Service de Recherches de Métallurgie Physique

CEA / DEN / DMN / SRMP

Multiscale Modeling of Materials Kinetics under Irradiation

from the atomic to the macroscopic scale :
a long standing activity at SRMP

- What for ? Technical & Scientific Stakes
- Tools, Scales, Coupling with experiment
- Applications
- Perspectives

Our basic research themes

In order to control behavior in service and design of materials :

- ***Understand the kinetic pathways***

↳ **microstructural evolution and resulting properties of « Driven materials » (submitted to various types of external forcing, mainly irradiation)**

- ***Develop predictive tools***

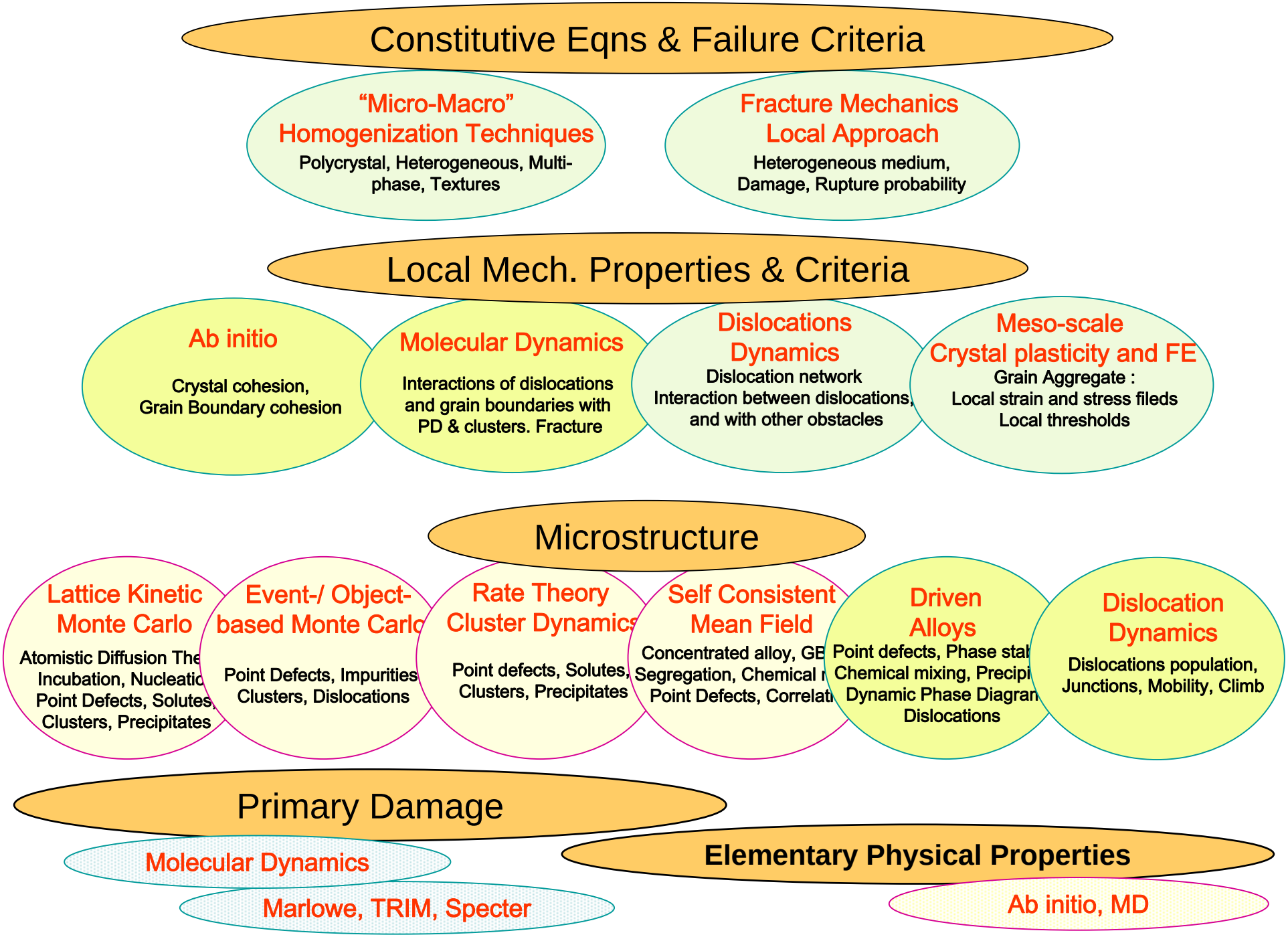
↳ **anticipate materials properties, assist in the development of new materials**

1. Identify and modelize stability criteria, kinetic pathways : « dynamic phase diagrams »

2. Provide the theory and modeling of kinetic pathways with the same level of robustness as that currently achieved for cohesion

↳ **point defects populations and elementary properties thermodynamics & diffusion (ab initio, MD)**

↳ **physical mechanisms of diffusion, evolution models**


Constitutive Eqns & Failure Criteria
"Micro-Macro" Homogenization Techniques
Polycrystal, Heterogeneous, Multi-phase, Textures
Fracture Mechanics Local Approach
Heterogeneous medium, Damage, Rupture probability
Local Mech. Properties & Criteria
Ab initio
Crystal cohesion, Grain Boundary cohesion
Molecular Dynamics
Interactions of dislocations and grain boundaries with PD & clusters. Fracture
Dislocations Dynamics
Dislocation network Interaction between dislocations, and with other obstacles
Meso-scale Crystal plasticity and FE
Grain Aggregate : Local strain and stress fileds Local thresholds
Microstructure
Lattice Kinetic Monte Carlo
Atomistic Diffusion The Incubation, Nucleatic Point Defects, Solutes, Clusters, Precipitates
Event-/ Object-based Monte Carlo
Point Defects, Impurities Clusters, Dislocations
Rate Theory Cluster Dynamics
Point defects, Solutes, Clusters, Precipitates
Self Consistent Mean Field
Concentrated alloy, GB Segregation, Chemical r Point Defects, Correlati
Driven Alloys
Point defects, Phase stal Chemical mixing, Precipi Dynamic Phase Diagran Dislocations
Dislocation Dynamics
Dislocations population, Junctions, Mobility, Climb
Primary Damage
Molecular Dynamics
Marlowe, TRIM, Specter
Elementary Physical Properties
Ab initio, MD

Cohesion & elementary properties at atomic scale

Point Defects, Extended defects :

- Diffusion, Kinetics
- Dislocations, Plasticity

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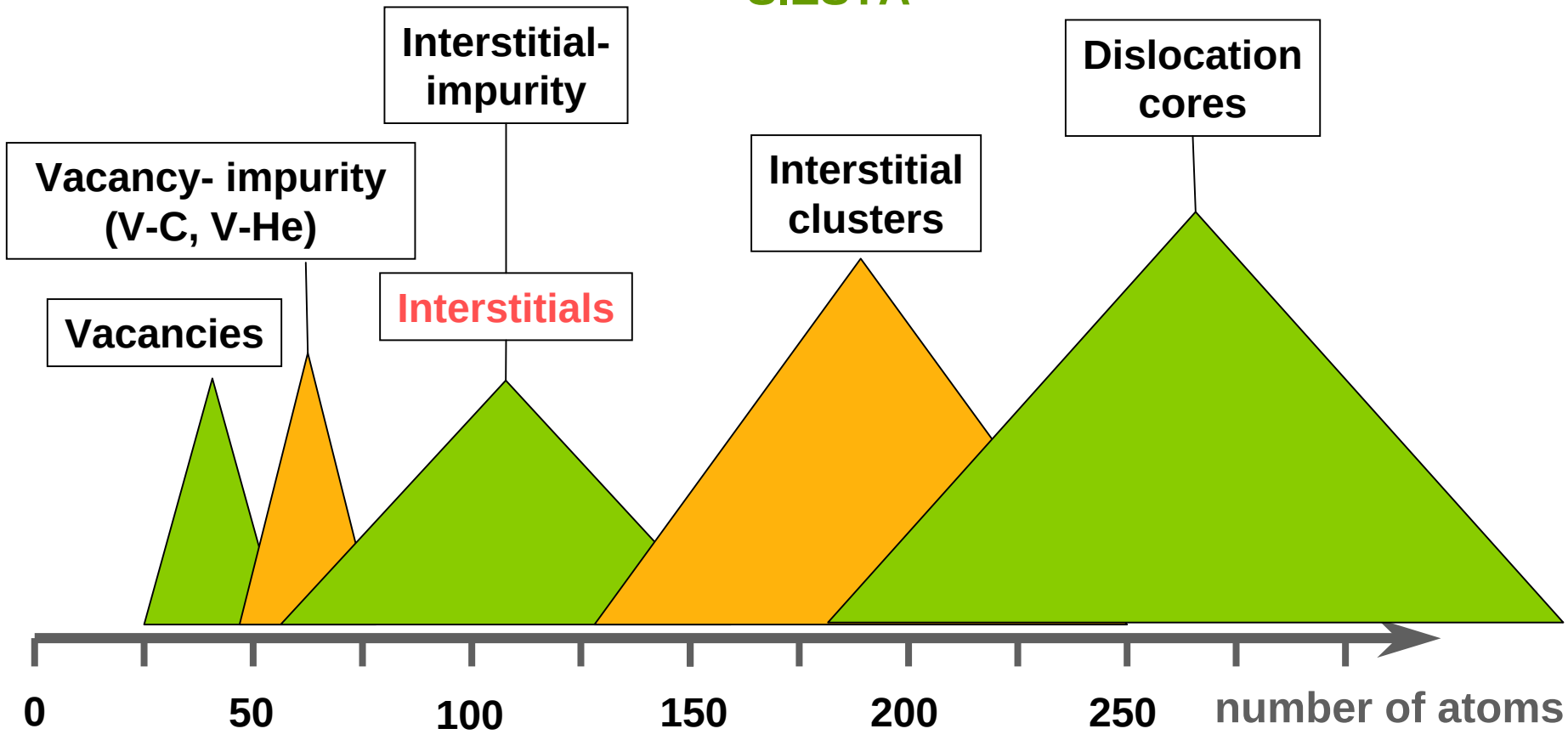
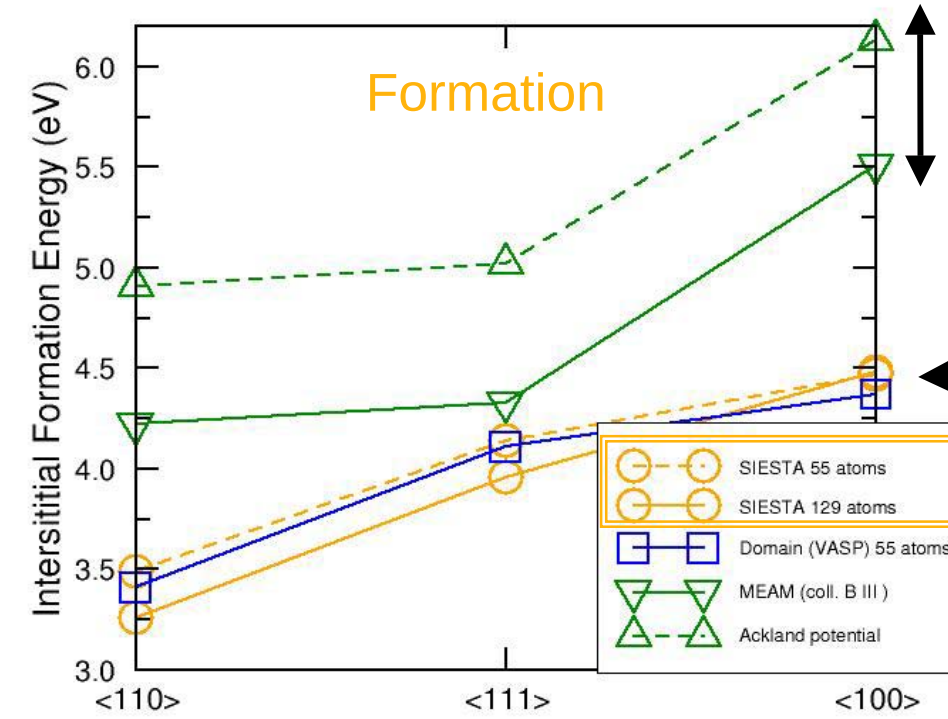


