



GPM

GROUPE DE PHYSIQUE DES MATERAUX



H. Zapolsky

GPM

Direction

Administration

**Service Technique de Maintenance
et de Recherche (STMR)**

Matériaux en Milieux Extrêmes et Nanostructurés
ERM MEN

Transformation de phases à l'échelle nanométrique
ERAFEN

Instrumentation Scientifique
ERIS

Matériaux Magnétiques pour Applications
ERMMA

Mécanique des Matériaux
ERMECA

Matériaux de la Microélectronique et Photonique
ER2MP

Matériaux et Surfaces
ERMES

Défaillances Electroniques et Fiabilité
ERDEFI

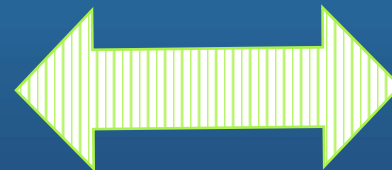
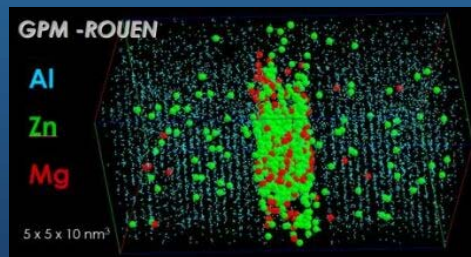
Groupe de Physique des Matériaux

Université et INSA de Rouen, UMR CNRS 6634

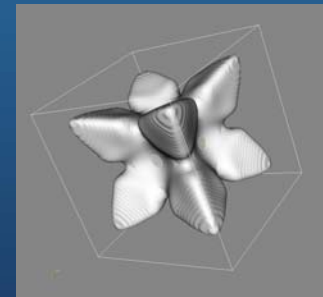
Instrumentation
Interaction laser - atom



Analyses
Physical metallurgy
and nanomaterials

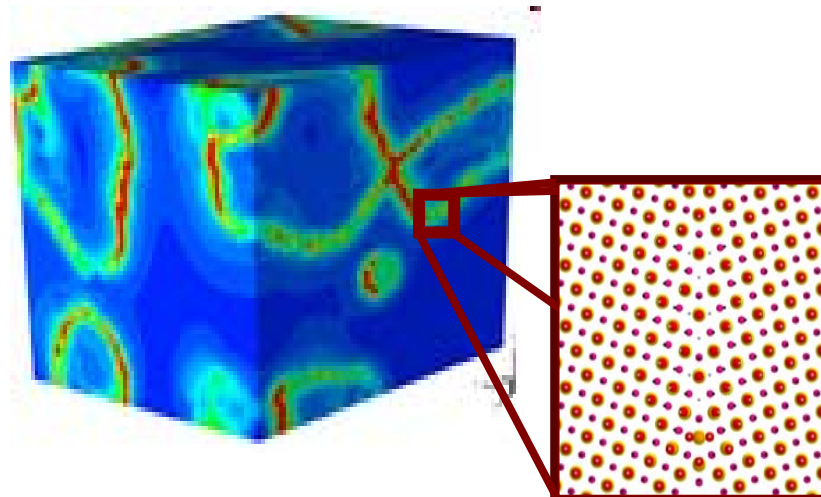
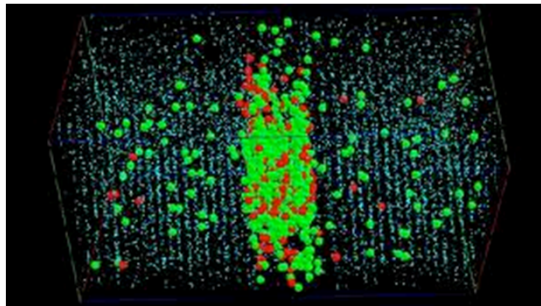


Modeling

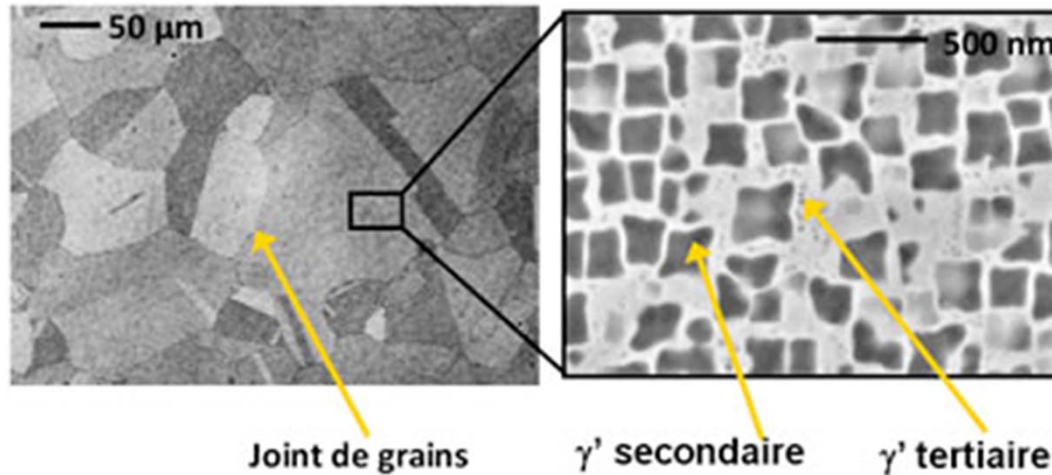




Modélisation des transformations de phases dans les matériaux

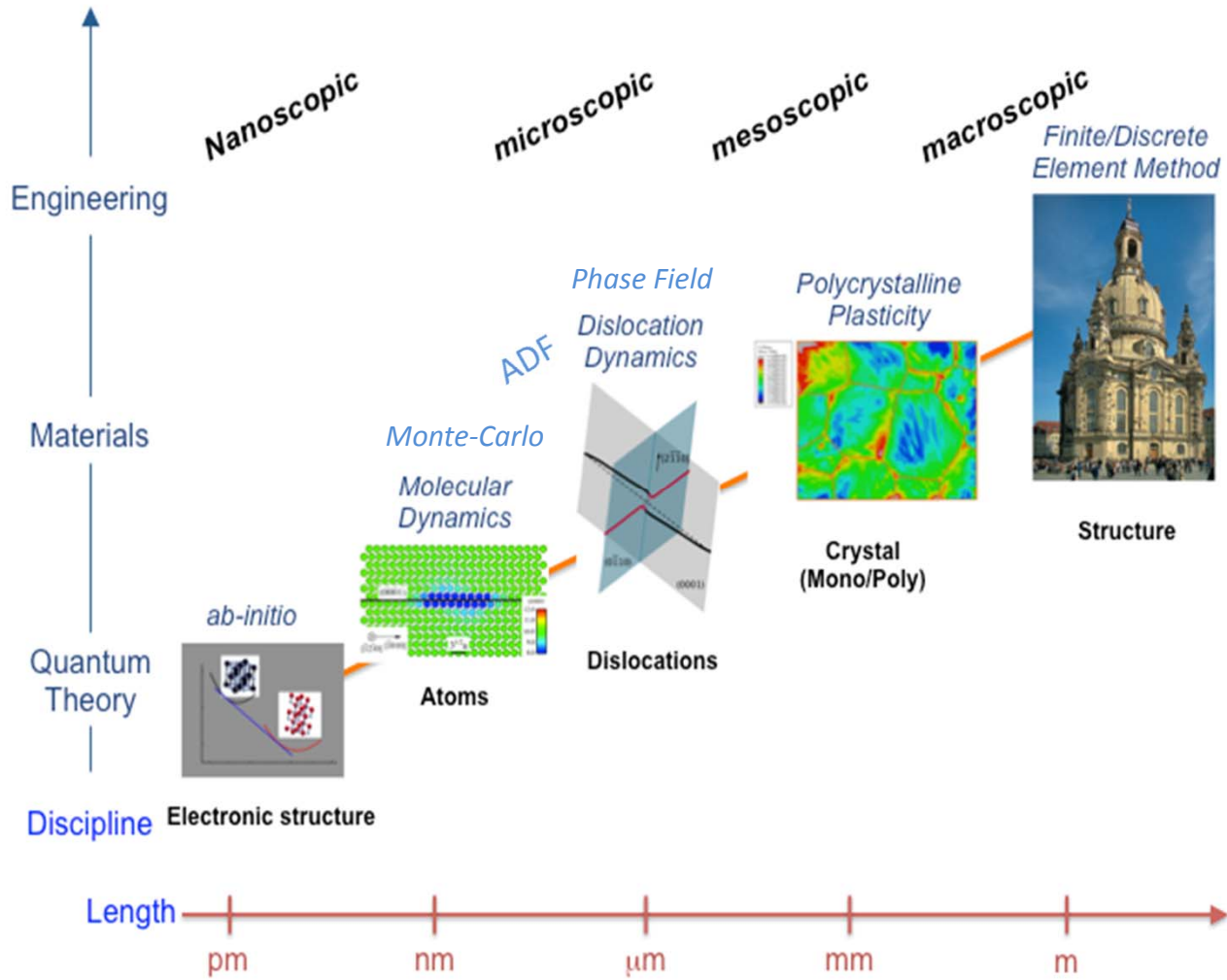


La métallurgie physique



Matériau N18 polycristallin pour disque de turbine d'un avion, formé d'un agrégat de grains. A droite, zoom dans un grain, révélant la présence de précipités durcissants.

MULTI-SCALE MODELING OF MATERIALS



**Based on
Mass
transport**

PHASE TRANSFORMATIONS

Diffusional

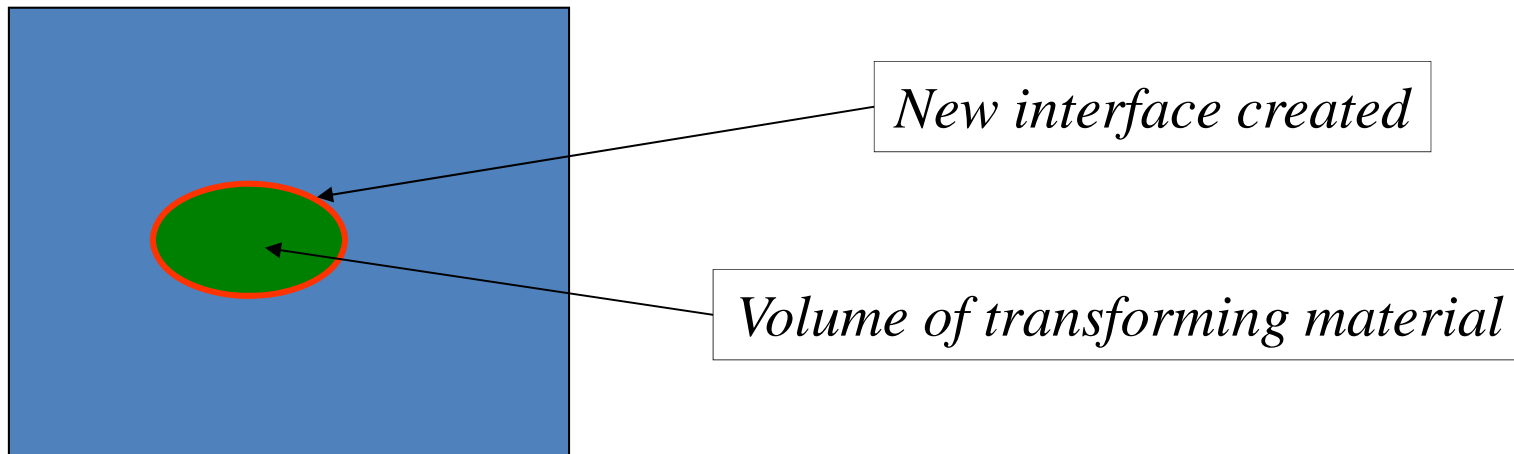
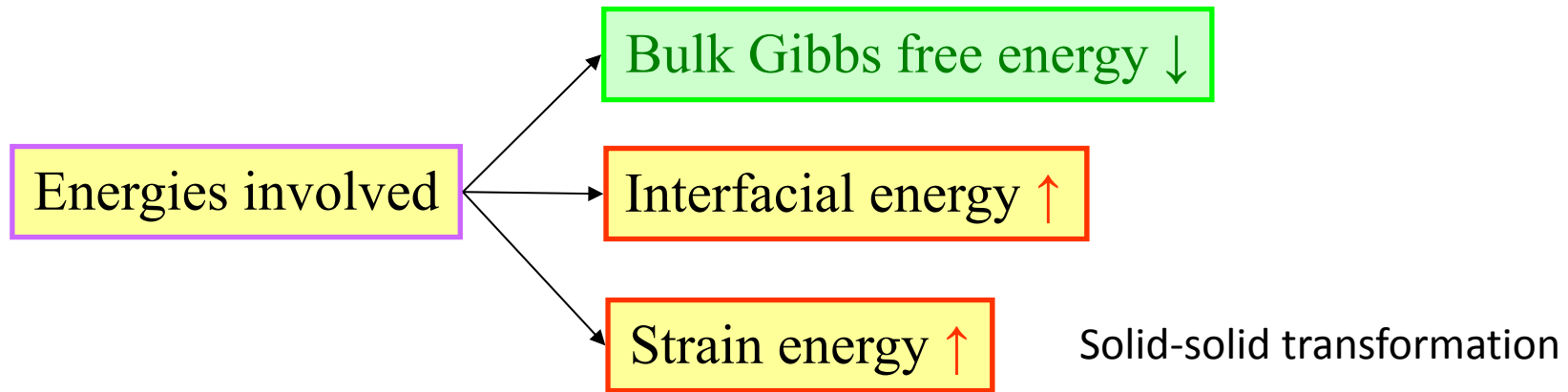
Displacive

**Based on
order**

PHASE TRANSFORMATIONS

1nd order
nucleation & growth

2nd order
Entire volume transforms

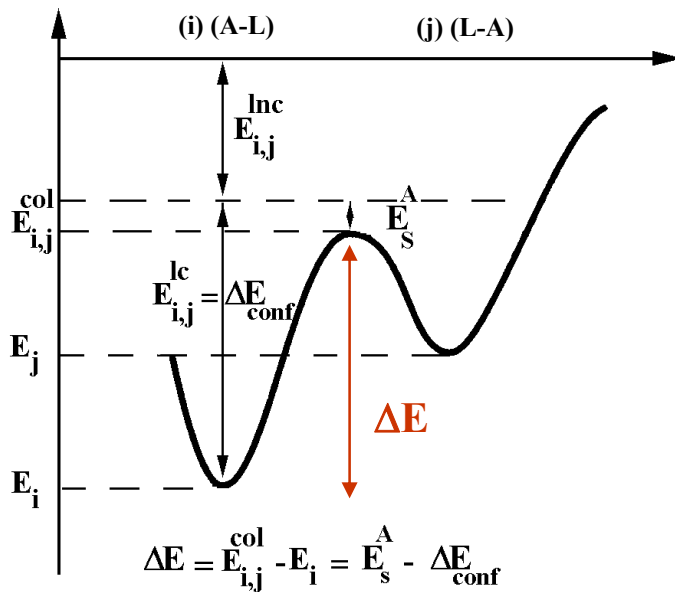
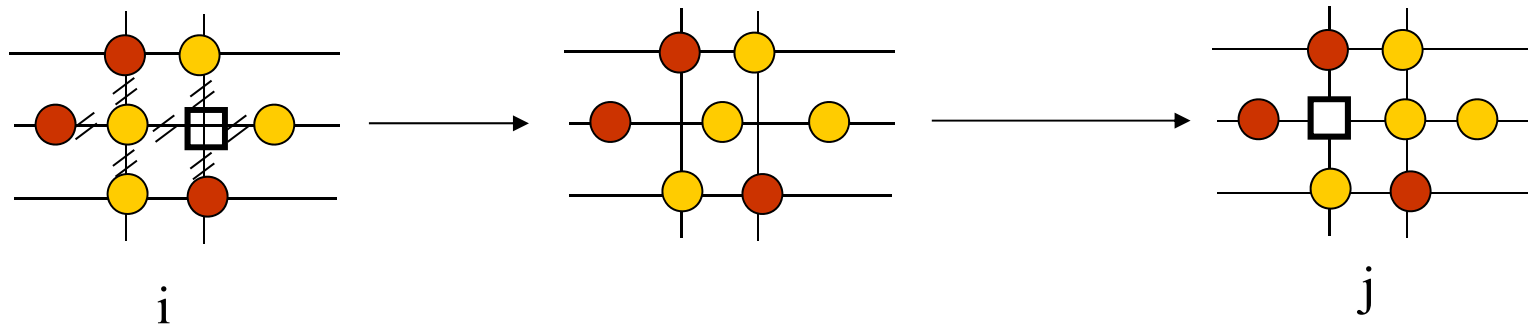


