Monte Carlo simulations of diffusive phase transformations: time-scale problems

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Outline

- Atomistic Kinetic Monte Carlo simulations (AKMC) : from an atomistic description of diffusion mechanisms to the kinetics of phases transformations in metallic alloys

- The precipitation kinetic pathways depends on point defect diffusion properties

  key points : the dependence of the *migration barriers* and the *vacancy concentrations* with the local configuration

Ab initio calculations (thermodynamics and diffusion)

Diffusion model on a rigid lattice

Atomistic Kinetic Monte Carlo simulations (AKMC)

- Applications to the decomposition of Fe-Cr concentrated solid solutions
  Comparison with experiments (3D atom probe and SANS)

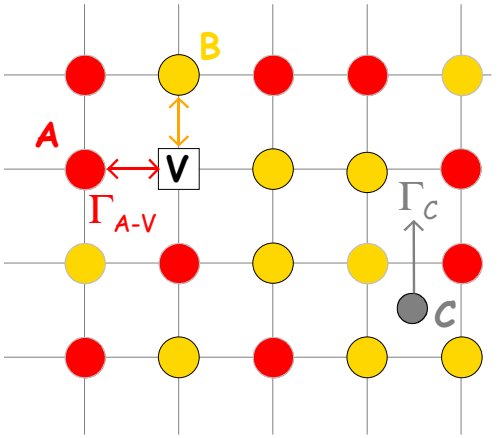
- Contributions of *ab initio* calculations (and their current limitations)

Rigid lattice diffusion model

· **A-B alloy – rigid lattice with pair interactions : εAA, εAB, εBB + εAV, εBV**

Possible improvements:
- many-body interactions (triangle, tetrahedron, etc.)
- composition dependent interactions (-> FeCr alloys)
- temperature dependent interactions (-> ΔSmig, ΔSfor)

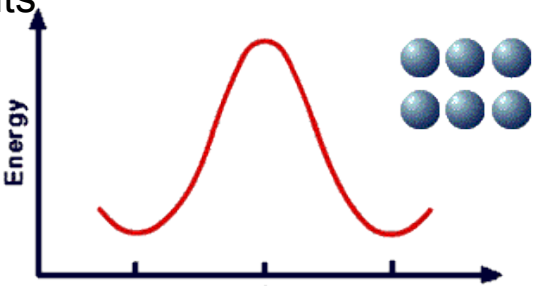
Alternative approach : interatomic potentials



· **Diffusion by thermally activated point defects jumps**

- jump frequency : depend on the local environments

$$\Gamma_{AV} = \nu_A \exp\left(-\frac{\Delta E^{mig}_{AV}}{k_b T}\right)$$



- migration barriers: broken-bond models

$$\Delta E^{mig}_{AV} = E_{sys}(SP) - E_{sys}(ini) = \underbrace{\varepsilon^{SP}_{Ai}}_{\text{saddle-point interactions}} - \underbrace{\varepsilon^{(n)}_{Aj} - \varepsilon^{(n')}_{k\lambda}}_{\text{broken-bonds}}$$

· **AKMC: residence time algorithm**

Simulations with 106-107 atoms, PBC and 1 vacancy -> time scale : $t_{MC} = \frac{1}{\sum_i \Gamma_i}$

Physical time scale and point defect concentrations

The kinetic pathways depends on the migration barriers but also on the point defect concentrations : simulations with a constant number of point defects (e.g. *NV* = 1) require a time rescaling

The time correction factor *is not constant*

$$t = t_{MC} \frac{\langle C_V^{MC} \rangle}{\langle C_V^{eq} \rangle} \quad \text{with} \quad \langle C_V^{MC} \rangle = N_V / N$$

$\langle C_V^{eq} \rangle$ usually evolves during the phase transformations

- For any local environment (α) $t = t_{MC} \frac{C_V^{MC}(\alpha)}{C_V^{eq}(\alpha)}$ with $C_V^{eq}(\alpha) = \exp\left(\frac{E_V^{for}(\alpha)}{kT}\right)$

also provides an estimation of $\langle C_V^{eq} \rangle = \langle C_V^{MC} \rangle \frac{C_V^{eq}(\alpha)}{C_V^{MC}(\alpha)}$ during the phase transformation

- A convenient choice for phase separation : pure A or pure B

$$E_V^{for}(\text{pure A}) = -\frac{z}{2} \varepsilon_{AA} + z\, \varepsilon_{AV}$$

- Only valid when vacancy concentration remains at equilibrium.

