Precipitation in a multicomponent alloy: combining atomic and mesoscopic simulations

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Multimat workshop
Institut Henri Poincarré

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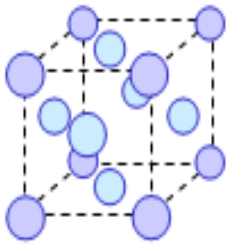
Introduction : Al-Zr-Sc Alloy

Zr and Sc precipitation in Al alloys



Al Zr/Sc

- → Al_3Zr ($L1_2$) $x^{eq}_{Zr} \leq 0.27$ at.%
- → Al_3Sc ($L1_2$) $x^{eq}_{Sc} \leq 0.24$ at.%
- → $Al_3Zr_xSc_{1-x}$ ($L1_2$)

Model system for ordering alloys

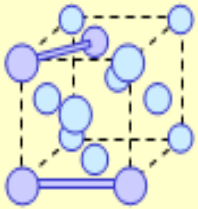
Interaction between solute atoms: - repulsive for 1st n. n.
- attractive for 2nd n. n.
- no interaction beyond

➡ Validate mesoscopic modeling of precipitation by confronting them with atomic simulations

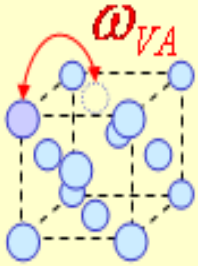
Introduction : Modeling Approach

Ab-initio calculations
Experimental data

Atomic model (KMC)



Rigid lattice



Vacancy - atom exchange

Mesoscopic models
(cluster dynamics)

Difficulties :
- validity of hypothesis
- predictions for ternary alloys

Comparison
(reachable super-saturations and annealing times)

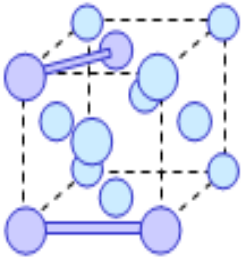
Experimental characterization of precipitation kinetics

No direct comparison
(super-saturations)

Thermodynamics :

Rigid lattice with pair interactions (Ising model)

- 1st nearest neighbours
- 2nds nearest neighbours

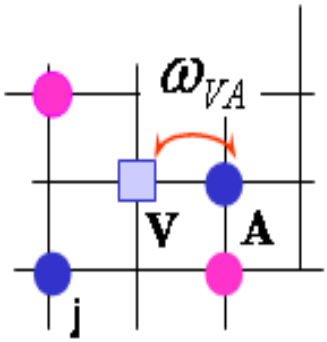


$$E = \frac{1}{2}\sum_{\substack{i \neq j \\ \alpha,\beta}} \varepsilon^{(1)}_{\alpha\beta} n_i^{\alpha} n_j^{\beta} + \frac{1}{2}\sum_{\substack{i \neq j \\ \alpha,\beta}} \varepsilon^{(2)}_{\alpha\beta} n_i^{\alpha} n_j^{\beta}$$

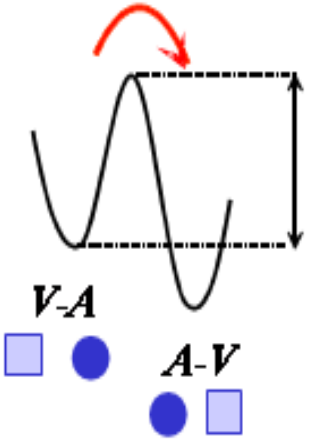
Atomic Model

Kinetics :

Atom-vacancy exchange thermally activated



$$\omega_{VA} = \nu_A \exp\left(-E_{VA}^{act} / k_B T\right)$$



$$E_{VA}^{act} = E_A^S - \sum_{\substack{j \\ \beta}} \varepsilon_{V\beta} n_j^{\beta} - \sum_{\substack{j \\ \beta}} \varepsilon_{A\beta} n_j^{\beta}$$

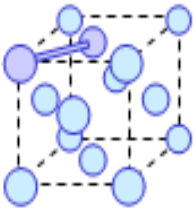
KMC using resident time algorithm :

At each time step :

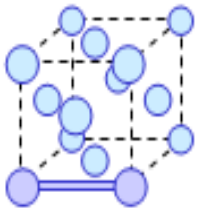
- calculate all transition probabilities ω_i of the vacancy (only 12)
- choose the next configuration according to this distribution of probabilities (random number)
- increment time with $\delta t = 1 / \Sigma_i \, \omega_i$

Atomic Model : Parameters

- Formation free energies $\Delta F(Al_3Zr)$ et $\Delta F(Al_3Sc)$
  - → ab initio calculations (energy + vibration entropy)



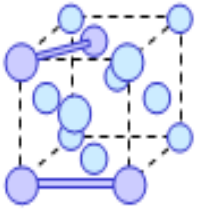
$\varepsilon^1_{Al\text{-}Zr}(T)$
$\varepsilon^1_{Al\text{-}Sc}(T)$



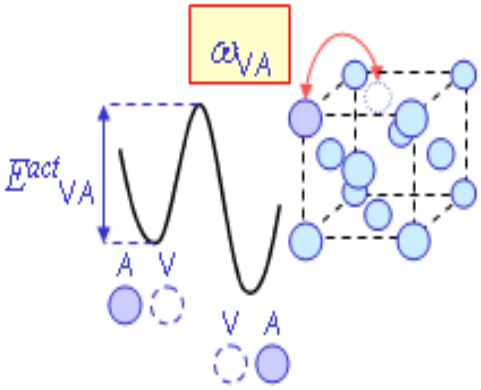
$\varepsilon^2_{Al\text{-}Zr}(T)$
$\varepsilon^2_{Al\text{-}Sc}(T)$

- Solubility limits
  - → Zr in Al : ab initio / experimental ♣
  - → Sc in Al : experimental data

- Formation energies of ternary ordered compounds
  - → ab initio calculations (energy)



$\varepsilon^1_{Sc\text{-}Zr}$
$\varepsilon^2_{Sc\text{-}Zr}$

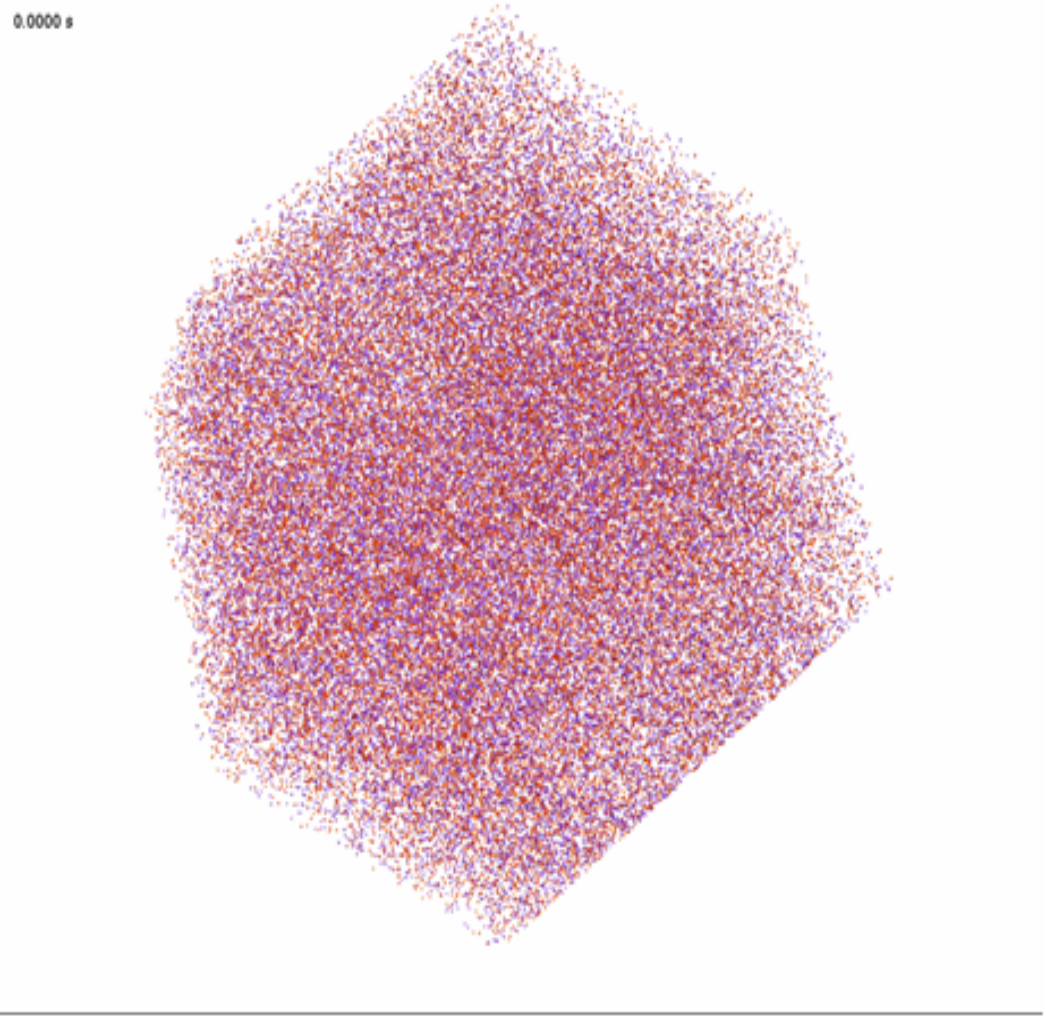


- Vacancy thermodynamics (E^{for}_V, E^{bin}_{ZrV}, E^{bin}_{ScV})
- Diffusion coefficients $D_{Al^*}(T)$, $D_{Sc^*}(T)$ et $D_{Zr^*}(T)$
  - → experimental data

♣ E. Clouet, J. M. Sanchez and C. Sigli, Phys. Rev. B **65** (2002) 094105

Atomic Model : Simulations

Precipitation in Al-Zr-Sc alloy



Aluminum solid solution

c^0_{Zr} = 0.5 at.%

c^0_{Sc} = 0.5 at.%

T = 550°C

200^3 lattice sites

1 vacancy

- Zr
- Sc

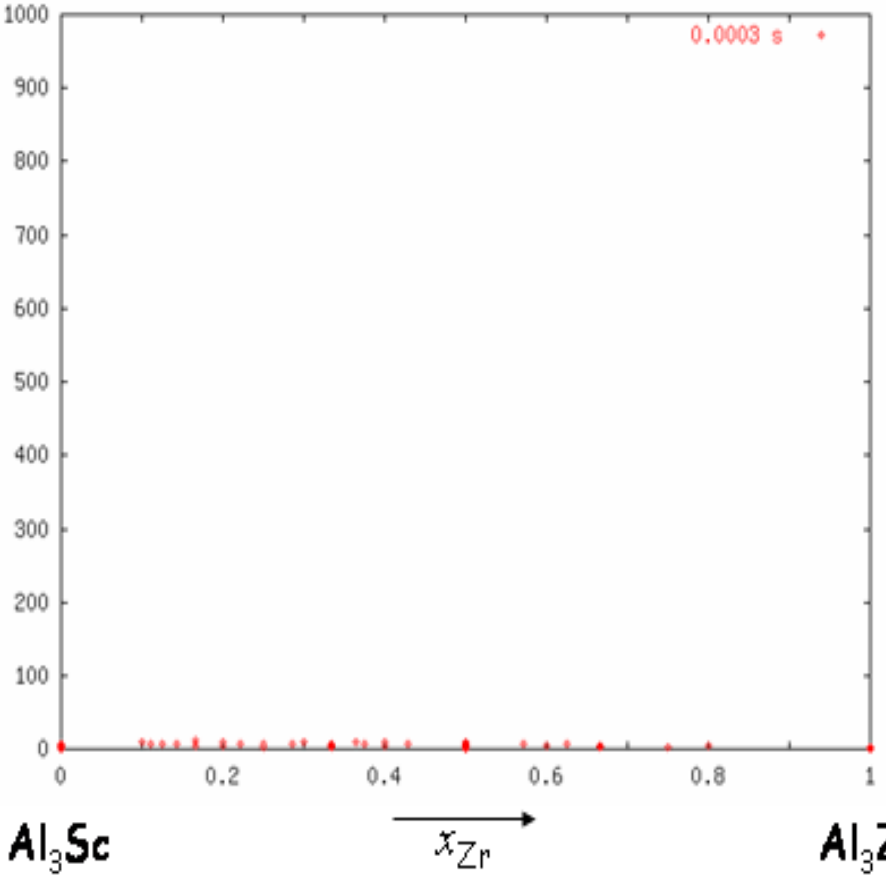
Explanation :