Modèle microscopique sur le réseau rigide

II - Simulation Monte Carlo

1- Modèle cinétique

La diffusion : mécanisme lacunaire thermiquement activé



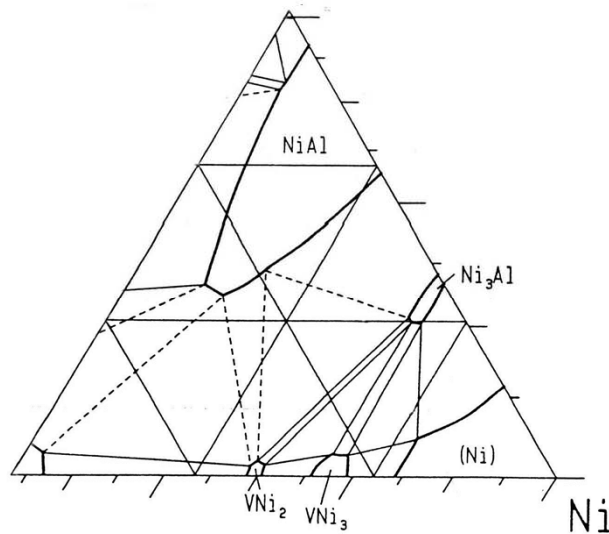
Fréquence d'échange de la lacune avec un atome voisin :

$$W_{A-V} = \nu_A \exp\left(-\frac{\Delta E}{kT}\right) = \nu_A \exp\left(-\frac{E_s^A - \Delta E_{conf}}{kT}\right)$$

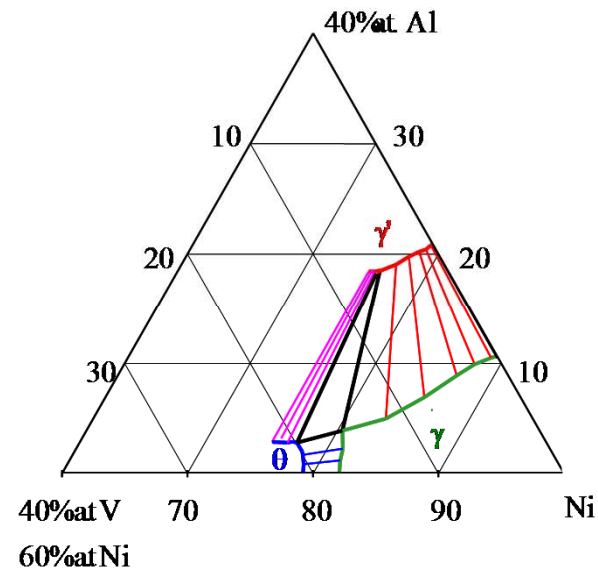
$$\Delta E_{conf} = \sum_{Y \in n(A)} V_{AY} - \sum_{\substack{Y \in n(L) \\ Y \neq A}} V_{LY}$$

Monte Carlo simulation : thermodynamic parameters

Experiment



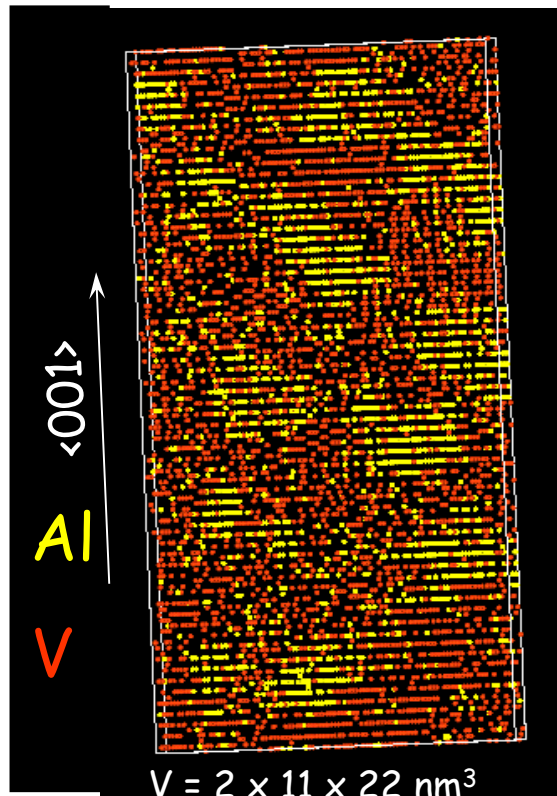
Simulation



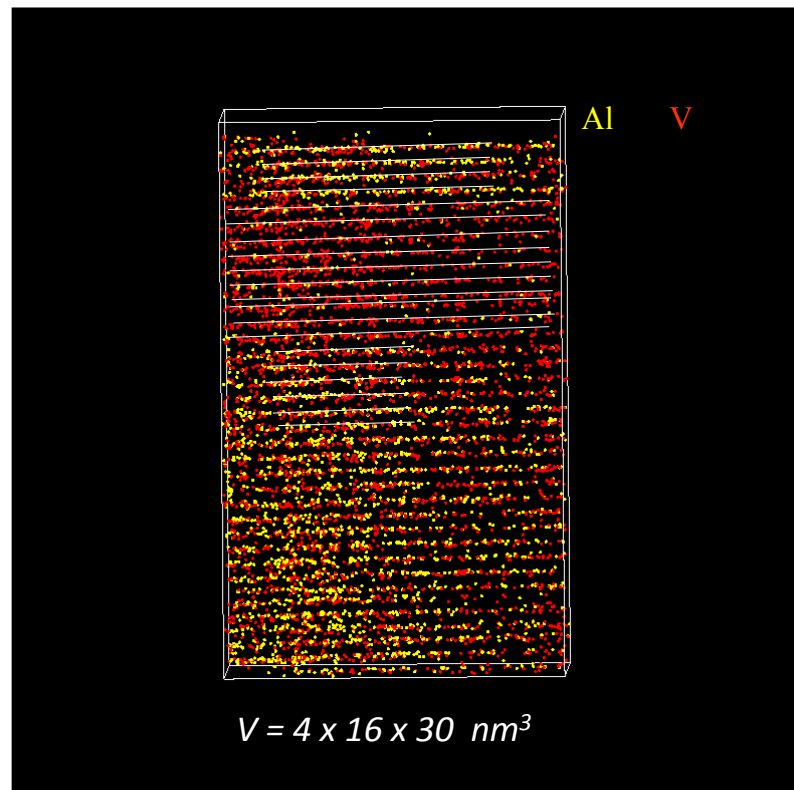
Ordering energy: $\omega_{X-Y}^i = \varepsilon_{XX}^i + \varepsilon_{YY}^i - 2\varepsilon_{XY}^i$

	ω_{X-Y}^1 (eV)	ω_{X-Y}^2 (eV)	ω_{X-Y}^3 (eV)	ω_{X-Y}^4 (eV)
Ni-Al*	0.16	-0.064	-	-
Ni-V	0.201	-0.0503	-0.01	0.027
Al-V	0.2	0.01	-0.01	0.03

Simulation



Experiment



L₁₂/DO₂₂ interface : one atomic plane - also observed experimentally

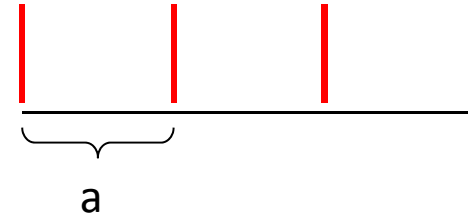
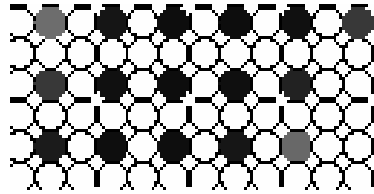
Problématiques: traitement statistique des données, barrière de la percolation, systèmes non-ergodiques, modèle de Potts et Heisenberg,....

1. D. Blavette, G. Grancher et A. Bostel « STATISTICAL ANALYSIS OF ATOM-PROBE DATA (I). DERIVATION OF SOME FINE-SCALE FEATURES FROM FREQUENCY DISTRIBUTIONS FOR FINELY DISPERSED SYSTEMS » J. Phys. Colloques 49 (1988) C6-433

2. F. Danoix, G. Grancher, A. Bostel, D. Blavette « Standard deviations of composition measurements in atom probe analyses—Part II: 3D atom probe » Ultramicroscopy, [Volume 107, Issue 9](#), September 2007, Pages 739–743.

Ising lattice Atomic density function (ADF)

$P(r)$ - probability to find atom at position r



Kinetic equation of relaxation dynamic:

$$\frac{dP(r,t)}{dt} = \frac{1}{k_B T} \sum_{\alpha,\beta} \sum_{r'} L_{\alpha\beta}(r-r') c_\alpha c_\beta \frac{\partial F}{\partial P(r',t)}$$

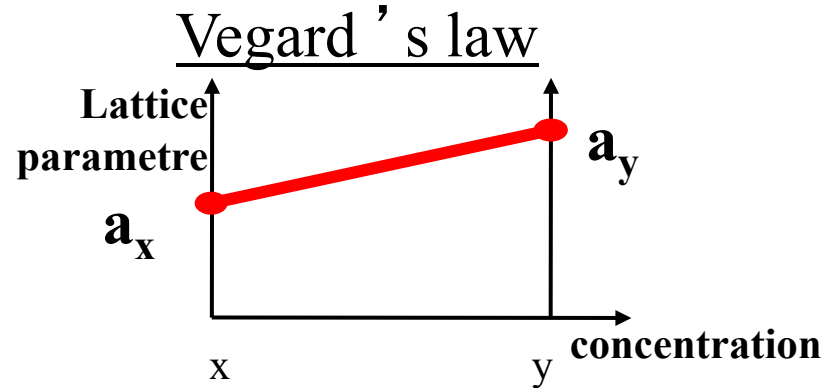
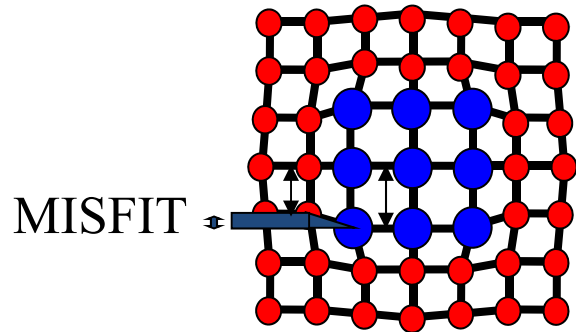
$L_{\alpha\beta}(r-r')$ is a matrix of kinetic coefficients.

$P_A(r,t)$ is the probability of finding of an A atom at a given lattice site r at a given time t .

$$F = F_{chem} + E_{elast}$$

$$F_{chem} = \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} V(\mathbf{r} - \mathbf{r}') P(\mathbf{r}) P(\mathbf{r}') + k_B T \sum_{\mathbf{r}} \{ P(\mathbf{r}) \ln(P(\mathbf{r})) + [1 - P(\mathbf{r})] \ln[1 - (P(\mathbf{r}))] \}$$

ELASTIC ENERGY



$$E_{elast} = \frac{1}{2} \sum_{pq} \int \frac{d^3k}{(2\pi)^3} B_{pq}(\mathbf{n}) |\theta(\mathbf{k})|^2$$

$$B_{pq}(\mathbf{n}) = c_{ijkl} \varepsilon_{ij}^0(p) \varepsilon_{kl}^0(q) - n_i \sigma_{ij}^0(p) \Omega_{jk}(\mathbf{n}) \sigma_{kl}^0(q) n_l$$

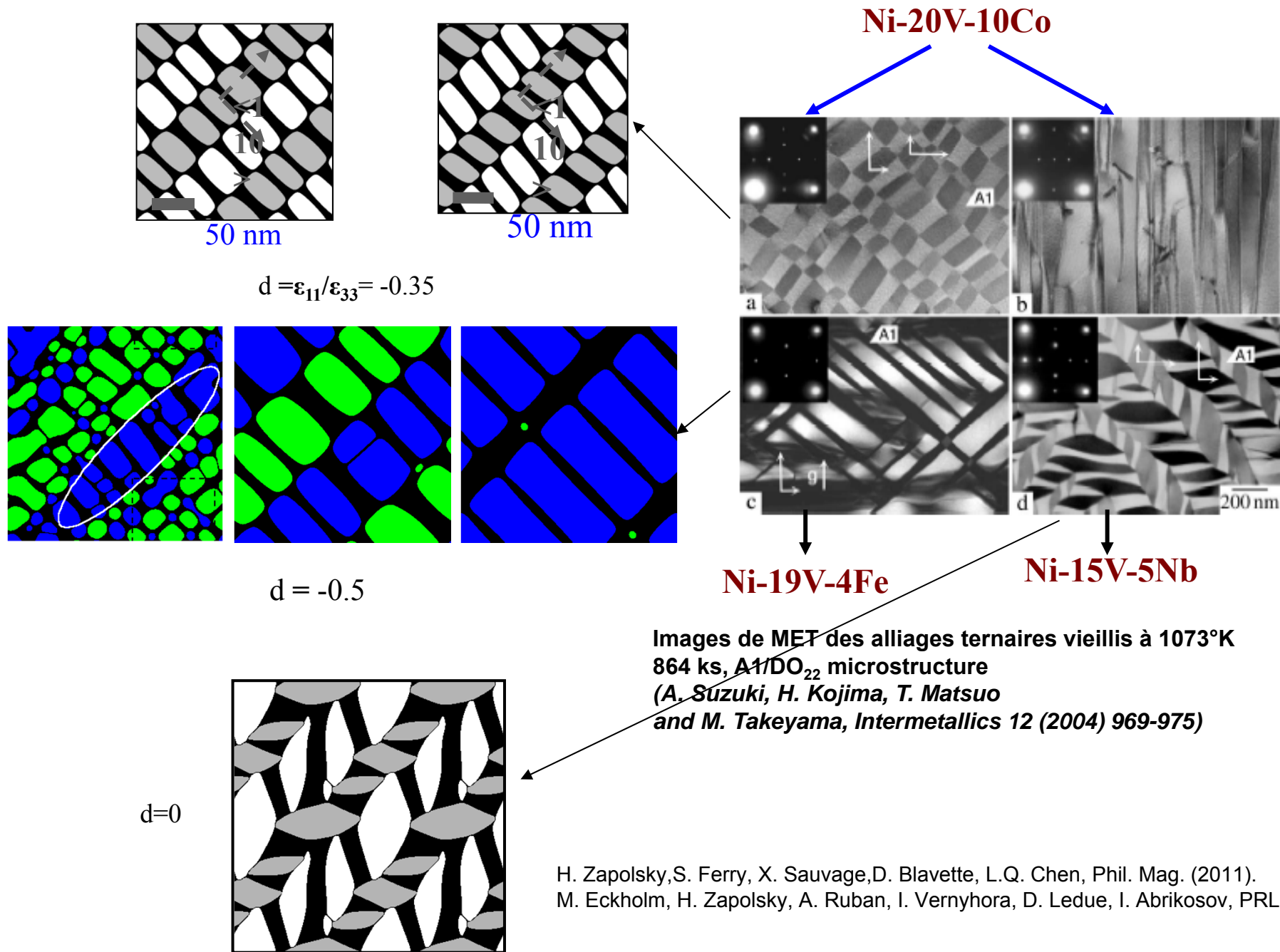


Strain-induced interaction between p and q inclusions located at the points R and R '

