Monte Carlo and Rate theory calculations Introduction
(Barbu2)

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Introduction

All models start from the master equation

$$\dot{P}(\mathbf{X},t) = \sum_{\mathbf{X}'} P(\mathbf{X}',t) W_{\mathbf{X}'\to\mathbf{X}} - P(\mathbf{X},t) \sum_{\mathbf{X}'} W_{\mathbf{X}\to\mathbf{X}'}$$

Impossible to solve analytically

Two kinds of methods

- **Monte Carlo**
- **Mean Field**

Two kinds of modeling:

- At the atom level
  - Atomistic Kinetic Monte Carlo (AMC)
  - Self Consistant Mean Field (SCMF)
- At a mesoscopic level
  - Object Kinetic Monte Carlo (OKMC)
  - Rate theory (RT)

Monte Carlo: basis

Simulation of the trajectory of the system in the phase space

Residence time algorithm

$p_{\mathbf{X}}(t)$ probability for the system to be in configuration $\mathbf{X}$ at time t , knowing that it is their at time zero

$$p_{\mathbf{X}}(t) = \exp\left(-t/\tau_{\mathbf{X}}\right) \qquad 1/\tau_{\mathbf{X}} = \sum_{\mathbf{X}'} W_{\mathbf{X}\to\mathbf{X}'}$$

Selection of the effective transition:

- all the probability of the possible transitions stack along a segment of length $1/\tau_{\mathbf{X}}$
- a marker randomly place on this segment.
- configuration $\mathbf{X}$ is replaced by the new one and the time t by the time , $t+\tau$ and so on.

Rate theory basis

Determinist description instead of the stochastic

- **Only the mean trajectory $\langle \mathbf{X}(t) \rangle = \sum_{\mathbf{X}} \mathbf{X} P(\mathbf{X}, t)$ in the phase space is considered.**
- **The system is described by the set of ODE's equations**

$$\frac{\partial}{\partial t}\langle \mathbf{X}(t) \rangle = \sum_{\mathbf{X}'} \langle \mathbf{X}'(t) \rangle W_{\mathbf{X}' \to \mathbf{X}} - \langle \mathbf{X}(t) \rangle \sum_{\mathbf{X}'} W_{\mathbf{X} \to \mathbf{X}'}$$

Within the most general situation the higher moments has to be considered $\langle \mathbf{X}_i(t) \mathbf{X}_j(t) ..... \rangle$

Atomistic scale calculations

Basis © G. Martin, M. Nastar, F. Soisson, …

- Rigid lattice
- Interacting atoms of species A, B, .. and vacancies and/or self interstitial atoms (SIA) distributed among the Ns sites of the lattice
- State of the system described by occupation numbers n_i^A = 1 if the site i is occupied by species A and zero otherwise.
- Configuration of the alloy defined by the state vector

$$\left\{n_1^A, n_1^B, ..., n_1^v, n_2^A, n_2^B, ..., n_2^v, ...\right\}$$

Main ingredients of the modeling

- The configurational Hamiltonian:

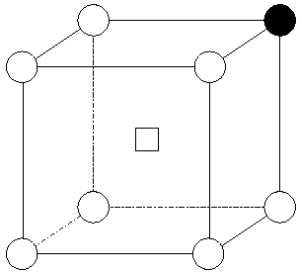
$$\hat{H} = \sum_{a,i} \varphi_i^a n_i^a + \frac{1}{2!} \sum_{ab\, i \neq j} V_{ij}^{ab} n_i^a n_j^b + \frac{1}{3!} \sum_{abc\, i \neq j \neq k} V_{ijk}^{abc} n_i^a n_j^a n_k^c + \cdots$$