Self-interstitials in BBC Fe

Chu Chun Fu & F. Willaime 2003-2004

Structure and formation energy



Very different from available empirical potentials

Excellent agreement with Plane Wave calculations

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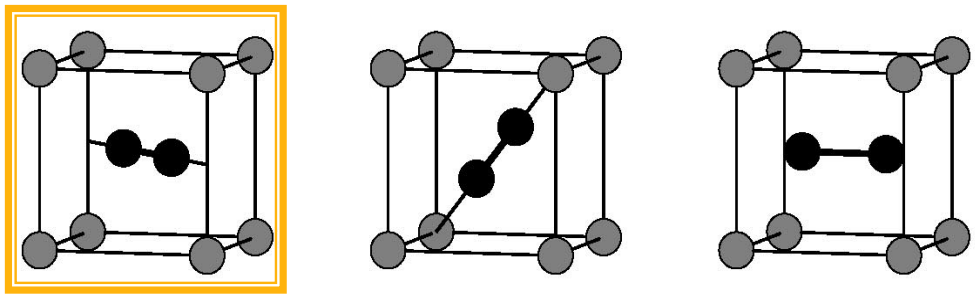
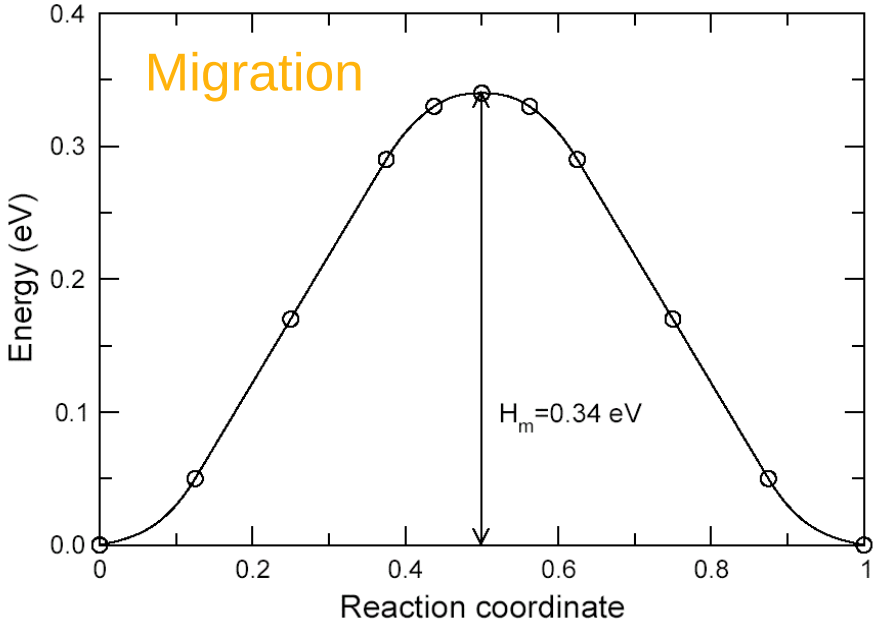


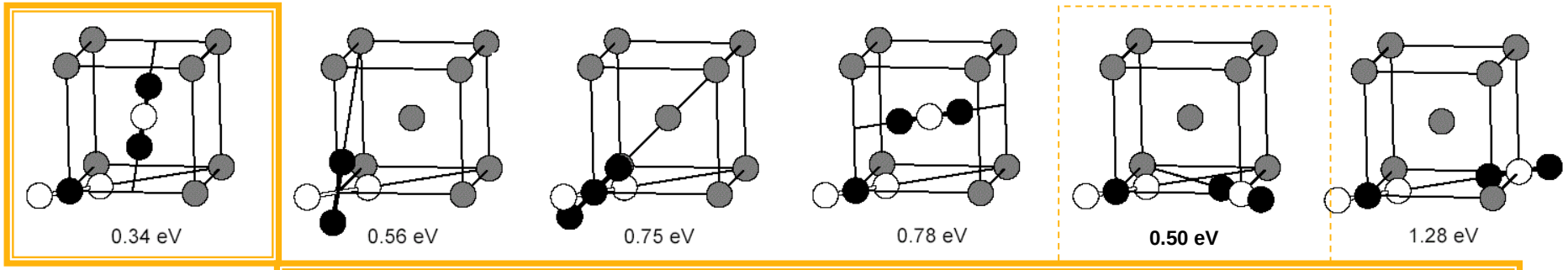
Self-interstitials in BBC Fe

Chu Chun Fu & F. Willaime 2003-2004

Migration mechanisms of <110> dumbbells

and diffusion path





Translation / rotation 1st neighbour jump → 3D Migration
Excellent agreement with experiment : H_m=0.3 eV

Point Defect clusters

- **Single-interstitials**
  - formation : <110> dumbbell (much more stable than <111>)
  - migration : 3D
    (combined jumps more favorable than pure rotation or translation)
- **Di- & tri-interstitials**
  - parallel dumbbells <110>
  - high binding energy 0.7eV (Di) – 0.8 eV (Tri)
  - low migration energy 0.4 eV → diffuse without dissociation at low temperature
- **n-interstitials** : under way …
  - <110>, <111> or <100> ? transition ?
  - mobiles or not?

  ⇒ **towards dislocations loops and other PD clusters**
- **Di-vacancy**
  - migration barrier of di-vacancy = 0.61 eV ≈ that of single vacancy (0.67 eV)
  - 3D motion

Solutes & PD-solutes complexes

➢ Carbon

- **V-C interactions :**
  - strongly attractive V-C : 0.41 eV
  - lowers effective formation energy & raise migration barriers of vacancies

    → Diffusion coeff^{t}, PD population

    ⇒ **coupling with E-KMC (Jerk) simulations**

- **V-C complexes V_mC_n :**
  - VC_n repulsive for n > 3, V_nC repulsive for n > 2
  - V-C complexes dissociate to migrate?
  - no attraction between <110> DB and nn C

➢ Helium

- **Insertion site :**
  - **substitutional** = stable configuration
  - **tetrahedral** = when produced in bulk from nuclear reactions (empirical potential predicts octahedral)
- **He-V, He_T-He_T, He_T-V, He_nV_m :**
  - all interactions are attractive