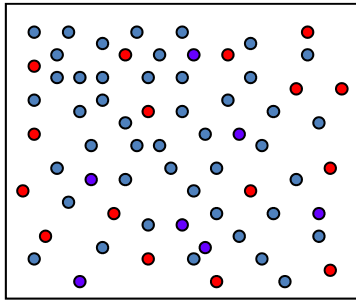
$$W_{pq}(\mathbf{R} - \mathbf{R}') = - \iiint_{-\infty}^{\infty} \frac{d^3k}{(2\pi)^3} (\mathbf{n} \hat{\sigma}^0(p) \hat{\Omega}(\mathbf{n}) \hat{\sigma}^0(q) \mathbf{n}) |\theta(\mathbf{k})|^2$$

$$\Omega_{ij}^{-1}(\mathbf{n}) = c_{ijkl} n_k n_l$$

$$\mathbf{n} = \frac{\mathbf{k}}{k}$$



Continuum Atomic Density Function model (Phase Field Crystal)



A small parameter determining the transition to microscopic continuum version of ADF model is:

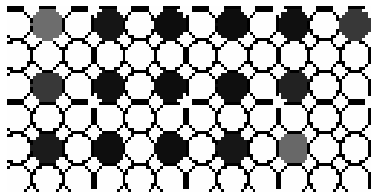
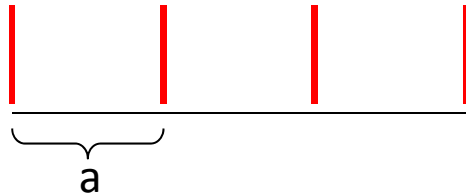
$$\frac{a}{R_{W\alpha\beta}} \ll 1$$

a - Ising lattice parameter

$R_{W\alpha\beta}$ - characteristic distance of interatomic interaction

ADF on constrained lattice

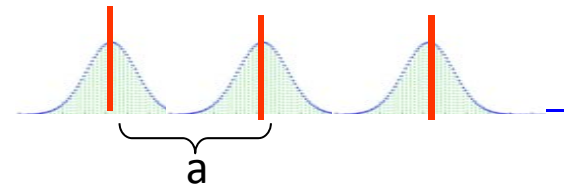
$P(r)$ - probability to find atom at position r



ADF on unconstrained lattice

$\rho(r)$ - atomic density

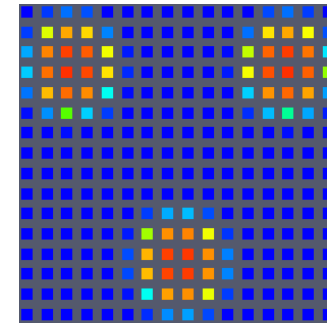
$$\{\rho(\mathbf{r})_\alpha\} = (\rho_1, \rho_2, \dots, \rho_\alpha, \dots, \rho_n)$$



$\rho(r)$ -> averaging over time :

$\Delta t >$ frequency of phonons

$\Delta t <$ characteristic diffusion time



- There is no Ising lattice constraint: atoms are free to continuously move to relax the free energy.
- The n -component system is described by the n **atomic density functions**:

$$\{\rho(\mathbf{r})_\alpha\} = (\rho_1, \rho_2, \dots, \rho_\alpha, \dots, \rho_n)$$

- **The ADF kinetic** equations are essentially the same but the integration is over continuum space is substituted for summation over lattice sites:

$$\frac{\partial \rho_\alpha(\mathbf{r}, t)}{\partial t} = \sum_{\beta=1}^{\beta=n} \int_V L_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \frac{\delta F}{\delta \rho_\beta(\mathbf{r}', t)} d^3 r' \quad \alpha = 1, 2, \dots, n$$

$F(\{\rho_\alpha(\mathbf{r})\})$ is a non-local free energy functional of n atomic density functions, $L_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is the mobility matrix.

The conservation of the number of atoms:

$$\int_V L_{\alpha\beta}(\mathbf{r}, \mathbf{r}') d^3 r' = 0.$$

Free energy approximations:

$$F[\{\rho_\alpha\}] = \frac{1}{2} \int_V \int_V \sum_{\alpha\beta} W_{\alpha\beta}(\mathbf{r}-\mathbf{r}') \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') d^3r d^3r' + \int_V f(\{\rho_\alpha(\mathbf{r})\}) d^3r$$

Non-local term **Local term**

The local free energy density $f(\{\rho_\alpha(\mathbf{r})\})$ can be approximated by the Landau polynomial expansion with respect to densities $\rho_\alpha(\mathbf{r})$.

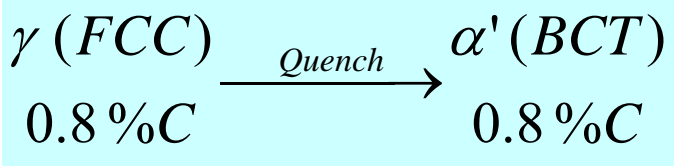
$$W_{\alpha\beta}(\mathbf{r}-\mathbf{r}')$$

the effective interaction potentials



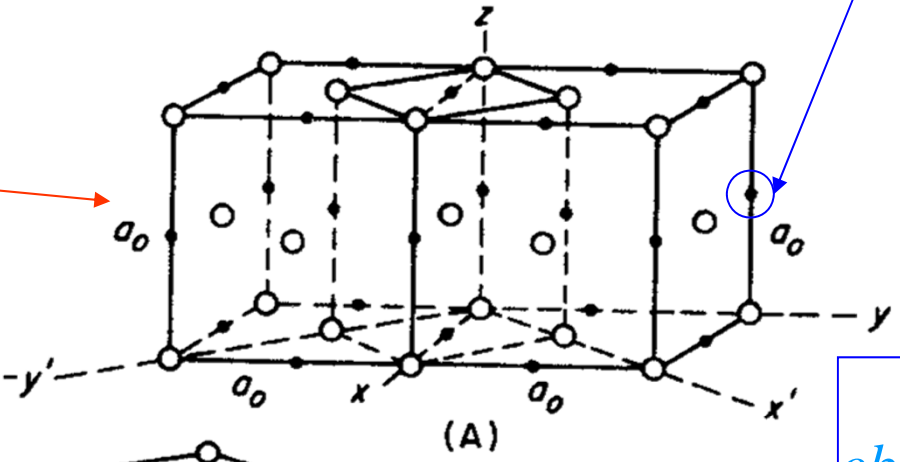
Embedded potential, effective pair potential, ...

Martensite



Possible positions of Carbon atoms
Only a fraction of the sites occupied

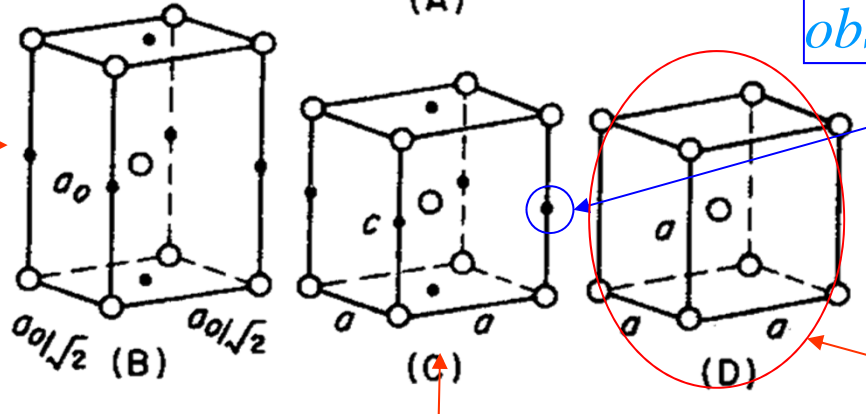
FCC Austenite



Bain distortion

C along the c-axis obstructs the contraction

FCC Austenite
 Alternate choice of Cell



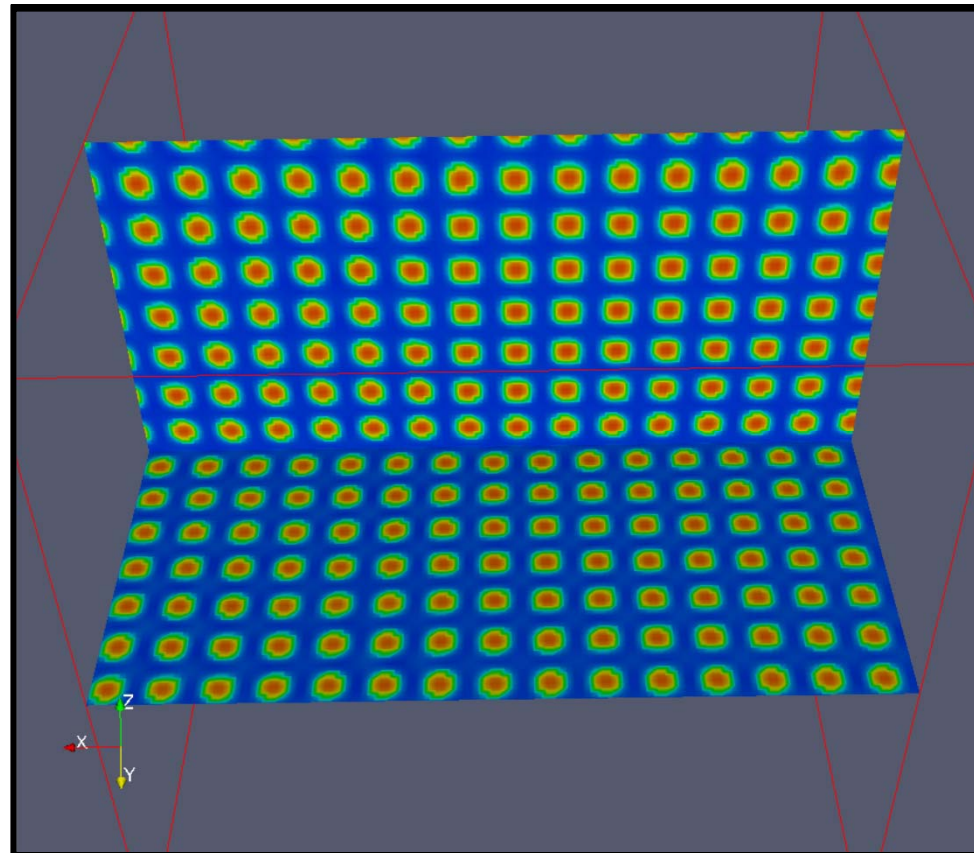
Tetragonal Martensite

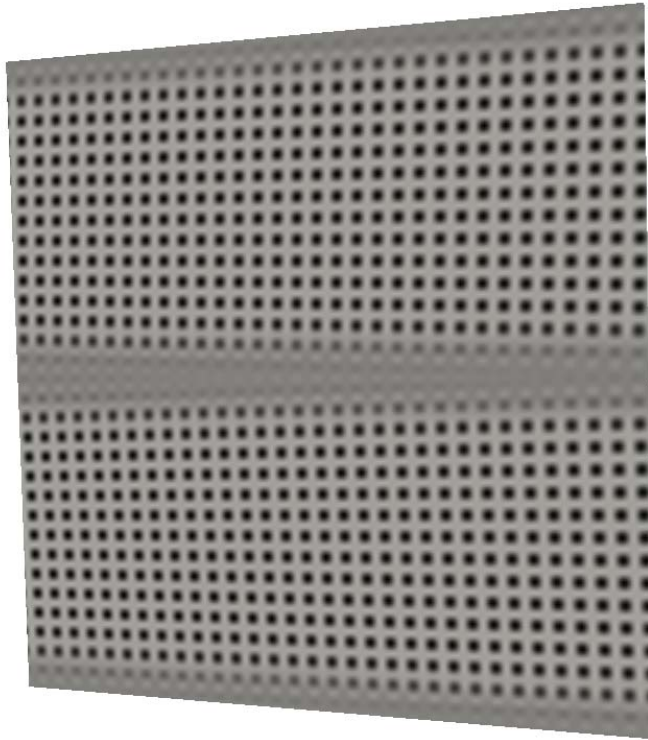
In Pure Fe after the Matensitic transformation
 $c = a$