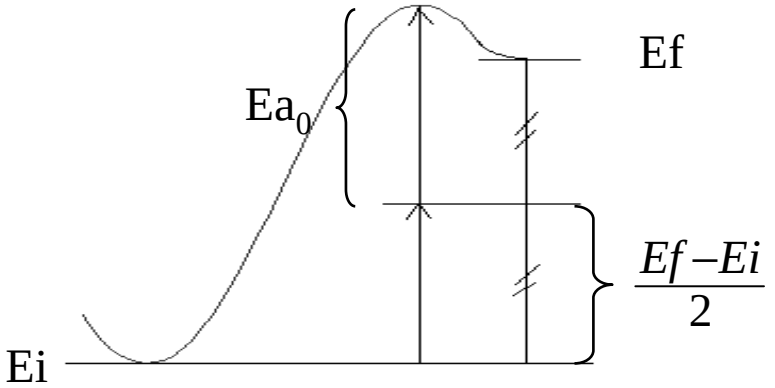
- V_{ij}^{AB} the pair interaction between a A atom on the i site and a B atom on the site j, the triplet interaction V_{ijk}^{ABC}, etc.
- The jumps frequencies of point defects (i or v).

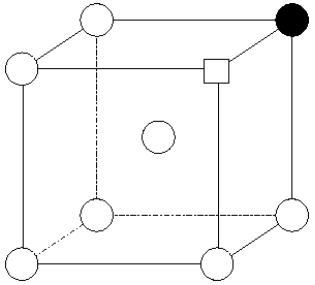
Jump frequencies I

$$\Gamma_{X,V} = \nu_X \exp\left(-\frac{Ea}{kT}\right)$$

$$Ea = Ea_0 + \frac{Ef - Ei}{2}$$

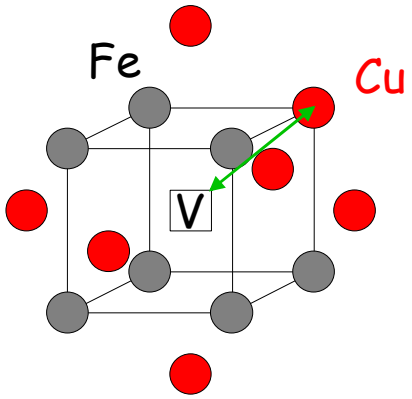


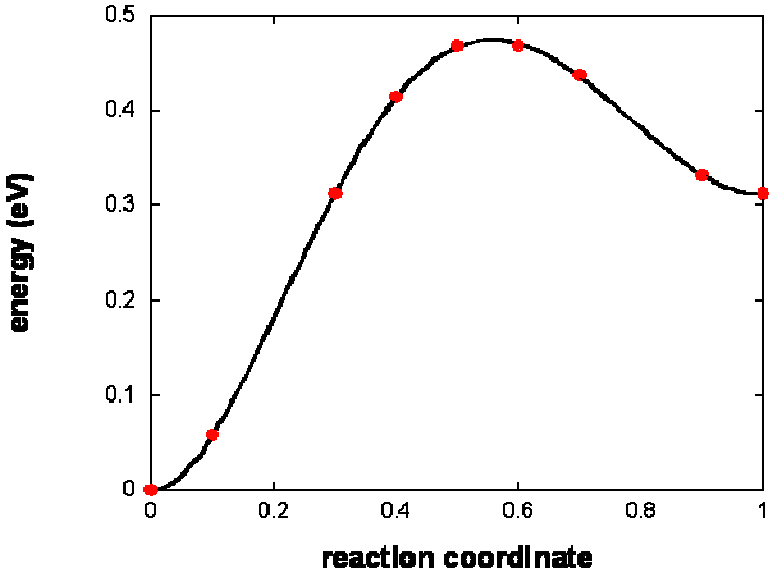




Jump frequencies II

More valuable method

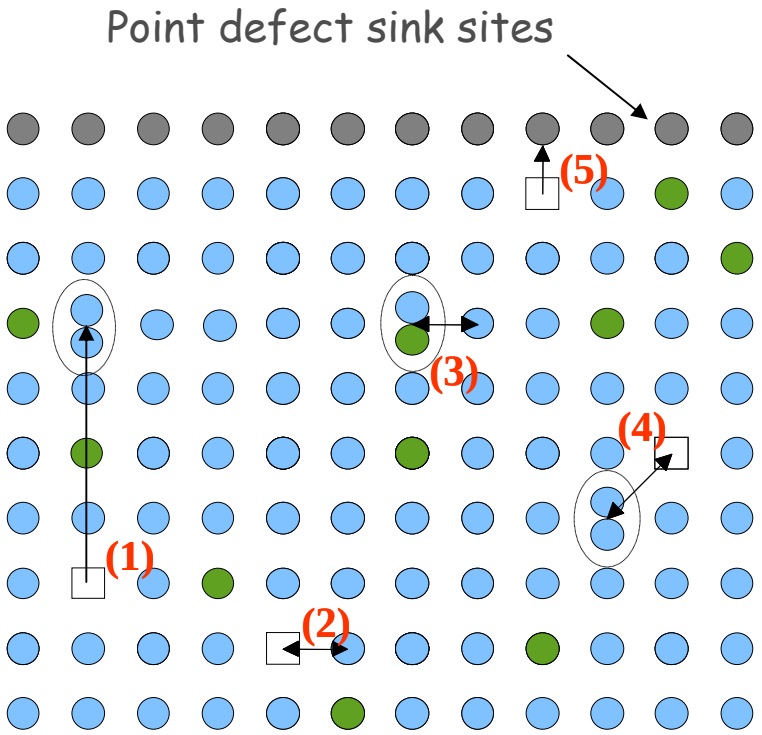




$$\Delta E_{CuV} = e_{Cu}^{SP} - \sum_i \varepsilon_{Cui} - \sum_j \varepsilon_{jV}$$

Atomistic Kinetic Monte Carlo (AKMC)

Energy = sum of pair interactions V_{ij} on rigid lattice



© F. Soisson

(1) Frenkel pair formation: $\Gamma_{FP} = \sigma\phi \quad (\mathrm{dpa.s^{-1}})$

(2) Vacancy jumps : $\Gamma_{AV} = \nu_A \exp\left(-\frac{E_{AV}}{k_B T}\right)$

© G. Martin

$$E_{AV} = e_A^{sp} - \sum_{\substack{\text{broken} \\ \text{bonds}}} V_{Ai}$$

(3) Interstitial jumps : XY « dumbbells »

$$\Gamma_{XY}^{int} = \nu_{XY}^{int} \exp\left(-\frac{E_{XY}^{int}}{k_B T}\right)$$

(4) V/I recombination $(d_{V-I} < l_{rec})$

(5) Point defect annihilation at sinks (perfect sinks)

Atomistic Kinetic Monte Carlo (AKMC)