$D_{Sc} >> D_{Zr}$

Atomic Model : Simulations

Precipitation in Al-Zr-Sc alloy

Precipitates' size (atoms)



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Atomic Model : Simulations

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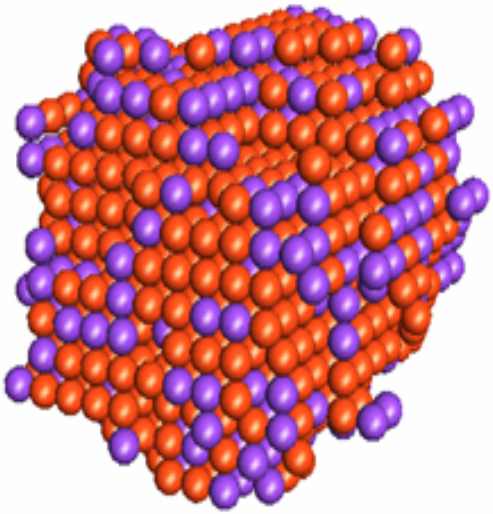
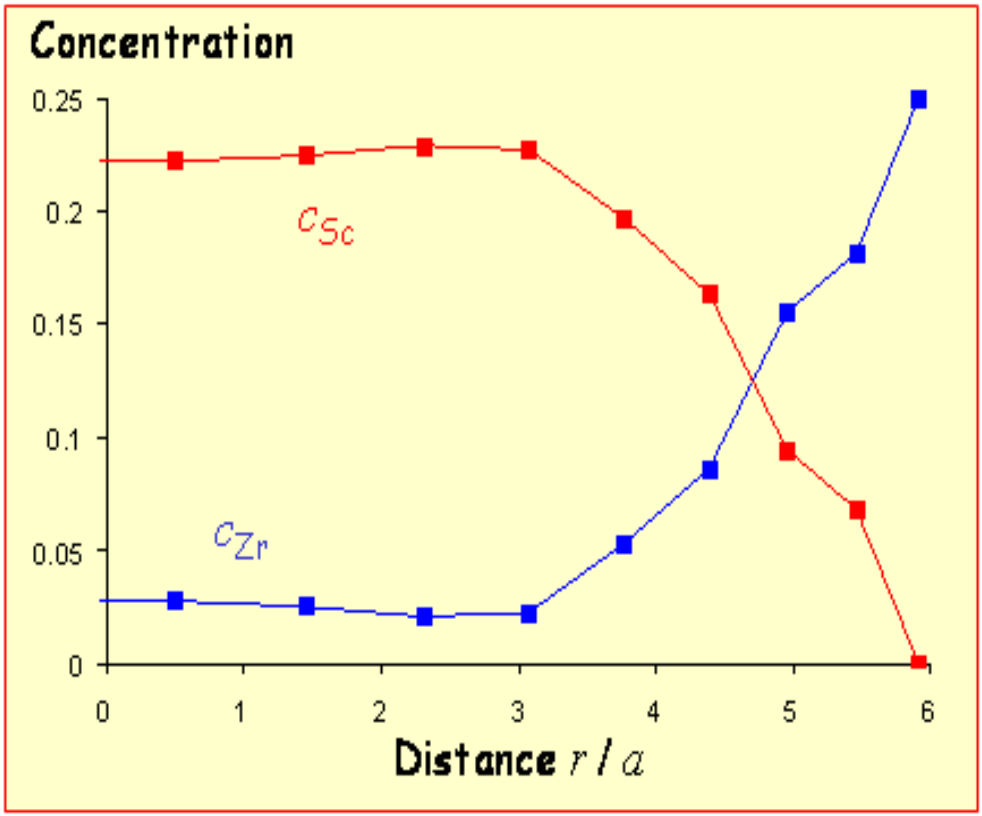


Zr Sc



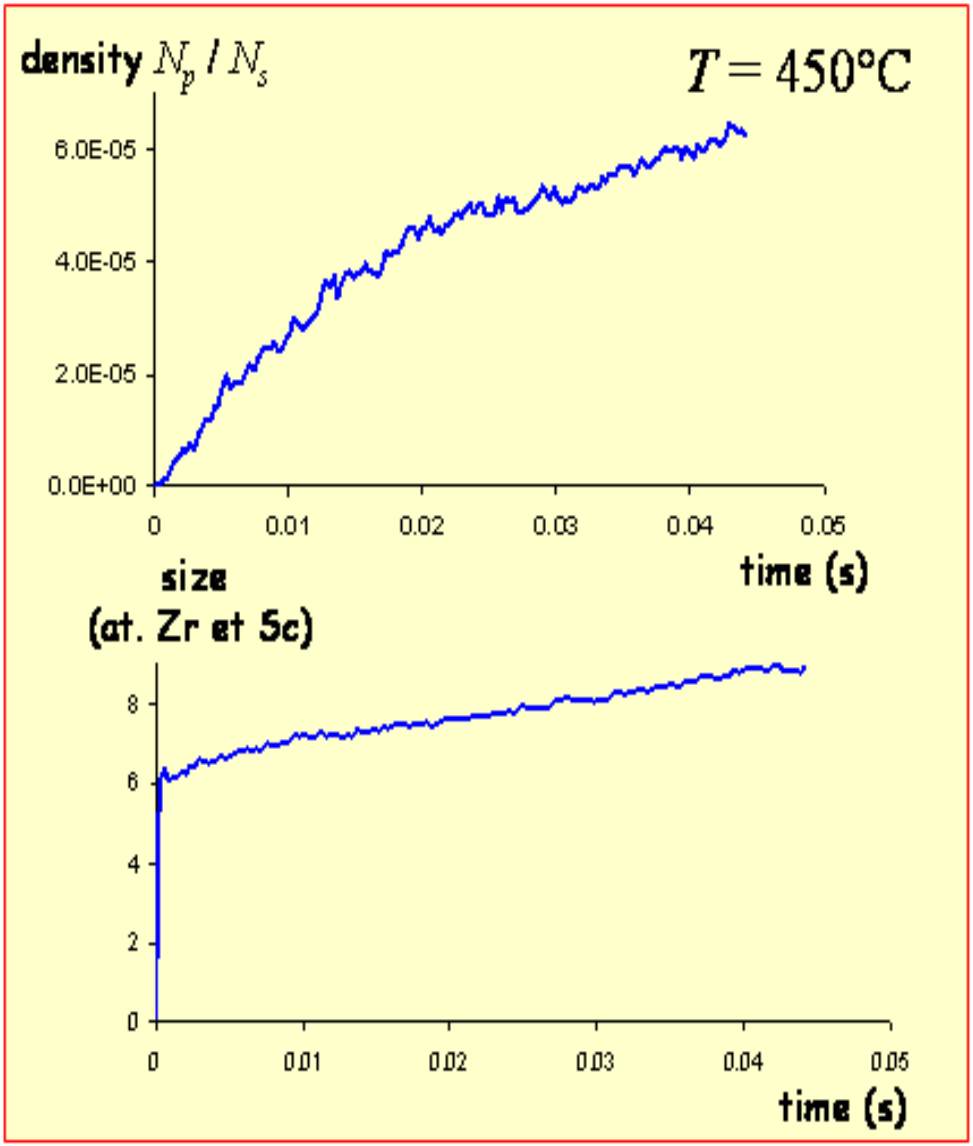
In agreement with experimental observations (3D atom probe[1] / HREM[2])

1 B. Forbord, W. Lefebvre, F. Danoix, H. Hallem and K. Marthinsen, Scr. Mater. **51** (2004) p.333
2 A. Tolley, V. Radmilovic and U. Dahmen, Scr. Mater. **52** (2005) p.621

Atomic Model : Simulations

c_{Sc} constant

- 0% Zr - 0.5% Sc



Atomic Model : Simulations

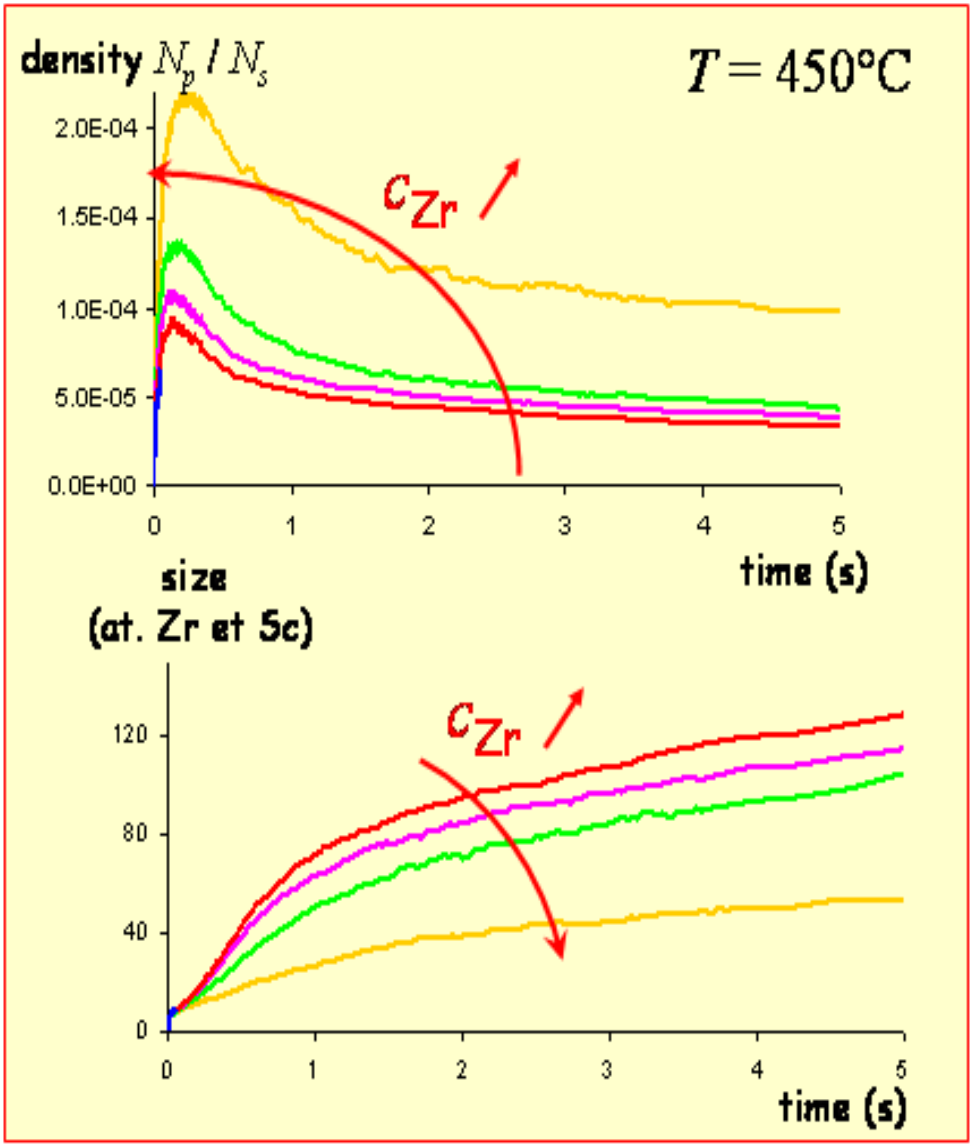
c_{Sc} constante

- 0% Zr - 0.5% Sc
- 0.05% Zr - 0.5% Sc
- 0.1% Zr - 0.5% Sc
- 0.2% Zr - 0.5% Sc
- 0.5% Zr - 0.5% Sc