20% contraction of *c*-axis
 12% expansion of *a*-axis

Austenite to Martensite \rightarrow 4.3 % volume increase

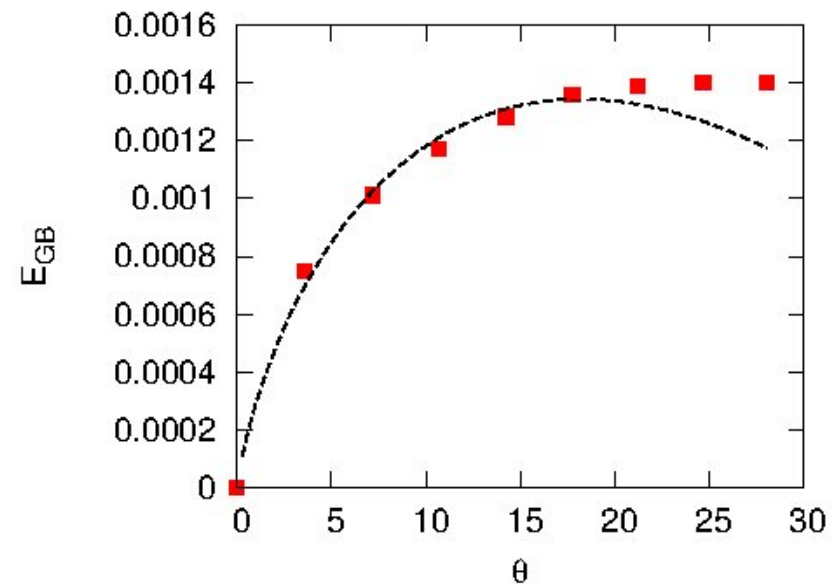
FCC-BCC Transition

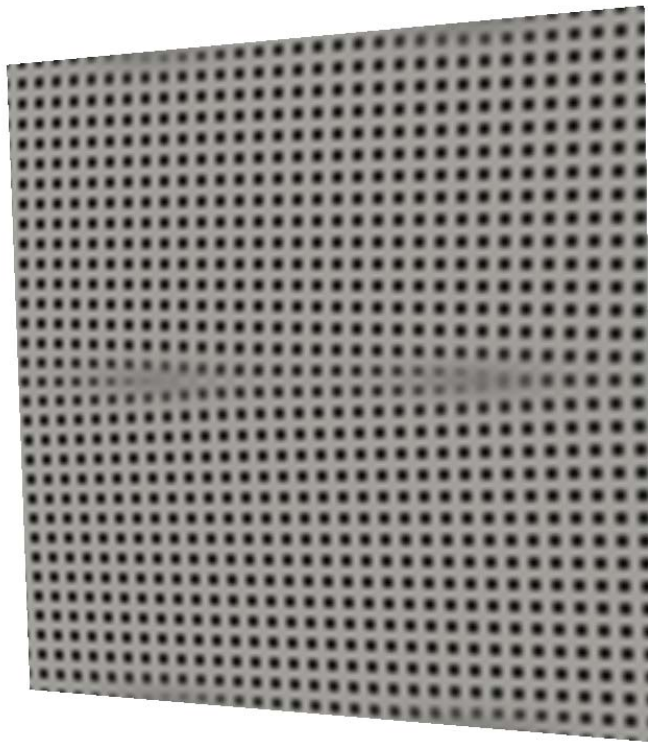




PFC, tilt angle $\theta = 3.58^\circ$

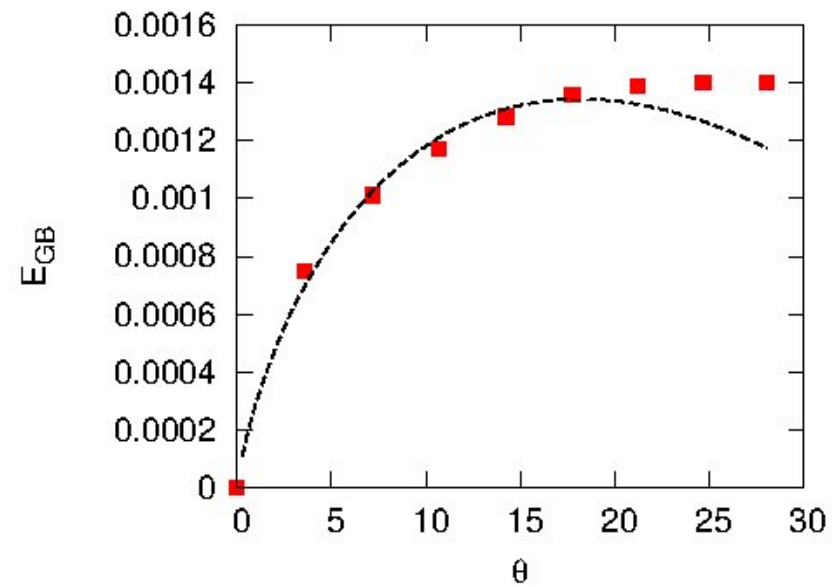
Read and Shockley fit

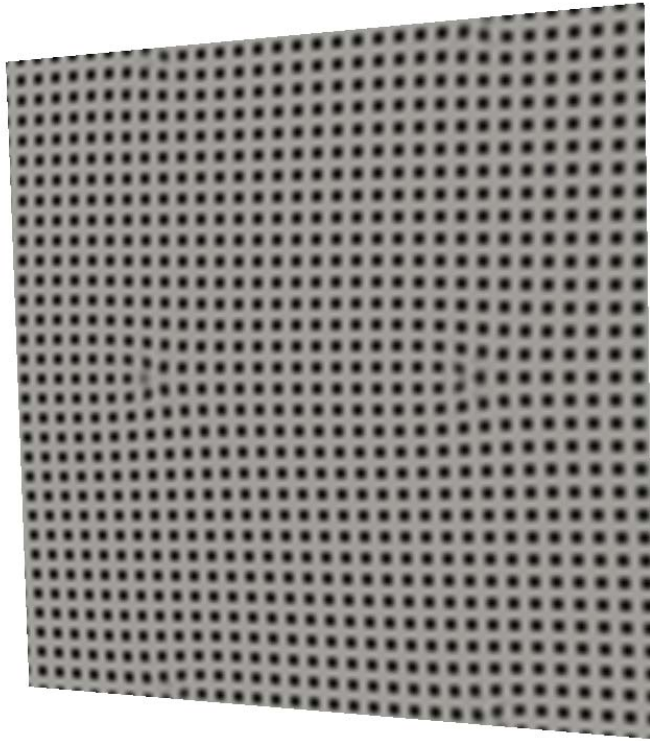




PFC, tilt angle $\theta = 3.58^\circ$

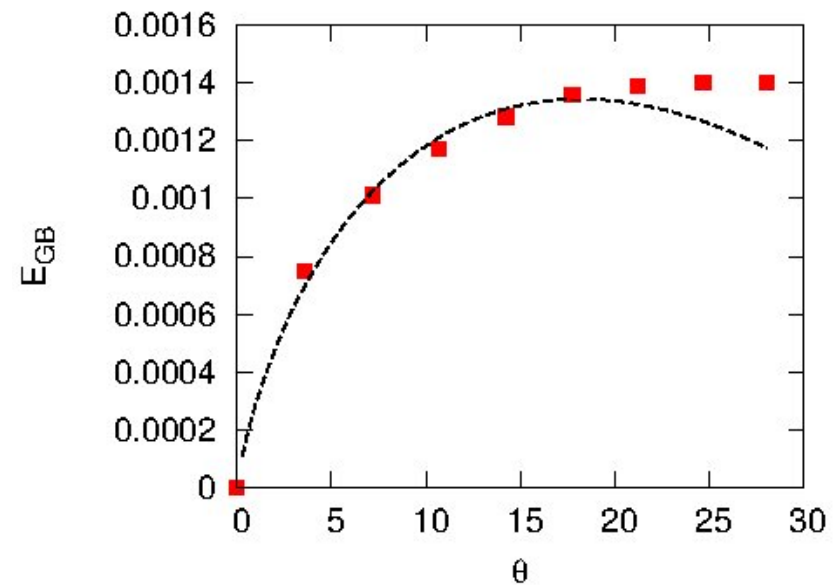
Read and Shockley fit

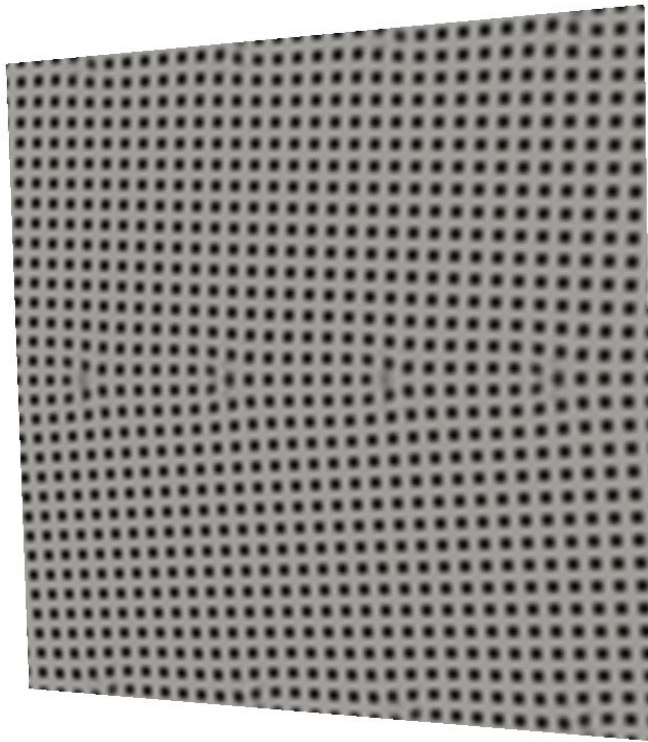




PFC, tilt angle $\theta = 3.58^\circ$

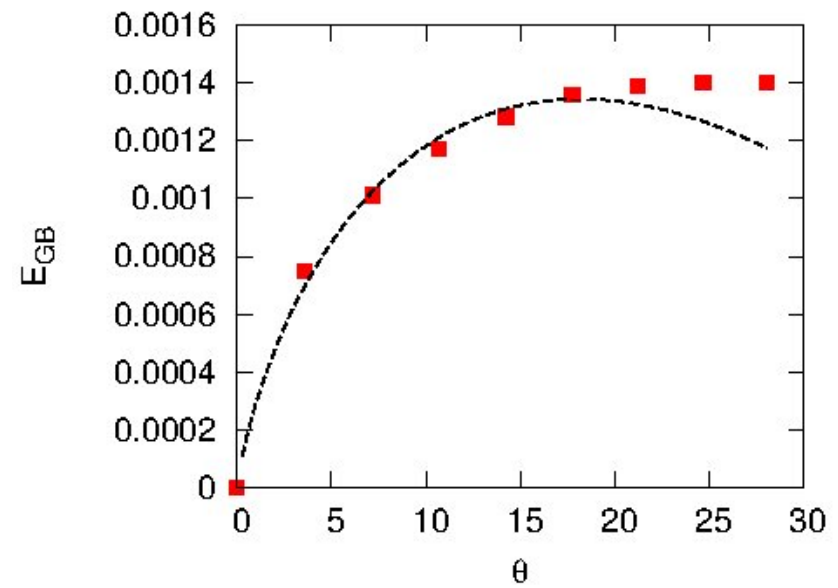
Read and Shockley fit

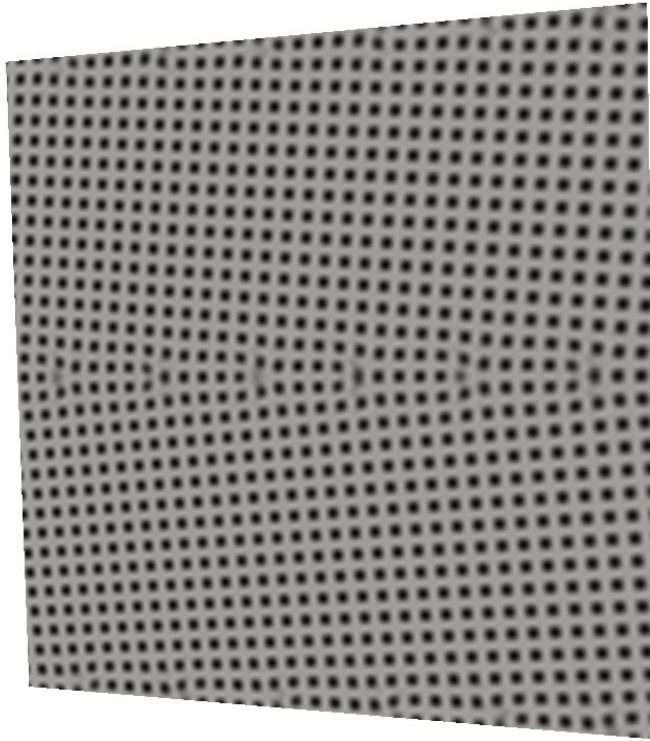




PFC, tilt angle $\theta = 7.17^\circ$

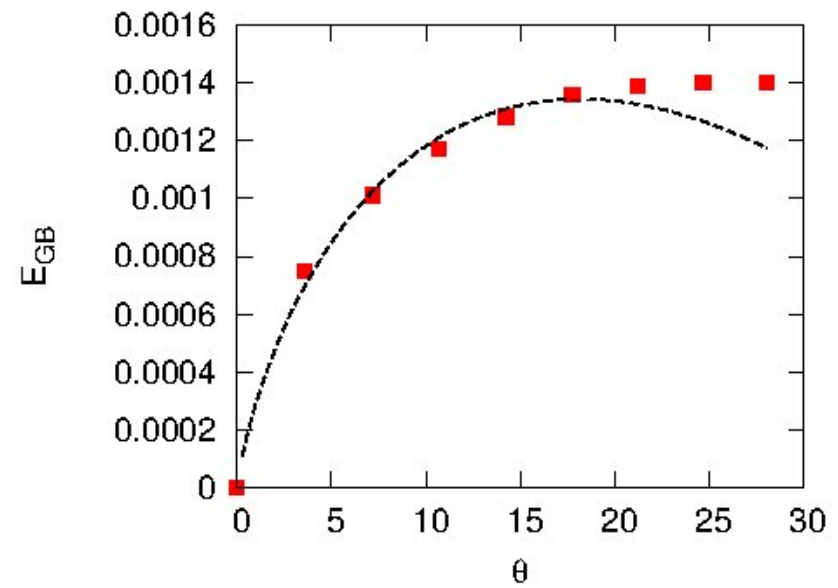
Read and Shockley fit

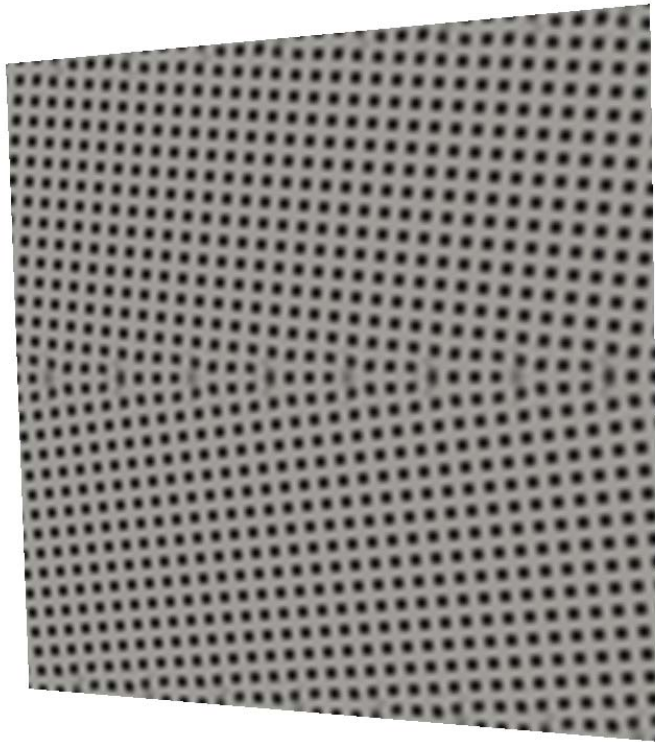




PFC, tilt angle $\theta = 10.17^\circ$

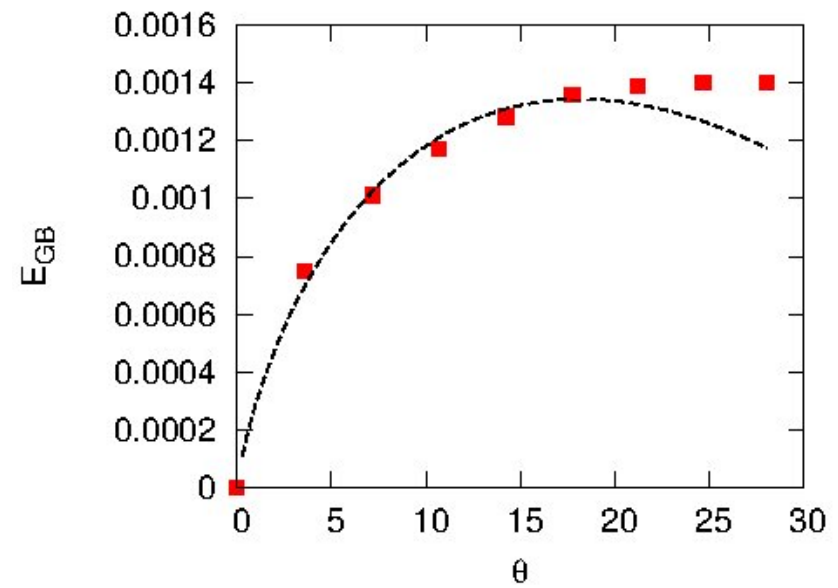
Read and Shockley fit

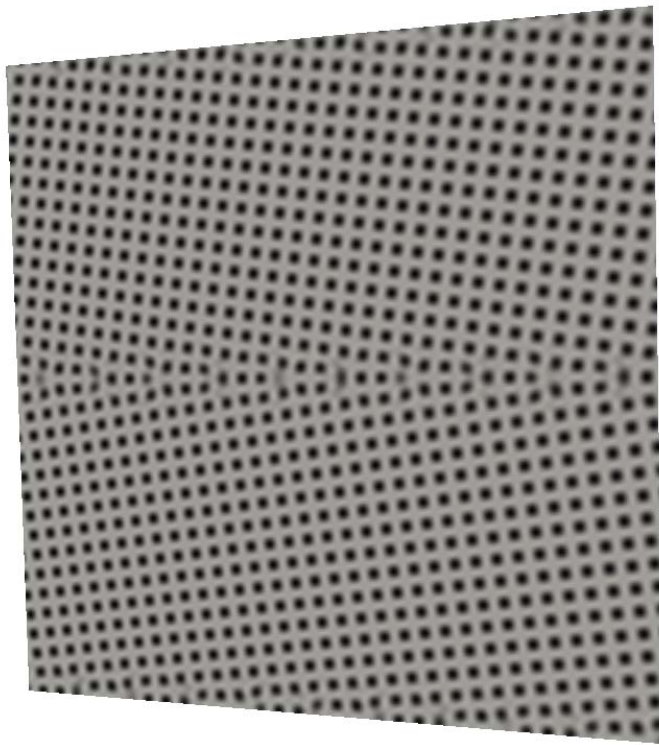




PFC, tilt angle $\theta = 14.25^\circ$

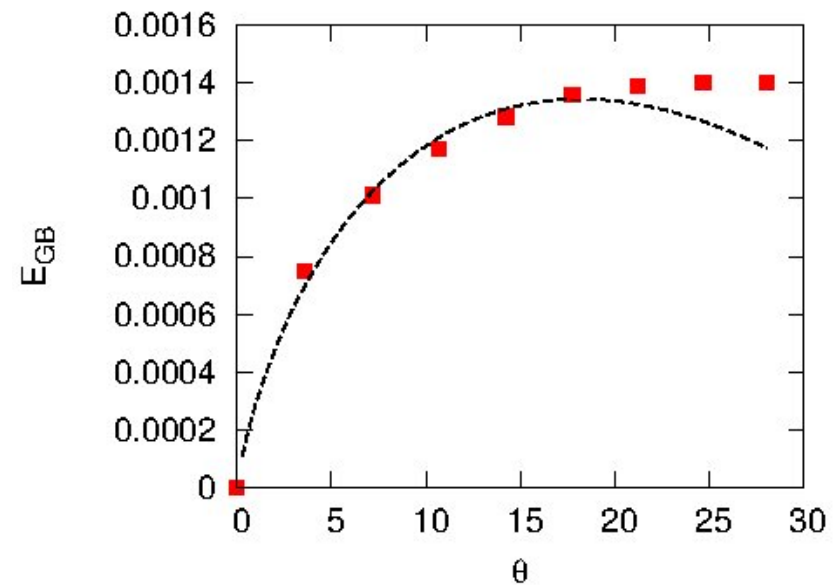
Read and Shockley fit

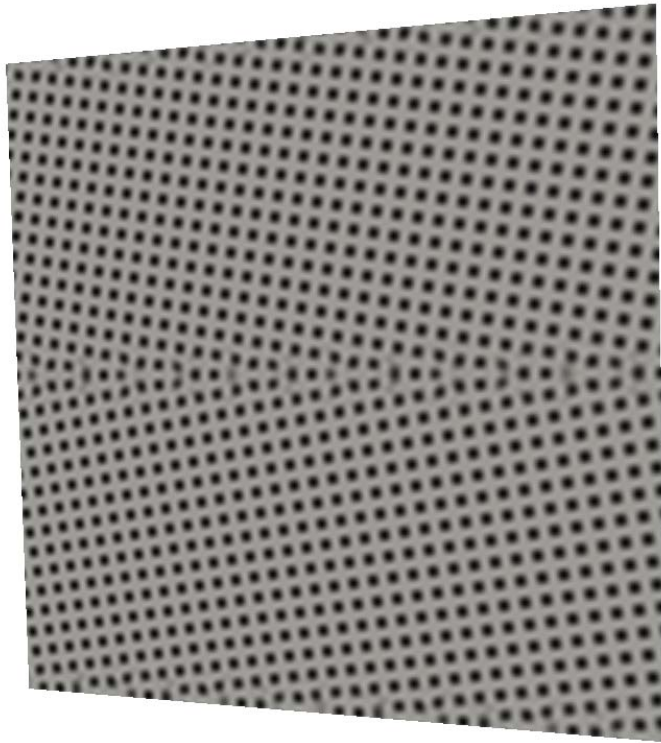




PFC, tilt angle $\theta = 17.76^\circ$

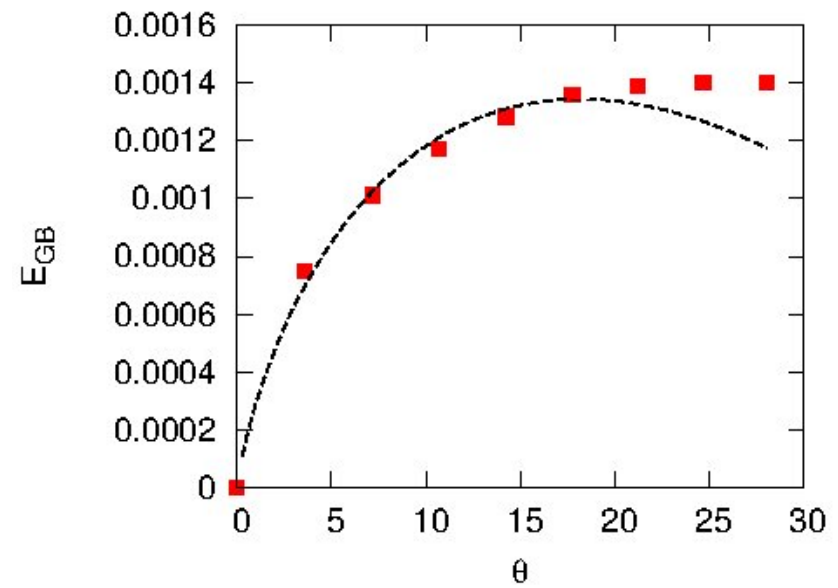
Read and Shockley fit

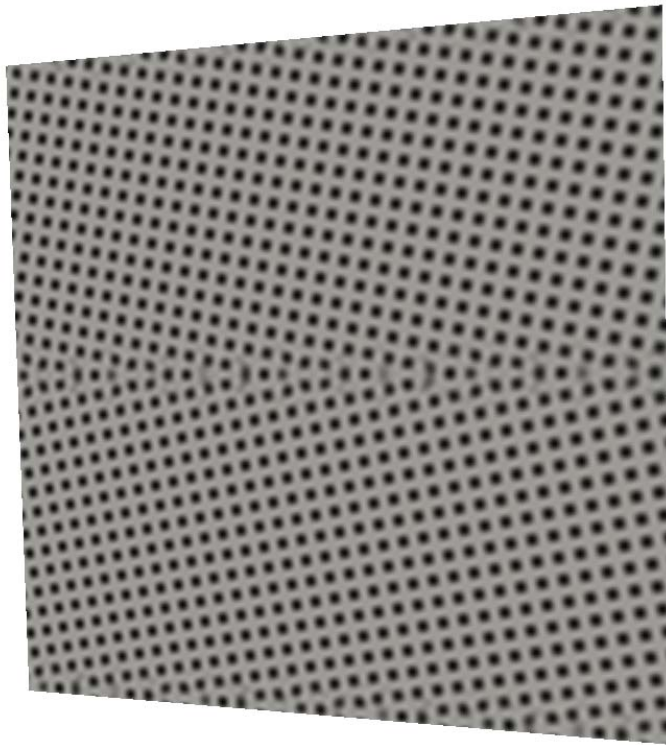




PFC, tilt angle $\theta = 21.24^\circ$

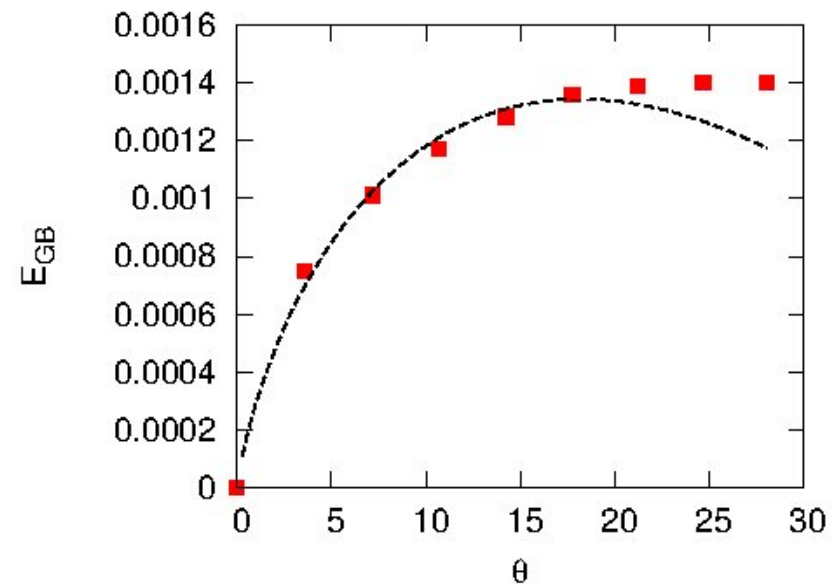
Read and Shockley fit



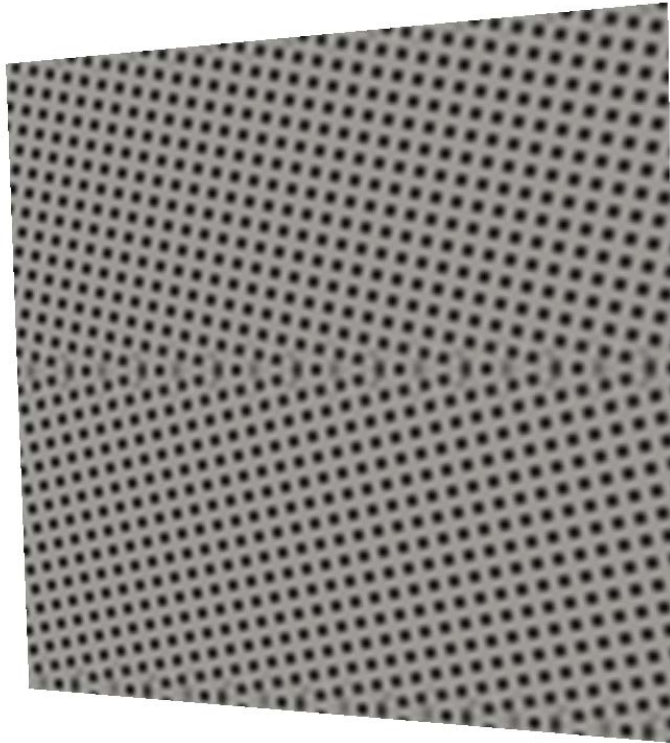


PFC, tilt angle $\theta = 24.68^\circ$

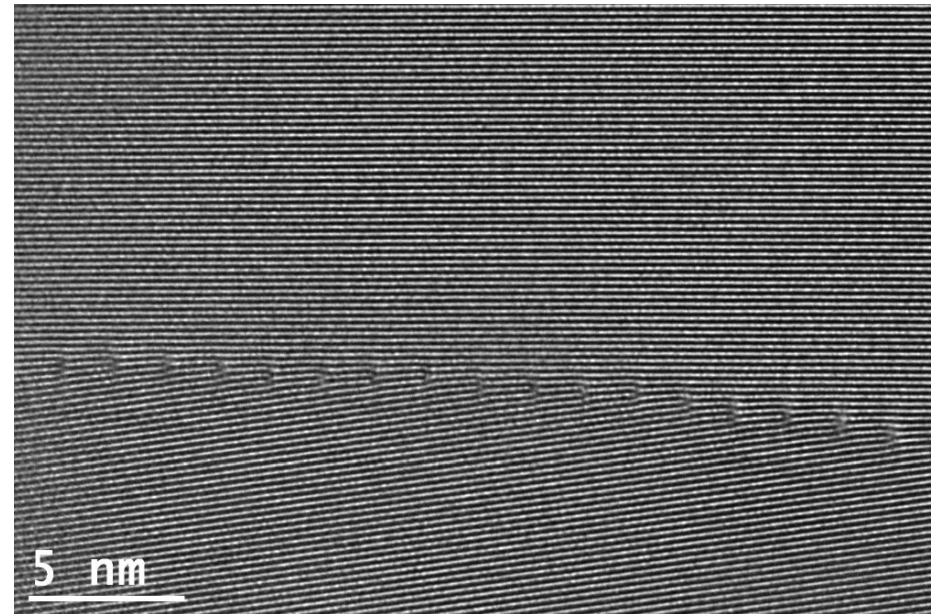
Read and Shockley fit



Simulation



Experimental image



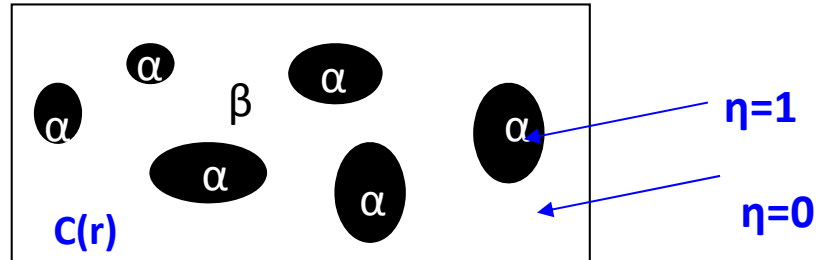
PFC, tilt angle $\theta = 28.07^\circ$

