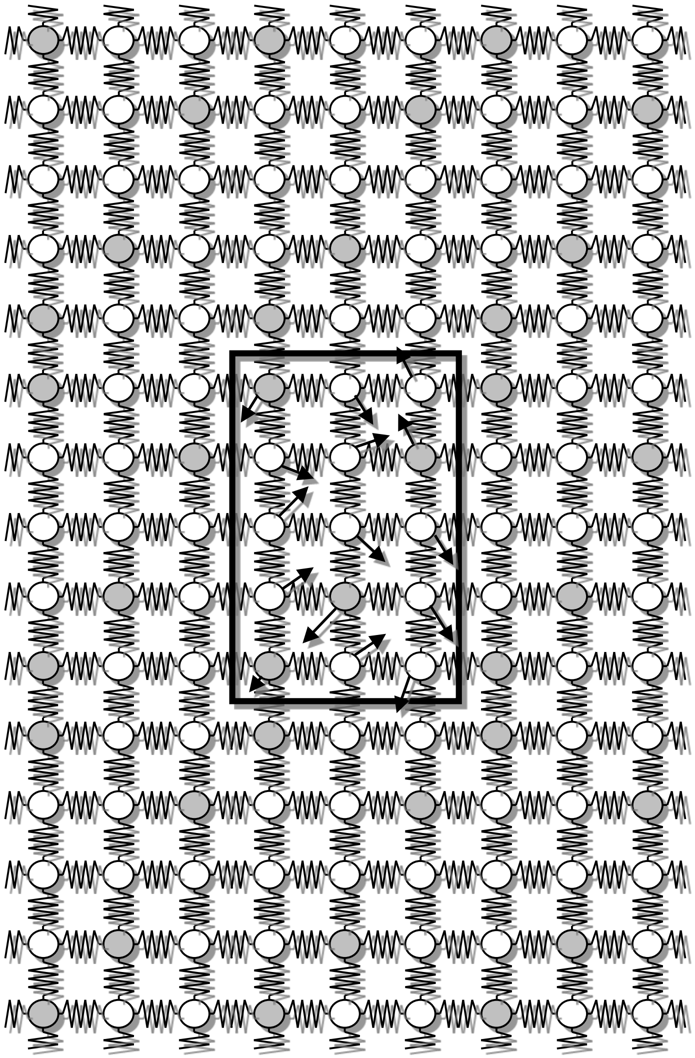
$$m\frac{d^2\bar{r}_i}{dt^2} = -\nabla V(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) \quad \rightarrow \quad \{\bar{r}_i, \bar{v}_i \,/\, i = 1, \ldots, N\}$$

- *From the knowledge of atomic positions and momenta all* ***statistical mechanics quantities*** *become directly accessible*
- *More importantly, the* ***properties of specific local atomic configurations*** *(e.g. lattice defects) can be studied in detail*

Core of the method: **interatomic potential**, V(r_i), or other Hamiltonian (can be also quantum mechanical), from which the interatomic forces are derived

Molecular Dynamics

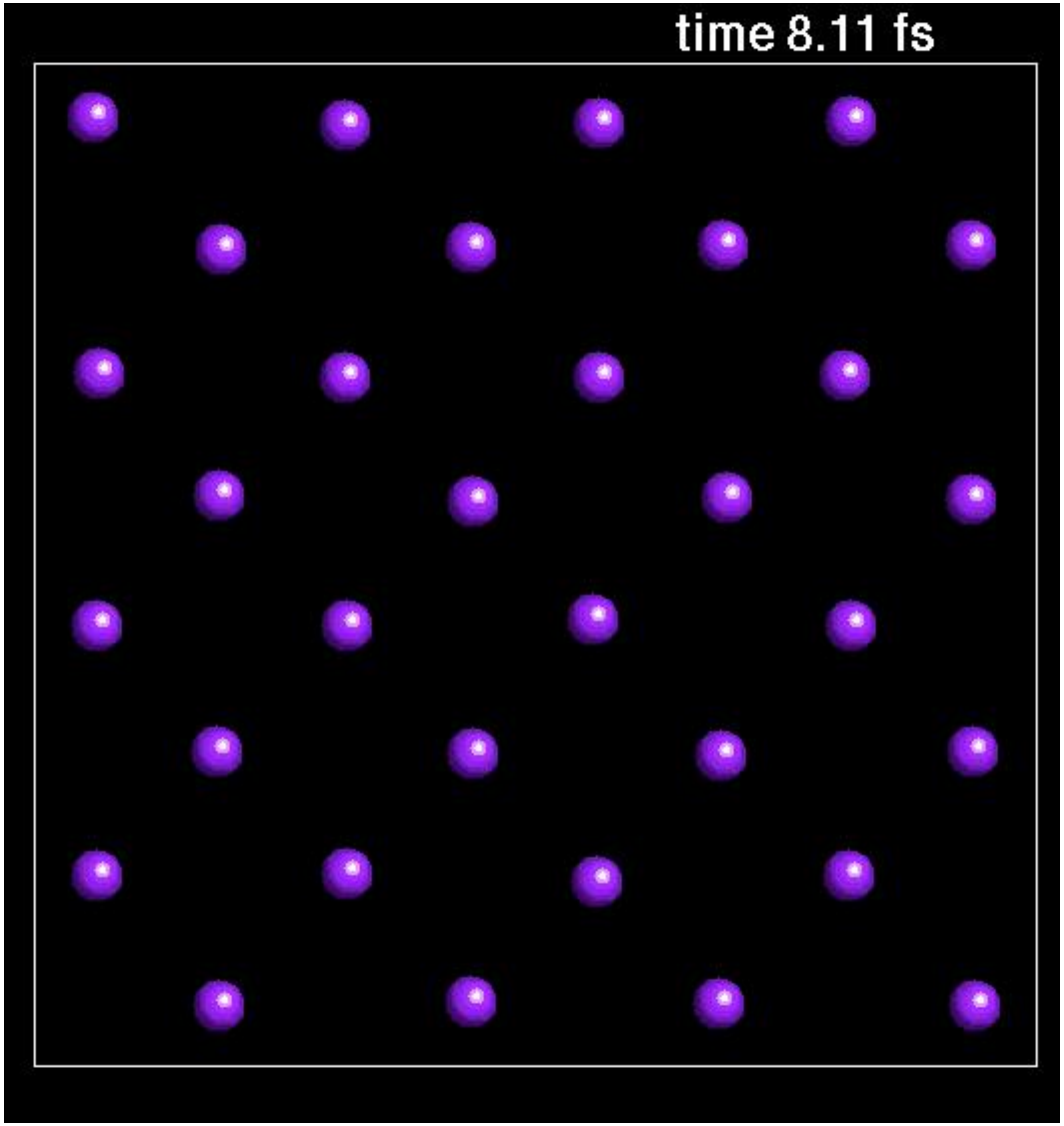
- ☐ Atoms are distributed in a simulation box, in initial positions corresponding to a crystal lattice