Zr Addition :

- → increases precipitates' density
- → decreases precipitates' size

In agreement with experimental observations



Atomic Model : Simulations

Precipitation in Al-Zr-Sc alloy

- Thermodynamic factor ($\omega^2_{ZrSc} \leq 0$)
  → Formation of nuclei containing Zr and Sc atoms

- Kinetic factor ($D_{Sc} >> D_{Zr}$)
  → Nuclei growth by Sc absorption

- Decreasing of Sc concentration in the solid solution
  → Precipitates' external shelves richer in Zr

Zr addition to Al-Sc alloy

- Nucleation's increase
  → Higher precipitates' density

- No influence on the growth stage
  → Smaller precipitates (less Sc available for growth after nucleation)

Modeling Approach

Ab-initio calculations
Experimental data

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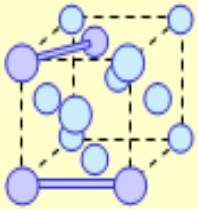
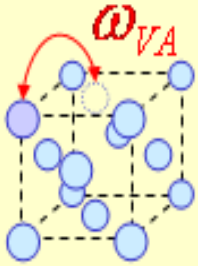


Rigid lattice



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Difficulties :

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Comparison
(reachable super-saturations and annealing times)

Experimental characterization of precipitation kinetics

No direct comparison
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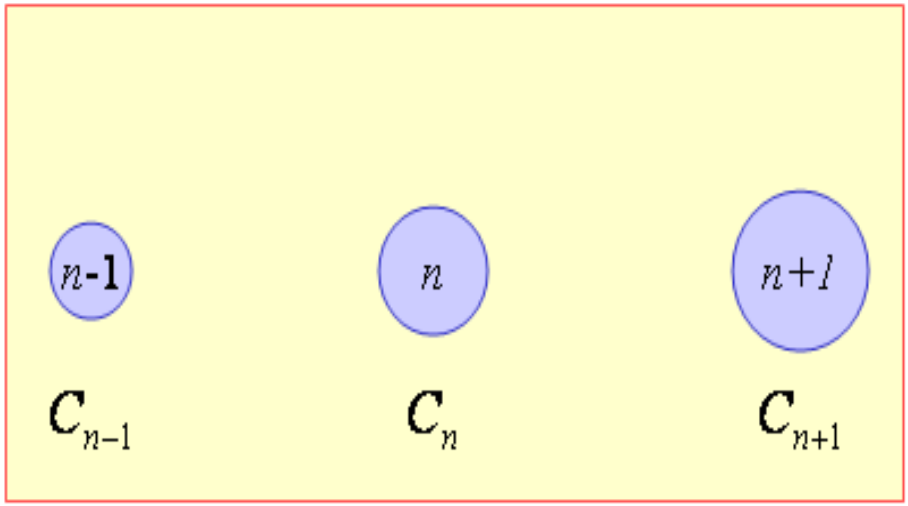
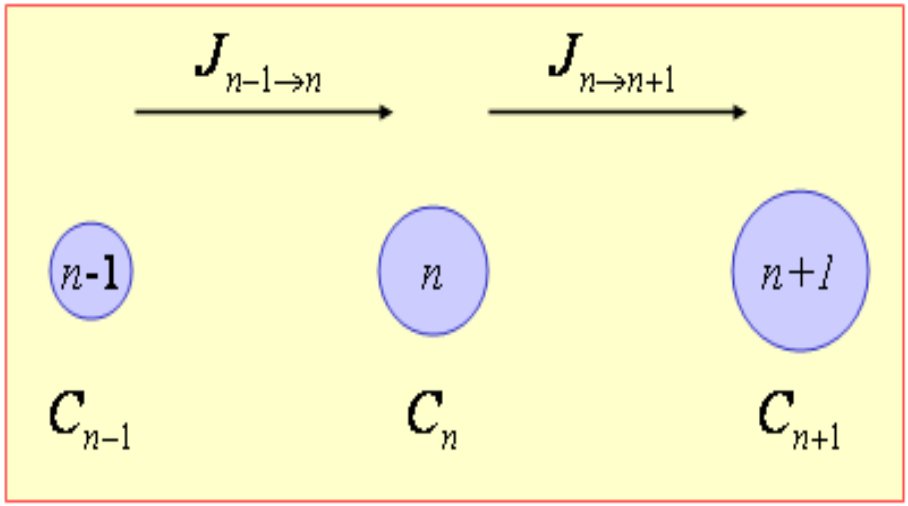
Cluster Dynamics : Theory



Cluster population described by its size distribution C_n

➡ No information on cluster position

Cluster Dynamics : Theory



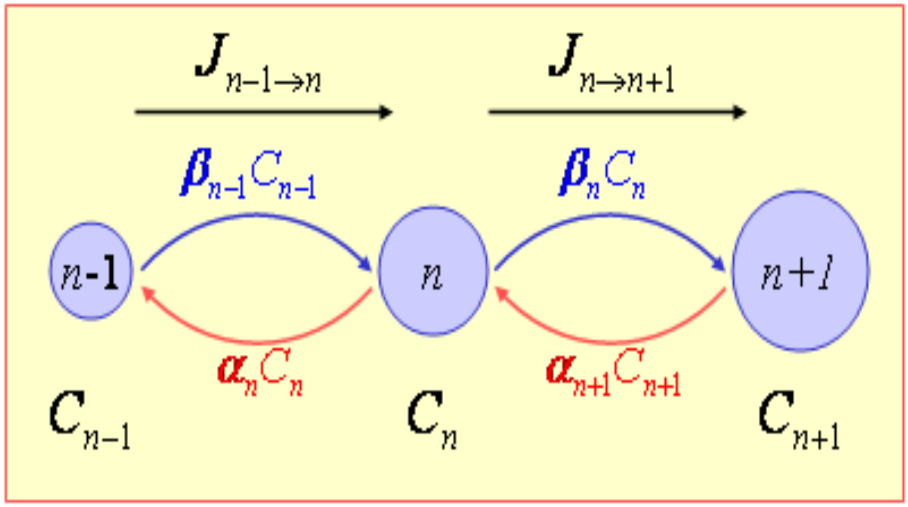
Time evolution of the distribution

$$\frac{dC_n}{dt} = J_{n-1\to n} - J_{n\to n+1} \quad , \quad \forall n \geq 2$$

$$\frac{dC_1}{dt} = -2J_{1\to 2} - \sum_{n\geq 2} J_{n\to n+1}$$

➡ Flux only between adjacent classes

Cluster Dynamics : Theory



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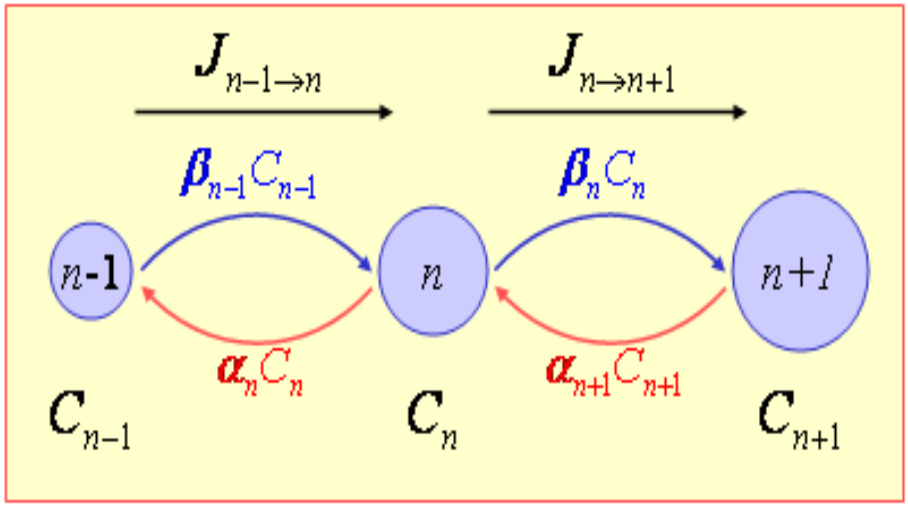
$$J_{n\to n+1} = \beta_n C_n - \alpha_{n+1} C_{n+1}$$

- Monomer absorption
- Monomer emission

Cluster Dynamics : Theory



- **Absorption** controlled by the long-range diffusion of monomers

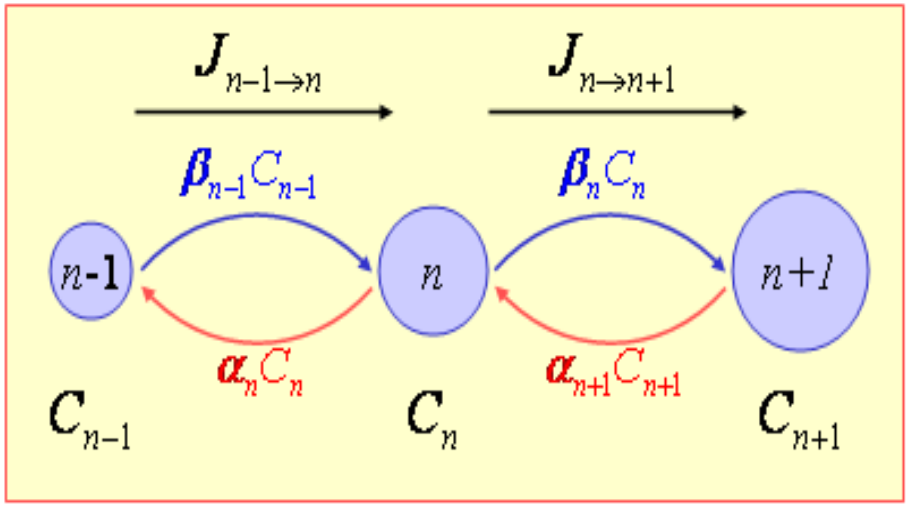
$$\beta_n = 4\pi R_n D_1 C_1$$

- **Emission** : intrinsic property of the cluster
  (do not depend of the embedding solid solution)

Fluxes equilibrium in a saturated solid solution

$$\Rightarrow \quad \alpha_{n+1} = \frac{\overline{\beta}_n \overline{C}_n}{\overline{C}_{n+1}} = 4\pi R_n D_1 \frac{\overline{C}_1 \overline{C}_n}{\overline{C}_{n+1}} = f(D_1, \sigma_n)$$

Cluster Dynamics : Theory



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$$\beta_n = 4\pi R_n D_1 C_1$$