To improve our simulation:

- ❖ More efficient numerical methods to solve TDLG equation
- ❖ Condition for Δt

Phase Field equations (mesoscopic description)

Phase field variables:
 Concentration $c(\mathbf{r})$
 Order parameter $\eta(\mathbf{r})$



- Time dependent Ginzburg-Landau equation for the Iro parameters

$$\frac{\partial \eta(\vec{r}, t)}{\partial t} = -L \left(\frac{\delta F}{\delta \eta(\vec{r}, t)} \right) + \zeta_{\eta}(\vec{r}, t)$$

Cahn-Hilliard equation for the concentrations

$$\frac{\partial c(\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot \mathbf{M} \vec{\nabla} \left(\frac{\delta F}{\delta c(\vec{r}, t)} \right) + \zeta_c(\vec{r}, t)$$

\mathbf{M} – mobility .

L – kinetic coefficient describing the motion of the interface

F – total free energy. $F = F_{\text{chemical}} + F_{\text{elastic}}$

$\zeta_c(\mathbf{r}, t)$ et $\zeta_{\eta}(\mathbf{r}, t)$ – Langevin noises.

Chemical energy

In the phase field model, the **chemical energy** is:

$$F_{\text{chim}} = \int_V \left[\underbrace{\frac{1}{2} \alpha (\vec{\nabla} c)^2 + \frac{1}{2} \sum_{\alpha=1}^v \beta (\vec{\nabla} \eta_{\alpha})^2}_{\text{Non-local term (interfacial energy)}} + \underbrace{f(c, \eta_1, \eta_2, \dots, \eta_v)}_{\text{Local term density of the bulk free energy}} \right] dV$$

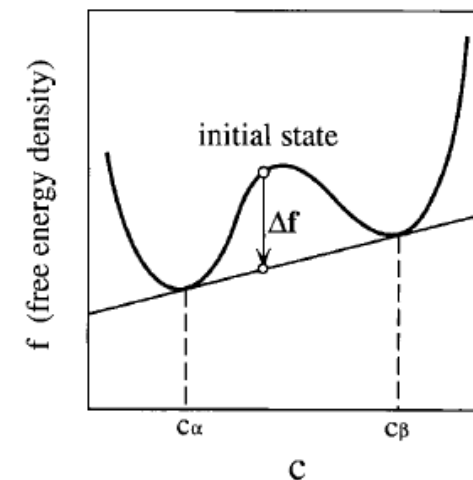
Non-local term (**interfacial energy**)

Local term
density of the bulk free energy

$$f(T, c, \eta) = f_{\text{des}} + A(T, c) \eta^2 + B(T, c) \eta^3 + C(T, c) \eta^4 + \dots$$

with **f_{des}** – the free energy density for the disordered phase.