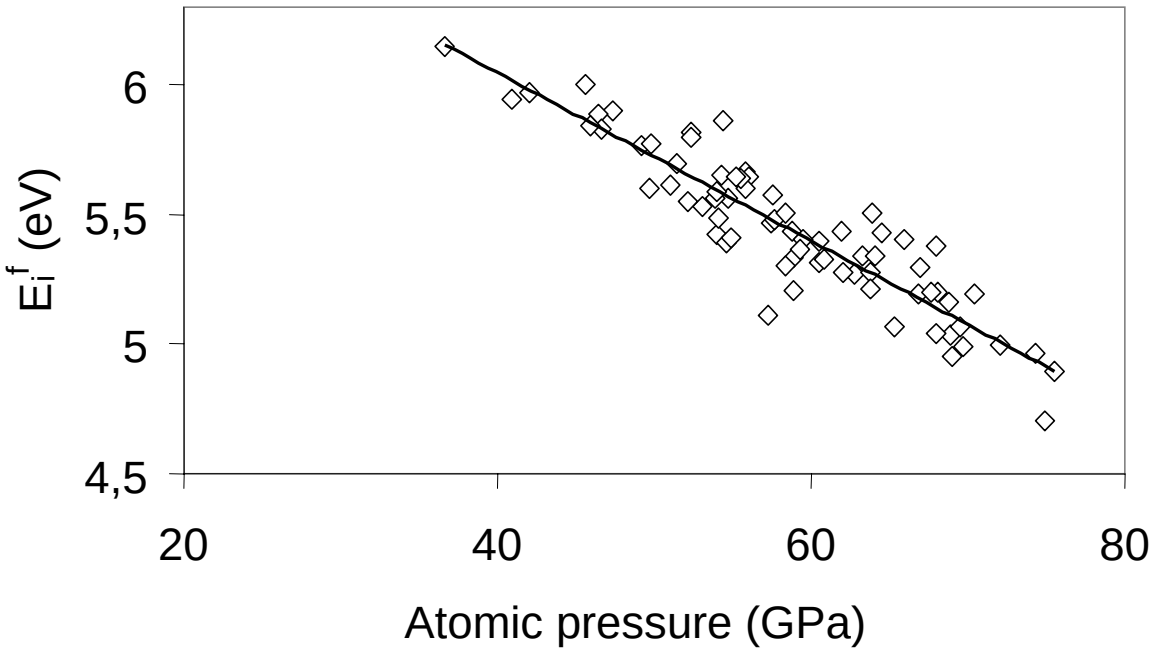
Point Defects & diffusion in Ceramics

Crystalline and amorphous SiO_2

Y. Limoge, G. Roma, L. Martin-Samos, 2003

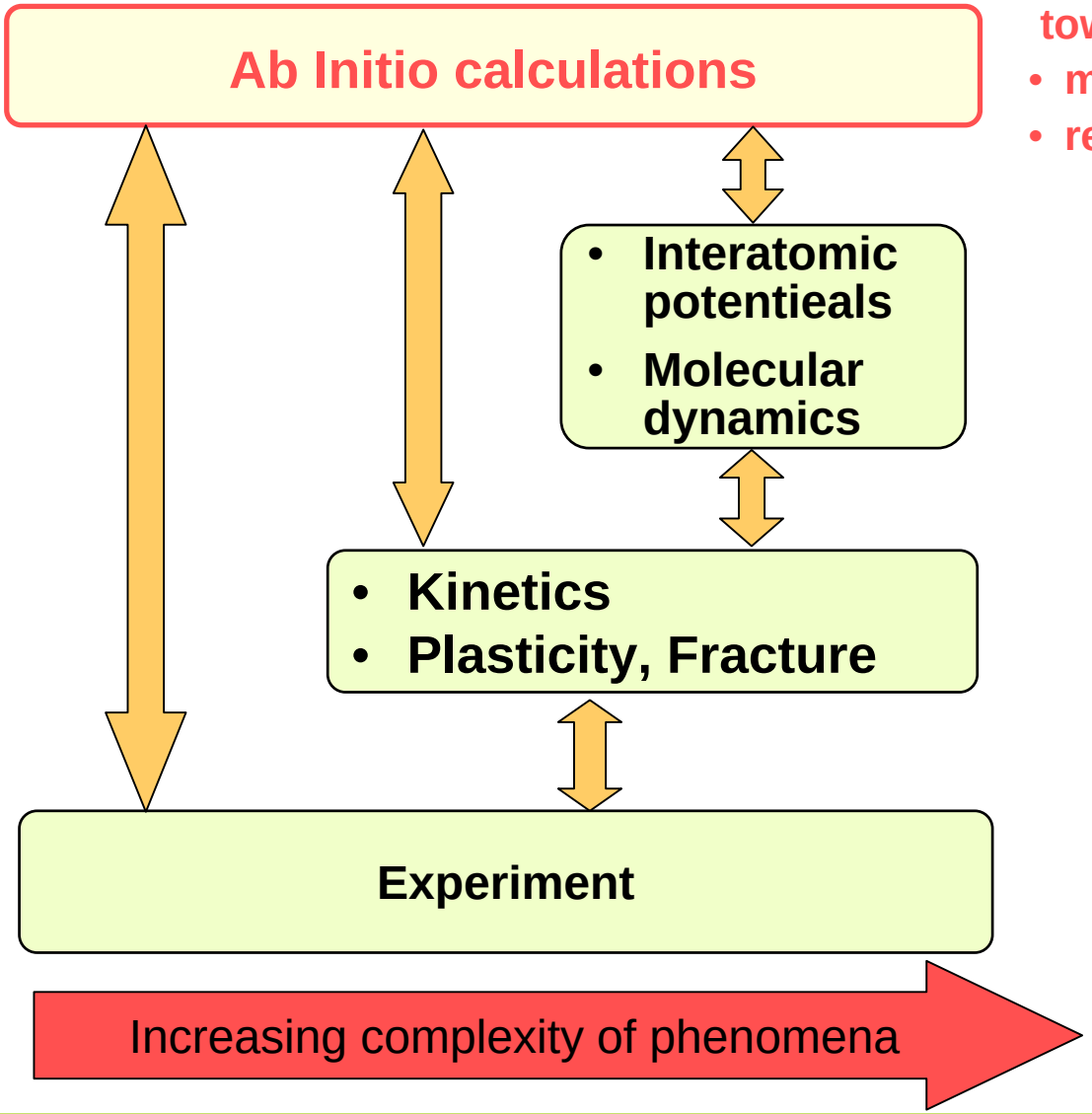
1 - Formation of neutral defects

Effect of local pressure Oxygen vacancy

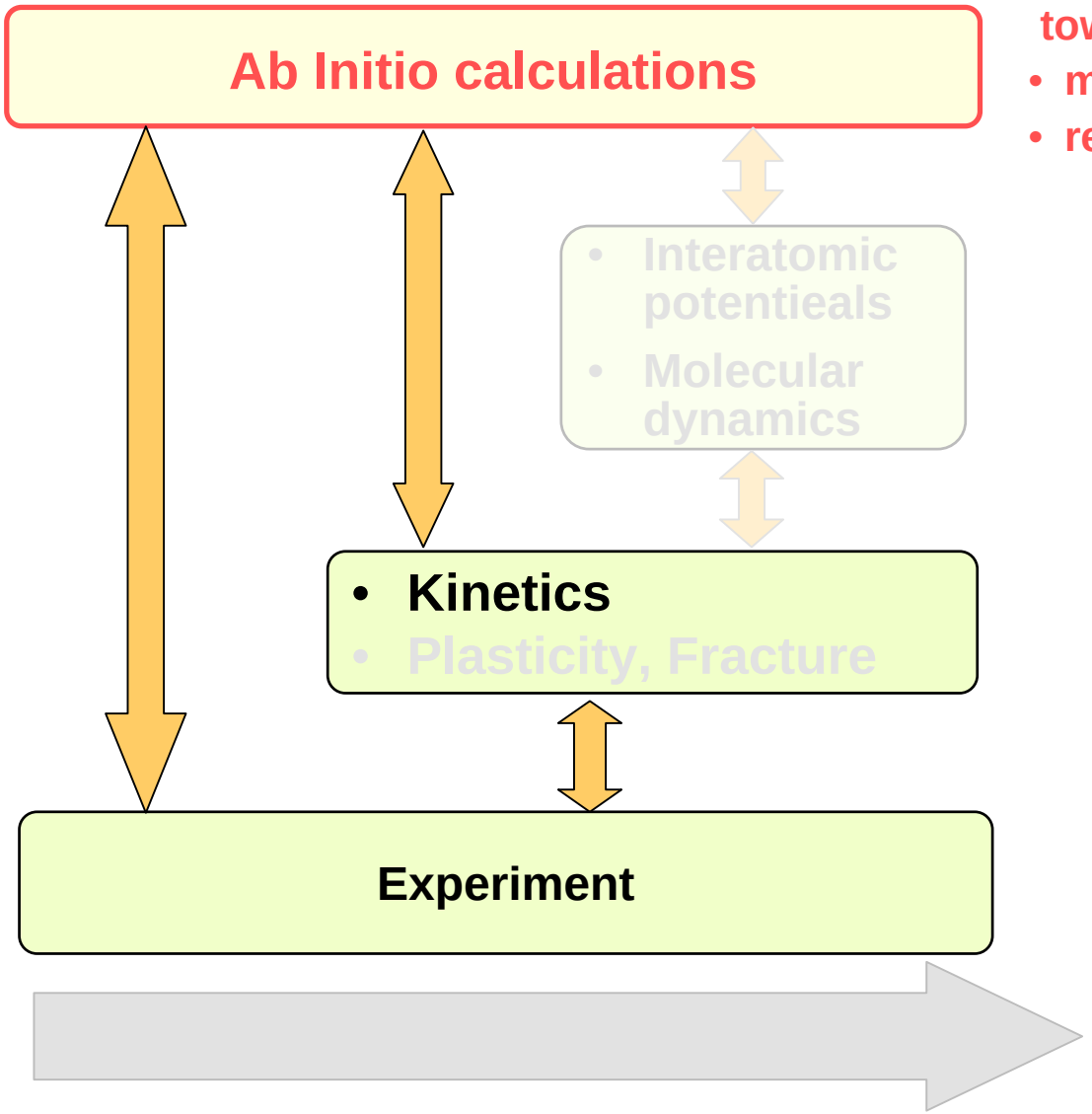


fluctuation of local atomic stress ⇒ scatter of E_f distribution

Ab initio calculations : the robust basis for multiscale modeling & model-experiment coupling



Ab initio calculations : the robust basis for multiscale modeling & model-experiment coupling



Coupling Ab initio with slow kinetics :

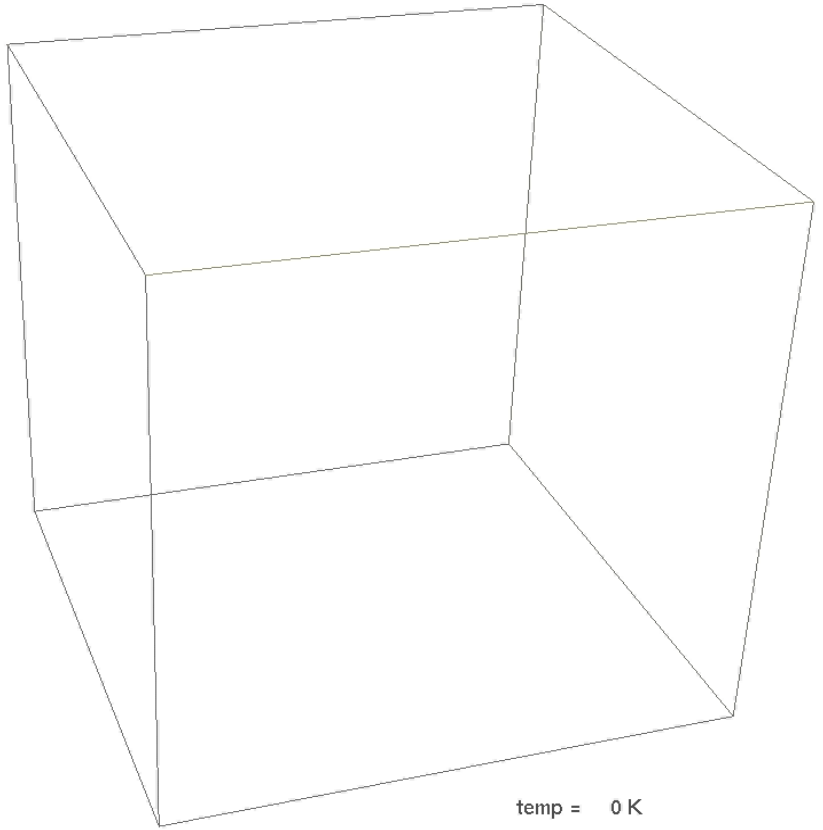
Event-based Monte Carlo

- « objects » (cavities, clusters, dislocations, GB, surfaces...) : position, size
- « mobile defects » (i, v, minor impurities...) : position, mobility
- « events » (defect + object → new configuration)
- probability laws for occurrence of events : impingement & dissociation

Recovery of pure BCC-Fe after irradiation with 3 MeV electrons

JERK Program coupled with Ab Initio

J. Dalla Torre, Chu Chun Fu, F. Willaime
2003



0.5 x 0.5 x 0.5 µm³

Point Defects & diffusion in Ceramics

Crystalline and amorphous SiO_2

Y. Limoge, G. Roma, L. Martin-Samos, 2003

1 - Formation of neutral defects

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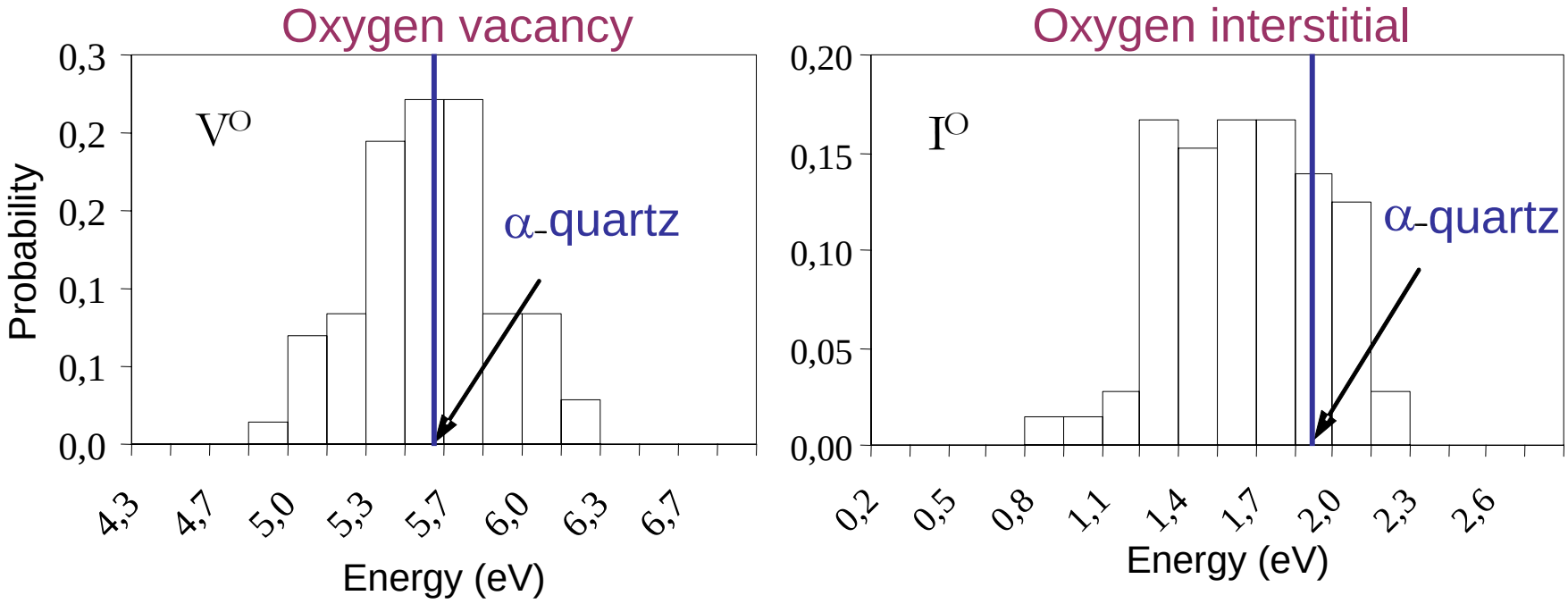


atomic disorder → wide variety of structures ⇒ wide distribution of E_f

Evolution of microstructure after irradiation

Recovery of pure iron after irradiation with 3 MeV electron

Resistivity measurements, Takaki et al. 1983

close pair

I_{D2} correlated

I_E uncorrelated

II I_2 migr.

III V migr.

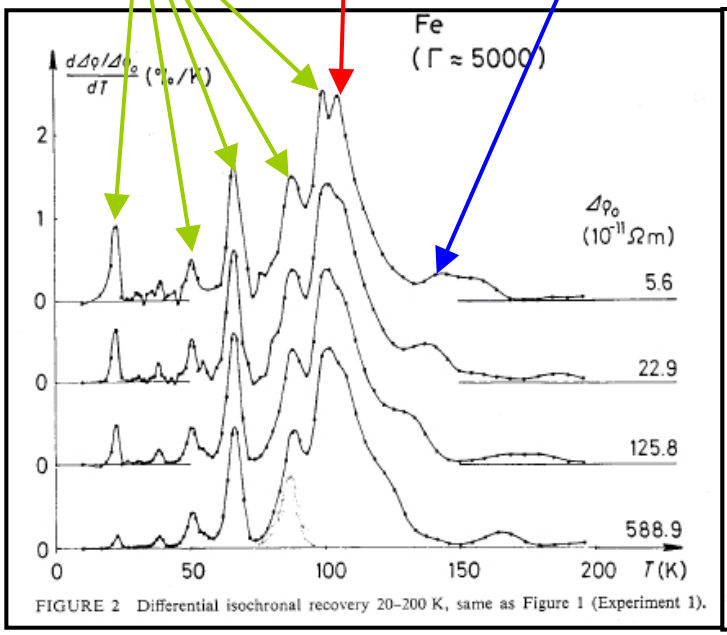


FIGURE 2 Differential isochronal recovery 20–200 K, same as Figure 1 (Experiment 1).

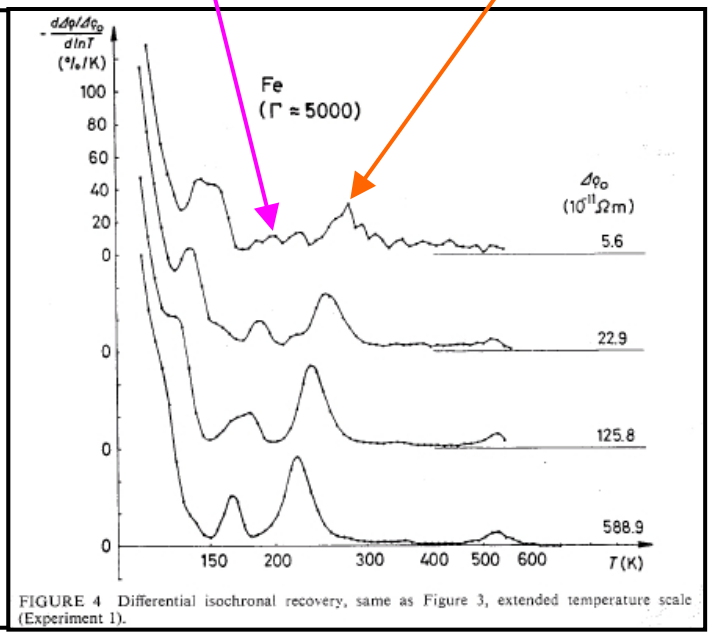
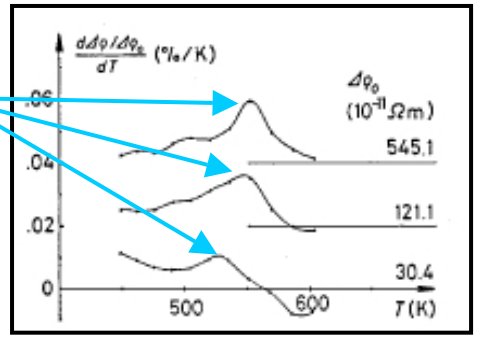


FIGURE 4 Differential isochronal recovery, same as Figure 3, extended temperature scale (Experiment 1).