Alternative approach : AKMC with formation and annihilation mechanisms (sources/sinks)

One simple example

Phase separation in an A95-B5 alloy : $E_V^{for}(\mathrm{A}) = 1.4\ \mathrm{eV} > E_V^{for}(B) = 1.0\ \mathrm{eV}$

AKMC simulation
with 1 vacancy
T = 573 K (0.6 Tc)

$$\left\langle C_V^{eq} \right\rangle = \left\langle C_V^{MC} \right\rangle \frac{C_V^{eq}(\mathrm{A})}{C_V^{MC}(\mathrm{A})} = \left\langle C_V^{MC} \right\rangle \frac{C_V^{eq}(\mathrm{B})}{C_V^{MC}(\mathrm{B})}$$

$$\left\langle C_V^{eq} \right\rangle$$

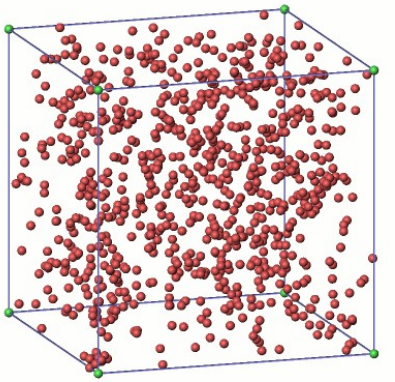
Strong variation of the time rescaling factor
Gibbs-Thomson effect :
Application: vacancy concentration in non-ideal concentrated solid solutions
(Mean-Field models, M. Nastar)

$\left\langle C_V^{eq} \right\rangle$ with ref. A slightly $\gtrless$ $\left\langle C_V^{eq} \right\rangle$ with ref. B

Copper precipitation in α-iron : clusters mobility

$E_V^{for}(Cu) = 0.9\ eV > E_V^{for}(Fe) = 2.1\ eV$

Classical theories of nucleation, growth and coarsening: emission/absorption of individual solute atoms



·**AKMC simulation :**

Small Cu clusters are mobile than monomers

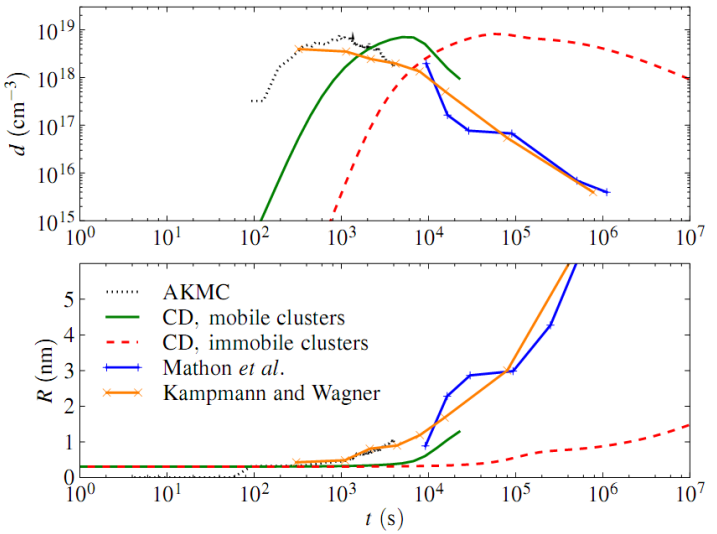
-> coagulation mechanisms

·**Measurements of the cluster diffusion coefficients**

·**CD and EKMC simulations (T. Jourdan)**

- the diffusion of clusters strongly accelerates the precipitation kinetics

- better agreement with experiments



α-α' decomposition in Fe-Cr alloys

Fe-Cr alloys : a model system for ferritic-martensitic steels
A special thermodynamic behavior :

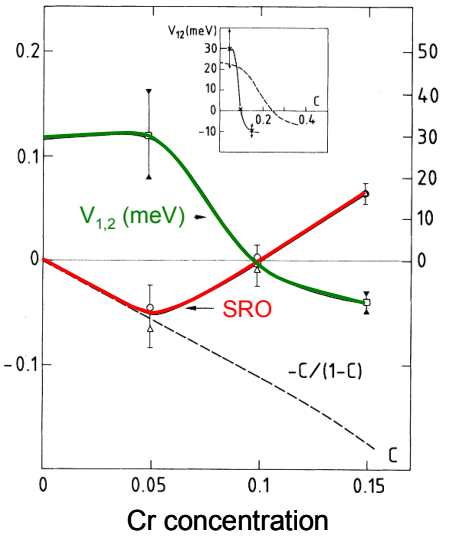
SANS and electrical resistivity experiments:

below 10%Cr : ordering tendency

above 10%Cr : unmixing tendency

(Mirebeau et al, 1984)