  - Initial velocities are randomly assigned, according to temperature, e.g. following a maxwellian distribution
  - Periodic boundary conditions simulate the infinite crystal

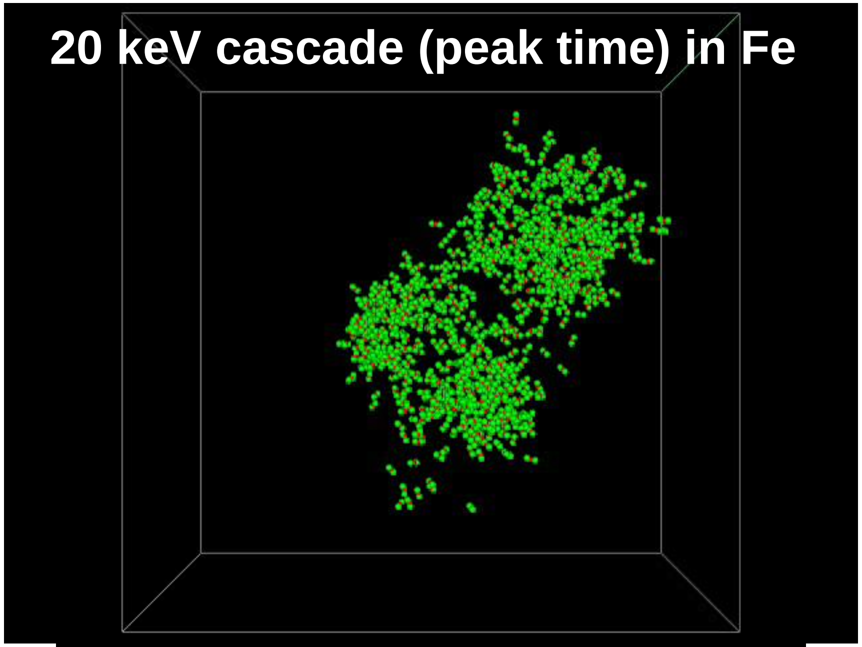
    L+dx → dx

The simplest molecular dynamics simulation

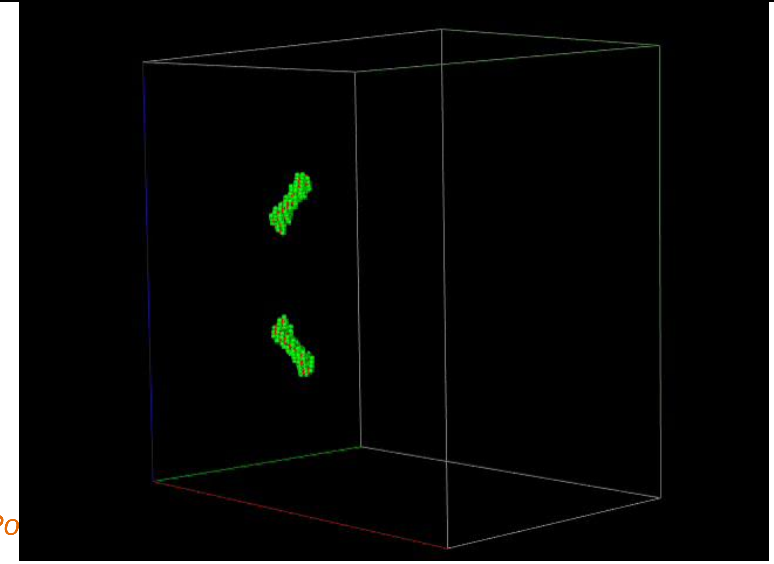


Applications of MD for irradiation problems

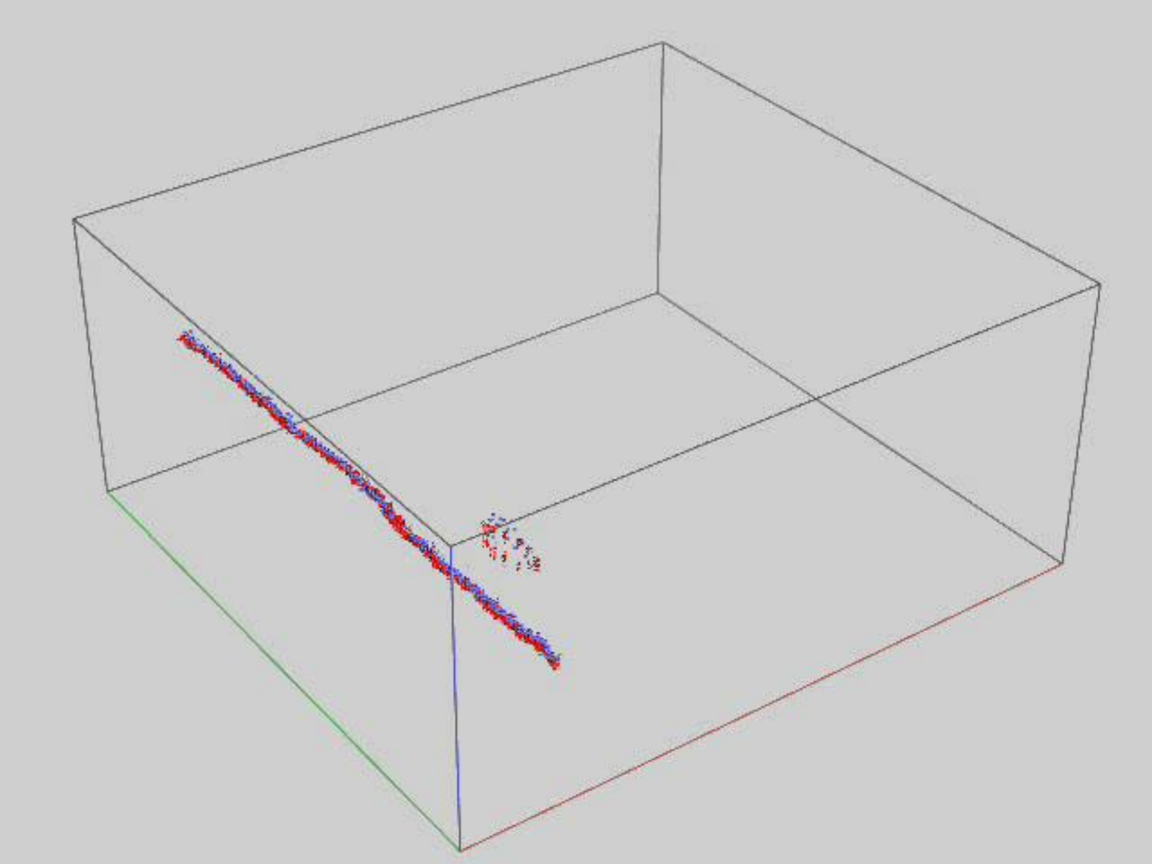
- MD is the technique "par excellence" for displacement cascade simulations:
  - one atom is given kinetic energy
  - the dynamic evolution of the system is followed
- MD also allows stability and mobility of (fast enough) defects to be studied
- Finally, MD can be used to model the interaction between dislocations and defects (at brutal strain rates)



20 keV cascade (peak time) in Fe



Interaction edge dislocation / prismatic loop



Edge dislocation interacting with SIA loop at 600 K