A, B, C – coefficients of the expansion.



Parameters of model

- *kinetics coefficients*
- *driving force Δf*
- *interfacial energy*
- *elastic constants*
- *misfit*

Applications of semi-implicit
Fourier-spectral method to phase field equations

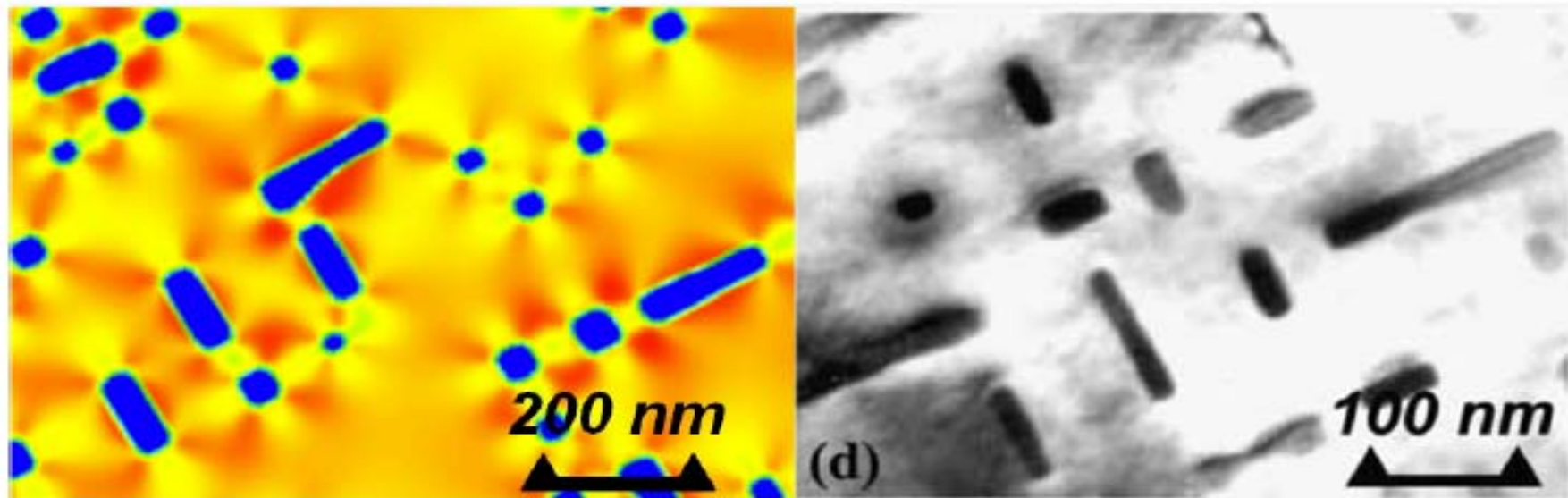


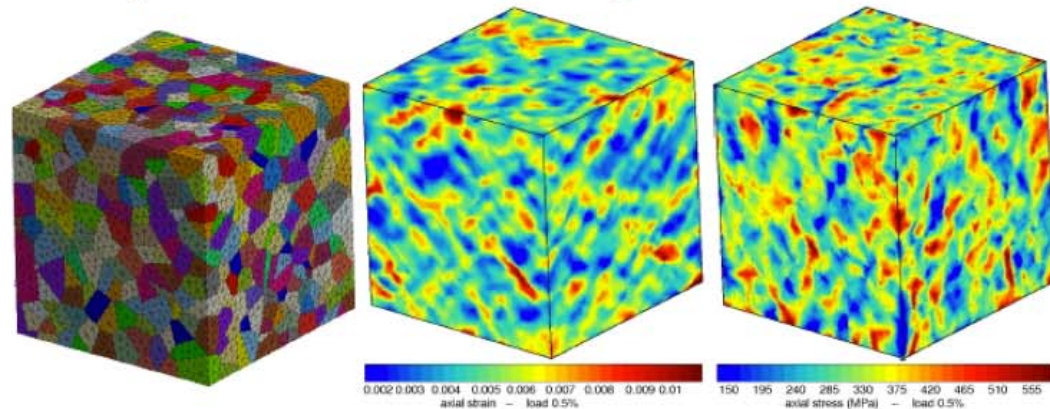
Figure 3.20 – A gauche : simulation d'un alliage $Ni - 21.1at.\%Al$ pour $t^* = 10000$; à droite : Image MET en champ sombre d'un alliage $Ni - 22.33at.\%Al$. Seulement 25% de la boîte de simulation est représenté.

Un problème mathématique pour la mécanique des matériaux :

caractériser les morphologies des motifs de localisation dans un polycristal

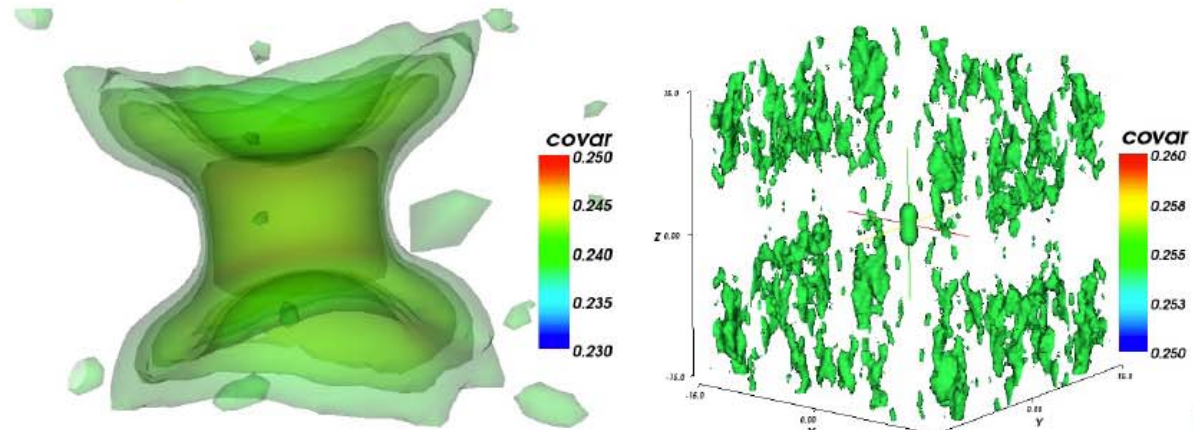
I - On fait une observation qualitative de la localisation en surface de champs mécaniques simulés par “Crystal Plasticity Finite Element Modelling” :

- localisation des déformations en bandes à 45° , confirmé par l'expérience
- localisation des contraintes dans les grains (pas d'observation expérimentale)
- **Qu'en est-il en 3D ?** (là où l'expérimental ne peut rien)
- **Qu'apporte l'analyse des contraintes ?** (là où l'expérimental est très limité)



II - On caractérise simplement les motifs de localisation en termes de covariance à 2 points sur les champs segmentés (Barbe et al, *Mech Res Comm*, 2009) :

- surfaces d'iso-intensité de covariance
- déformation : **morphologie en bandes à 45° “isotropes” d'une longueur ≈ 2 grains**
- contrainte : **localisation orientée selon la charge sur une longueur ≤ 1 grain**



Un problème mathématique pour la mécanique des matériaux : caractériser les morphologies des motifs de localisation dans un polycristal

III - Bilan et Perspectives

- **Points forts** : caractérisations **encourageantes** sur données **simulées** :
 - motifs en 3D, représentativité statistique assurée, analyse étendue à toutes les variables méca et pour \neq effets :
 - propriétés mécaniques
 - microstructure (texture cristallographique / morphologique, distribution bimodale, ...)
 - chargement (monotone / cyclique / multi-axial / ...)
- **Points faibles** : des caractérisations **sommaires** des morphologies de motifs
 - analyses basées uniquement sur la covariance à 2 points
 - caractérisation essentiellement qualitative pour l'instant
- **Voies d'amélioration** :
 - caractériser quantitativement les motifs :
quelles longueurs / largeurs de bandes / ogives ?
 - compléter la caractérisation avec des **outils de morphologie mathématique plus adaptés** aux objectifs :

Calculs, modelisation et simulation pour l' amélioration de la sonde atomique tomographique

F.Vurpillot, A. Vella, J. Houard, L. Arnoldi, E. Silaeva

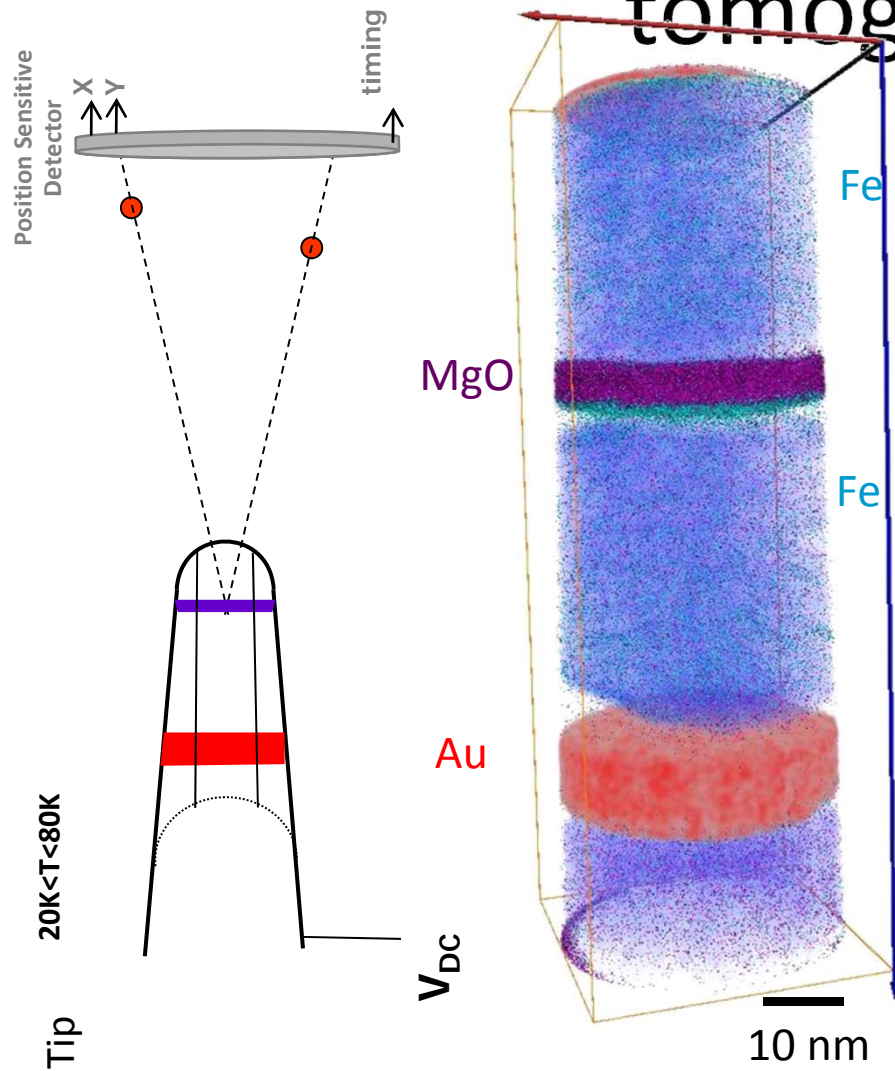
**Equipe de Recherche en Instrumentation Scientifique*

Groupe de Physique des Matériaux
UMR 6634 CNRS,

Université de Rouen Avenue de l' Université, B.P. 12 76801
Saint – Etienne du Rouvray Cedex, France

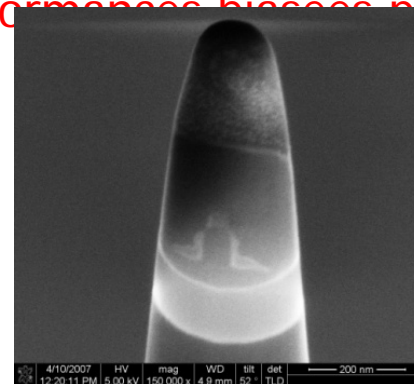


Principes de la sonde atomique tomographique



- ✓ Une pointe soumise à un potentiel en face d'un détecteur
- ✓ Projection quasi déterministe des ions
- ✓ Erosion contrôlée de la pointe (field evaporation)
- Reconstruction tomographique
- ⊘ Spectroscopie de masse à temps de vol

Performances liées par

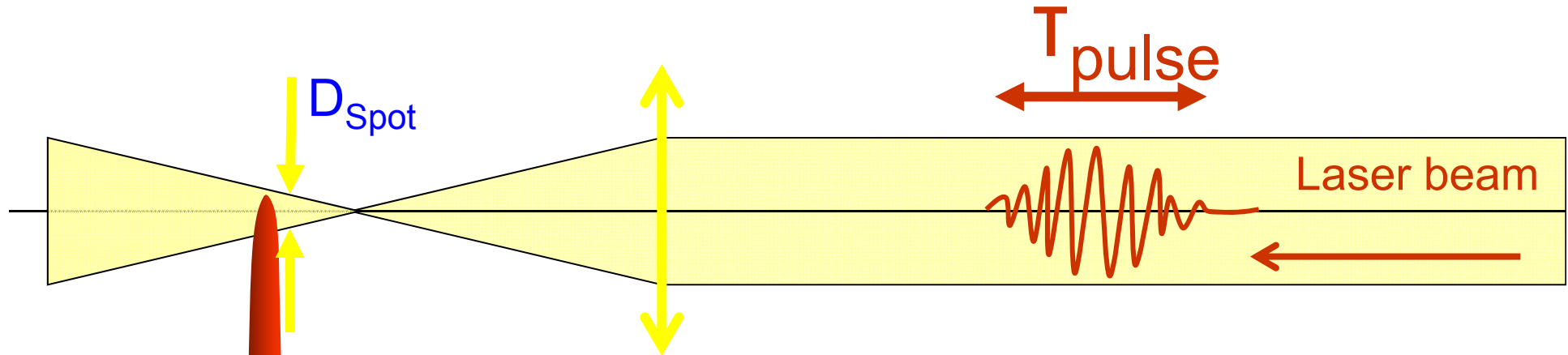


tionnaire des ions

nte non stationnaire

ctoires

Une sonde atomique assistée par impulsion laser



Energy ~ 1 – 500 nJ /pulse
 D_{spot} ~ 10 - 100 μm
: intensity 1-100 J/m^2

τ_{pulse} ~100-500 fs
variable wavelength (infrared-visible)
repetition rate 1-100 kHz

Tip

Role de la modélisation

Modeliser les processus physique est essentiel pour evaluer les limites de l'instrument en terme de

- ✓ 1. Resolution spatiale (fidélité)
- ✓ 2. Distortions (justesse)
- ✓ 3. Corréler les propriétés du matériaux aux effets lors de l'analyse
- ✓ 4. Controler les paramètres d'analyse