Stage I

Stage II & III

Stage 500- 600K
only high dose

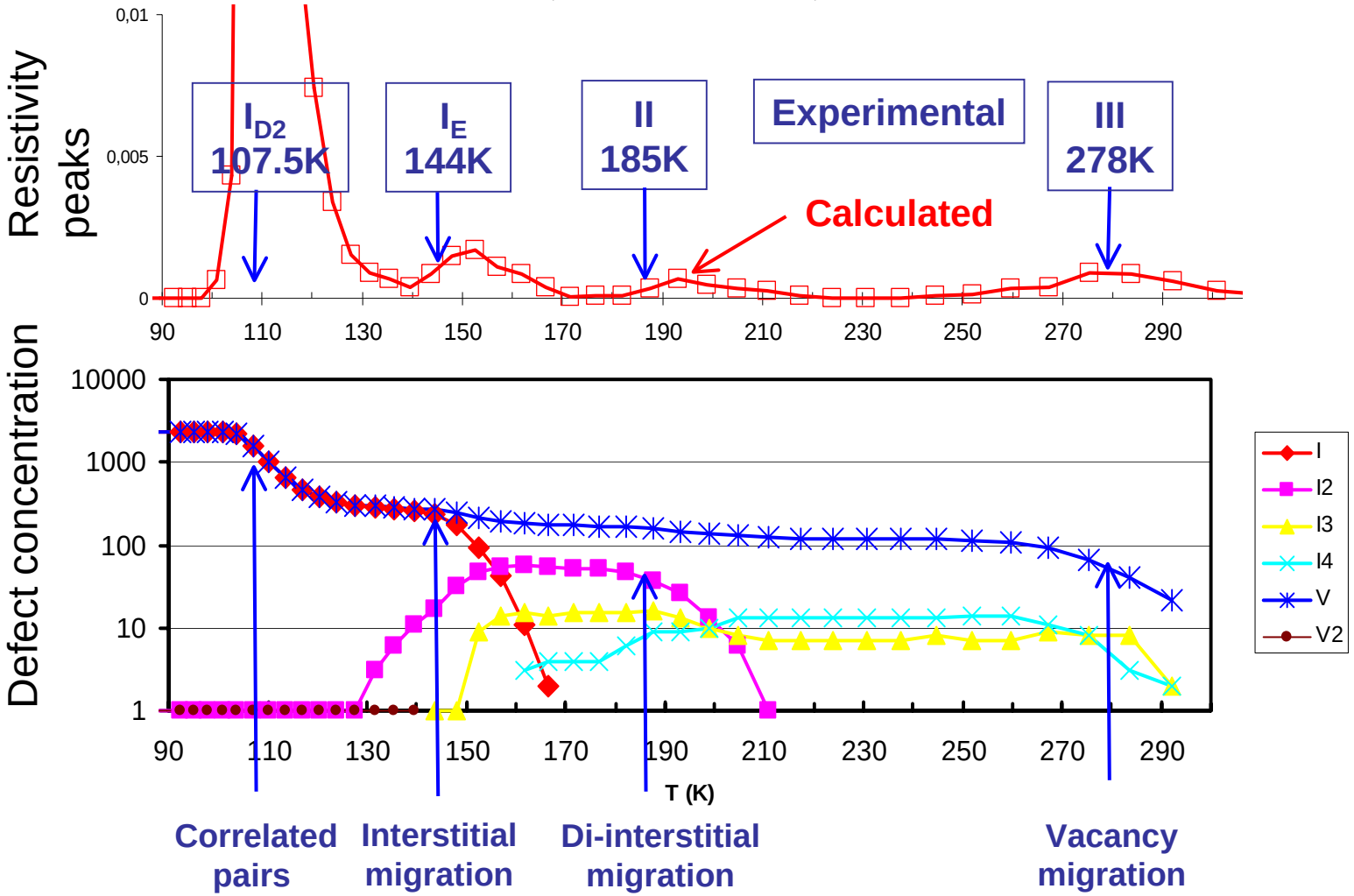


Evolution of microstructure after irradiation

Recovery of pure iron after irradiation with 3 MeV electron

Modeling : EKMC (JERK) coupled with Ab Initio calculations

J. Dalla Torre, Chu Chun Fu, F. Willaime 2003



film

Evolution of microstructure after irradiation

Recovery of pure iron after irradiation with 3 MeV electron

Conclusions – Coupling Ab Initio-EKMC (Jerk)

- **Monte Carlo simulations in excellent agreement with measurements**
  - temperature peaks reproduced within 10 K
  - dose effects as well :
    - ✓ IE, II, III stages shift towards lower temperatures
    - ✓ 500-600K stage appears at high doses only

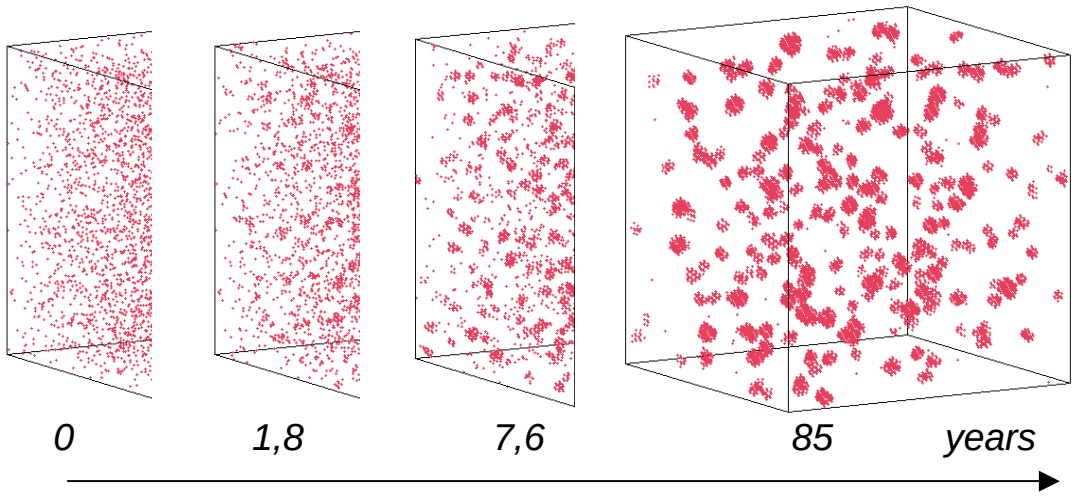
- **Identification/ validation of associated mechanisms**
  - confirms identification of recovery stages
    - ✓ stage 500-600K : associated with vacancy clusters dissociation
    - ✓ stage III : migration of di-vacancies improves agreement / experiment
  - confirms E_f calculations for vacancies :
    - ✓ ab initio values agree with high experimental values (2.1–2.4 eV) ; lower experimental values (1.6 eV) are incompatible : due to C-V binding E

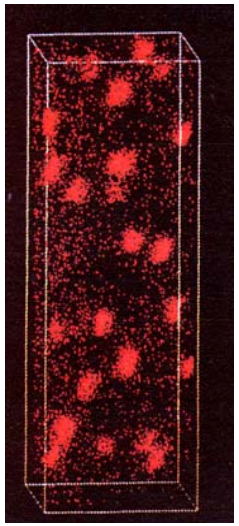
Slow kinetics : Thermal aging

Thermal aging

Demixtion of Fe-Cu : precipitation of Cu in Fe and steel

A. Barbu, F. Soisson, Y. Le Bouar 2000-2002

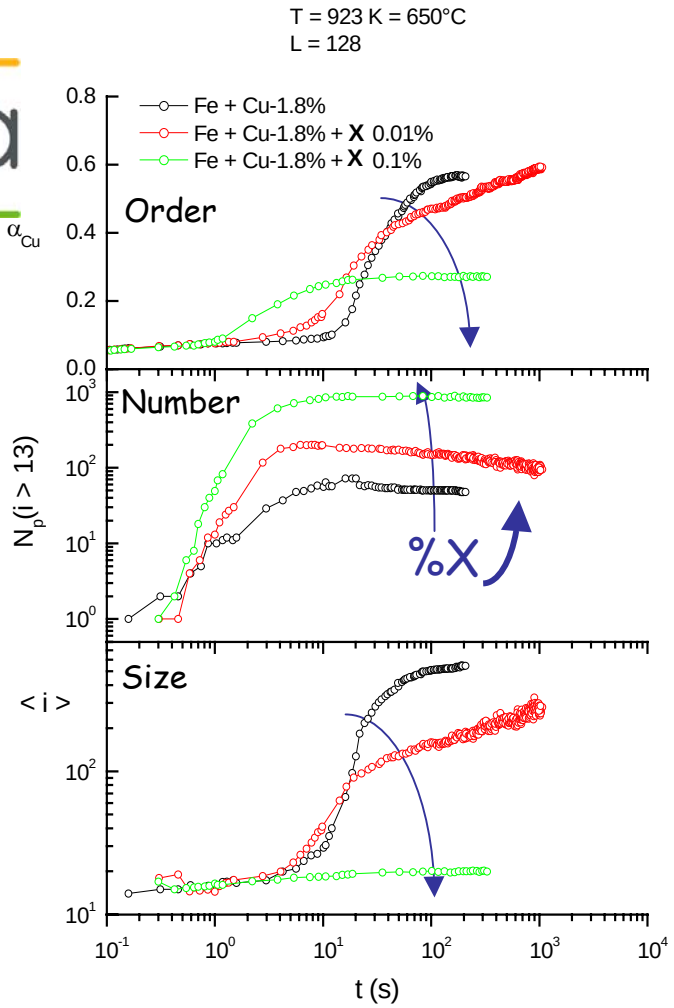




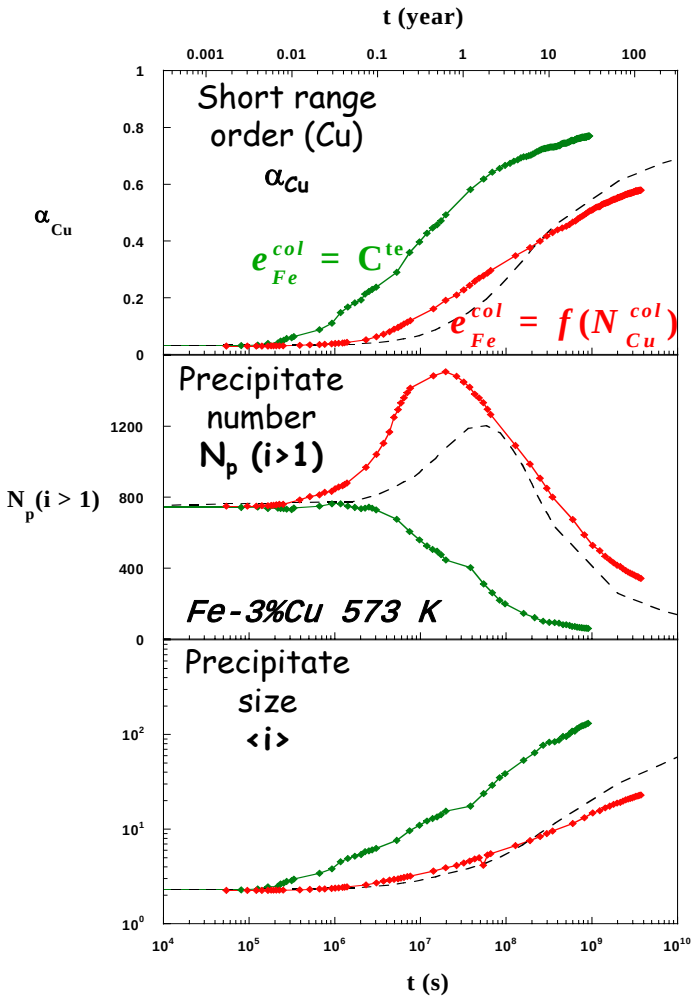
Modelization :
Kinetic Monte Carlo
(Rigid Lattice)

Observation :
Tomographic (3D)
Atom pROBE

Slow kinetics : Kinetic Monte Carlo (Rigid Lattice)



Fe-Cu



❖ **Ternary Fe-Cu-X alloy :**
effects of interactions,
addition of nucleating agent X