RIP in under-saturated solid solutions

$D_A^{vac} >> D_B^{vac}$

undersaturated

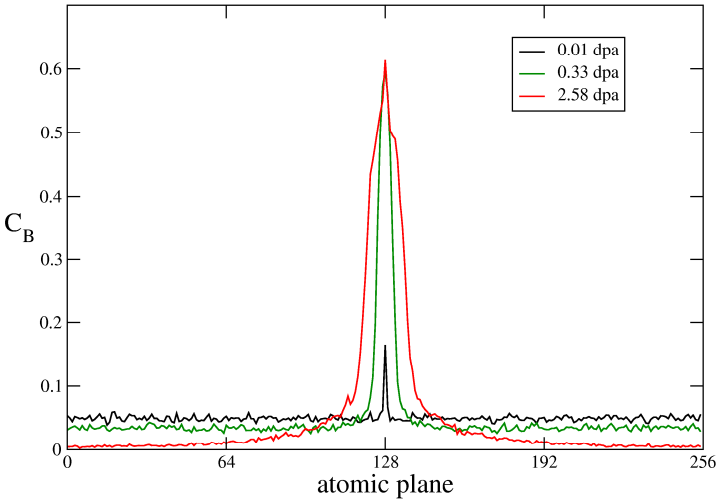
$T = 800\ K$

$C_B = 5\%$ $(C_B^{eq} = 8\%)$

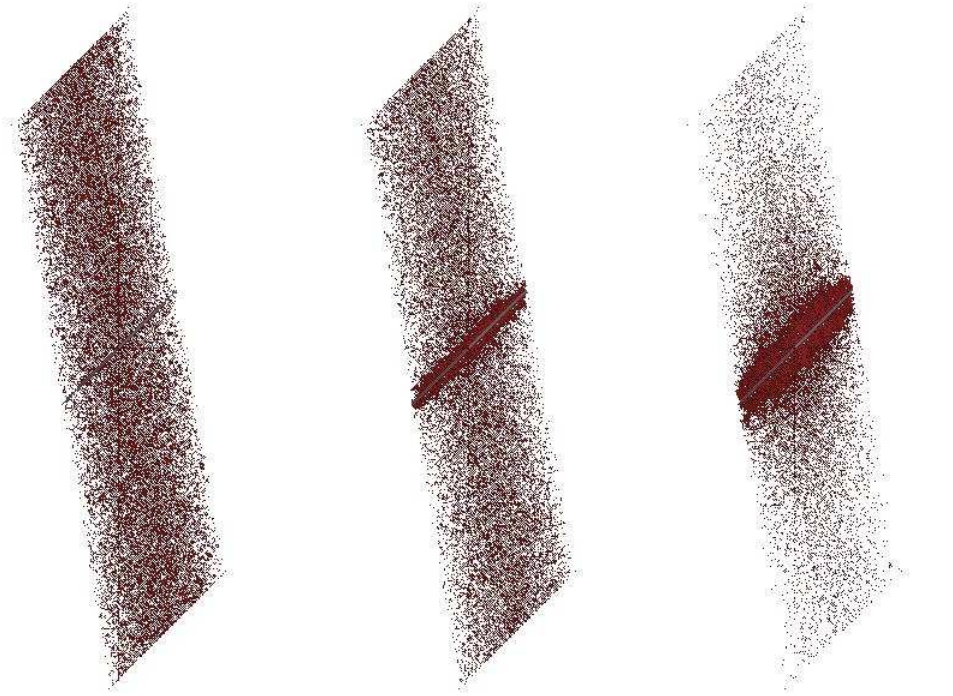
$\phi = 10^{-6}\ dpa.s^{-1}$

$D_B^v / D_A^v = 0.075$

planar point defect sink



Concentration Profile



0.01 dpa 0.33 dpa 2.58 dpa

Atomistic Kinetic Monte Carlo (AKMC)