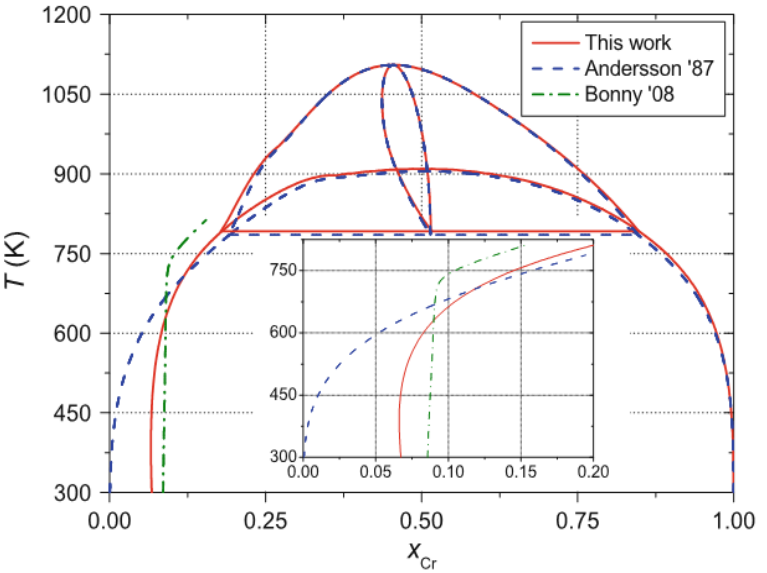
Ab initio calculations: connected to magnetic properties
Strong vibrational entropy (exp. + *ab initio*)



Phase diagram

"old Calphad": no Cr solubility at low

↝ new phase diagram
takes into account DFT calculations
and experiments at low T
(Bonny et al, 2010)



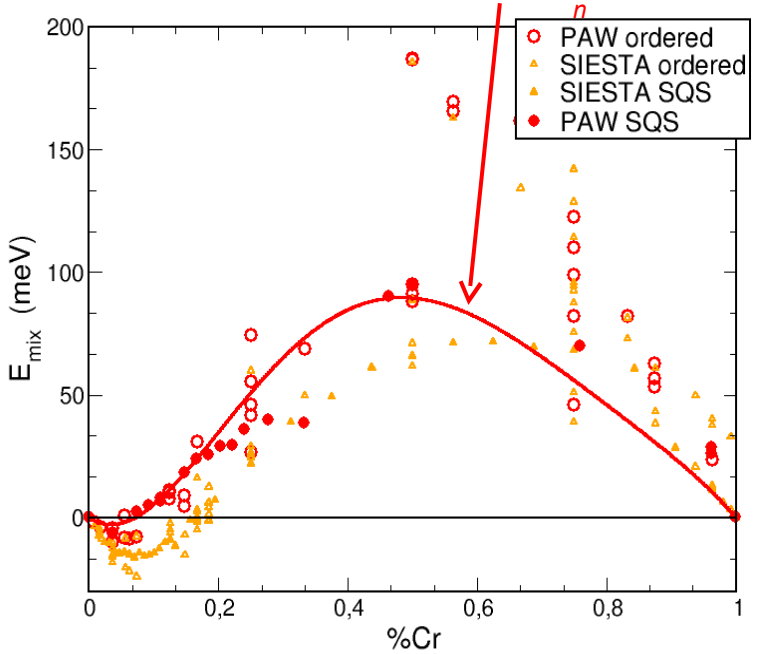
Thermodynamics: pair interaction model (M. Levesque et al. 2010)

· **Constant pair interactions**: $\Delta E_{mix} = x(1-x)\Omega$ with $\Omega = \sum_n \frac{z_n}{2}\left(\varepsilon^n_{AA} + \varepsilon^n_{BB} - 2\varepsilon^n_{AB}\right)$
symmetrical mixing energies and phase diagram