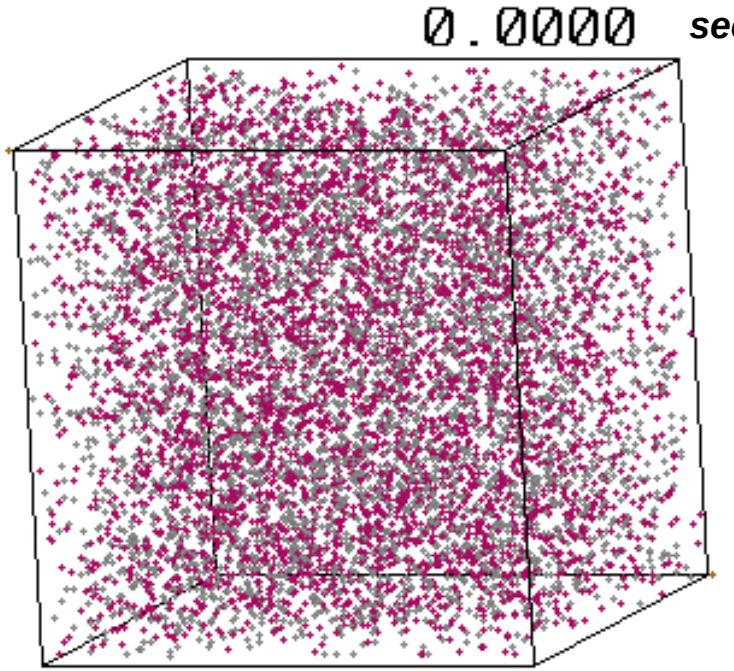
❖ **Refinement of diffusion model :**
taking into account atomic
environment at saddle point

Slow kinetics : Kinetic Monte Carlo (Rigid Lattice)

Thermal aging

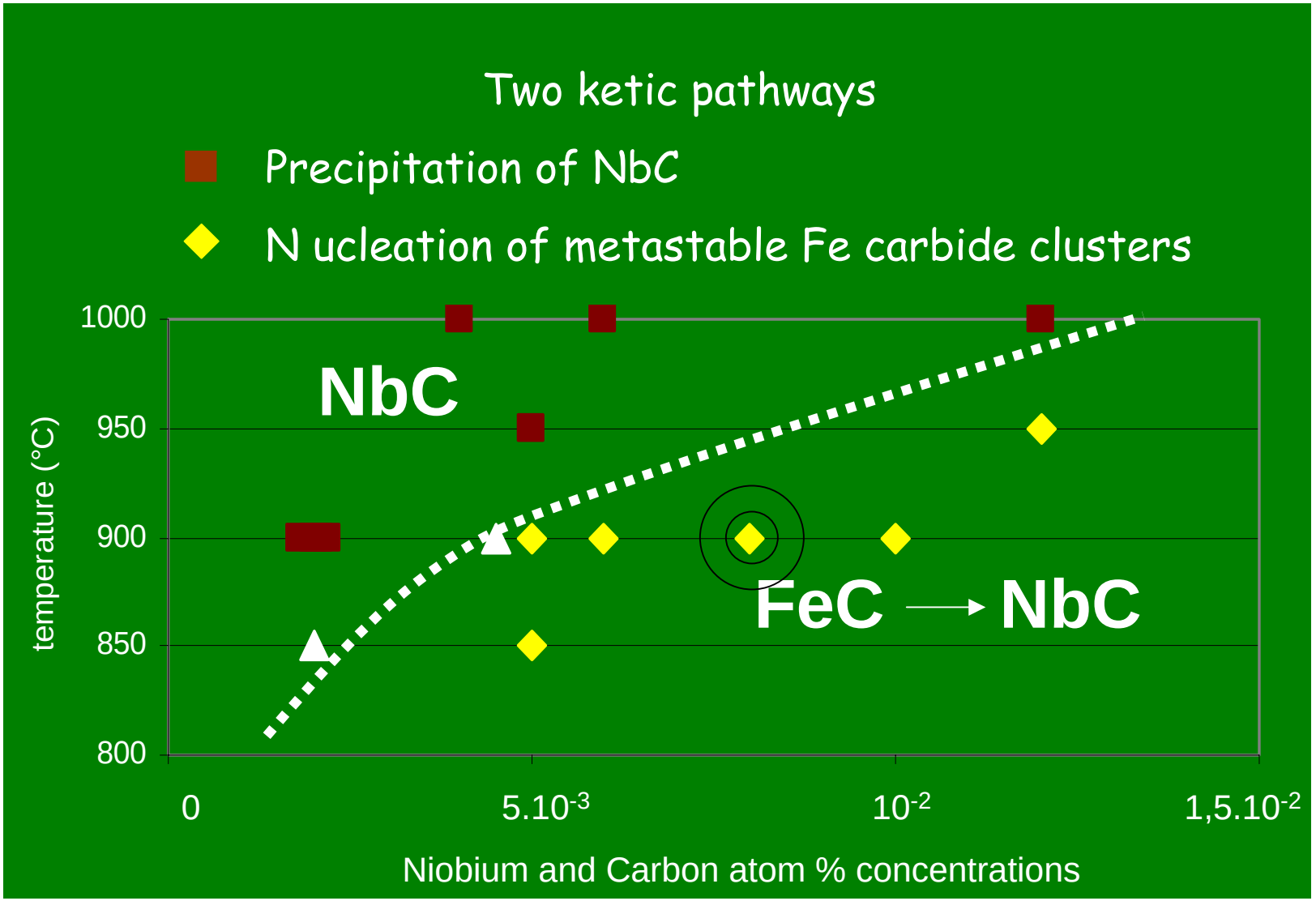
Precipitation of NbC in Fe and steel…

D. Gendt, F. Soisson, C. Hin 2001 - 2004 (collaboration Arcelor)



… with a transient Fe carbide

Slow kinetics : Kinetic Monte Carlo (Rigid Lattice)

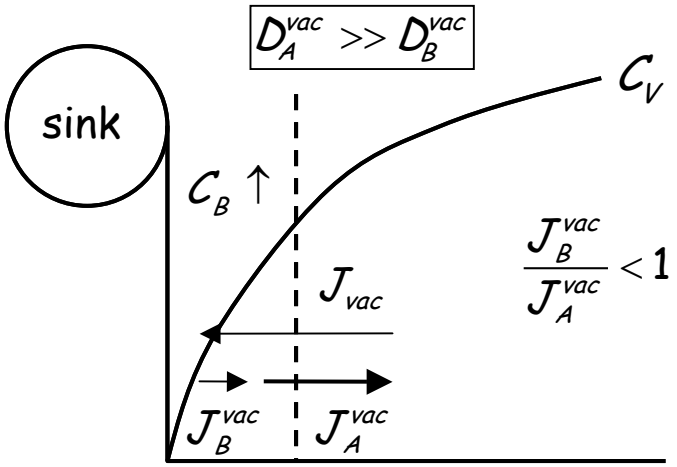


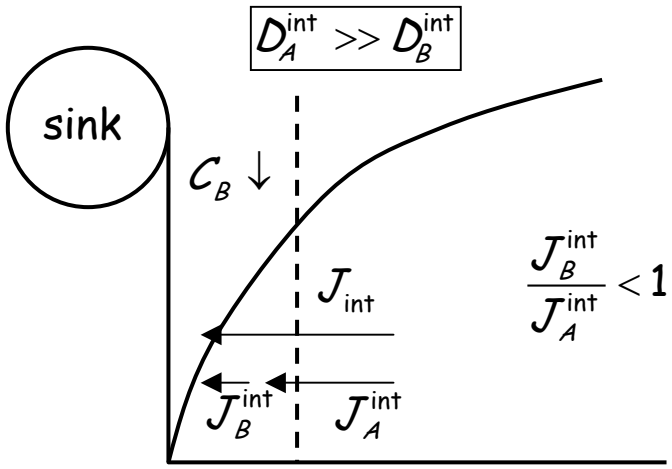
Slow kinetics : Aging under irradiation

→ Radiation Induced Segregation / Precipitation

Alloys under irradiation :

- far from equilibrium
- other diffusion mechanisms
- kinetic control of path ***and*** steady state
- DP-solute flux coupling
  - point defects fluxes towards sinks
  - inverse Kirkendall effects





Slow kinetics : Kinetic Monte Carlo (Rigid Lattice)

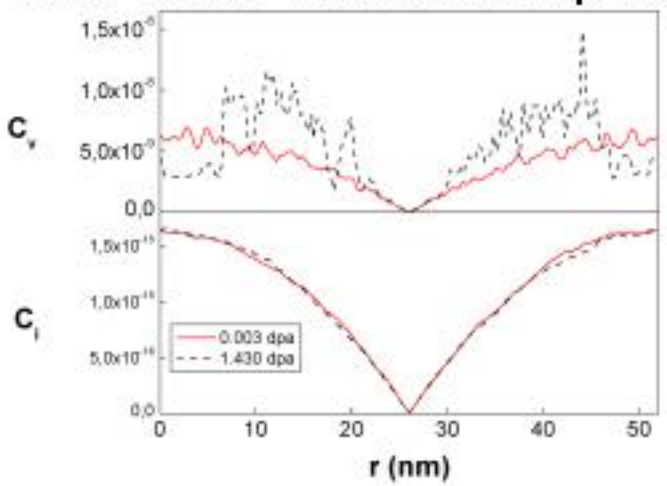
Aging under irradiation, F. Soisson (2003)

Supersaturated solid solution

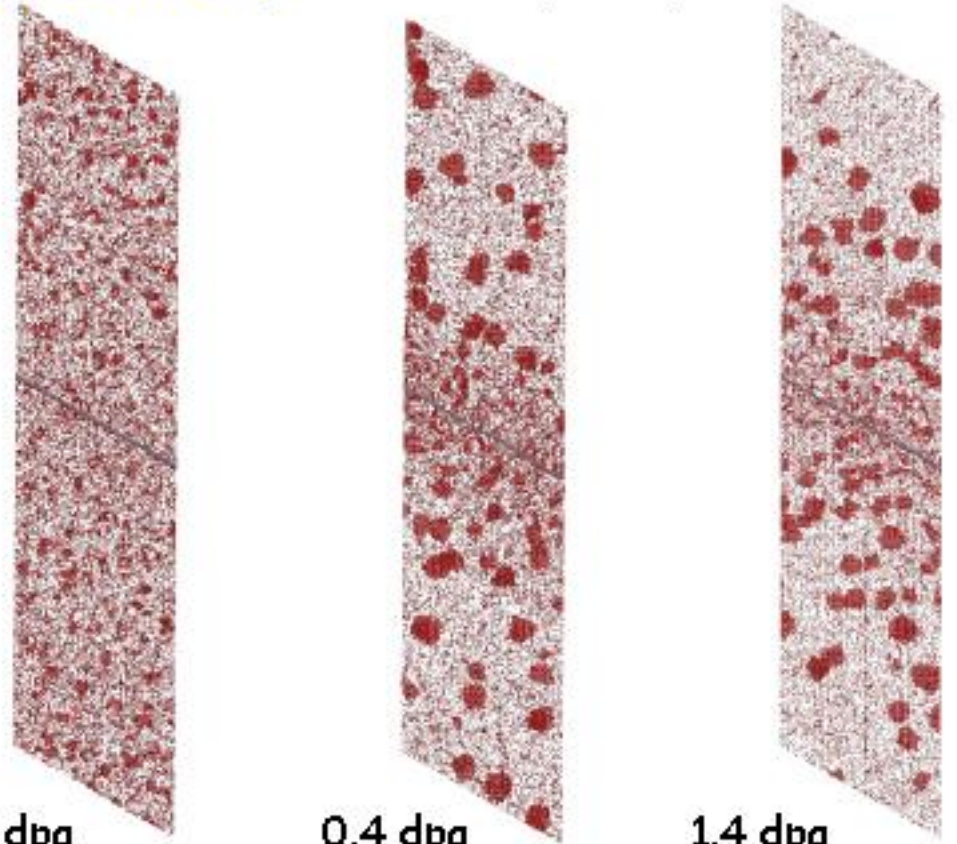
$D_A^{vac} >> D_B^{vac}$

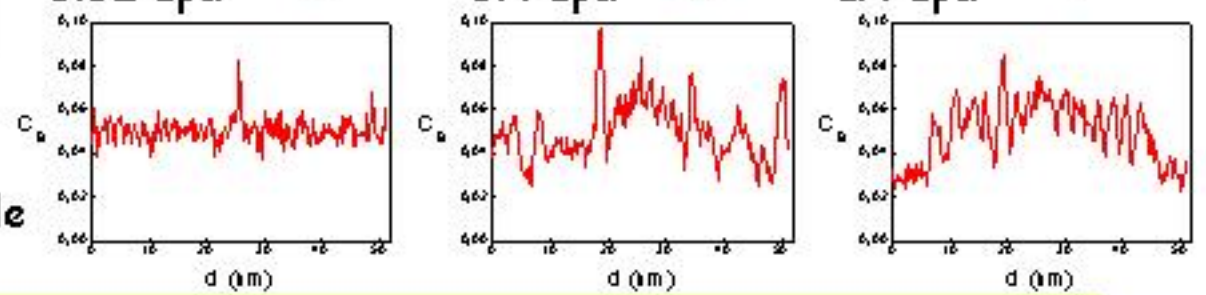
solute enrichment at sink
high supersaturation