Pros & Cons of MD

❑ Advantages

- Wide applicability (bulk, surfaces, crystals, amorphous, liquids, ...)
- No analytical simplifications or approximations in the description of an atomic system
- Treats spontaneously complex systems and phenomena at equilibrium or far from it, not accessible to analytical approaches

❑ Limitations

- Evolution of the system calculated by timesteps of ~1 **femto**second

  → Limited timescale (tens of nanoseconds, trade-off size/time)
- Limited volumes (up to 10^7 atoms): not big enough for e.g. extended defects
- All the physics is contained in the interatomic potential

STOCHASTIC ATOMISTIC MODELLING TOOLS

Metropolis Monte Carlo

Kinetic Monte Carlo

Stochastic Monte Carlo Algorithms

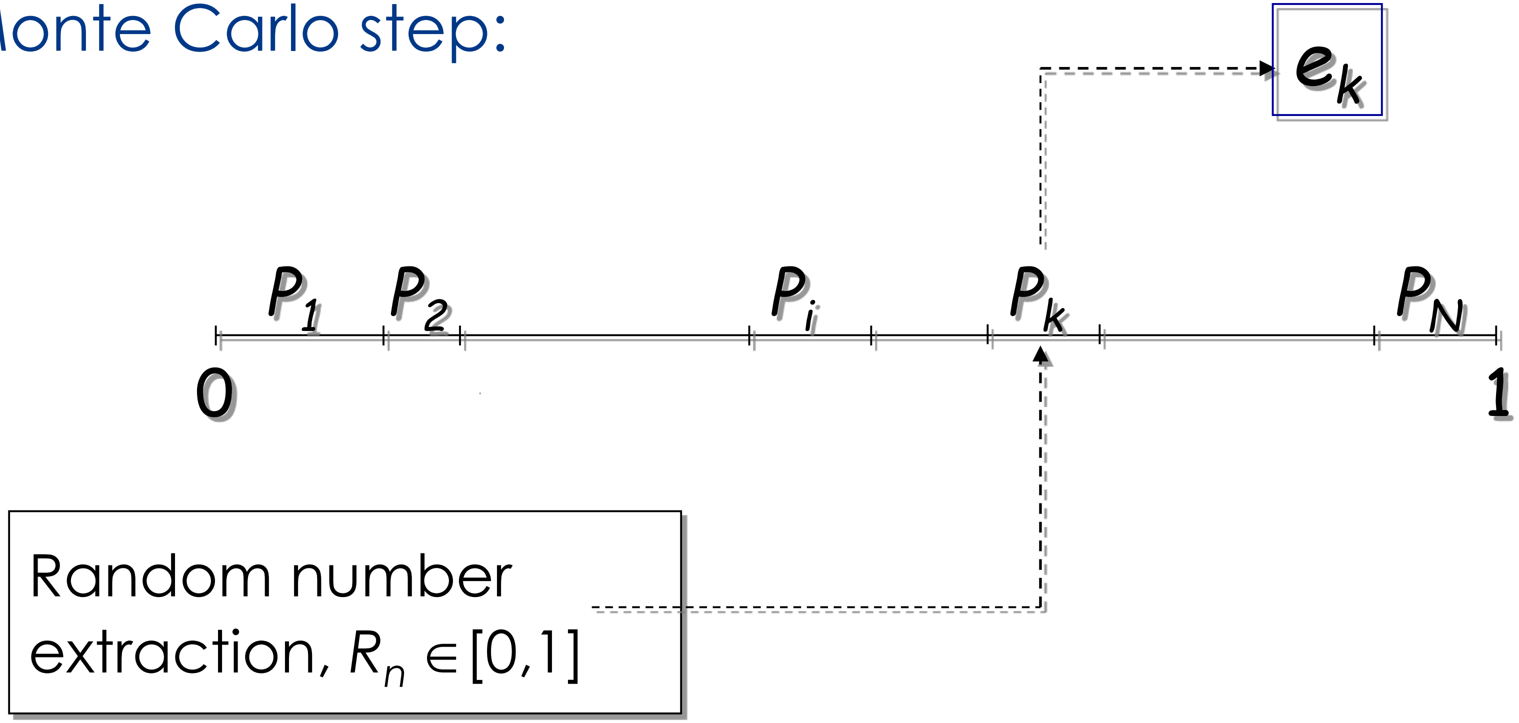
- ☐ MD **cannot** be used to simulate the evolution of a system to equilibrium if the kinetics is slower than **nanoseconds**