- **Emission** : intrinsic property of the cluster

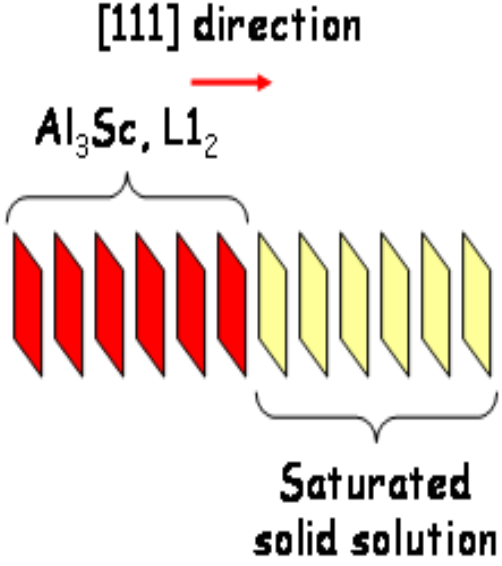
$$\alpha_n = f(D_1, \sigma_n)$$

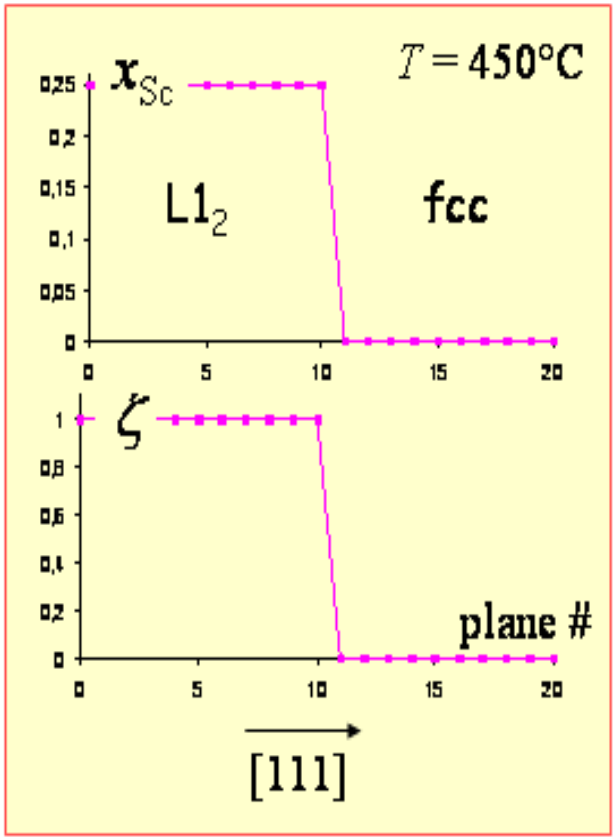
➡ No information on the nucleation driving force
assumed thermodynamics = lattice gas

➡ Only 2 parameters : D_1 and σ_n

Interface Free Energy

Al_3Sc, $L1_2$ / Al fcc: planar interface



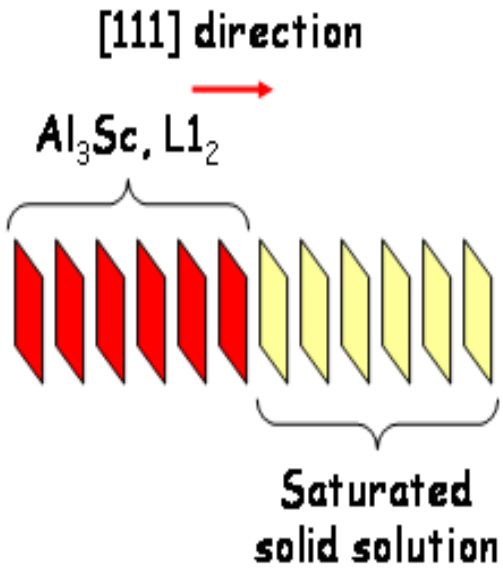


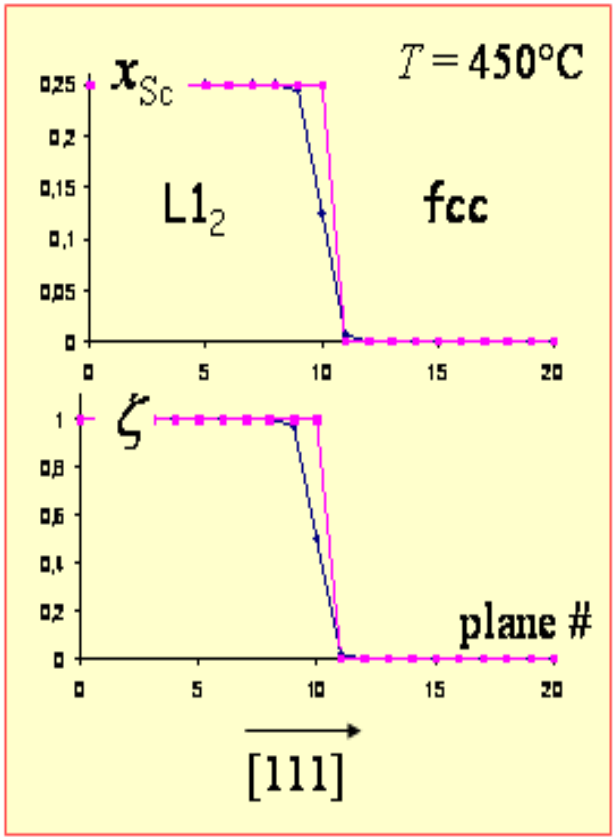
Interface Free Energy

Al_3Sc, $L1_2$ / Al fcc: planar interface

Relaxation within Bragg-Williams approximation:

- concentration
- order parameter





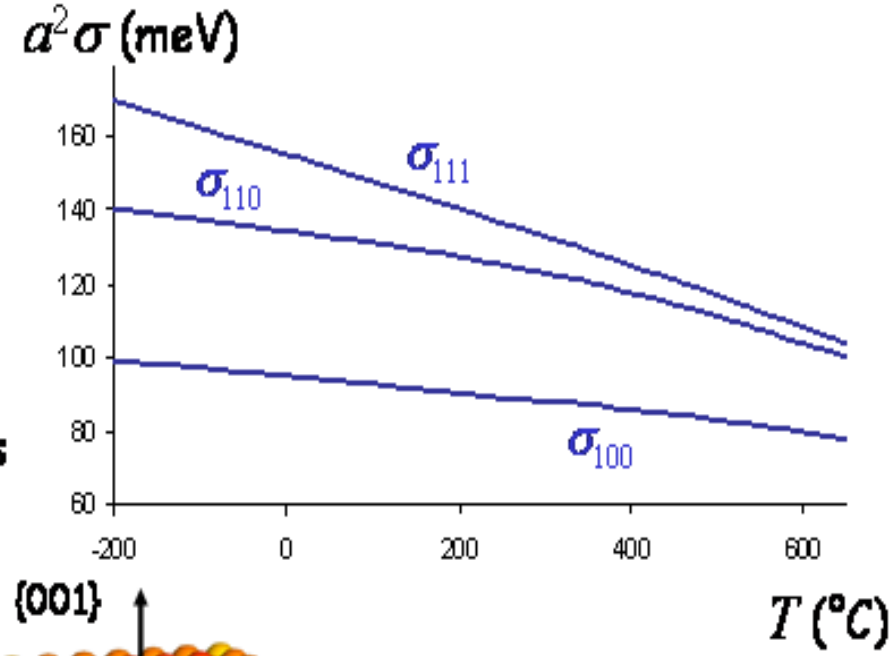
Interface Free Energy

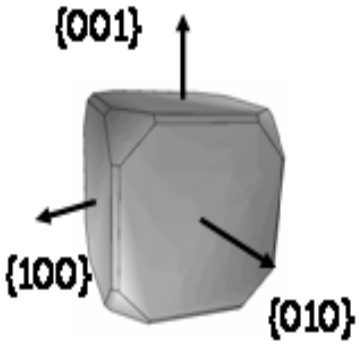
Interface free energy

Planar interfaces

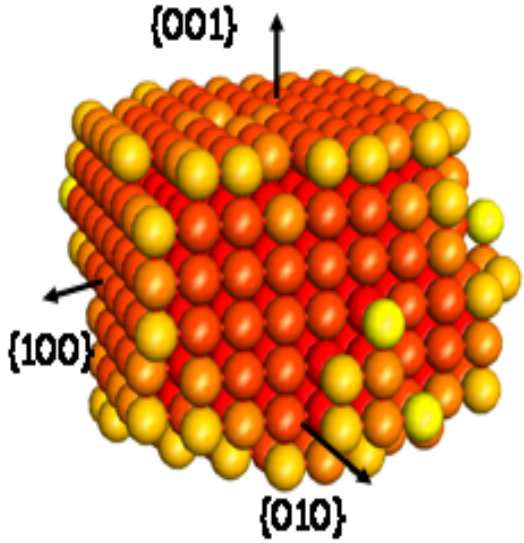
$\sigma_{100} < \sigma_{110} < \sigma_{111}$

➡ Facetted precipitates





Al_3Sc at 450°C



Al_3Sc precipitate (KMC simulation, 450°C, C^0_{Sc} = 0.5 %)