RIP in super-saturated solid solutions

$D_A^{vac} >> D_B^{vac}$

high mixing energy

high supersaturation

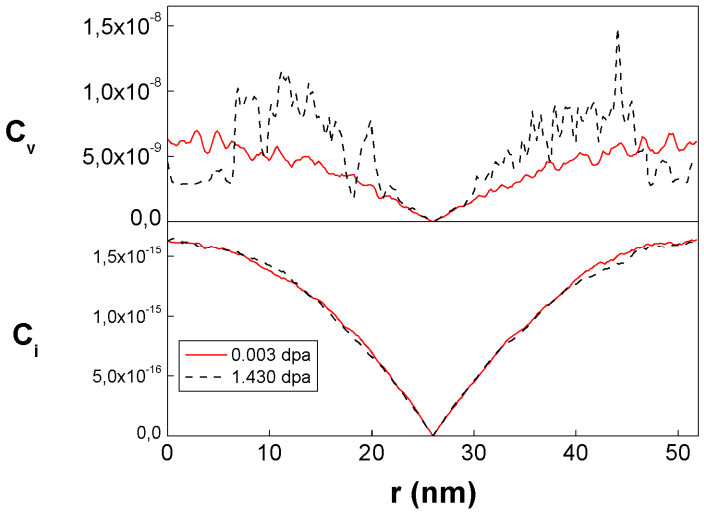
$T = 800\ K$

$C_B = 5\%$ $(C_B^{eq} \sim 0)$

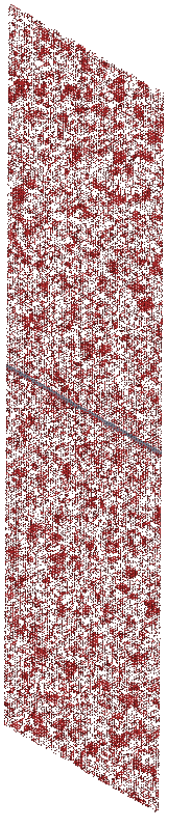
$\phi = 10^{-8}\ dpa.s^{-1}$

$D_B^v / D_A^v = 0.075$

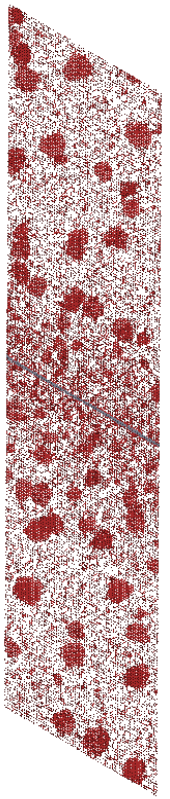
planar point defect sink



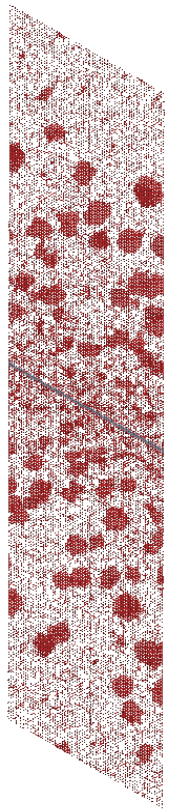
Concentration profiles



0.02 dpa



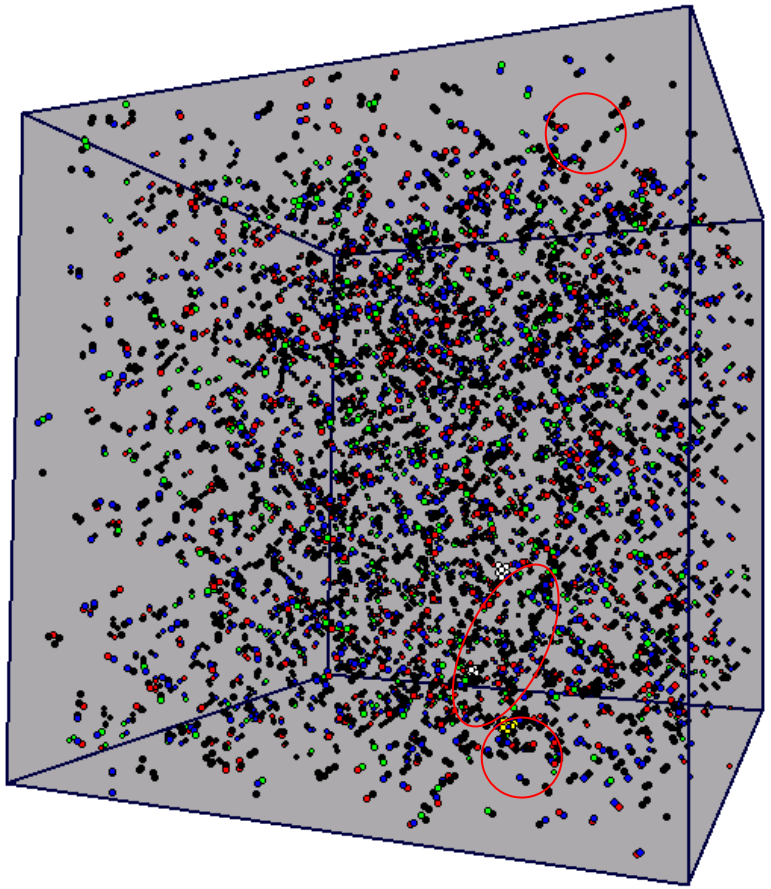
0.41 dpa



1.42 dpa

Atomistic Kinetic Monte Carlo (AKMC)

NEUTRON IRRADIATION OF AN FeCuNiMnSi ALLOY



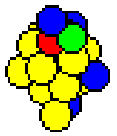
Flux: 6.5 10^{-5} dpa.s^{-1}

Dose: 1.3 10^{-3} dpa

T: 300℃

Fe-0.2Cu-0.53Ni-1.26Mn-0.63Si (at.%)

V-solute complex (4.2 10^{22} m^{-3})



SIA-solute complexes

Small solute clusters (3Cu + 3Si + 4Mn)