- ☐ MC methods can be used for this purpose or, more generally, to extend the timespan of radiation damage atomistic simulations to **progressively allow comparison with experiments**

- ☐ Three different techniques:
  1. Metropolis Monte Carlo
  2. Kinetic Monte Carlo
     - Atomistic KMC
     - Object KMC

The Monte Carlo Algorithm

- List of possible events: e_i / $i=1, \ldots, N_e$
- A probability P_i is associated to each event
- $\Sigma_i P_i = 1$
- Monte Carlo step:



Random number extraction, $R_n \in [0,1]$

1. Metropolis Monte Carlo

- ☐ System of *N* atoms, defects can be included
- ☐ Total energy must be calculable, e.g. using an interatomic potential
- ☐ One trial event is chosen between:
  - atomic position exchange
  - small atomic displacement
  - global expansion or contraction

- ☐ If $E_{after} - E_{before} = \Delta E < 0$, the trial is accepted
- ☐ If $\Delta E > 0$, the trial is accepted with probability

$$\exp(-\Delta E/kT) < 1$$

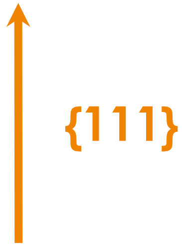
(by extracting a random number, which can fall only in one out of two possible probability intervals)

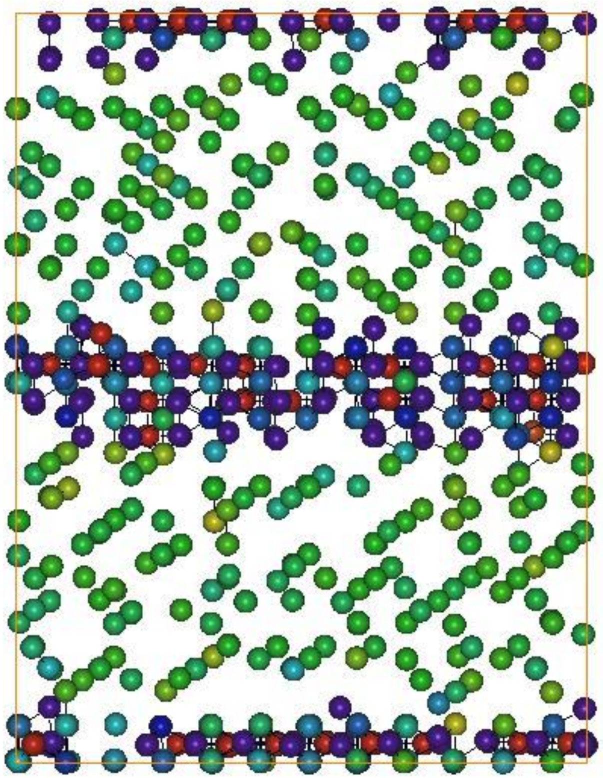
Application of Metropolis MC

Study solute redistribution in presence of a grain boundary: is segregation favoured or not?