Interface Free Energy

Interface free energy

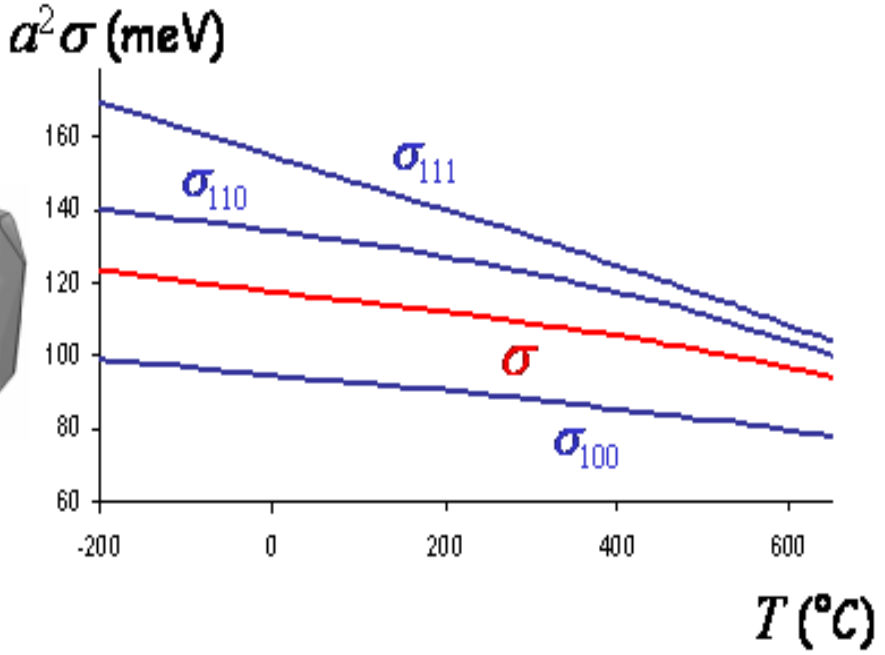
Planar interfaces

$\sigma_{100} < \sigma_{110} < \sigma_{111}$

Wulff construction

σ

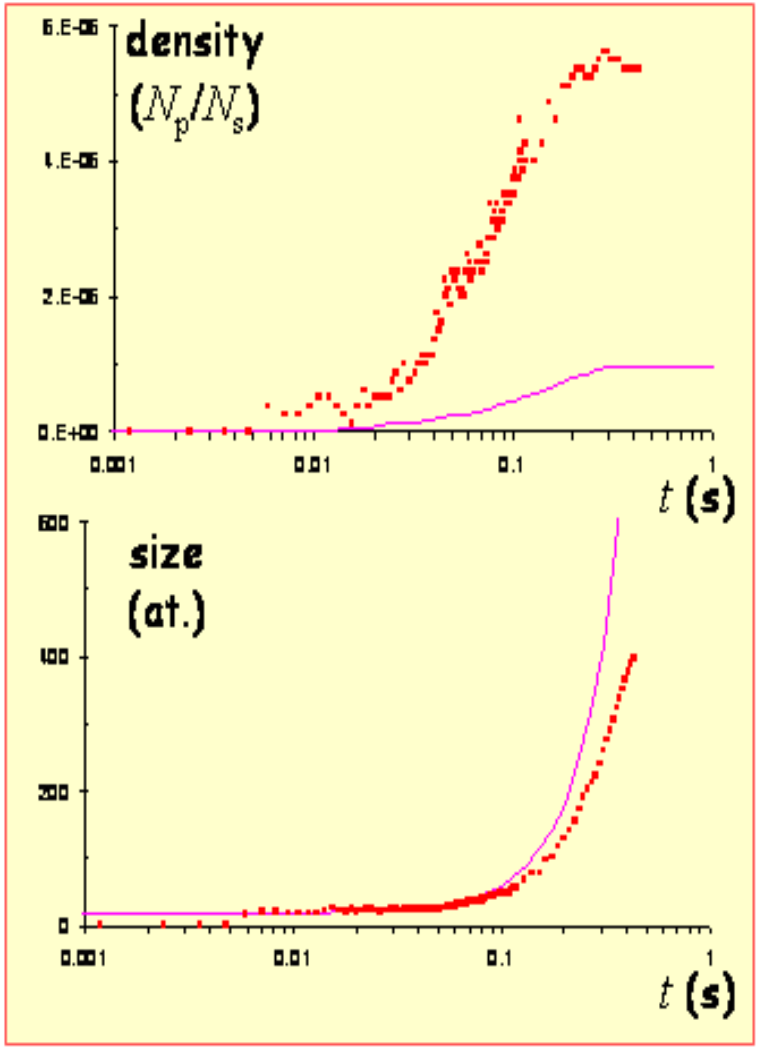
Spherical precipitate



$$\sigma_n = \sigma, \quad \forall\, n$$

Cluster Dynamics : Simulations

Al + 0.4% Sc – T = 500°C



Kinetic Monte Carlo

Cluster Dynamics

Cluster Dynamics : Simulations

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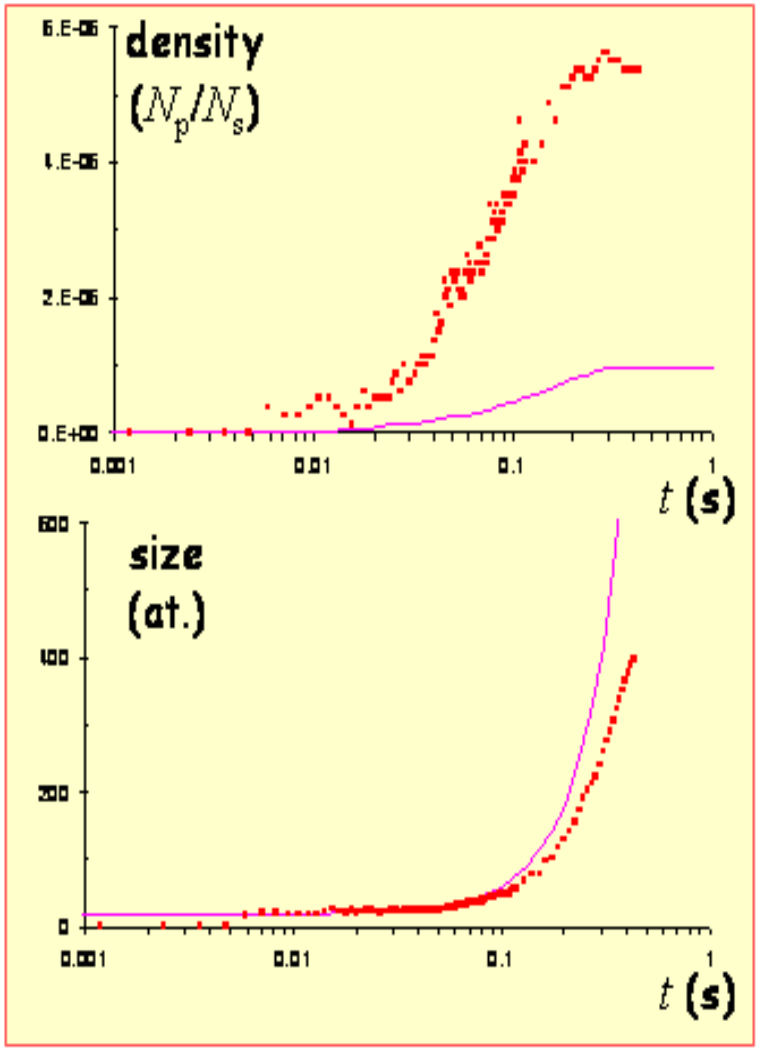
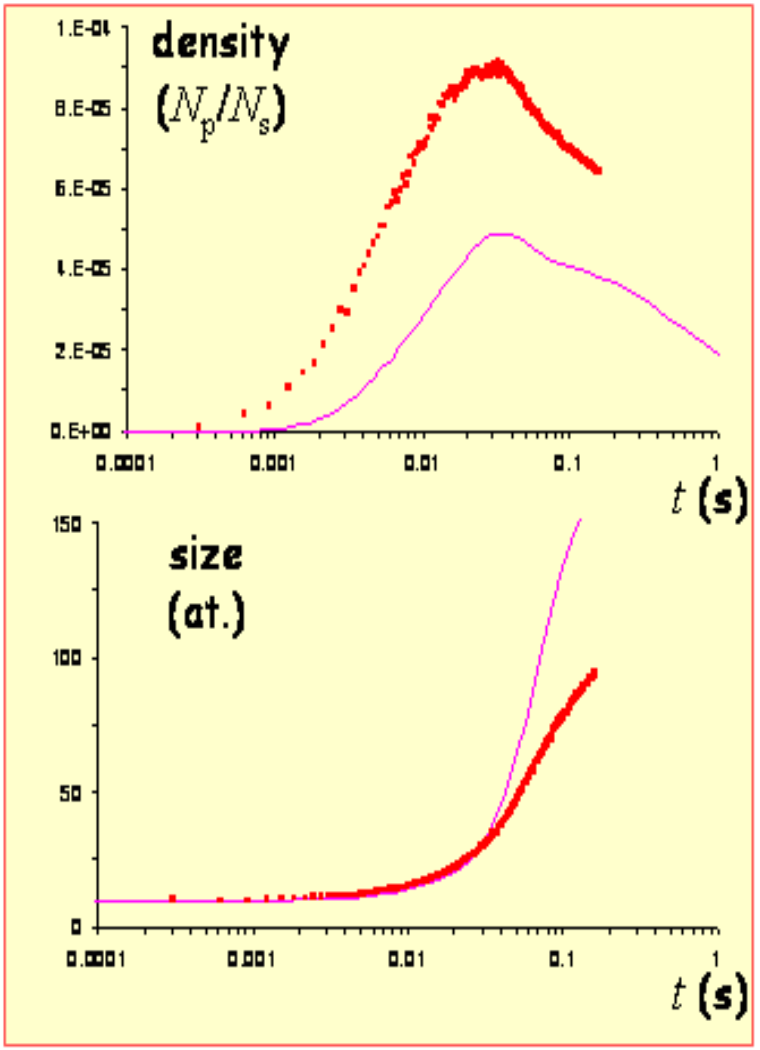


Al + 0.75% Sc – T = 500°C



Interface Free Energy

Dependence with size of σ_n

Counting of all reachable configurations of the cluster for

- each size n ($n < 10$)
- each energy class α

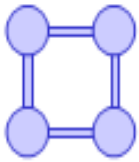
➡ Cluster interface free energy

$$G_n = -kT \ln \left(\Sigma_\alpha D_{n,\alpha} \exp(-H_{n,\alpha} / kT) \right)$$

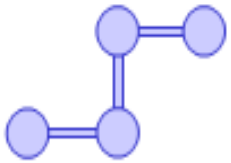
Example : $n = 4$

2 energy classes

↳ σ_n

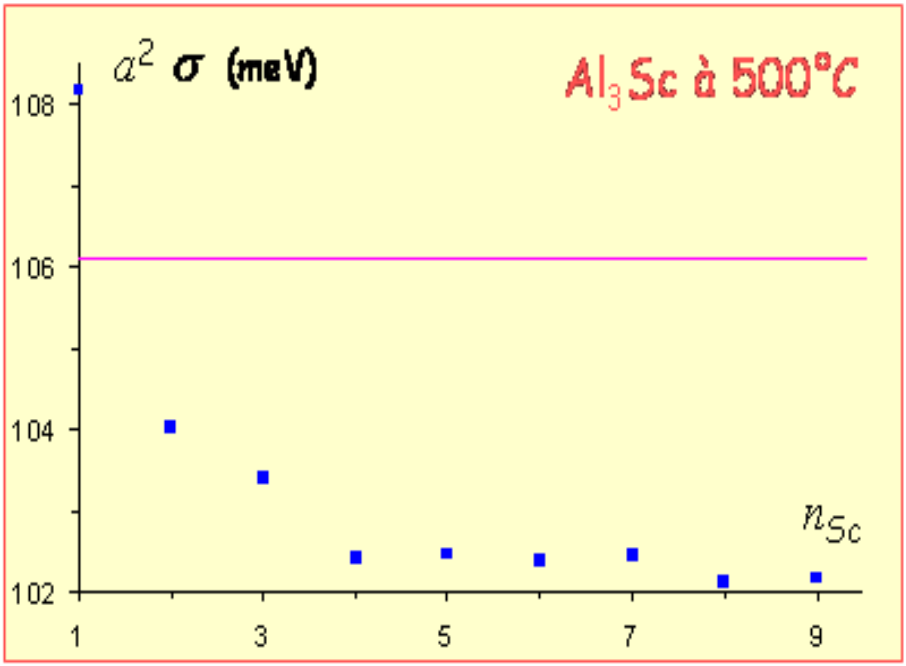


$$H_{4,1} = 16\ \omega^{(2)} \qquad D_{4,1} = 3$$



$$H_{4,2} = 18\ \omega^{(2)} \qquad D_{4,2} = 83$$

Interface Free Energy



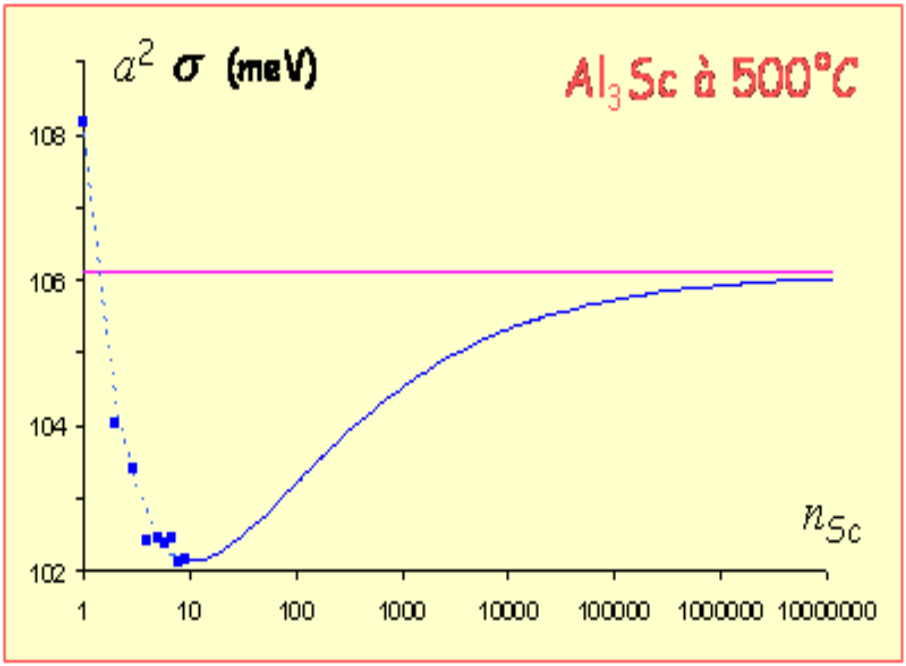
Constant interface free energy

- $\sigma_n = \sigma$ (Bragg-Williams + Wulff)