Difficultés

Echelles de temps : *de la fs à la microseconde*

Echelles d'espace : *du pm au cm*

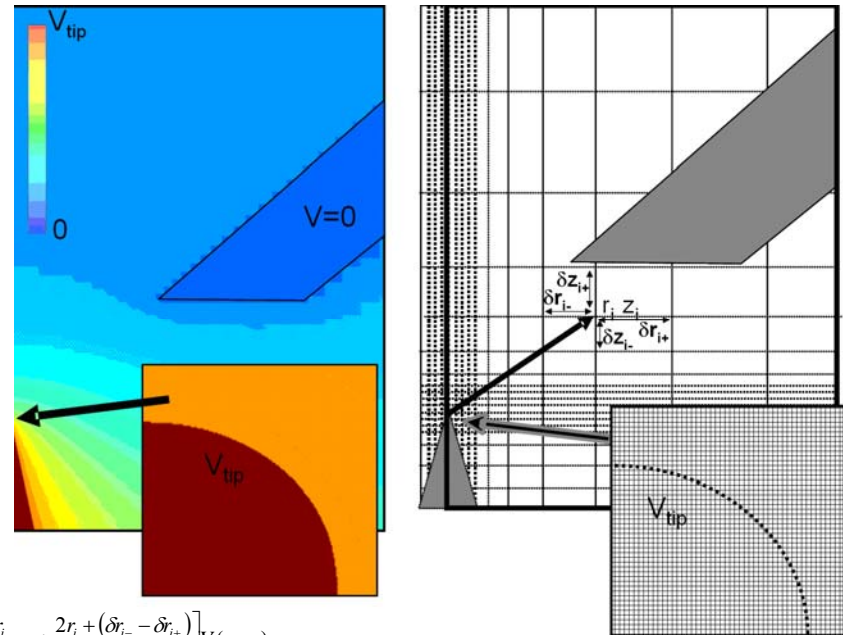
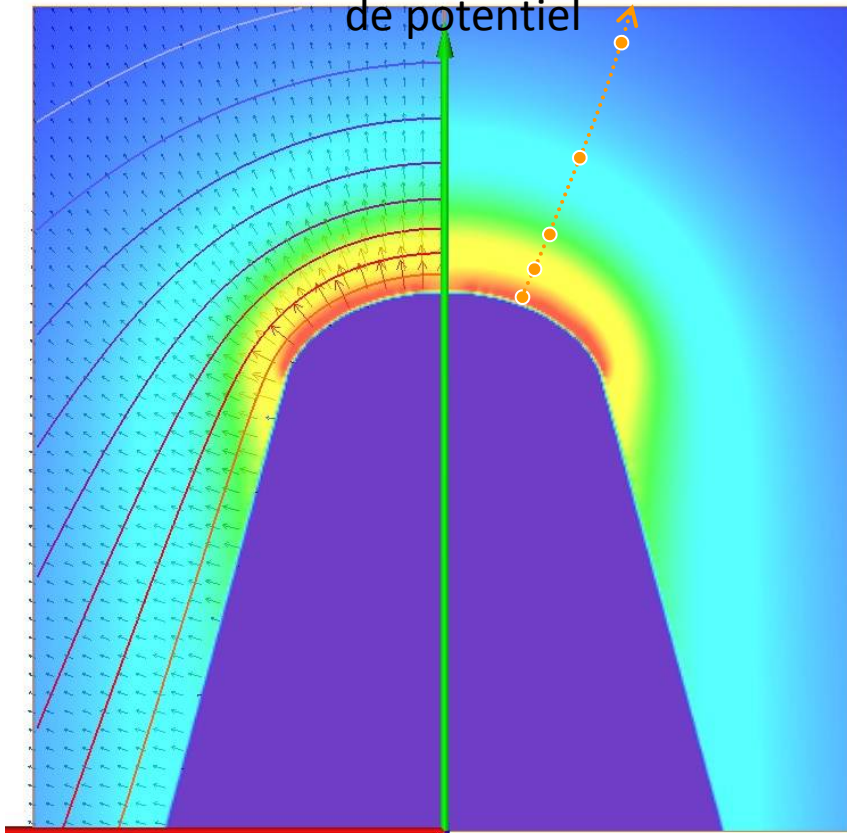
Intensités : *Eclairement intense (TW)*

Champ electrostatiques intenses (10^{10} V/m)

Multiphysique : *Physique des champs intenses, thermiques à l'échelle nano, interaction laser matière, Electrostatique, physique du solide, mecanique quantique (ionisation , evaporation par effet de champ)*

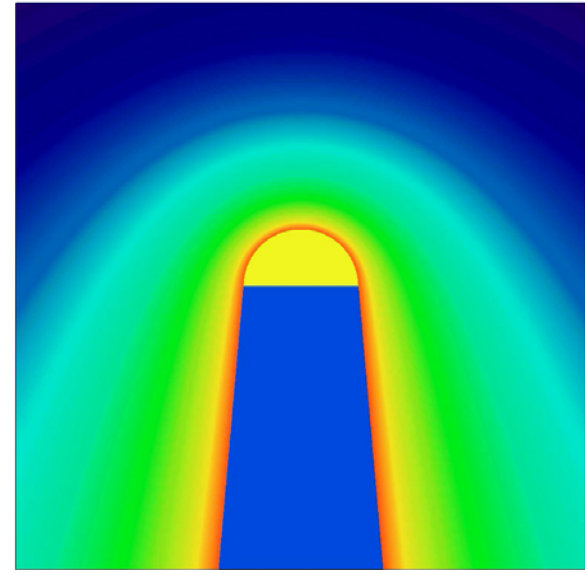
Exemple 1 : Trajectoires ioniques: optique electrostatique

Resolution numérique du PFD pour calculer les trajectoires ioniques dans la distribution de potentiel



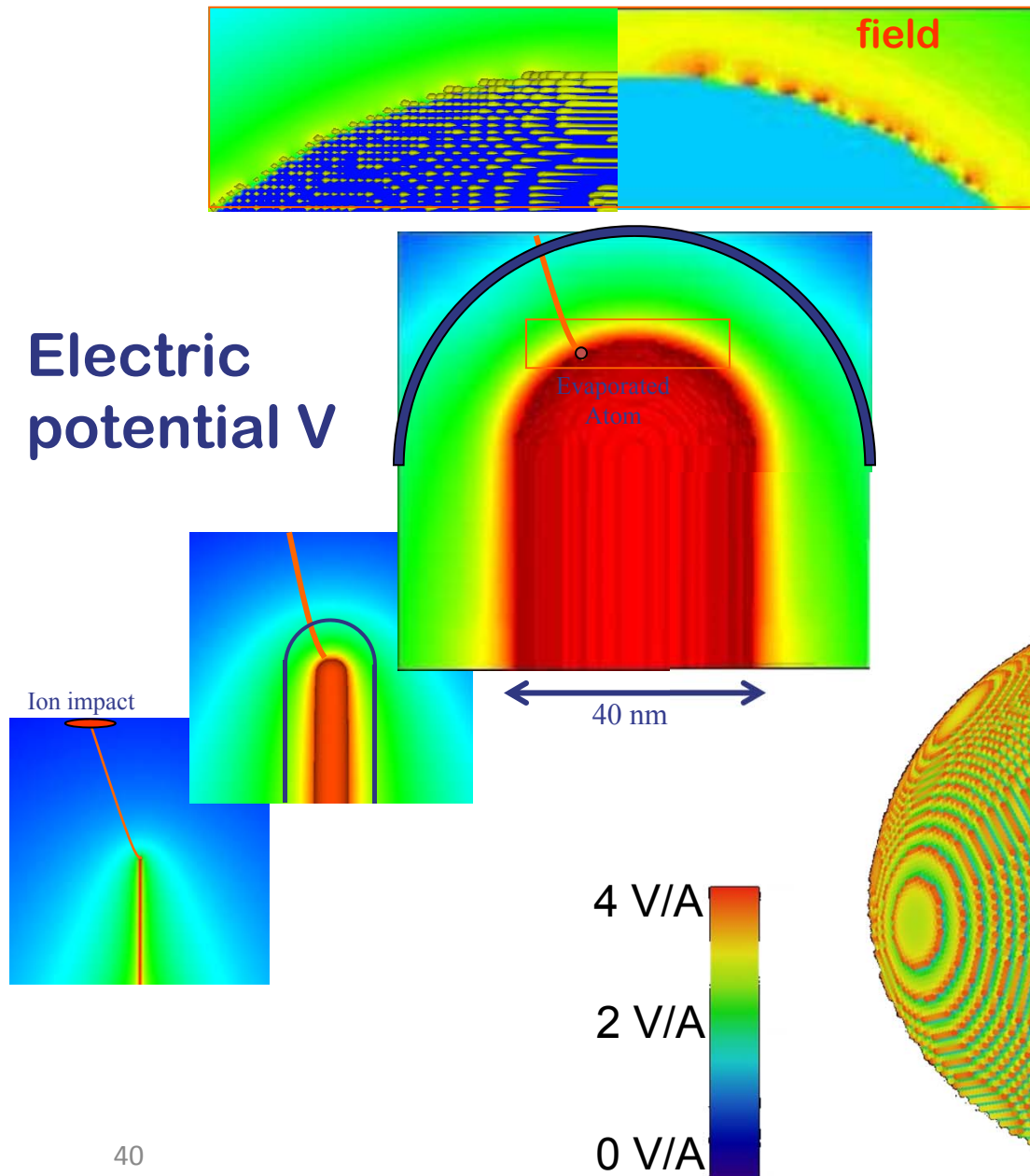
$$\left[\frac{2r_i}{\delta z_{i+} \cdot \delta z_{i-}} + \frac{2r_i + (\delta r_{i-} - \delta r_{i+})}{\delta r_{i+} \cdot \delta r_{i-}} \right] V(r_i, z_i) =$$

$$\left[\frac{2r_i}{\delta z_{i+} \cdot (\delta z_{i+} + \delta z_{i-})} \right] V(r_i, z_{i+1}) + \left[\frac{2r_i}{\delta z_{i-} \cdot (\delta z_{i+} + \delta z_{i-})} \right] V(r_i, z_{i-1}) + \left[\frac{2r_i + \delta r_{i-}}{\delta r_{i+} \cdot (\delta r_{i+} + \delta r_{i-})} \right] V(r_{i+1}, z_i) + \left[\frac{2r_i - \delta r_{i+}}{\delta r_{i-} \cdot (\delta r_{i+} + \delta r_{i-})} \right] V(r_{i-1}, z_i)$$

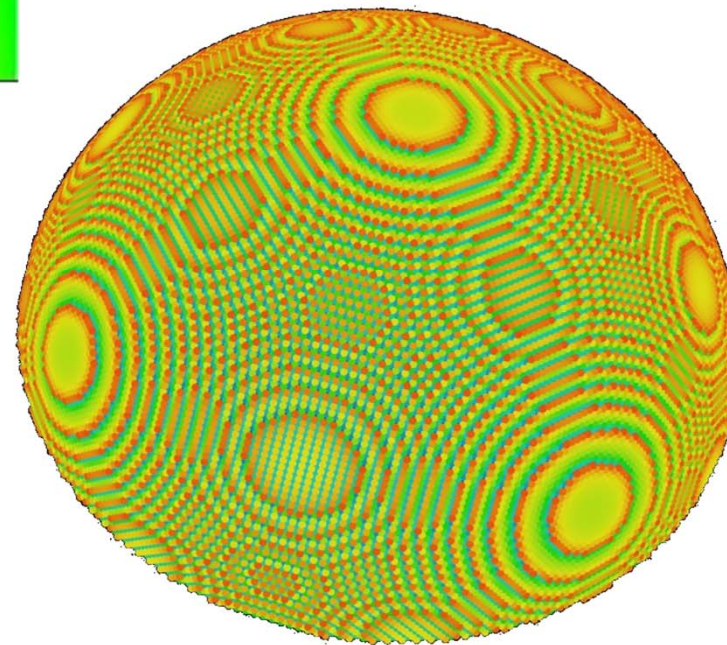


- $\Delta V=0$

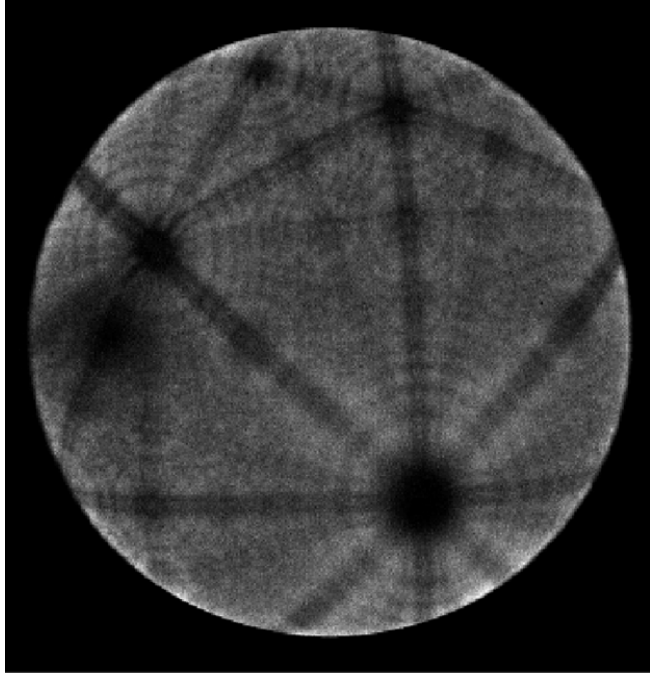
Difficulté de la mise en oeuvre : Multi-échelle et dynamique



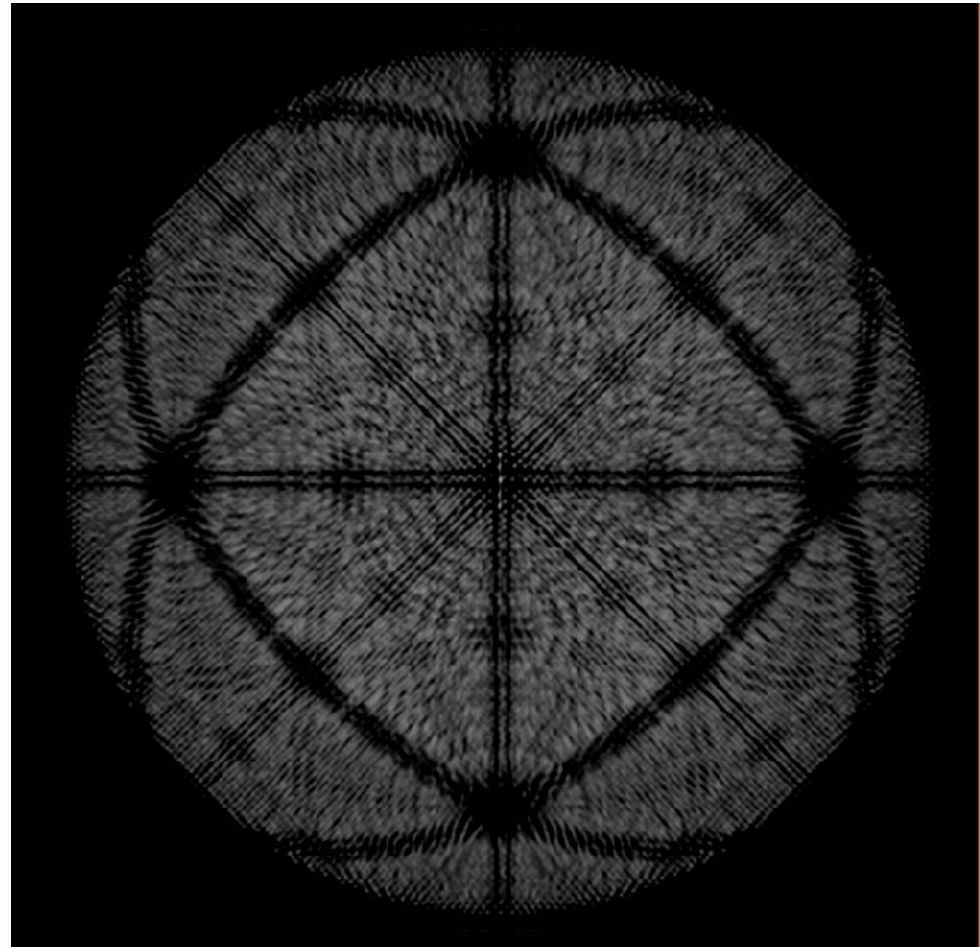
- De l'échelle atomique à l'échelle macroscopique
- Champ derive de V ($\Delta V = 0$)
- Trajectoires (PFD)