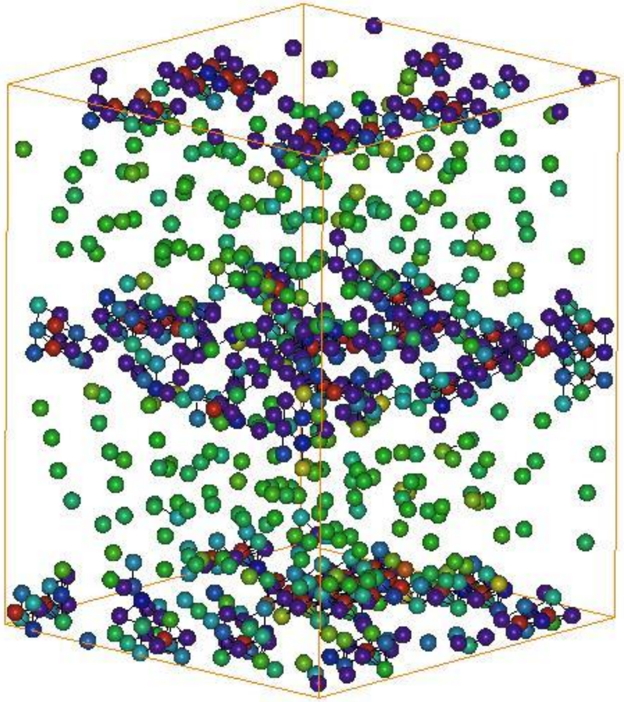
Solute atoms only – energy distribution

GB enrichment favoured





2D distribution



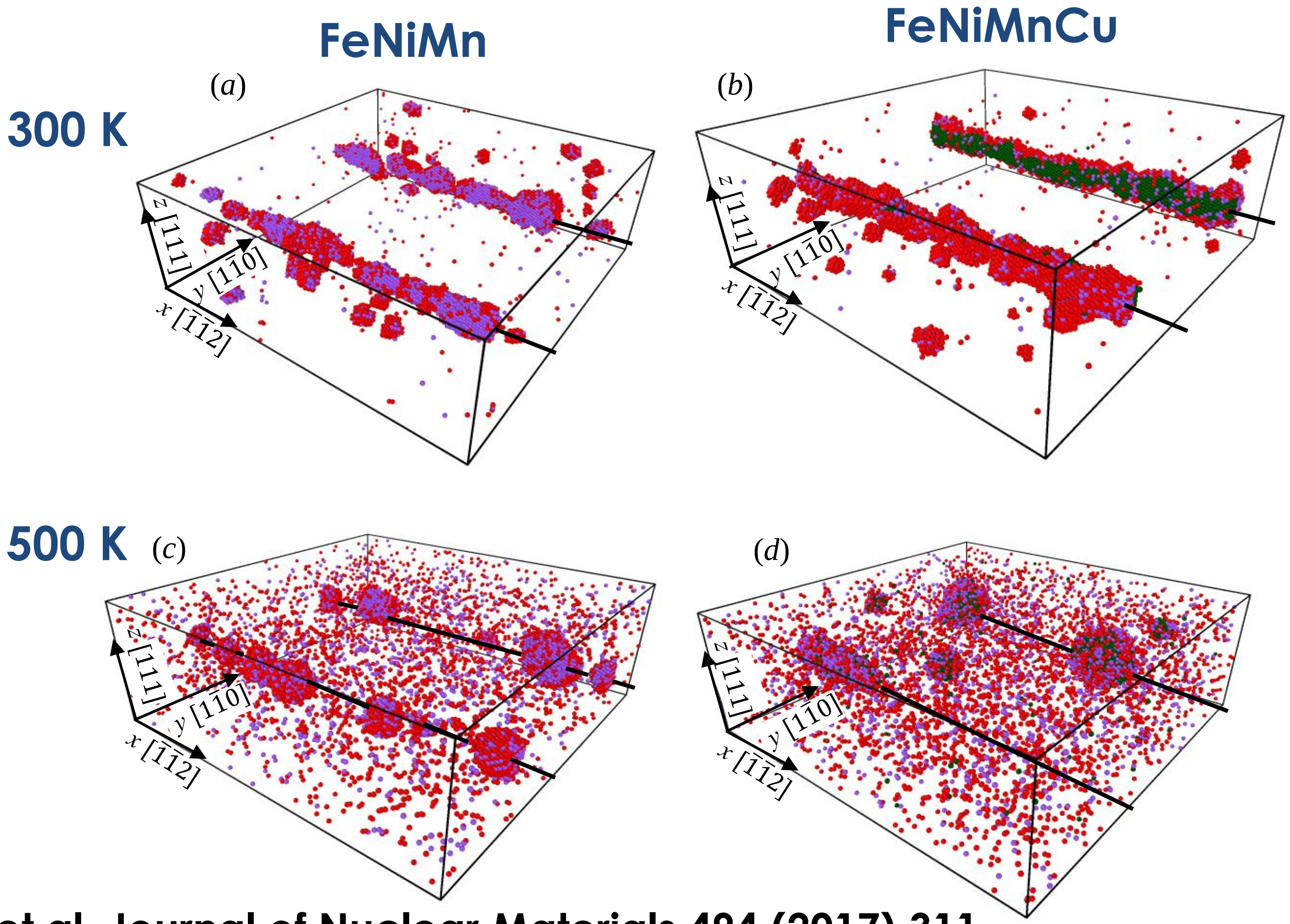
3D distribution

E. Zhurkin et al. Nucl. Instr. & Meth. B 269 (2011) 1679

Application of Metropolis MC

Study Ni, Mn, Cu, tendency to segregation at dislocations

Segregation of Ni, Mn and Cu at dislocations is energetically favoured in addition to being the consequence of solute transport towards sinks

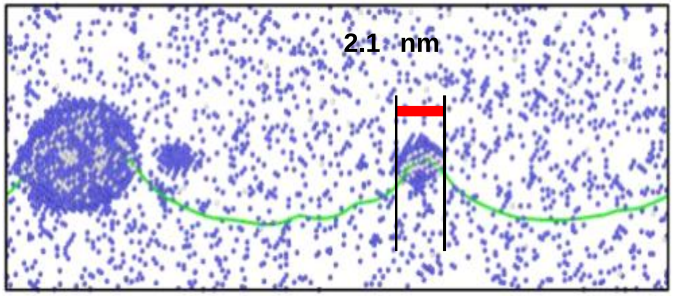


M.I. Pascuet et al. Journal of Nuclear Materials 494 (2017) 311

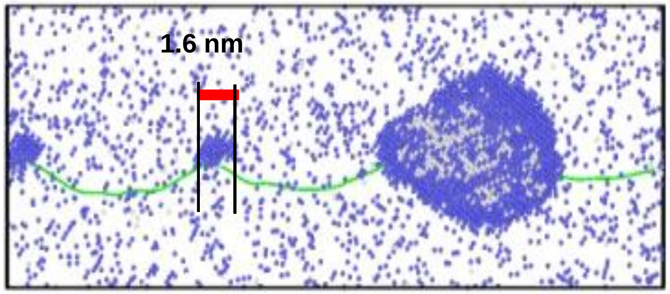
Combination MMC with MD

Study dislocation unpinning from precipitates formed on them

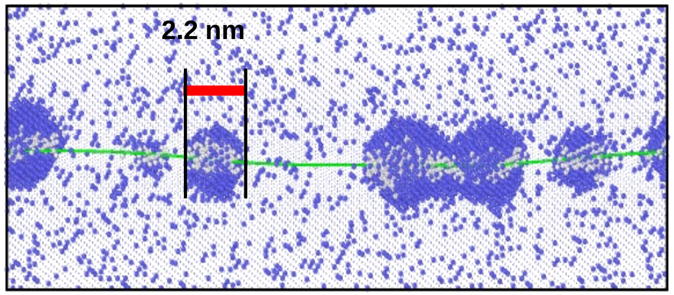
The atomic configurations obtained by MMC are used for dynamic simulations of dislocation motion