Interface energy depending on cluster size

- Direct calculation

Interface Free Energy



Constant interface free energy

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Interface energy depending on cluster size

- Direct calculation
- Fitting of

$$\sigma_n = \sigma(1 + cn^{-1/3} + dn^{-2/3})$$

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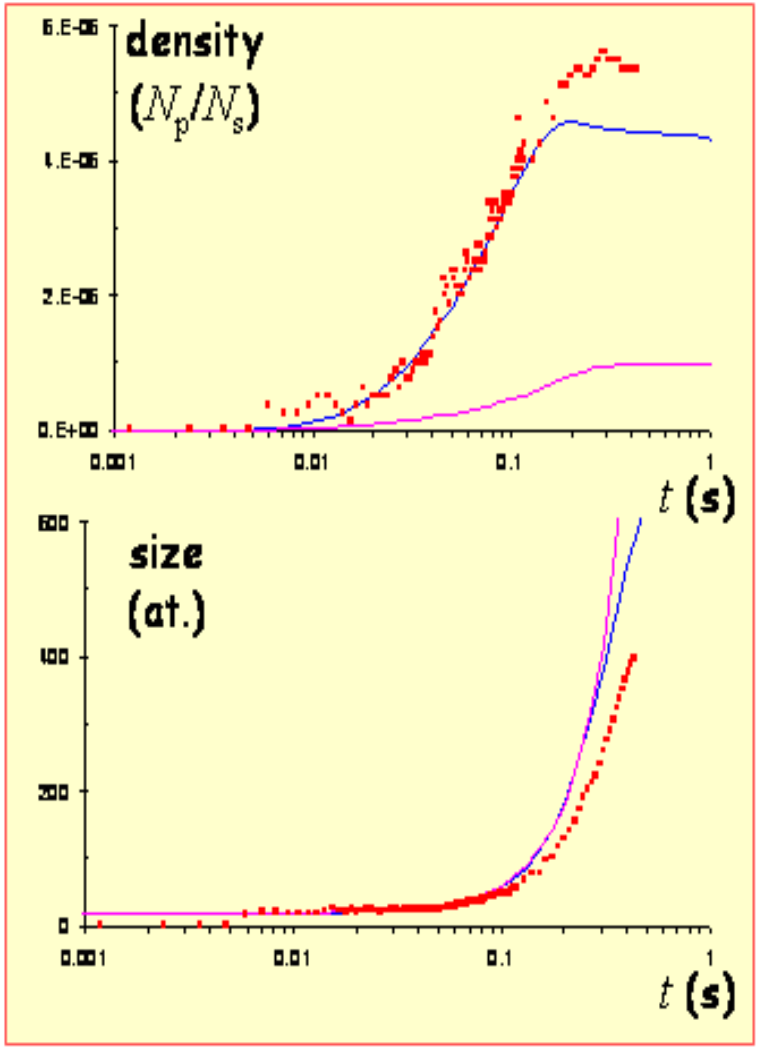
Al + 0.4% Sc – T = 500°C



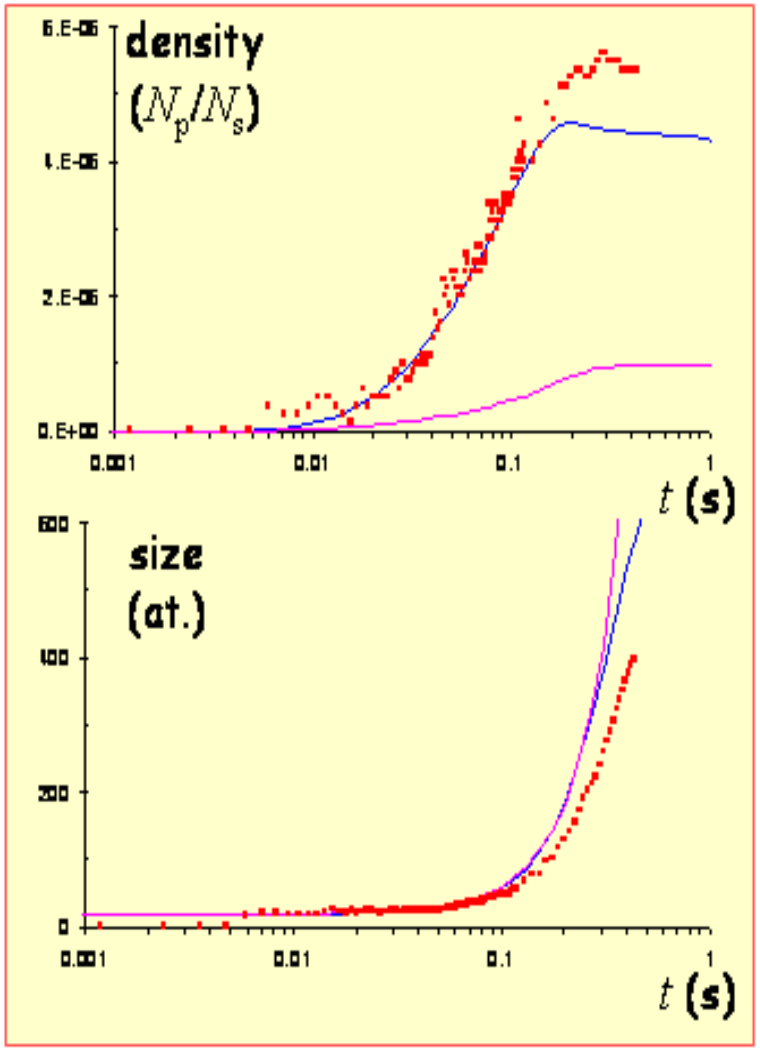
- Kinetic Monte Carlo

Cluster Dynamics

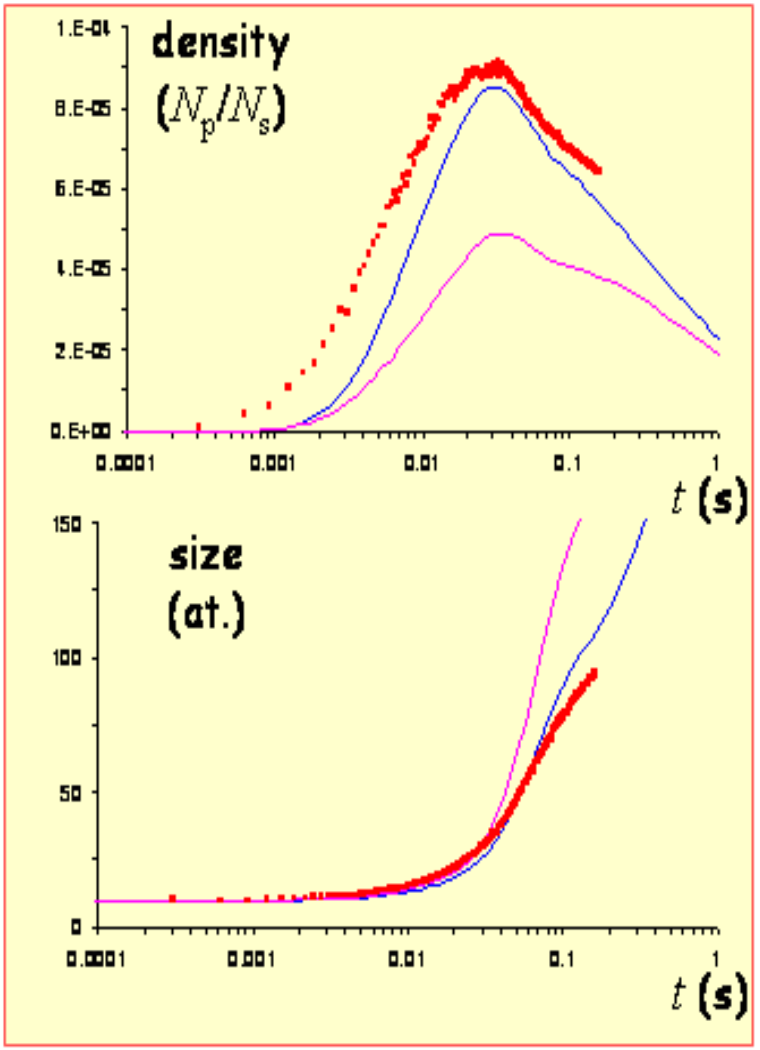
- σ_n constant
- $\sigma_n = f(n)$

Cluster Dynamics : Simulations

Al + 0.4% Sc – T = 500°C



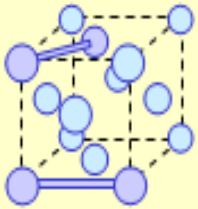
Al + 0.75% Sc – T = 500°C



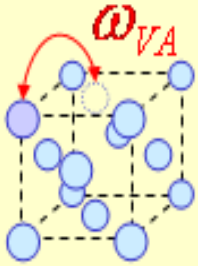
Modeling Approach

Ab-initio calculations
Experimental data

Atomic model (KMC)



Rigid lattice



Vacancy - atom exchange

Mesoscopic models
(cluster dynamics)

Difficulties :

- validity of hypothesis
- predictions for ternary alloys

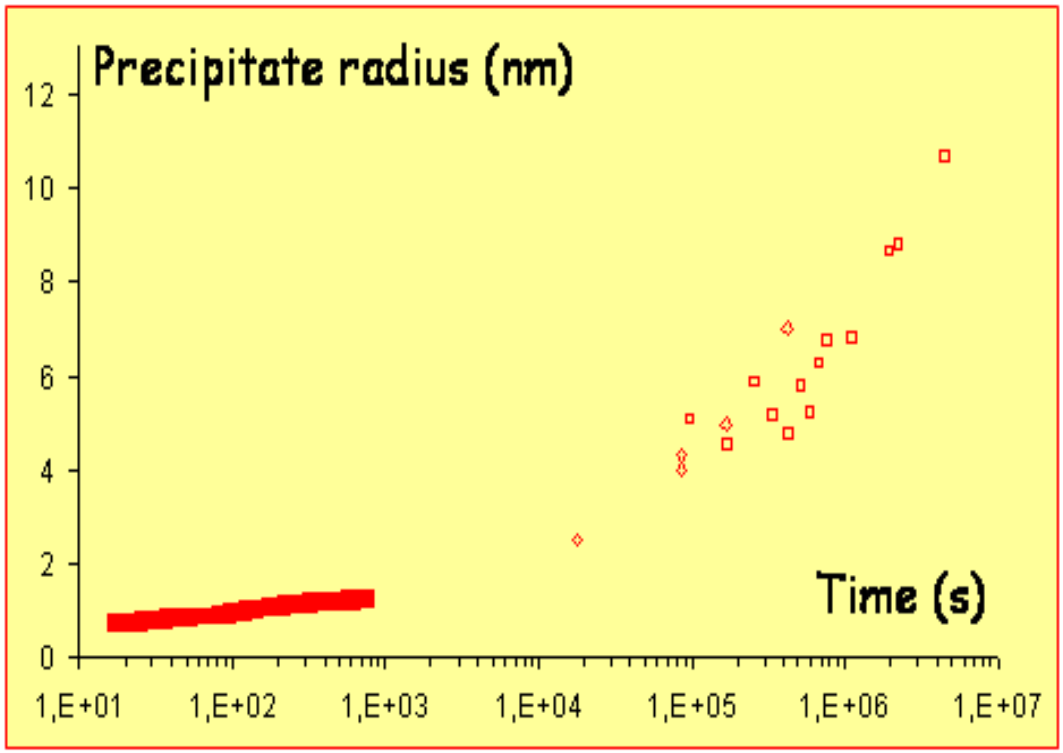
Comparison
(reachable super-saturations and annealing times)