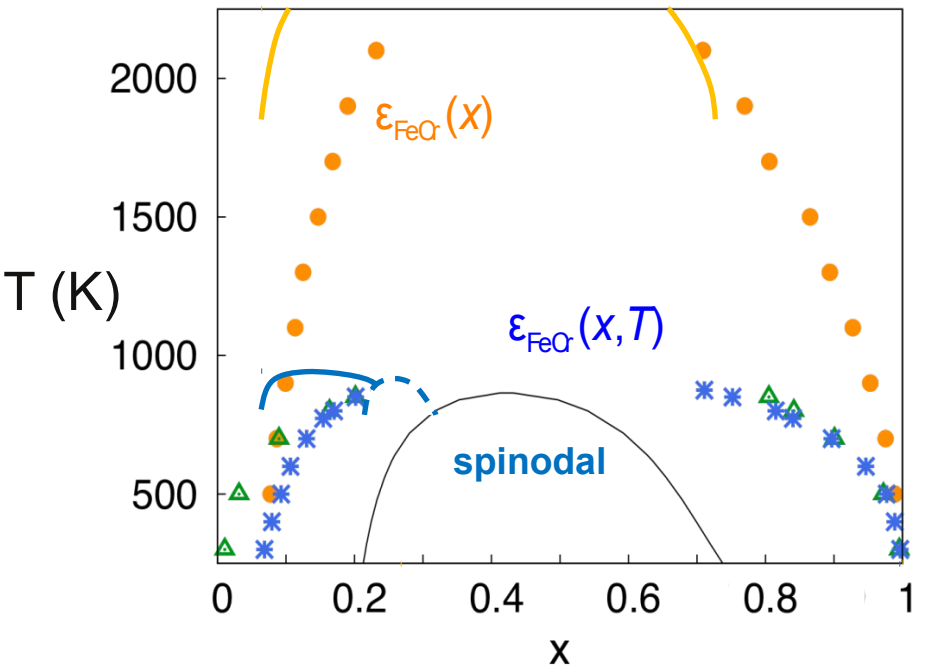
· **Composition dependent pair interactions** fitted on DFT calculations (1st and 2nd nearest-neighbor) -> asymmetrical phase diagram

· Temperature dependence: εFeCr(x,T) = εFeCr(x,0) (1-T/θ) (magnetic effects, vibrational entropy)

$\Delta E_{mix} = x(1-x)\sum_n L^n (1-x)^n$



Phase Diagram



· Alternative approach : Classical and Magnetic Cluster Expansion (Lavrentiev et al)

Diffusion properties: migration barriers

- Vacancy migration barriers : *vacancies-atom* and *saddle-point* (SP) pair interactions fitted on DFT calculations of vacancy formation energies and migration barriers (DFT-SIESTA)

  attempt frequencies *vFe* and *vCr* fitted on *ab initio*, or the experimental pre-exponential factors

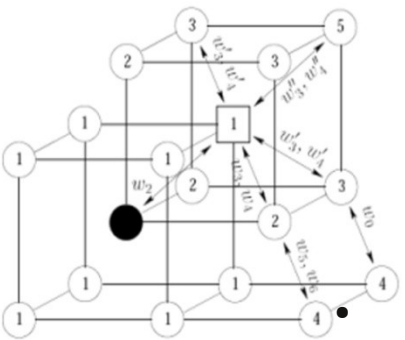
- Self diffusion in pure metals

$$D_A^* = a^2 C_V(A) \Gamma_0 \nu_0$$

	Fe	Cr
E_V^{for}	2.18	1.91 (Spin-wave)
E_V^{mig}	0.69	1.25 (AFM configuration)
Q	2.87 exp: 2.91	3.16 exp: 3.2-3.6 (at low T)

- Diffusion in dilute alloys : (10-frequency model)

$$D_B^* = a^2 C_V(A) \frac{\Gamma_2}{\Gamma_3} \nu_2$$



Activation energy	in Fe		in Cr	
at 0 K (eV)	SIESTA	RLA	SIESTA	RLA
ΔH_0	0.69	0.69	1.25	1.25
ΔH_2	0.57	0.57	1.16	1.16
ΔH_3	0.64	0.80	1.04	1.12
$\Delta H_3'$	0.69	0.70	1.10	1.24
$\Delta H_3''$	0.67	0.70	1.07	1.24
ΔH_4	0.66	0.79	1.14	1.12
$\Delta H_4'$	0.65	0.67	1.31	1.25
$\Delta H_4''$	0.66	0.67	1.27	1.25
ΔH_5	0.74	0.69	1.32	1.25
ΔH_6	0.74	0.68	1.20	1.25

Migration barriers are computed at 0K, in magnetic configurations extrapolation above the transitions temperature ?