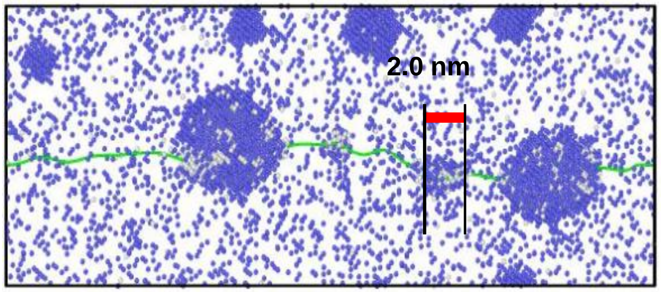
(*a*) 0.7%Ni - 0.8%Mn



(*b*) 0.7%Ni - 2%Mn



(*c*) 1%Ni - 1%Mn



(*d*) 0.5%Cu - 1%Ni - 1%Mn

M.I. Pascuet et al. Journal of Nuclear Materials 494 (2017) 311

Metropolis Monte Carlo

- ☐ Advantages
  - Phenomena such as segregation or precipitation, out of scope for MD, can be studied
    - (given a suitable hamiltonian and on the condition that these correspond to equilibrium states)
  - All contributions to the free energy can be included in the calculation
    - powerful tool to evaluate phase diagrams, including effect of pre-existing defects, e.g. dislocations

- ☐ Problems:
  - Evolution does not involve physical mechanisms, only total energy
  - Intermediate configurations are physically not meaningful
  - No information is given about time necessary to reach equilibrium

2. Kinetic Monte Carlo

Kinetic ⇒ time is introduced !

- Probabilities are calculated for physical transition mechanisms as Boltzmann factor frequencies :

$$\Gamma_i = \nu_i \exp\left(-\frac{E_{a,i}}{kT}\right)$$

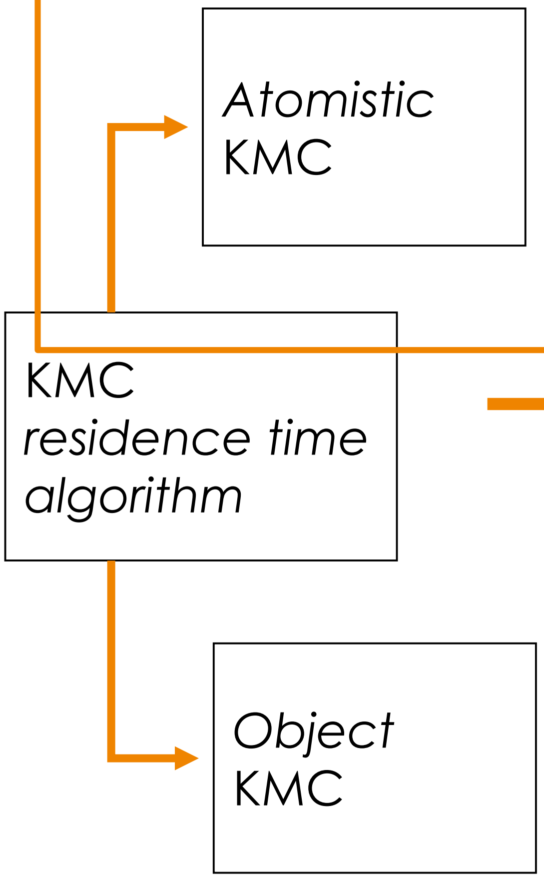
Most physics (kinetics and thermodynamics) contained in the activation energies !

- After a certain event is chosen, time is increased by an amount:

$$\Delta\tau = \frac{-\ln(rand)}{\sum_{i=1}^{N_e}\Gamma_i} \overset{average}{=} \frac{1}{\sum_{i=1}^{N_e}\Gamma_i}$$

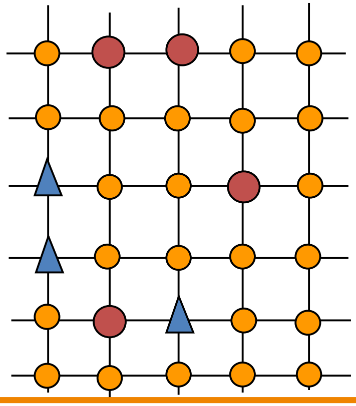
(residence time algorithm)

Kinetic Monte Carlo Families



KMC
residence time algorithm

Atomistic KMC

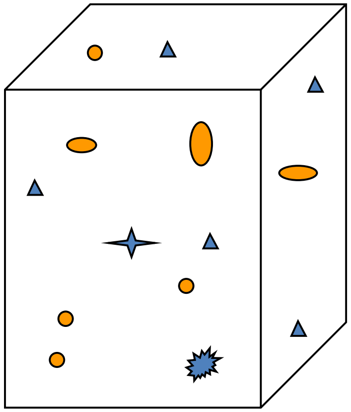


Atoms generally on rigid lattice

Vacancy & SIA jumps

Energy parameters from interatomic potentials or DFT

Object KMC



"Objects" on *non-atomic* lattice (V, SIA, clusters, …)

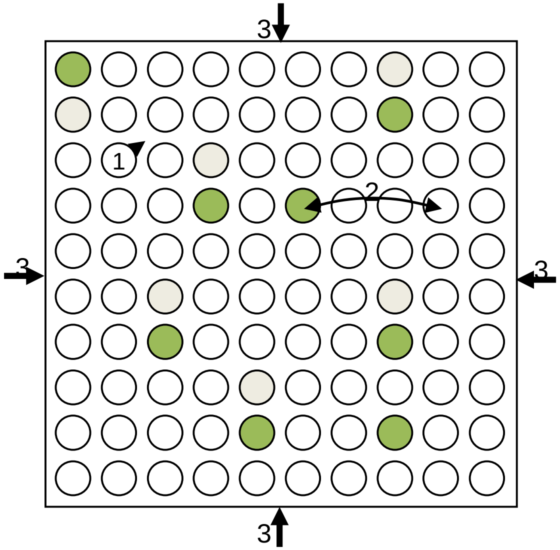
Many possible reactions between "objects"