Experimental characterization of precipitation kinetics

No direct comparison
(super-saturations)

Confrontation with Experimental Data

Al + 0.18 % Sc at 350°C : precipitate growth



Experimental data

Ref. 1 □

Ref. 2 ◇

KMC ■

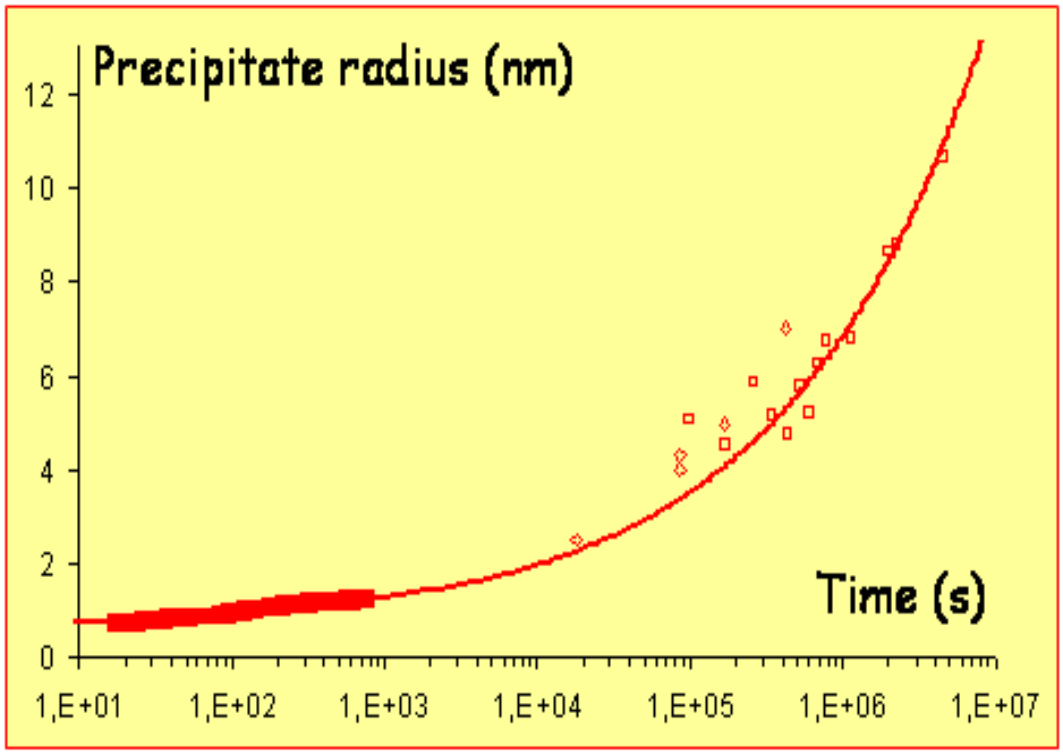
(R^{cut} ~ 0.75 nm)

[1] G. M. Novotny and A. J. Ardell, *Precipitation of Al_3Sc in binary Al-Sc alloys*, Mater. Sci. Eng. **A318** (2001) 144-154

[2] E. Marquis and D. Seidman, *Nanoscale structural evolution of Al_3Sc precipitates in Al(Sc) alloys*, Acta Mater. **49** (2001) 1909

Confrontation with Experimental Data

Al + 0.18 % Sc at 350°C : precipitate growth



Experimental data

Ref. 1 □

Ref. 2 ◇

Cluster dynamics

(R^{cut} ~ 0.75 nm)

KMC ■

(R^{cut} ~ 0.75 nm)

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Confrontation with Experimental Data

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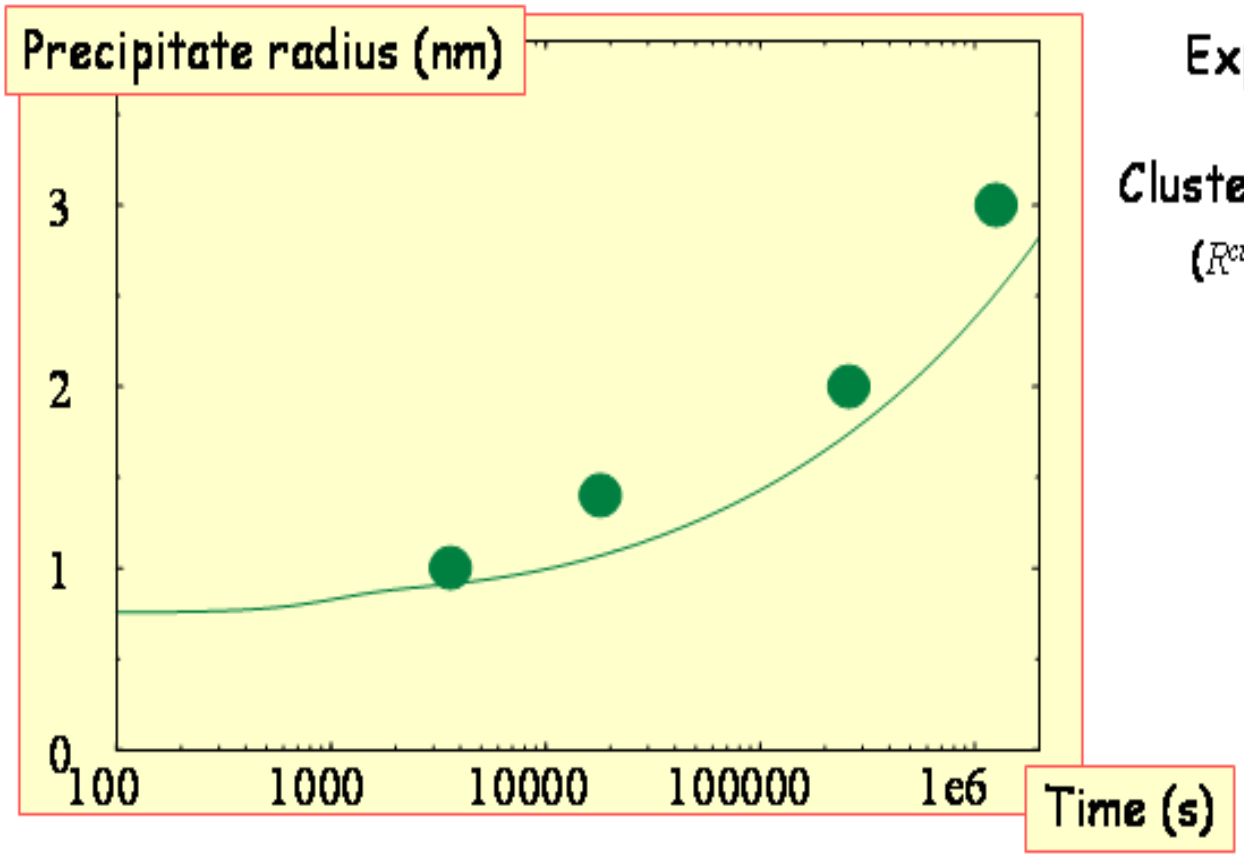


Exp. data.[2]

Cluster dynamics

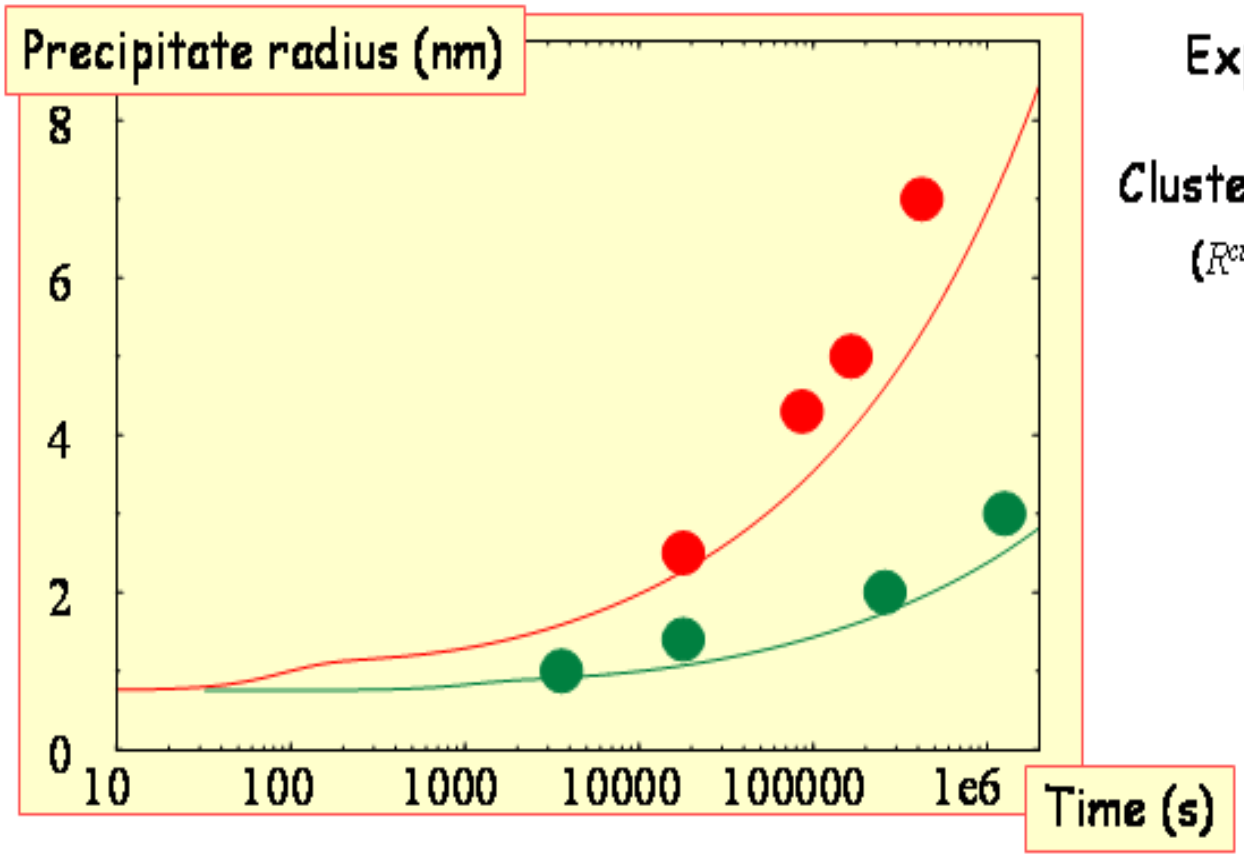
(R^{cut} ~ 0.75 nm)

300°C

[2] E. Marquis and D. Seidman, *Nanoscale structural evolution of Al_3Sc precipitates in Al(Sc) alloys*, Acta Mater. **49** (2001) 1909

Confrontation with Experimental Data

Al + 0.18 % Sc : precipitate growth



Exp. data.[2]

Cluster dynamics

(R^{cut} ~ 0.75 nm)