Cu Ni

Si V

Mn SIA

© E. Vincent et al

Mesoscopic approach

“gas” of dilute objects

Nature

- **point defects**
- **solute atoms**
- **clusters,**
- **etc.**

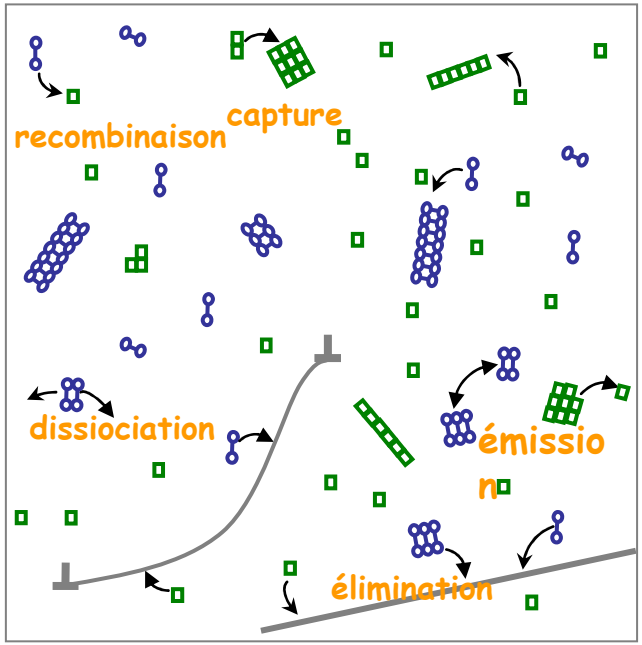
- **Object Monte Carlo (OKMC)**
- **Rate theory (RT)**

Object Monte Carlo (OKMC)

Object positions: ‘discreet’ or continuous coordinates

OKMC
BIGMAC (LLNL)
LAKIMOCA (EDF)

Even Based Monte Carlo (EBMC)
JERK (CEA)



Object Monte Carlo (OKMC)

Objects execute random diffusion jumps at first neighbors with a probability given by the jump frequency:

$$\Gamma = \Gamma_0 \exp\left(-E^m / kT\right)$$

Dissociation rate of a cluster, usually the emission of a monomer:

$$\Gamma = \Gamma_0 \exp\left(-\left(E^B + E^m\right) / kT\right)$$

E^B binding energy of the emitted particle to the cluster.

Algorithm :

1. $R = \sum_e \Gamma_e N_e$ the total rate for all events
2. An event is chosen randomly between 0 and R .
3. Time is increased by $\Delta t = -\log(\zeta) / R$
4. An object among the N_e is chosen randomly and the event is carried out.
5. The next step is perform coming back to 1 and so on.

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Even Based Monte Carlo (EBMC)

Elementary event = binary encounters of two objects (the migration of a mobile object is not an even in itself).

Probability distribution that two defects 1 and 2 at distance d reacts:

$$P(d,t) = \frac{r}{d} erfc\left\{\frac{d-r}{2\sqrt{Dt}}\right\}$$

r reaction radius

$$D = D_1 + D_2$$

The delay of interaction τ obtained by sampling $P(d,t)$:

$$\tau = \frac{1}{4D}\frac{(d-r)^2}{\left\{erfc^{-1}(\xi d / r)\right\}^2}$$

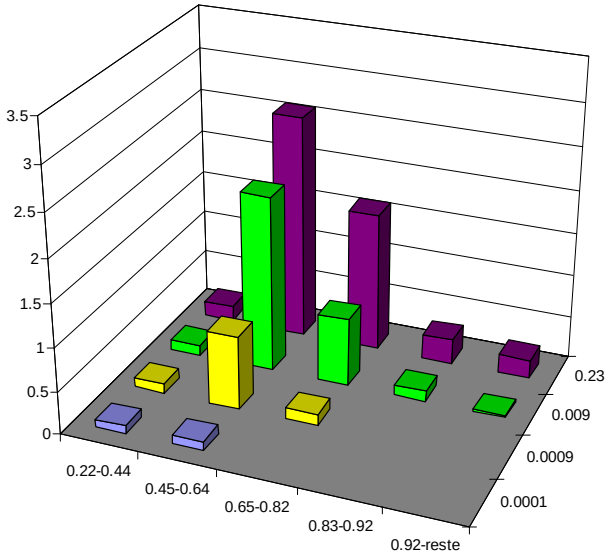
ξ *random number over [0,1]*

Algorithm

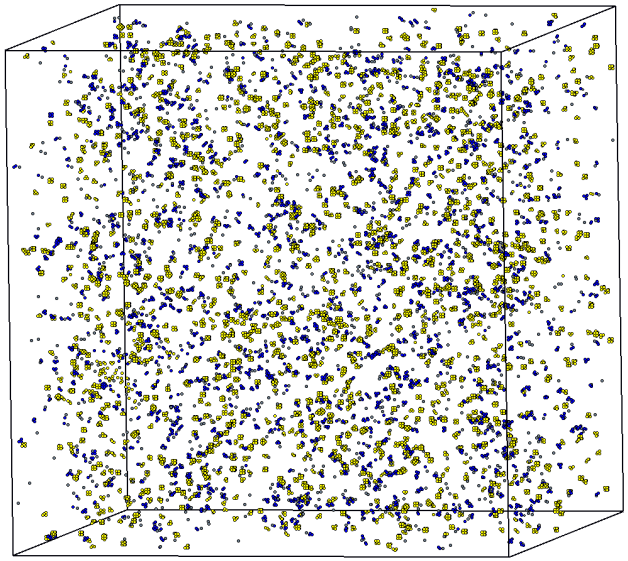
- **chooses a time step Δt**
- **calculates the delay τ of each possible reaction**
- **selects the shortest event τ_s in the list of all possible events**
- **executes the event deleting if necessary the defects that have interacted and computing the delay associated with the newly created defect if any**
- **updates the actual time by adding τ_s**
- **reduces the remaining delays by τ_s**
- **repeats steps 3, 4 and as far as no other event is possible before the end of Δt**