Large set of parameters covering all possible reactions is needed

Difference between AKMC and MMC

Initial state

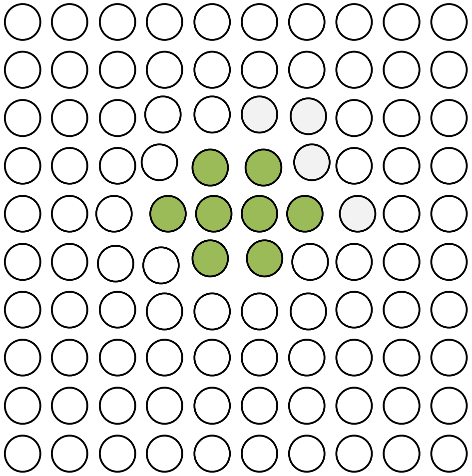
Final state

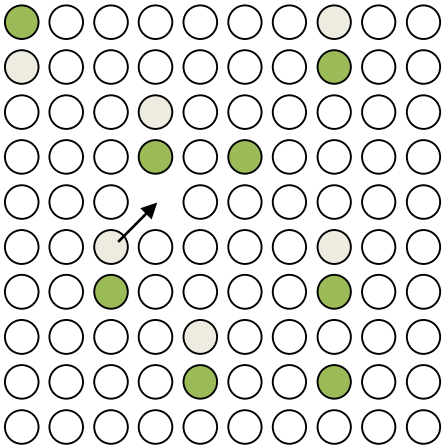


MMC

Time is unknown

Atomic coord. may be relaxed

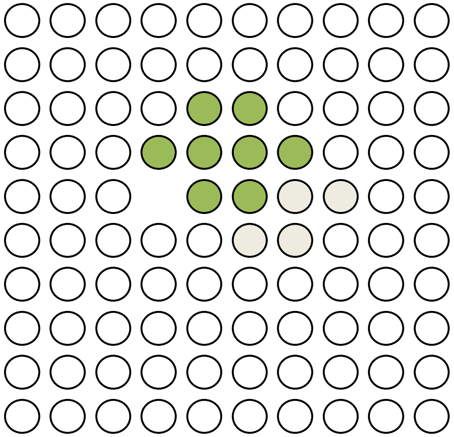




AKMC

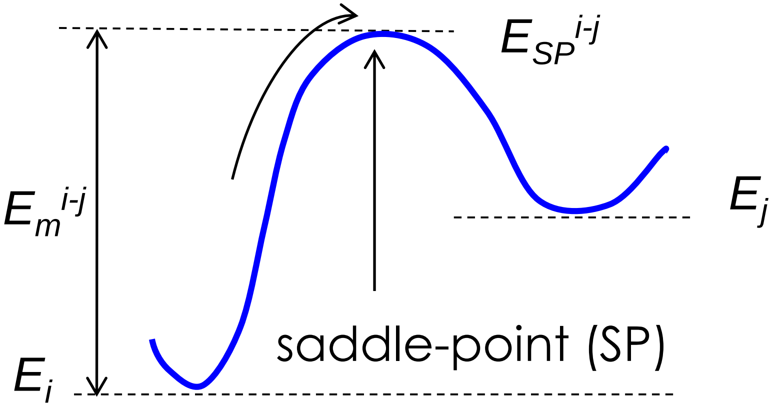
Time required is computed

Atomic coord. generally not relaxed



Main bottleneck: migration energy calculation takes time

$$E_m^{i\to j} \overset{def}{=} E_{SP}^{i\to j} - E_i$$



Point-defect migration energies can be calculated very accurately:

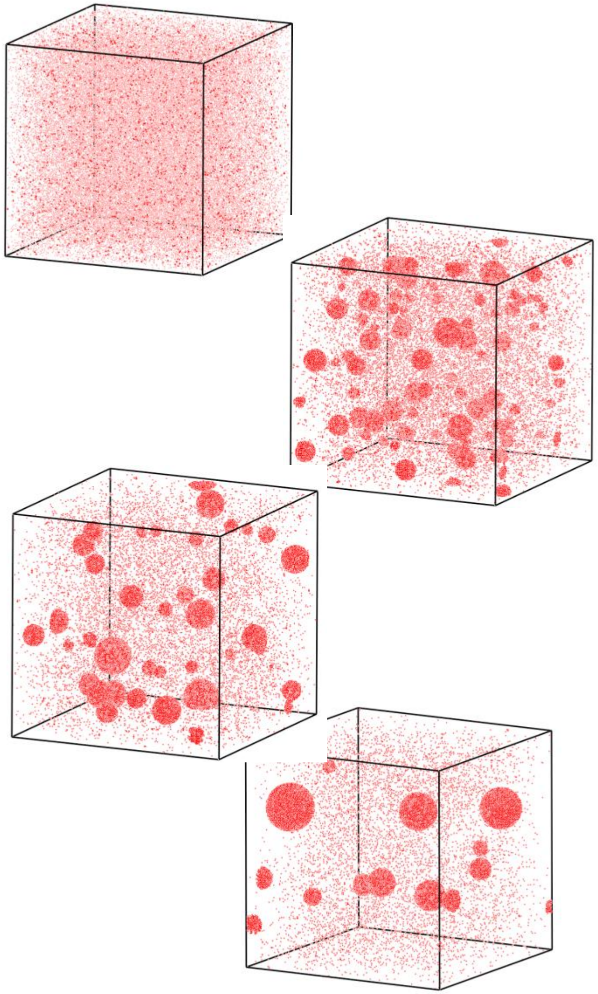
- DFT, interatomic potentials, …
- Drag method, nudged elastic-band (NEB) method, …