Point Defect concentration profile



Solute concentration profile





Slow kinetics : Kinetic Monte Carlo (Rigid Lattice)

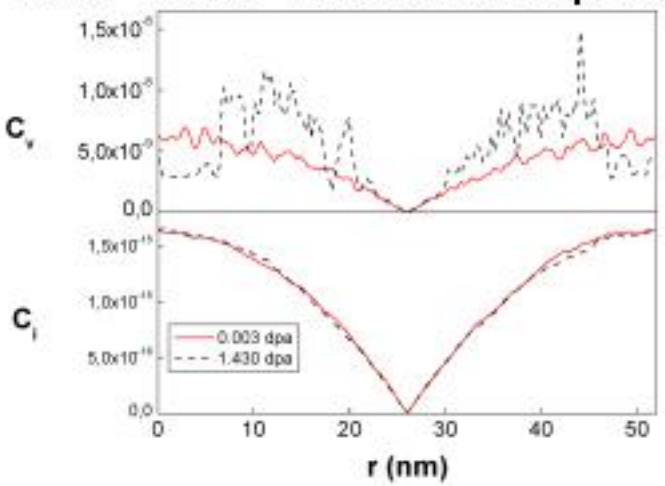
Segregation & precipitation in grain boundary region

Supersaturated solid solution

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

solute enrichment at sink
high supersaturation

Point Defect concentration profile



Solute concentration profile

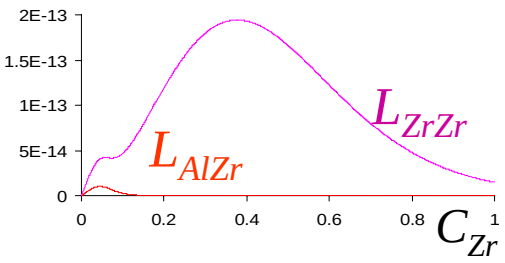
Slow kinetics : Self-consistent Mean Field

Onsager matrix

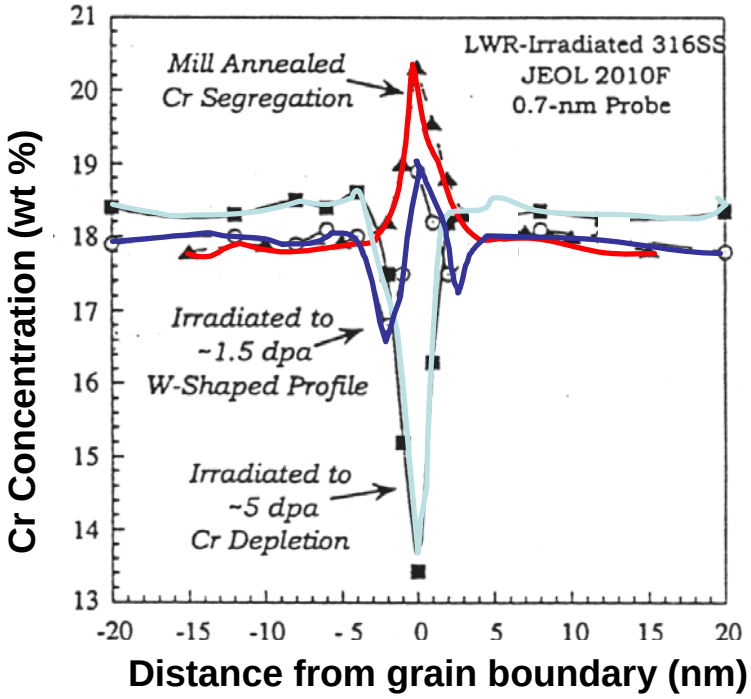
Compare DICTRA

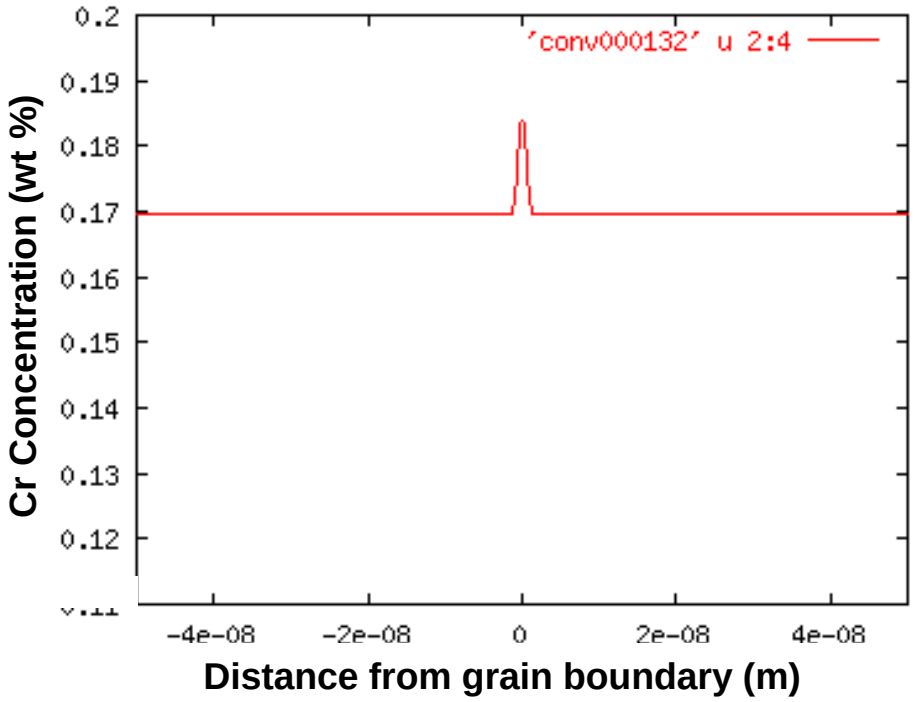
$$\vec{J}_A = -L_{AA}\vec{\nabla}\mu_A - L_{AB}\vec{\nabla}\mu_B$$
$$\vec{J}_B = -L_{AB}\vec{\nabla}\mu_A - L_{BB}\vec{\nabla}\mu_B$$

Kinetic coupling



Radiation Induced GB Segregation, M. Nastar, 2001





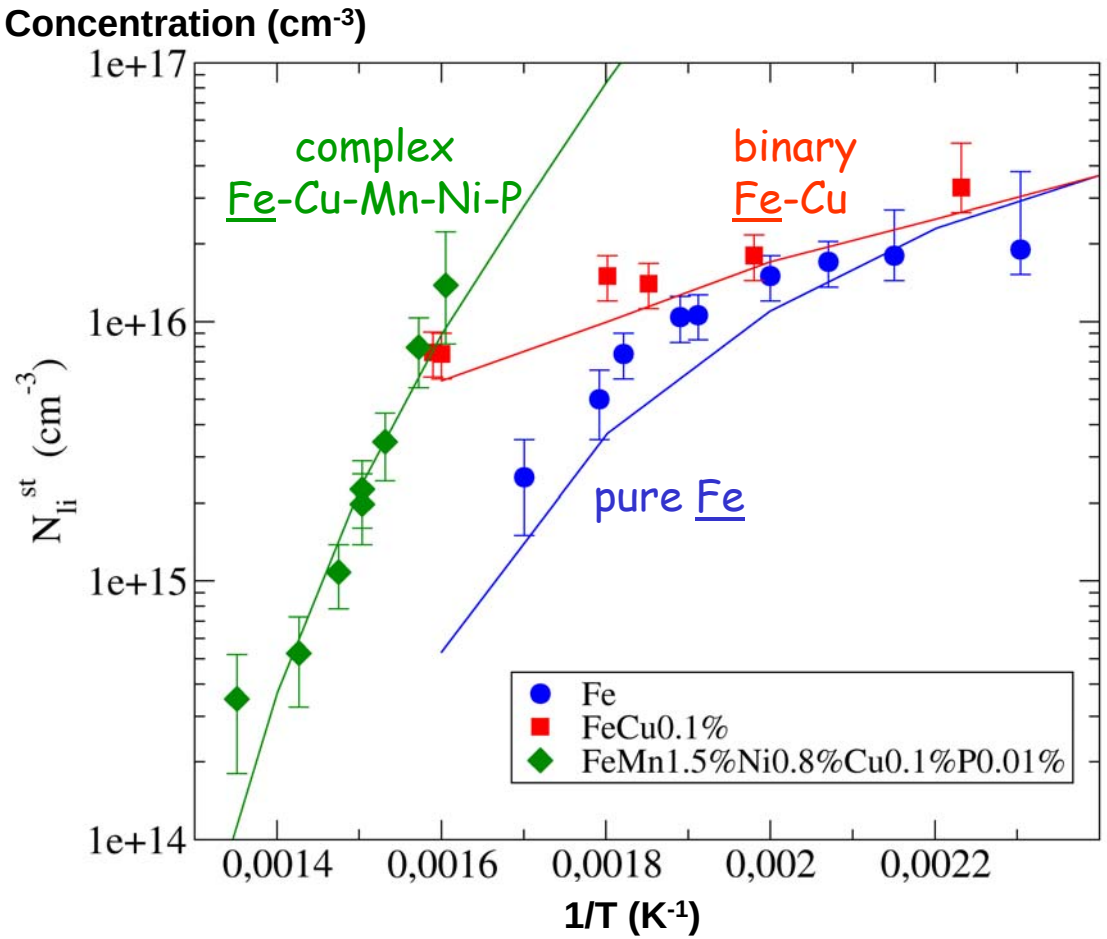
Evolution of grain boundary composition in 316 SS under irradiation

Slow kinetics : Rate theory (« Cluster dynamics »)

Evolution of defect cluster population under irradiation

A. Hardouin-Duparc, A. Barbu, 2002

Dislocation loops



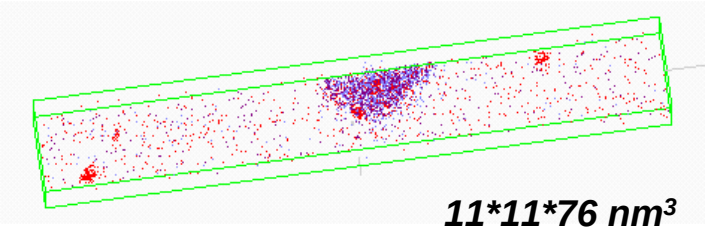
1 MeV HV-TEM
1,5.10^{-4} dpa/s
200-470°C

Slow kinetics : Rate theory (« Cluster dynamics »)

Solute clustering under neutron irradiation

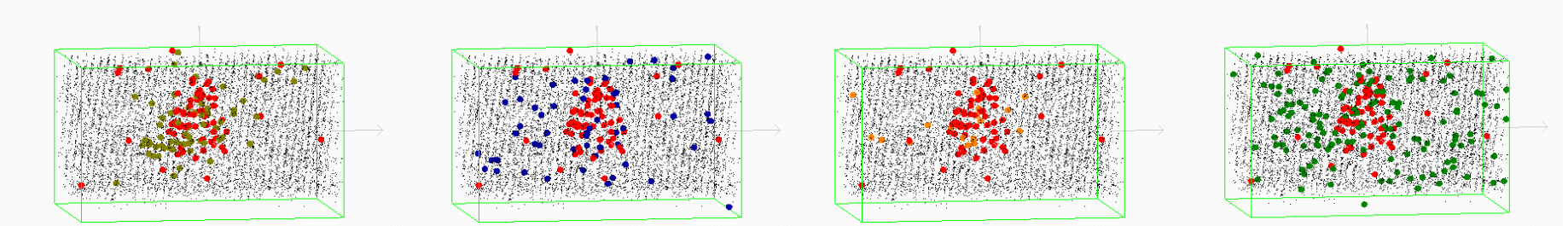
B. Radiguet, Ph. Pareige (GPM Rouen University), A. Barbu, 2002-2004

flux : $1{,}5.10^{15}$ n.m^{-2}.s^{-1}
fluence: $9{,}7.10^{23}$ n.m^{-2}
T ≈ 300 °C