Diffusion coefficients

Pre-exponential factor : $\nu_D = 10^{13}\, s^{-1}$

$S_V^{for}(Fe) = 4.1 k_B$ (DFT, Lucas & Schaüblin, 2009)

$S_V^{mig}(Fe) = 2.1 k_B$ (Athènes and Marinica, 2010)

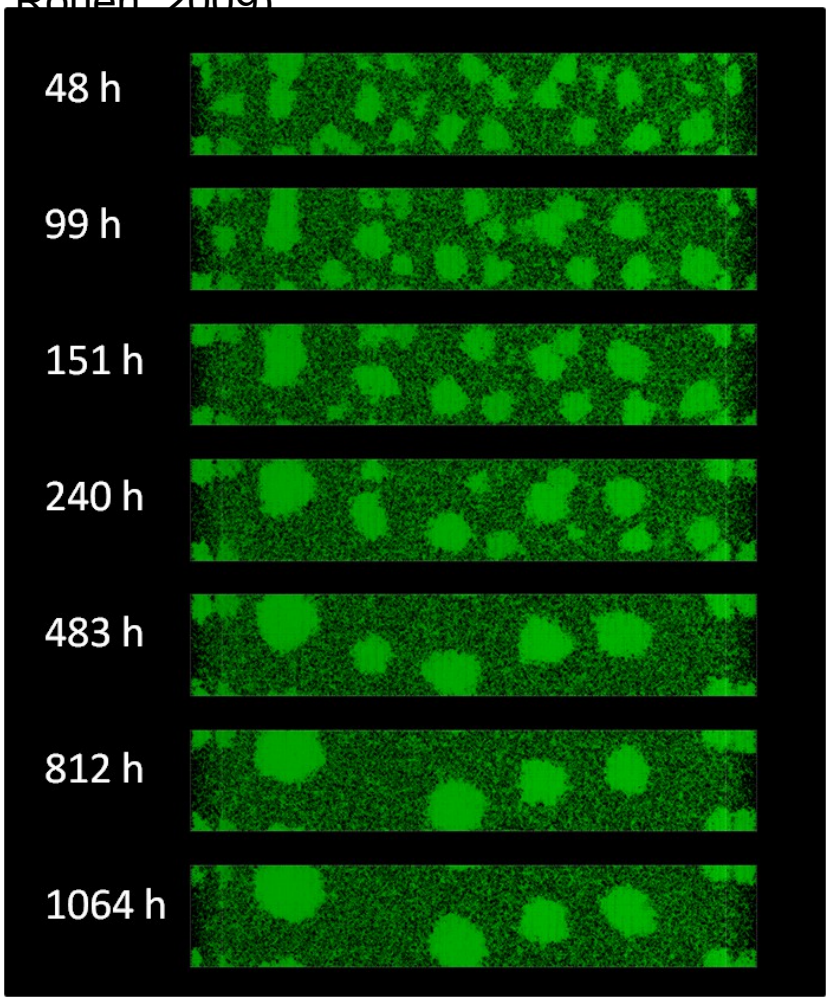
- Good agreement with the experimental *D0* (in iron)