OKMC

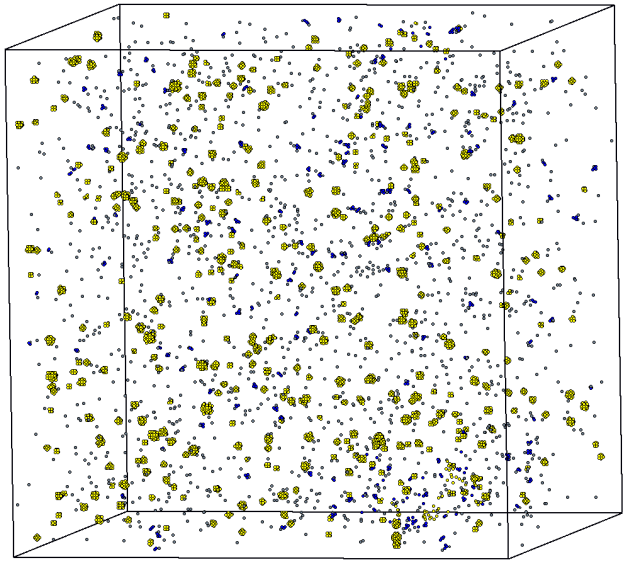
Ferritic model alloy 70℃



DEFECT POPULATION at 0.1 dpa



flux effect

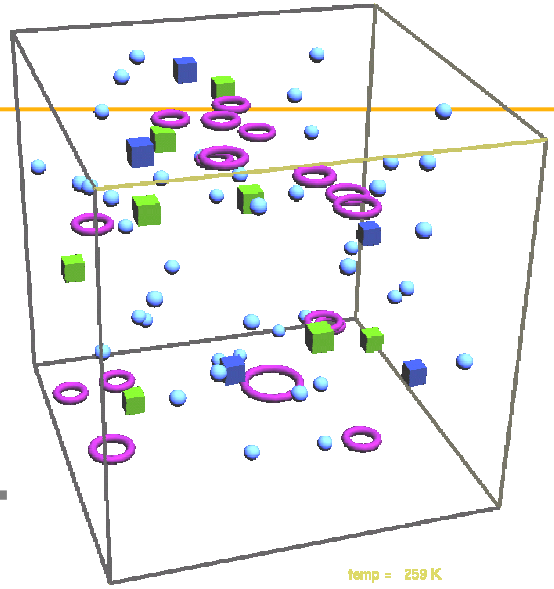


7 10^{-5} dpa/s

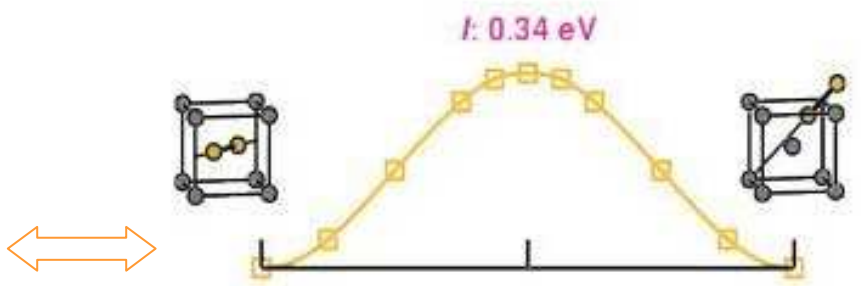
7 10^{-11} dpa/s

EBMC

Numerical simulations / experimental resistivity recovery

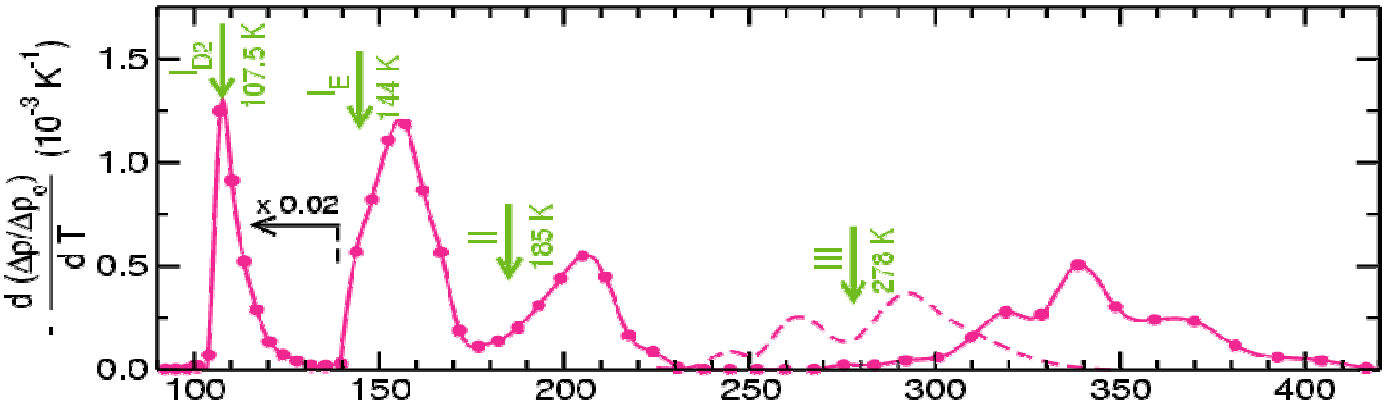


Macroscopic Resistivity recovery Experiments by Takaki et al.



Ab initio *SIESTA* Energetics and migration of defects

Kinetic Monte Carlo *Jerk* size and time evolution of the defect population



- **Excellent agreement with the experimental results.**
- **I_n (≥ 4) migration not required to reproduce the experiments.**
- **Peak position very sensitive to mechanisms rates.**

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Rate theory basis

Location of the object no more considerate

If N_j the number of object of type j, in a volume Ω

- If only SIA (dislocation loops) and vacancy clusters (voids), the state vector is:

$$\mathbf{X} = \{N(V_1), N(V_1), ..., N(I_1), N(I_2), ...\}$$

$N(V_n)$ the number of vacancy clusters (voids) made of n vacancies and $N(I_n)$ the number interstitial clusters (loops) made of n SIA's.

- Average number of SIA clusters, for example:

$$\langle N(I_n) \rangle = \sum_{\mathbf{X}} N_{I_n}(\mathbf{X}) P(\mathbf{X})$$

-

- Rate theory is obtained in the thermodynamic limit:

$$N(I_n) = \lim_{\Omega \to \infty} \langle N(I_n) \rangle_{\Omega}$$

Rate theory basis

Concentration per unit volume of object $C(I_n) = N(I_n)/\Omega$

Master equation for rate theory (deterministic equation)

$$\frac{\partial C(I_n)}{\partial t} = \sum_m C(I_m) w_{m \to m} - C(I_n) \sum_n w_{n \to m}$$

If I_n is a mobile, elimination term of clusters on fix sinks

$$-L(I_n) C(I_n)$$ **must be added**

If clusters are generated in cascades, a source term

$$G(I_n)$$ **must be added**