Champ local induit des artefacts

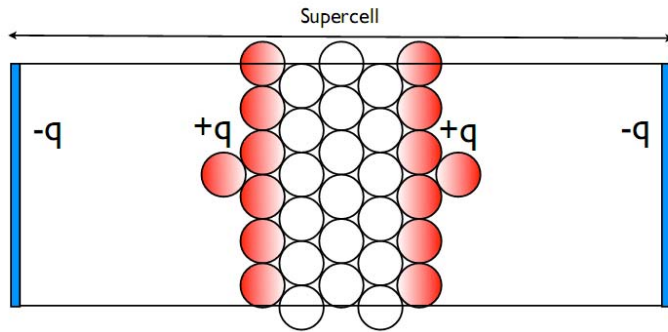


Experimental desorption
image (pure Al)
Image CAMECA



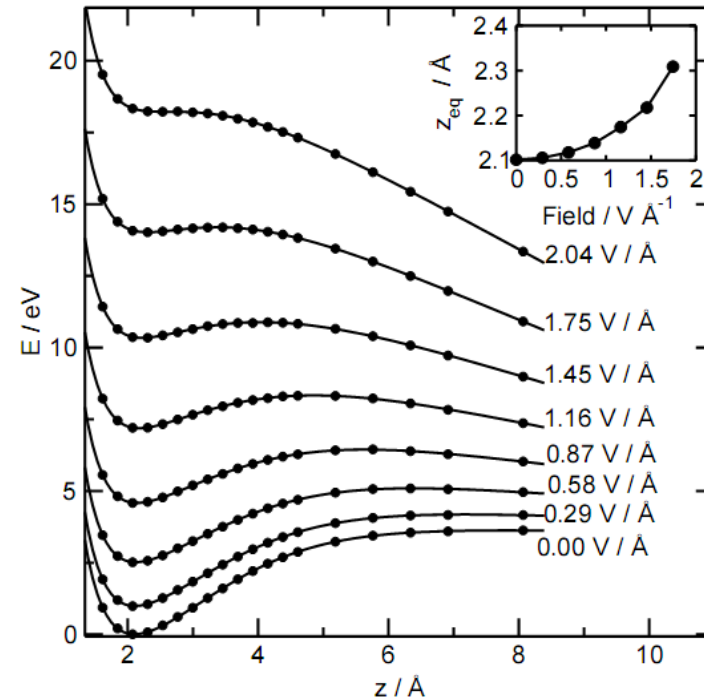
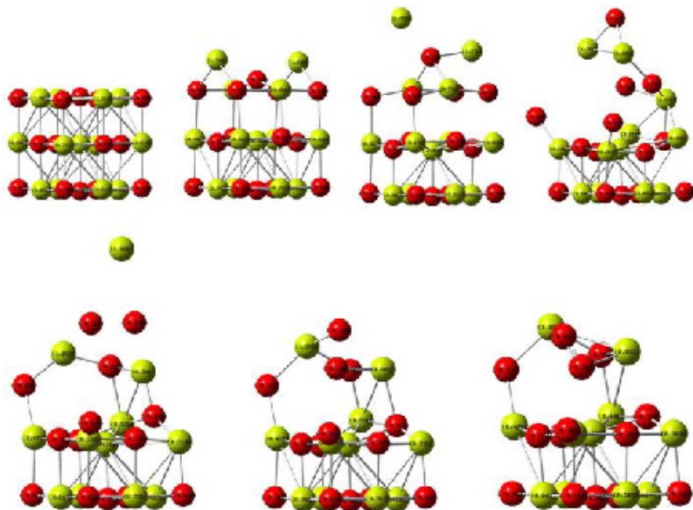
Simulated desorption image

A l'échelle local : effet quantique à prendre en compte...



- Calcul Ab-Initio, ex: Sanchez
(numerical model)

MgO field evaporation (courtesy of J. Kreuzer)



*Processus pas encore
décrit de manière
satisfaisante*

Exemple 2 : Interaction laser matière

FDTD : finite difference time domain
FDTD solution from Lumerical

Resolution numérique des équations de Maxwell en 3D

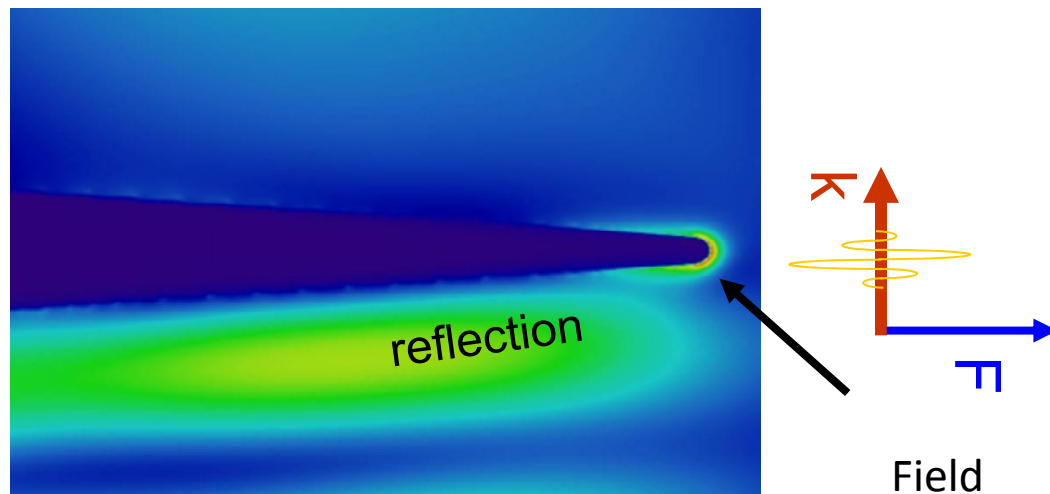
Maxwell equations

$$\nabla \times \vec{E} = -\frac{\partial \mu \vec{H}}{\partial t}$$

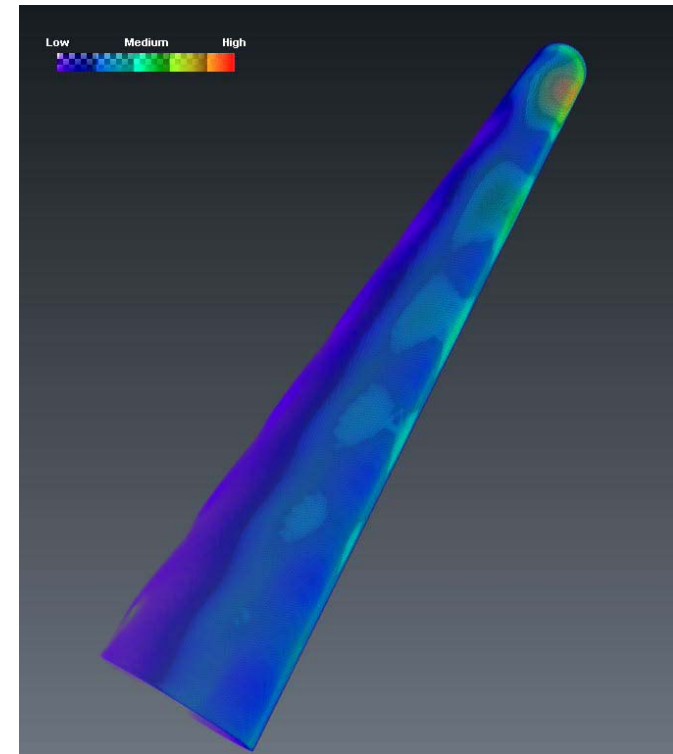
$$\nabla \times \vec{H} = \vec{J} + \frac{\partial \epsilon \vec{E}}{\partial t}$$

Absorbed energy

$$Q_{abs} = \text{div}(\vec{E} \times \vec{H})$$



Absorption map



Electronic temperature

Evolution de la température (modèle 3D)

$$C_e(T_e(\vec{r}, t)) \frac{\partial T_e(\vec{r}, t)}{\partial t} = -\vec{\nabla} \cdot \vec{Q}_e(\vec{r}, t) - g \{T_e(\vec{r}, t) - T_l(\vec{r}, t)\} + S(\vec{r}, t)$$

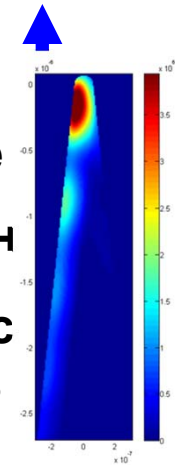
Heat flux

electron-phonon coupling constant

Lattice temperature

$$C_l \frac{\partial T_l(\vec{r}, t)}{\partial t} = -\vec{\nabla} \cdot \vec{Q}_l(\vec{r}, t) + g \{T_e(\vec{r}, t) - T_l(\vec{r}, t)\}$$

Heat source : FDTD + ballistic effects



**Electronic
temperature**

2500 K

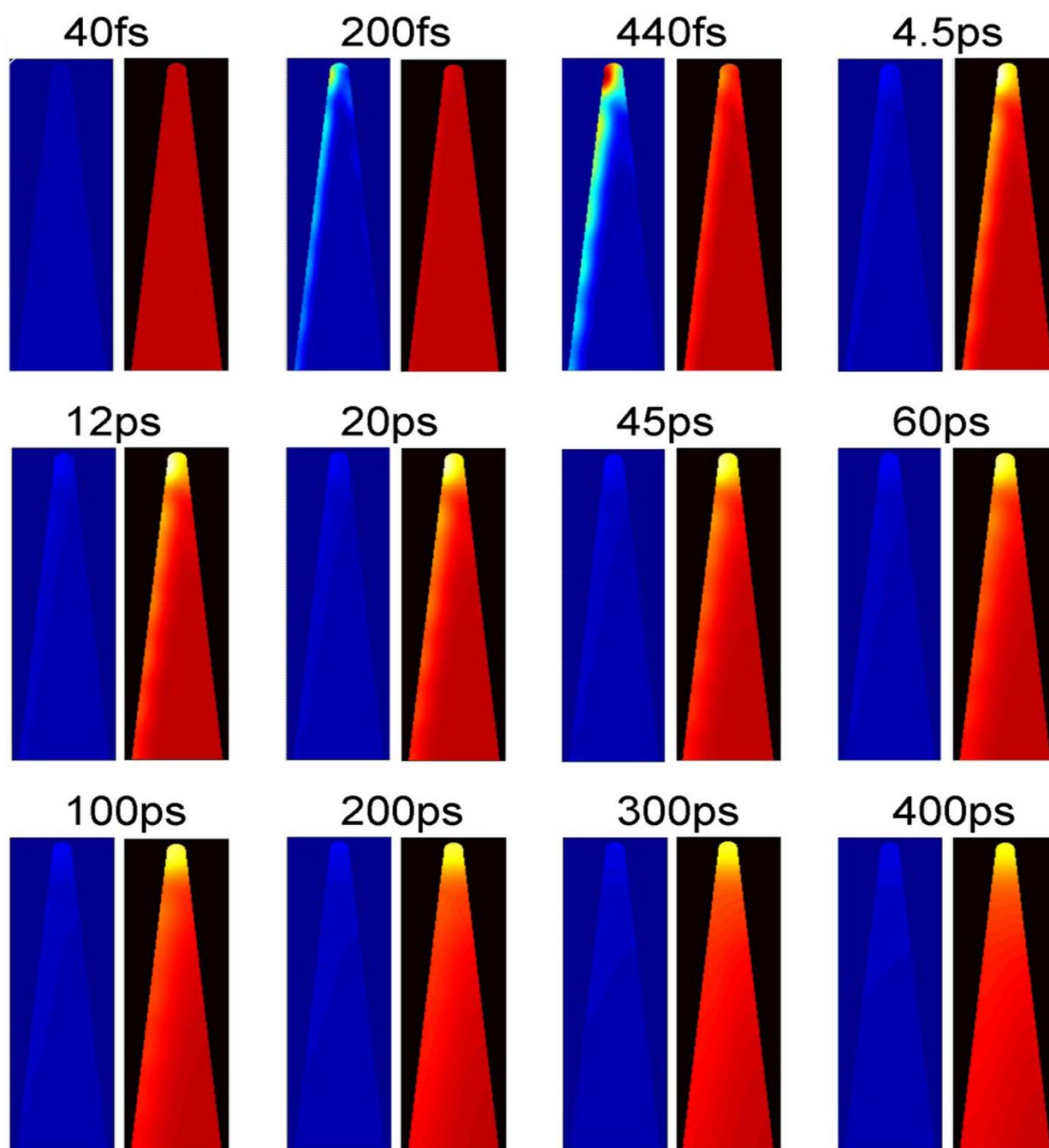
2000 K

1500 K

1000 K

500 K

0 K



**Lattice
temperature**

300 K

250 K

200 K

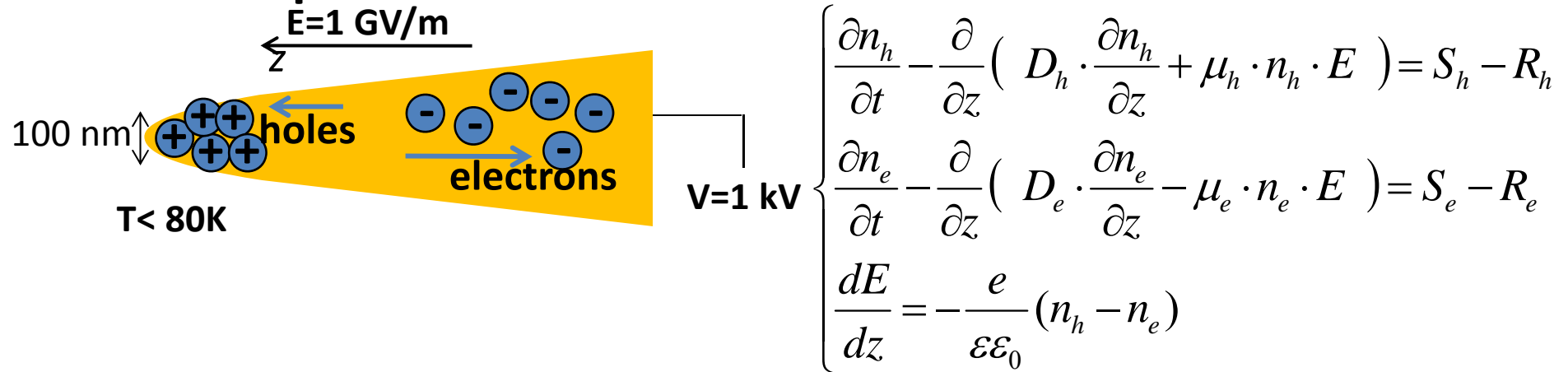
150 K

100 K

50 K

0 K

Exemple 3 : Dans les semiconducteurs



- Free carriers in silicon move under huge electric field $E = 1 \text{ GV/m}$
- Mobility is high at low temperature $\mu = 20\,000 \text{ cm}^2(\text{Vs})^{-1}$
- Carrier accumulation zone at the tip apex $\sim 1 \text{ nm}$
- Required spatial resolution $\Delta z = 1 \text{ \AA}$

- Explicite finite-difference method gives stable solution if $\Delta t \leq \frac{\Delta z}{\mu E} = 5 \cdot 10^{-20} \text{ s}$

we need results at 1 ns → very long calculation time → 3D calculation almost impossible