350°C

300°C

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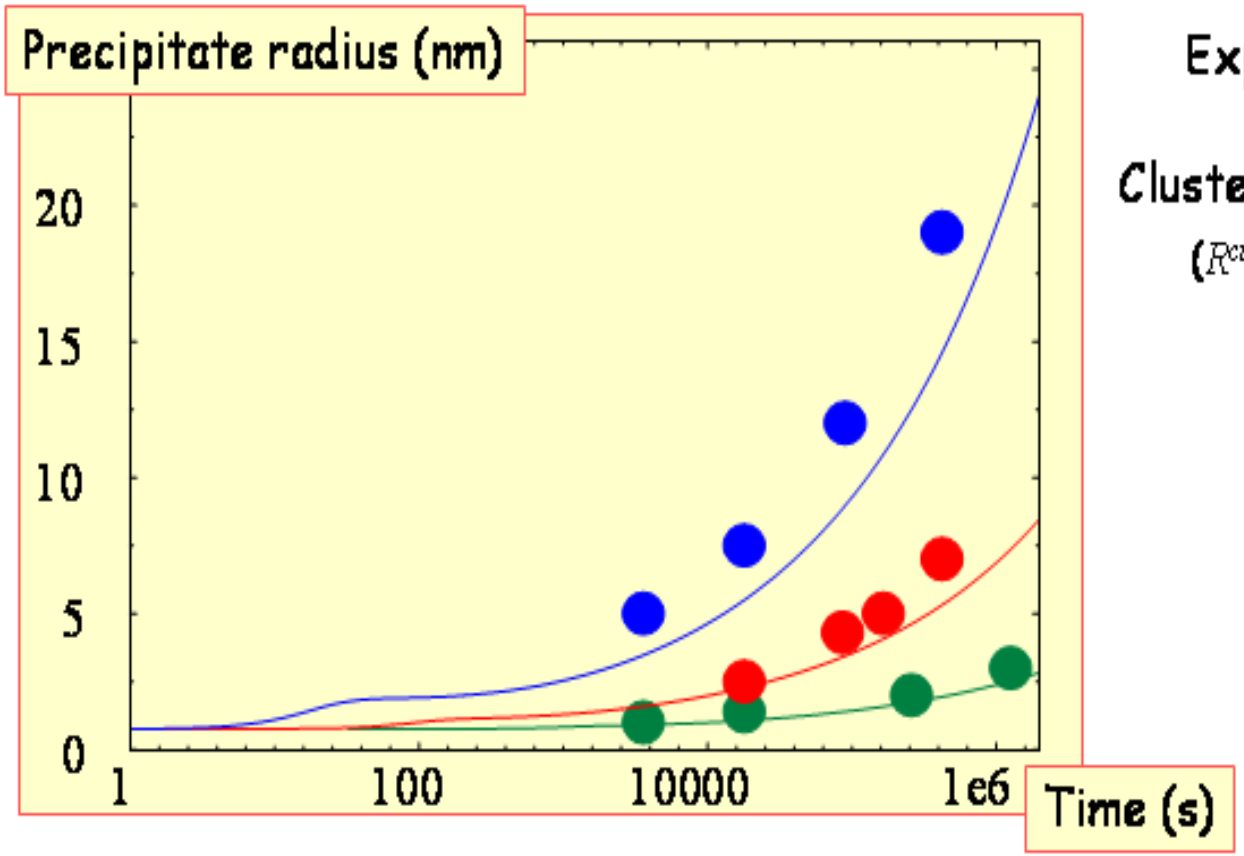
Confrontation with Experimental Data

Al + 0.18 % Sc : precipitate growth



Exp. data.[2]

Cluster dynamics

(R^{cut} ~ 0.75 nm)

400°C

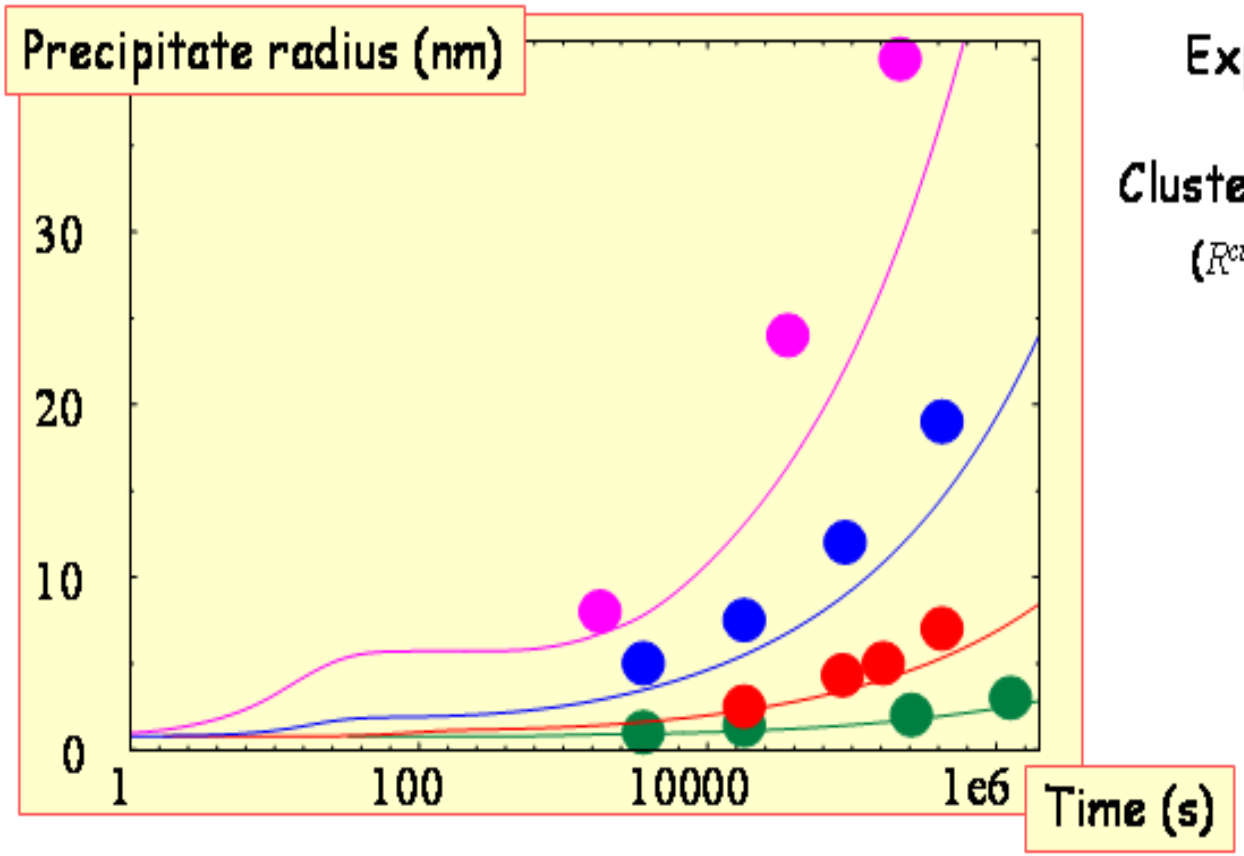
350°C

300°C

[2] E. Marquis and D. Seidman, *Nanoscale structural evolution of Al_3Sc precipitates in Al(Sc) alloys*, Acta Mater. **49** (2001) 1909

Confrontation with Experimental Data

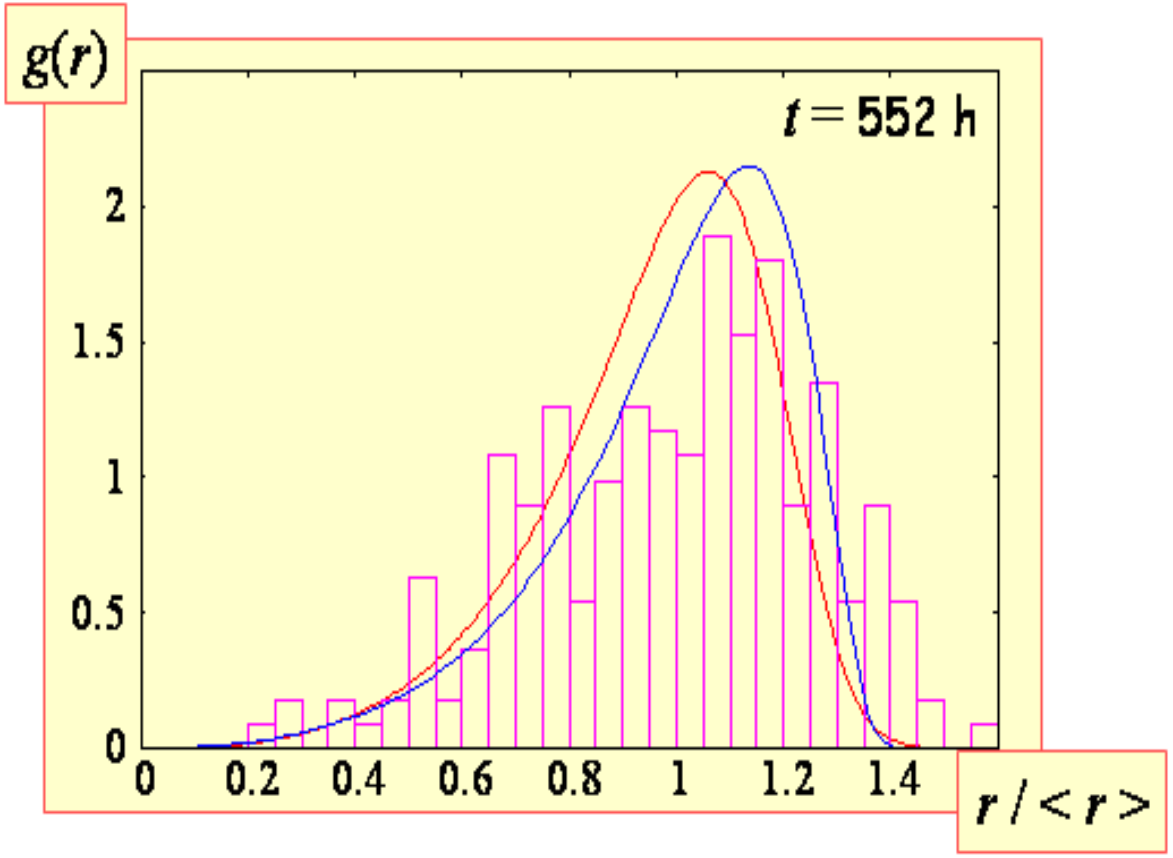
Al + 0.18 % Sc : precipitate growth



[2] E. Marquis and D. Seidman, *Nanoscale structural evolution of Al_3Sc precipitates in Al(Sc) alloys*, Acta Mater. **49** (2001) 1909

Confrontation with Experimental Data

Al + 0.18 % Sc at 350°C : size distribution



[1] G. M. Novotny and A. J. Ardell, *Precipitation of Al_3Sc in binary Al-Sc alloys*, Mater. Sci. Eng. **A318** (2001) 144-154

Conclusions

✓ Binaries Al-Zr and Al-Sc

Good agreement between :

- KMC / cluster dynamics
- cluster dynamics / experimental data

➡ Quantitative multiscale modelling of the precipitation kinetics

✓ Precipitation in ternary alloy Al-Zr-Sc

- Nucleation of a compound $Al_3Zr_xSc_{1-x}$ predicted by KMC
- Growth mainly controlled by Sc

➡ Need to generalize mesoscopic model to ternary alloys in order to increase range of supersaturations and annealing times that can be predicted

E. Clouet, M. Nastar and C. Sigli, Phys. Rev. B **69** (2004) 064109
E. Clouet, A. Barbu, L. Laé and G. Martin, Acta Mater. (2005) in press