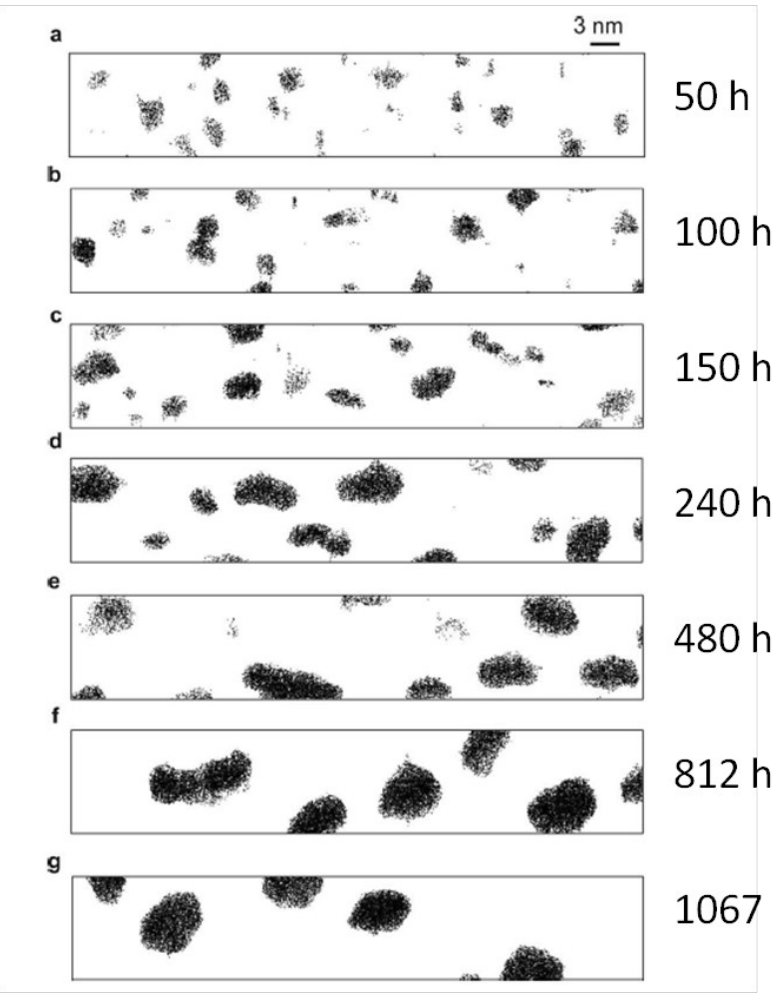
in iron in chromium

AKMC: α-α' decomposition during thermal ageing

Fe-20%Cr T = 500°C

AKMC (E. Martinez, O. Senninger, CEA) 3D atom probe (Novy et al, GPM Rouen, 2009)





AKMC vs SANS experiments (E. Martinez, O. Senninger, 2011)

Small Angle Neutrons Scattering experiments : Bley 1994, Furusaka et al 1986

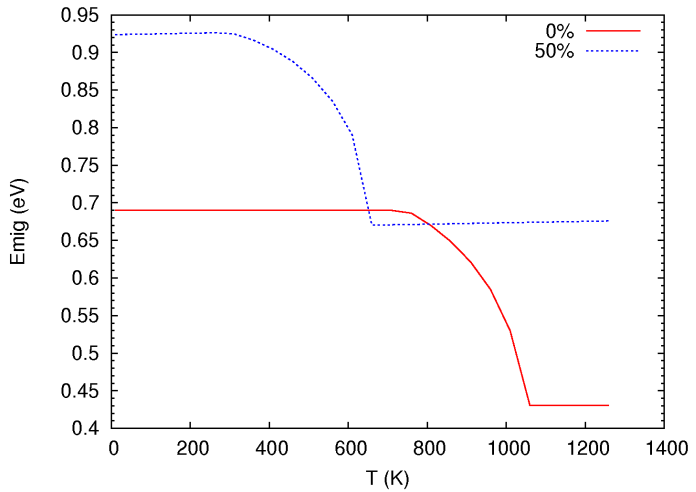
Fe – 20, 35 and 50% Cr, 500°C: good agreement with SANS experiments
Fe – 40%Cr, 540°C : AKMC much slower than SANS experiments
The Curie temperature decreases with the Cr content: effect of the ferro-paramagnetic transition?

Effect of the magnetic transition on the kinetics

O. Senninger, E. Martinez et al. 2012

Evolution of the Curie temperature
with the composition

Decrease of the migration barriers at TC (fitted on the experimental diffusion coefficients)



Radiation induced segregation and precipitation

Undersaturated solid solution with an unmixing tendency ($\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB} < 0$)