11*11*76 nm³

Solute clusters : 2 nm - 5×10^{23} m^{-3}



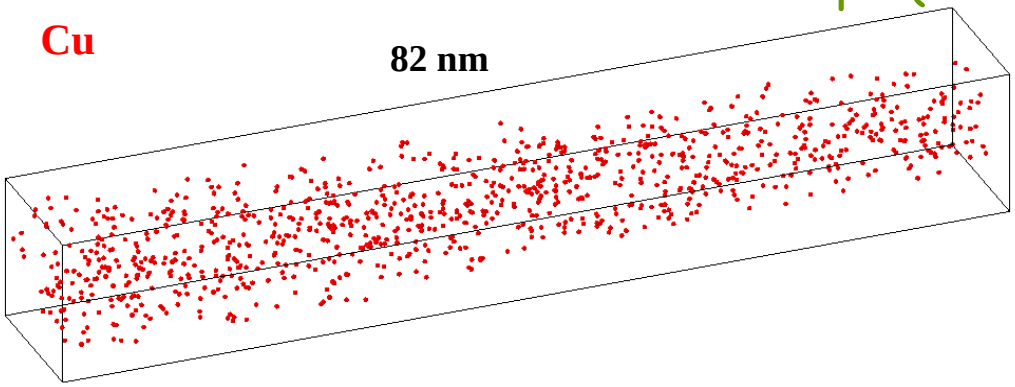
5*5*8 nm³

Fe	*Cu*	*P*	*Mn*	*Ni*	*Si*
bal	20.3±2.7	3.4±1.2	4.2±1.3	3.3±1.2	3.7±1.1

Mechanisms of Cu clustering in Fe-0.1% Cu

3D APFIM

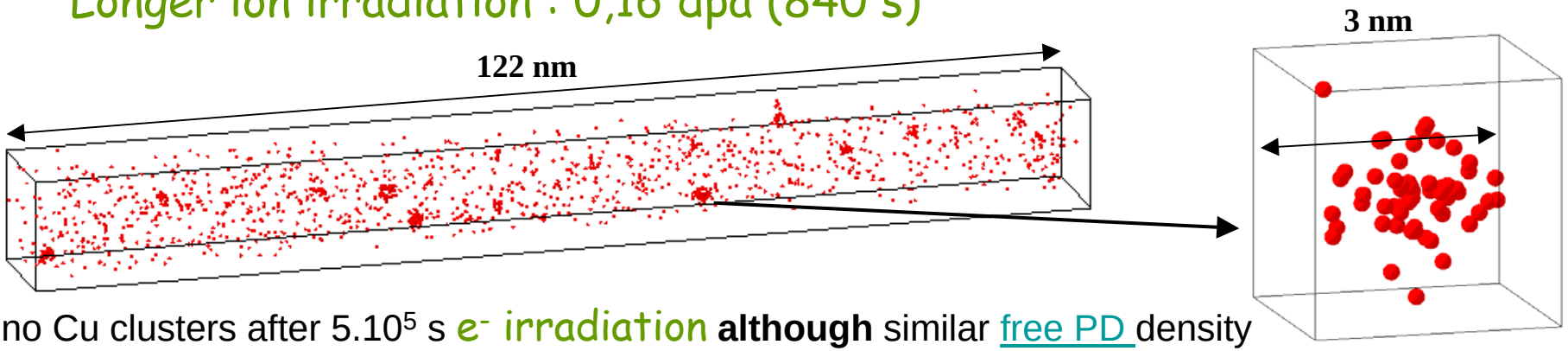
Short ion irradiation : 3.10^{-3} dpa (17 s)



- Cu remains in solid solution **although** 10 cascades (> 10 keV) in box

→ Cu clusters do not form in cascade cores

Longer ion irradiation : 0,16 dpa (840 s)



- no Cu clusters after 5.10^5 s e^- irradiation **although** similar free PD density
- **but** much higher PD cluster density with ions

→ Cu clusters form by RIS on PD clusters

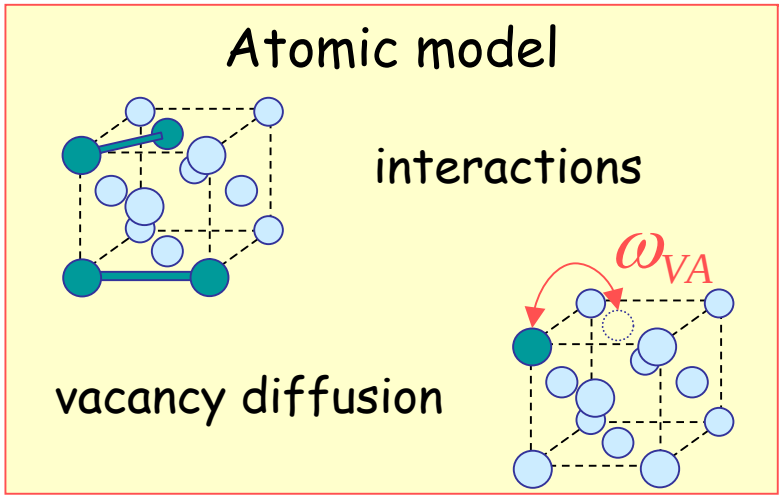
$(1,1 \pm 0,8).10^{24}$ m^{-3}
1 - 2 nm diameter
(63±12) % Cu

Slow kinetics : from atomistic to mesoscopic models

Validate and improve Nucleation Growth & Coarsening theory

E. Clouet, M. Nastar, 2003-2004

Ab-initio calculations
Experimental data



Input
- nucleation driving force
- interface free energy
- diffusion coefficients, …

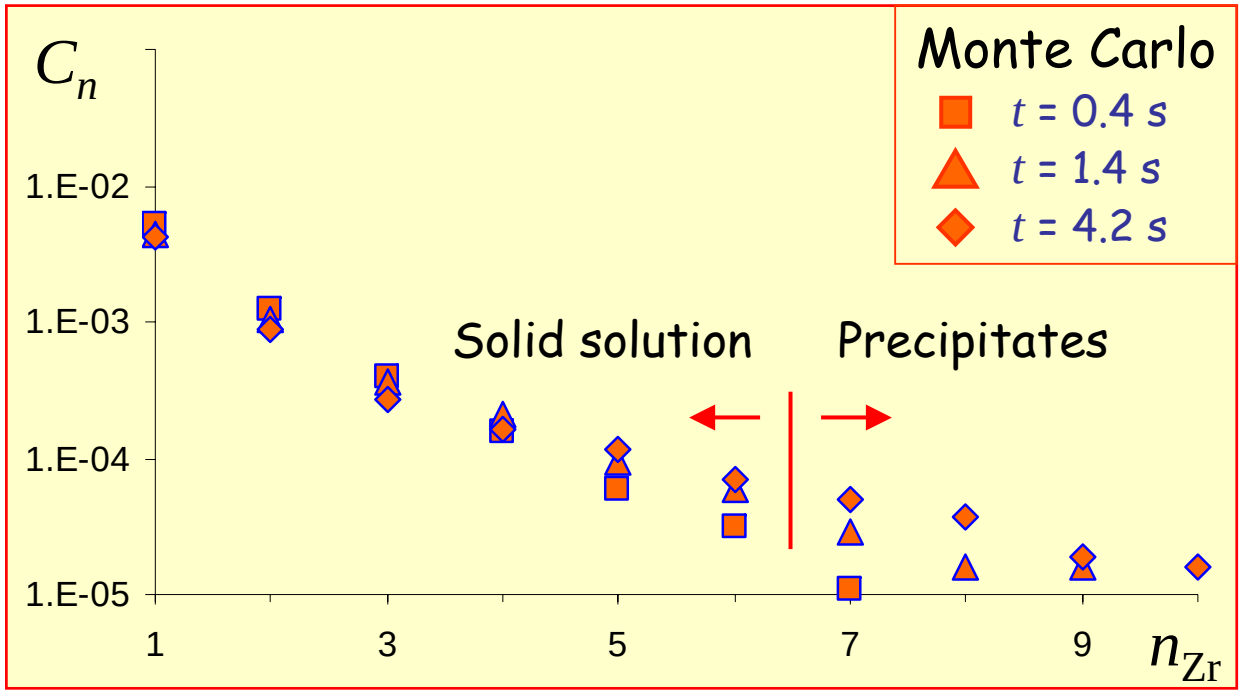
Mesoscopic N G C model

Monte Carlo model

Slow kinetics : from atomistic to mesoscopic models

Monte Carlo simulation

Steady state cluster size distribution



Al - 1 at.% Zr
450°C

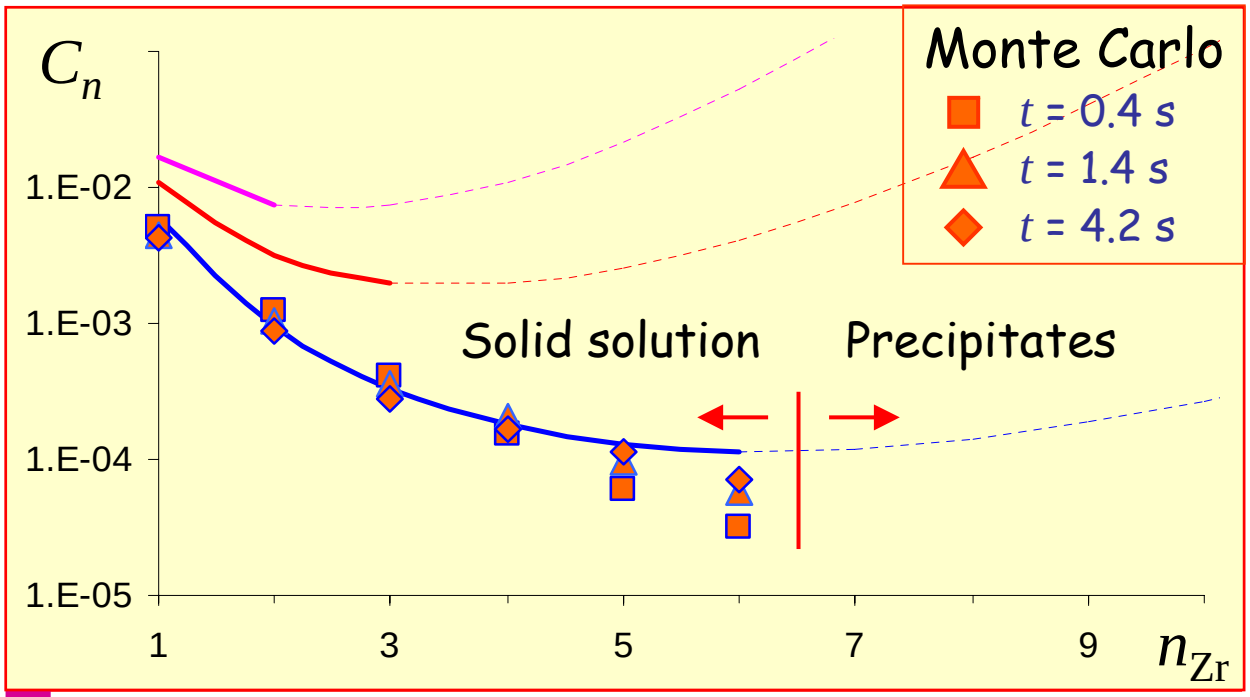
Slow kinetics : from atomistic to mesoscopic models

Improved NGC calculation : test solution models

Steady state cluster size distribution

Capillary approximation

$$C_n = \exp\left(-\frac{\Delta G_n}{kT}\right)$$



- ideal solution
- regular solution
- CVM

Al - 1 at.% Zr
450°C

identify CVM as the correct approximation for this ordering system

Slow kinetics : from atomistic to mesoscopic models

Validation of improved classical NGC model

Steady state nucleation flux of Al_3Zr $L1_2$

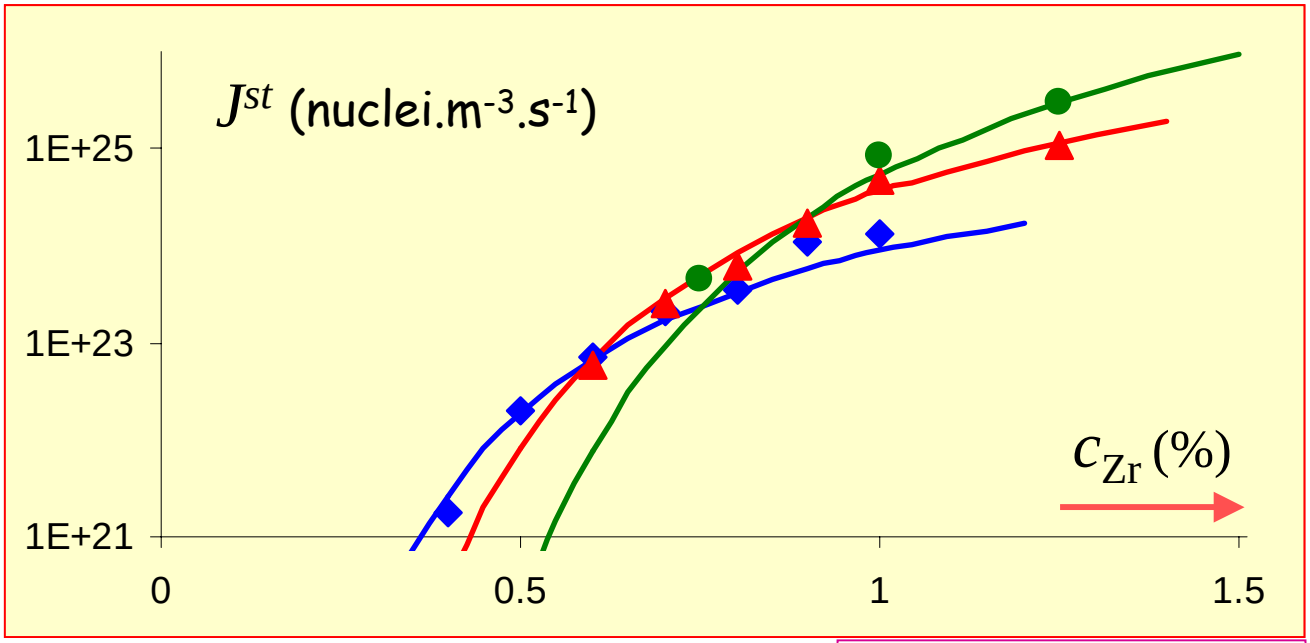
Classical nucleation theory

Monte Carlo

ideal solution

regular solution

CVM



T = 450°C

T = 500°C

T = 550°C

Input
- ΔG^{nuc} (CVM)
- σ (BW+Wulff)
- D_{Zr} (exp), ΔF (AbI)