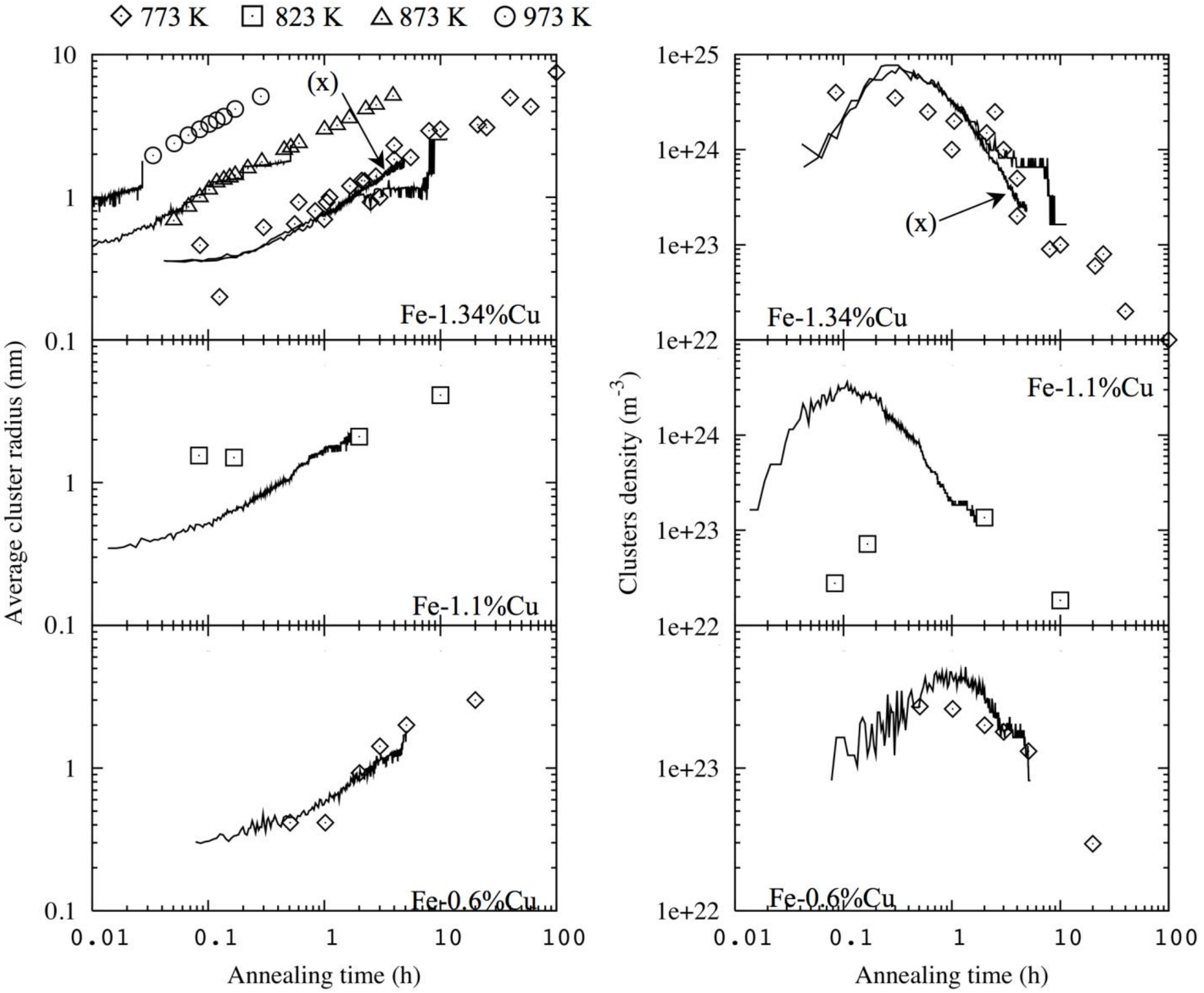
Problem: AKMC simulations require migration energy in **chemically changing** enviroments to be known for each possible point-defect jump, at each Dt

→ The more accurate the calculation, the less effective the timescale extension as compared to MD

→ **Approximations are used to speed up on-the-fly calculation**

Example of application of ANN-based AKMC: precipitation in FeCu





Castin, Pascuet & Malerba, J. Chem. Phys. 135, 064502 (2011)

Still open challenge: large strain fields

- ❑ SIA clusters:
  - Many initial and final configurations that are ‘topologically’ possible on rigid lattice are unstable
  - Method including relaxation needed
- ❑ Presence of grain boundaries or other interfaces; dislocations; phases with different crystallography

→ These situations are addressed with **on-the-fly AKMC**, where no pre-defined list of events exists, saddle-points are searched for and the the energy calculated using interatomic potentials

→ These are more acceleration methods for MD than AKMC methods producing results comparables with experiments

AKMC: Pros & Cons

- Advantages:
  - *Atomic-level method: can treat diffusion processes including proper atomic level mechanisms*
  - *Can be extended to relatively long timescales (it depends on the problem), much longer than MD any way (seconds to hours easily, under some conditions years) and potentially be compared with experiments*

- Limitations:
  - *Computationally expensive: the volumes that can be simulated remain fairly small*
  - *The treatment of SIA is not fully physical*
  - *Large strain fields, interfaces, etc still remain an open problem*
  - *Ideally, events should not be pre-determined but found on-the-fly → adaptive, or on-the-fly KMC*

Summary

- The multiscale modelling approach allows in principle the development of fully physical simulation tools for the prediction or at least description of radiation effects
- Some tools have been developed to study processes not obviously observed in experiments, especially at the atomic and nanometre scales
- DFT calculations and MD with interatomic potentials are the most widespread “deterministic” techniques at the atomic level
- Stochastic Monte Carlo methods allow the time scale of atomistic simulations to be expanded at the price of additional approximations