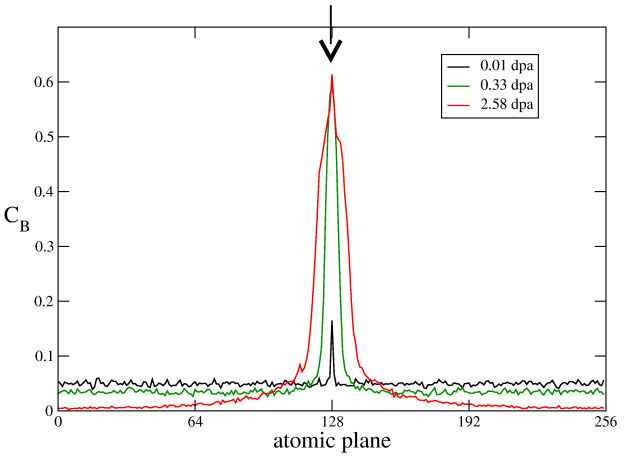
$C_B = 5\% - C_B^{eq} = 8\%$

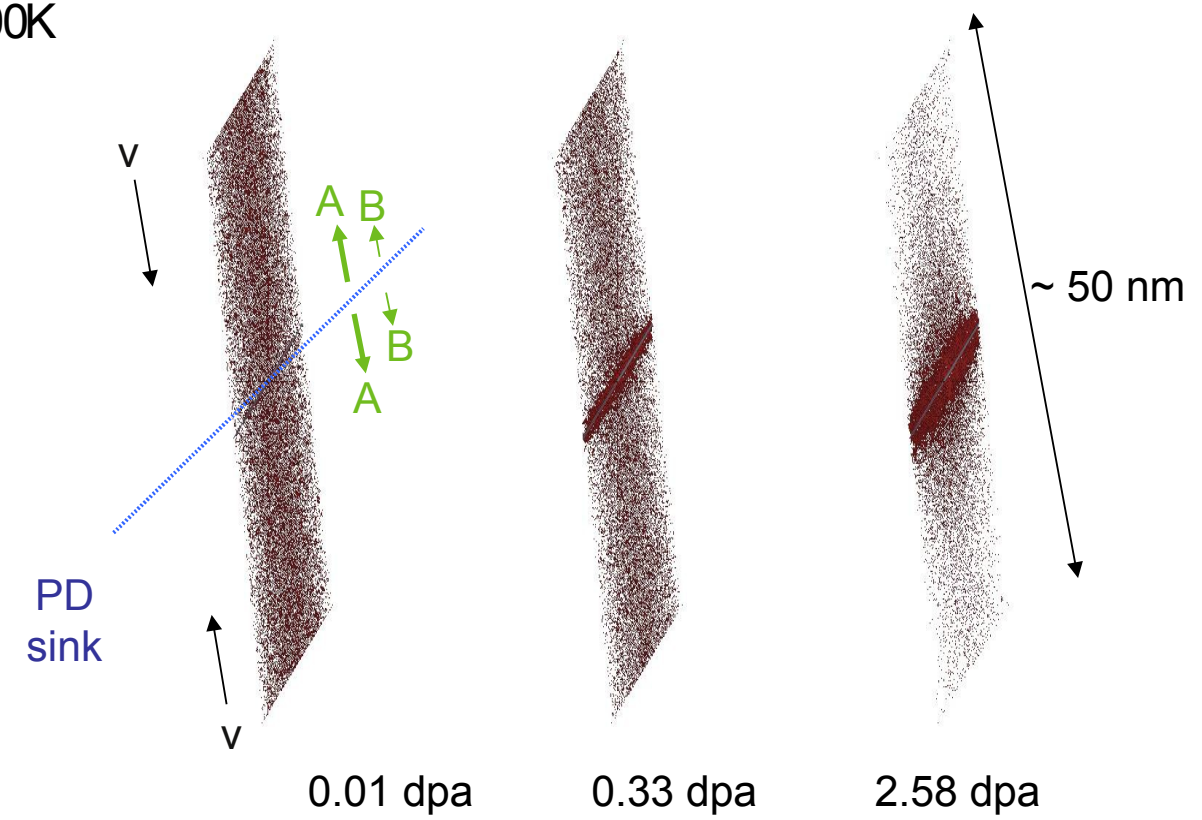
D_B^v / D_A^v 0.06 and D_B^i / D_A^i 1

$G = 10^{-6}\,\mathrm{dpa.s^{-1}}$ $T = 800\mathrm{K}$

Solute concentration profile

Point defect sink





Conclusions

AKMC simulations: a detailed description of thermodynamic and diffusion properties

- dependence of point defect jump frequencies and concentrations with the local atomic environment
- correlation effects (↔ theory of diffusion in alloys)

But time consuming: → cluster dynamics, OKMC, EKMC

Ab initio calculations : → reliable parameters at 0K

temperature effects : vibrational entropy of mixing, vacancy formation and migrations entropies

- in pure metals
- - in concentrated alloys ?

Fe-Cr alloys: importance of magnetic transitions

Perspectives : radiation induced segregation, spinodal decomposition in Fe-Cr alloys