Upgraded classical theory reproduces KMC results

Kinetic evolution of radiation damage : basic challenges

Towards increased complexity :
real materials and conditions

I. Elementary atomic transport mechanisms

- **more refined and reliable input data in kinetic models**
- « difficult » materials : Fe, Zr, oxides, carbides (all !)
- complex defect population and migration pathways in alloys

II. Kinetic models of μ-chemistry & μ-structure evolution

- **beyond the models for isolated point defects and clusters in pure or dilute binary alloys, account for :**
- multi-component, concentrated, heterogeneous alloys
- incidence of mesoscale microstructure (GB's, dislocations, surfaces…)
- wider space and time scales
- multiscale coupling with I
- atomistics enrich rather than discard classical theories: another multiscale coupling

Physics under construction :
numerical simulation still a tool to build safe physical bases

- explore, test and improve models : numerical experimentation
- couple with dedicated physical experiments

Coupling experiment and simulation

→ Associate versatile irradiation & characterization tools

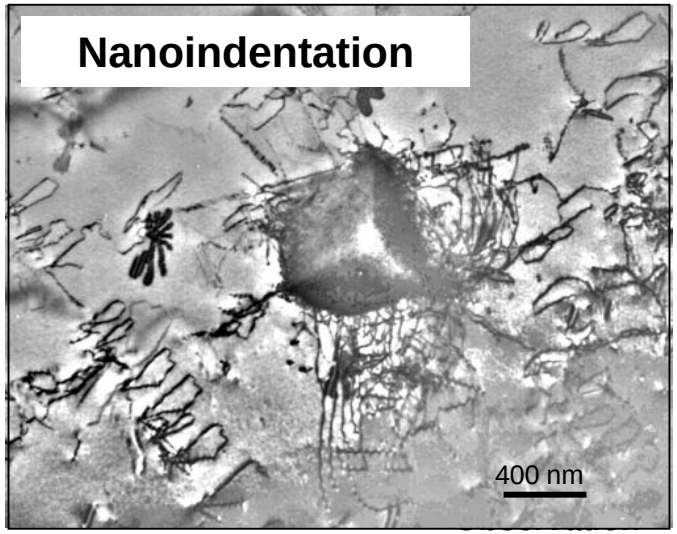
at the same scale

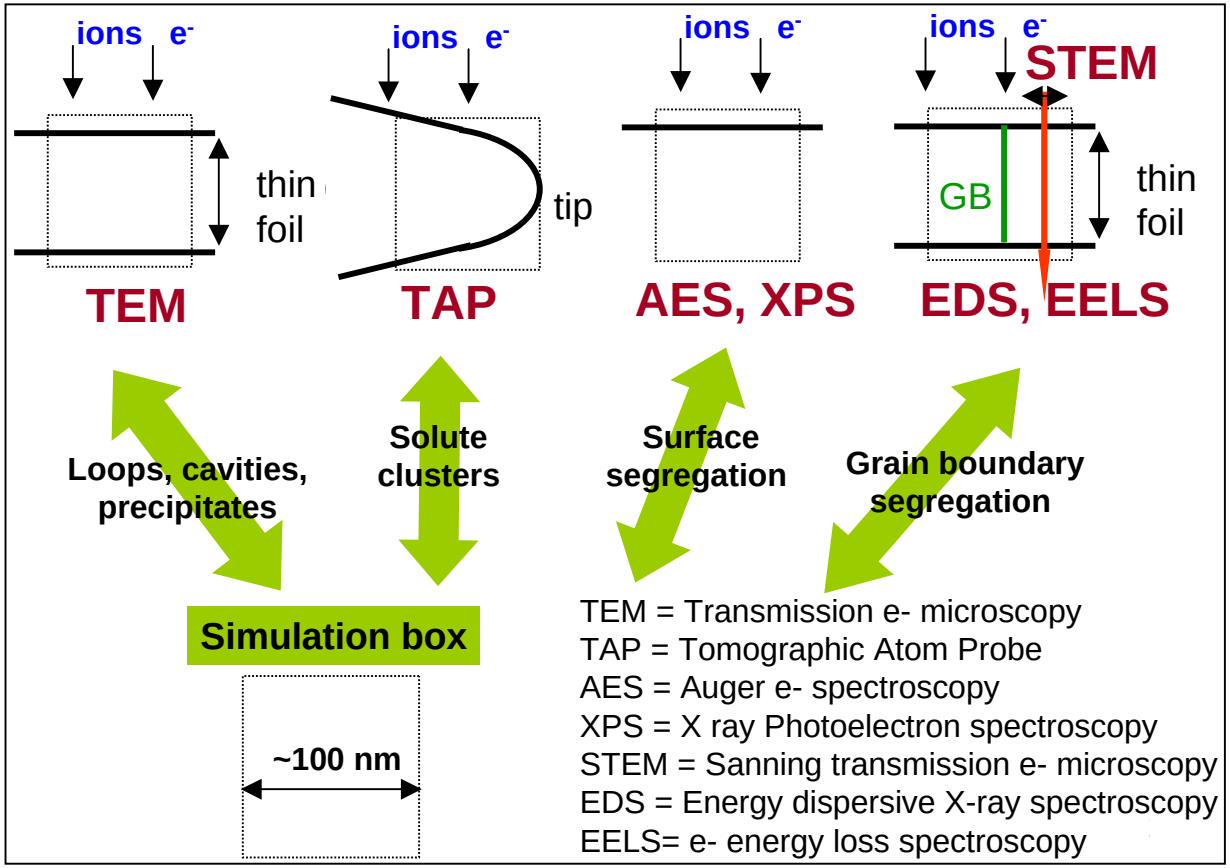
- Volume → identical in experiments and simulations
- Surfaces → taken into account

Irradiation → **Charged particles: Triple Beam + in situ TEM, e⁻ VDG, HVTEM**

Direct observation

Mechanical testing



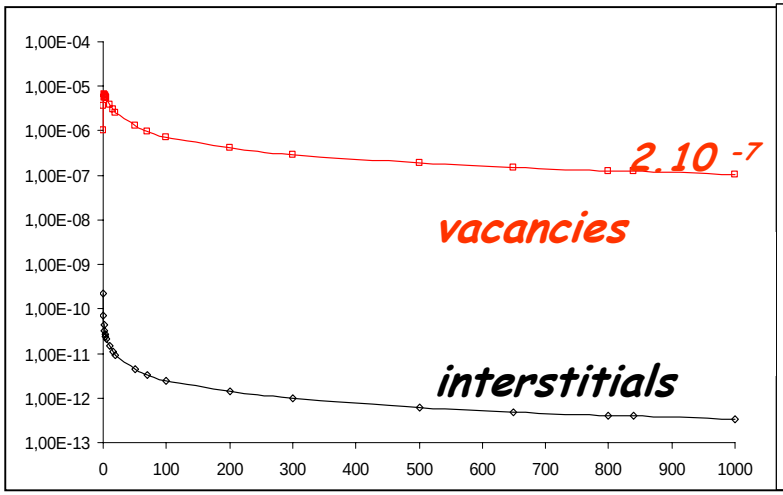


Thank you

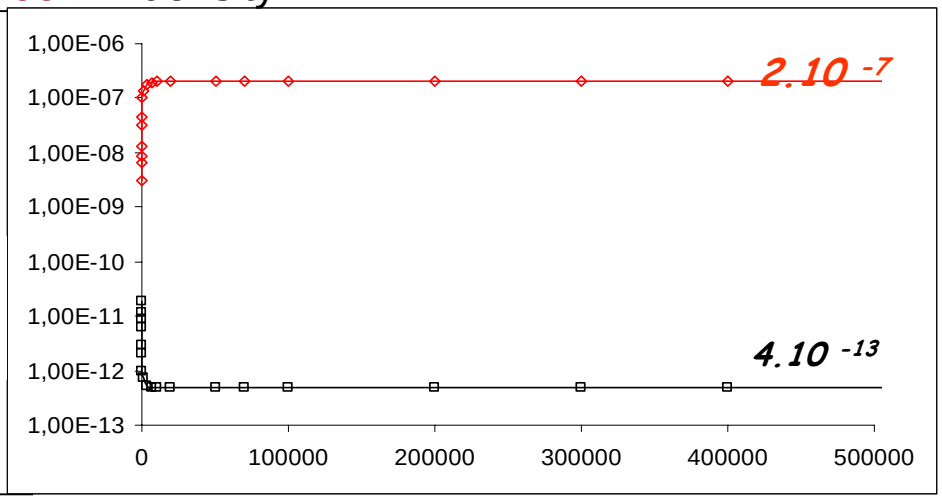
RT calculation of free PD and PD-cluster population

ions (840 s) similar free PD density *electrons (5.10^5 s)*

Free PD (mobile) atom fraction



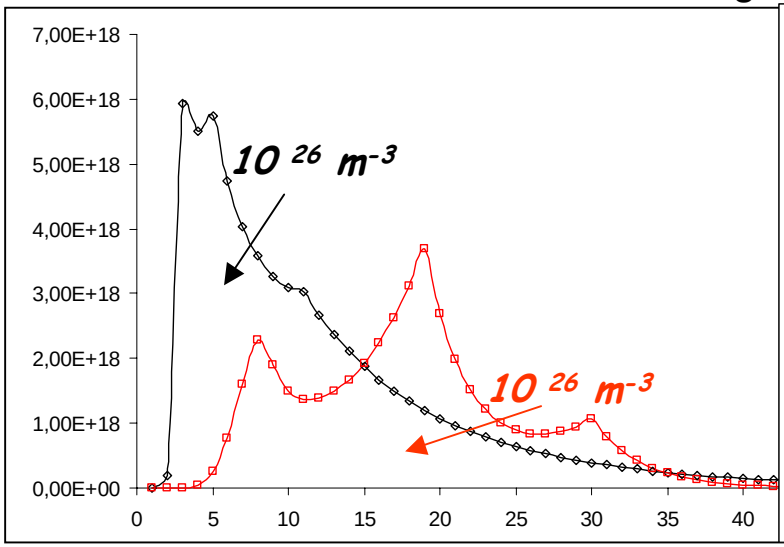
Time (s)



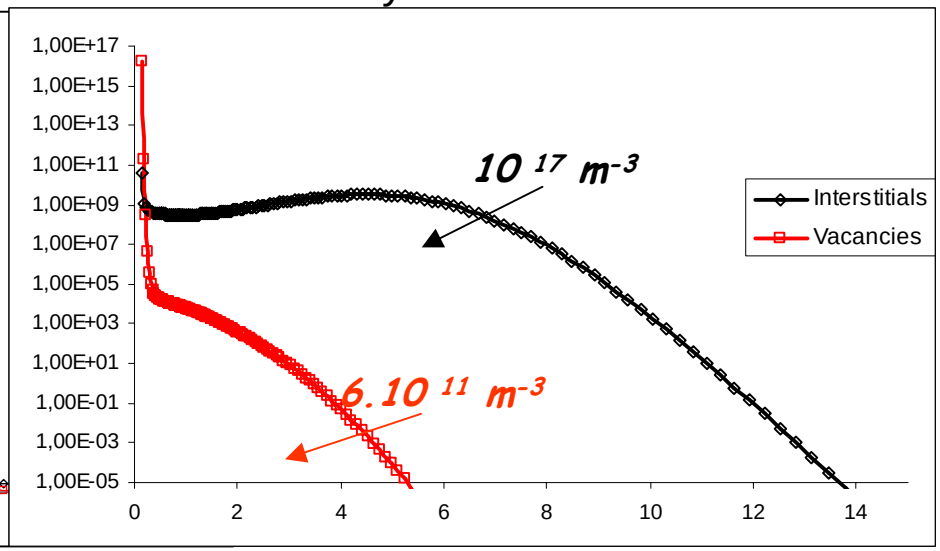
Time (s)

much higher PD cluster density

PD-cluster density (cm^{-3})



PD cluster diameter (monomers)



PD cluster radius(nm)