DE LA RECHERCHE À L'INDUSTRIE

Bridging space-time scales in the field of diffusion-controlled phase transformations

Maylise Nastar
CEA Saclay, France

in collaboration with

Thomas Schuler[1,2], Thomas Jourdan[1], Frédéric Soisson[1]

[1]CEA Saclay, France
[2]University of Illinois

Luca Messina[1,3], Pär Olsson[3]

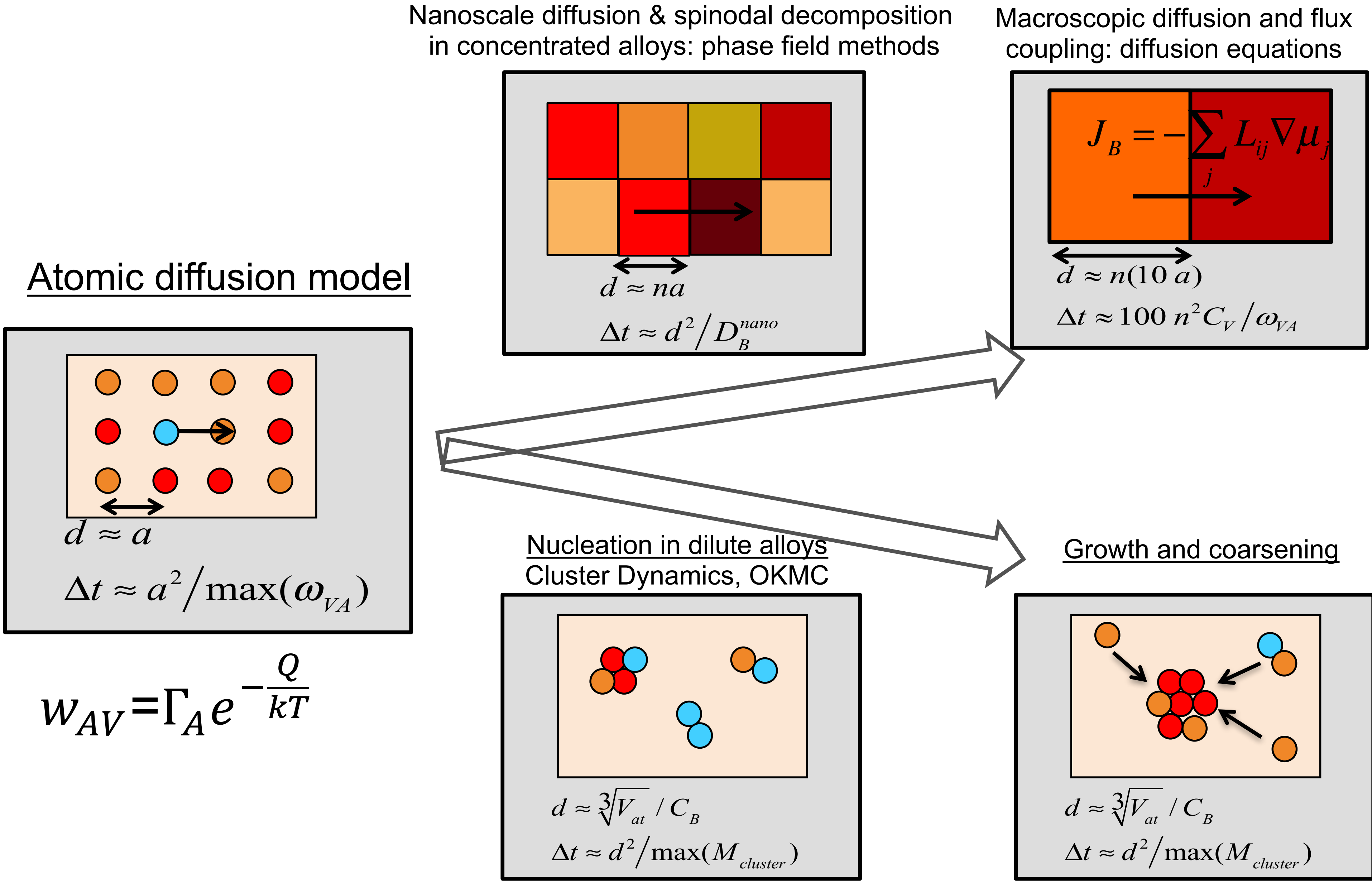
[3]KTH, Sweden

Part of this work was supported by
- *the joint program "CPR ODISSEE" funded by AREVA, CEA, CNRS, EDF and Mécachrome under contract n° 070551.*
- *NEEDS Materiaux*
- *JPNM/Matisse/Mefisto*

www.cea.fr

Workshop « bridging space-time scale… »,
DRESDEN, September 2016

A multiscale approach for diffusion and phase transformations



Atomic diffusion model

$$d \approx a$$

$$\Delta t \approx a^2 / \max(\omega_{VA})$$

$$w_{AV} = \Gamma_A e^{-\frac{Q}{kT}}$$

Nanoscale diffusion & spinodal decomposition in concentrated alloys: phase field methods

$$d \approx na$$

$$\Delta t \approx d^2 / D_B^{nano}$$

Macroscopic diffusion and flux coupling: diffusion equations

$$J_B = -\sum_j L_{ij} \nabla \mu_j$$

$$d \approx n(10\,a)$$

$$\Delta t \approx 100\, n^2 C_V / \omega_{VA}$$

Nucleation in dilute alloys

Cluster Dynamics, OKMC

$$d \approx \sqrt[3]{V_{at}} / C_B$$

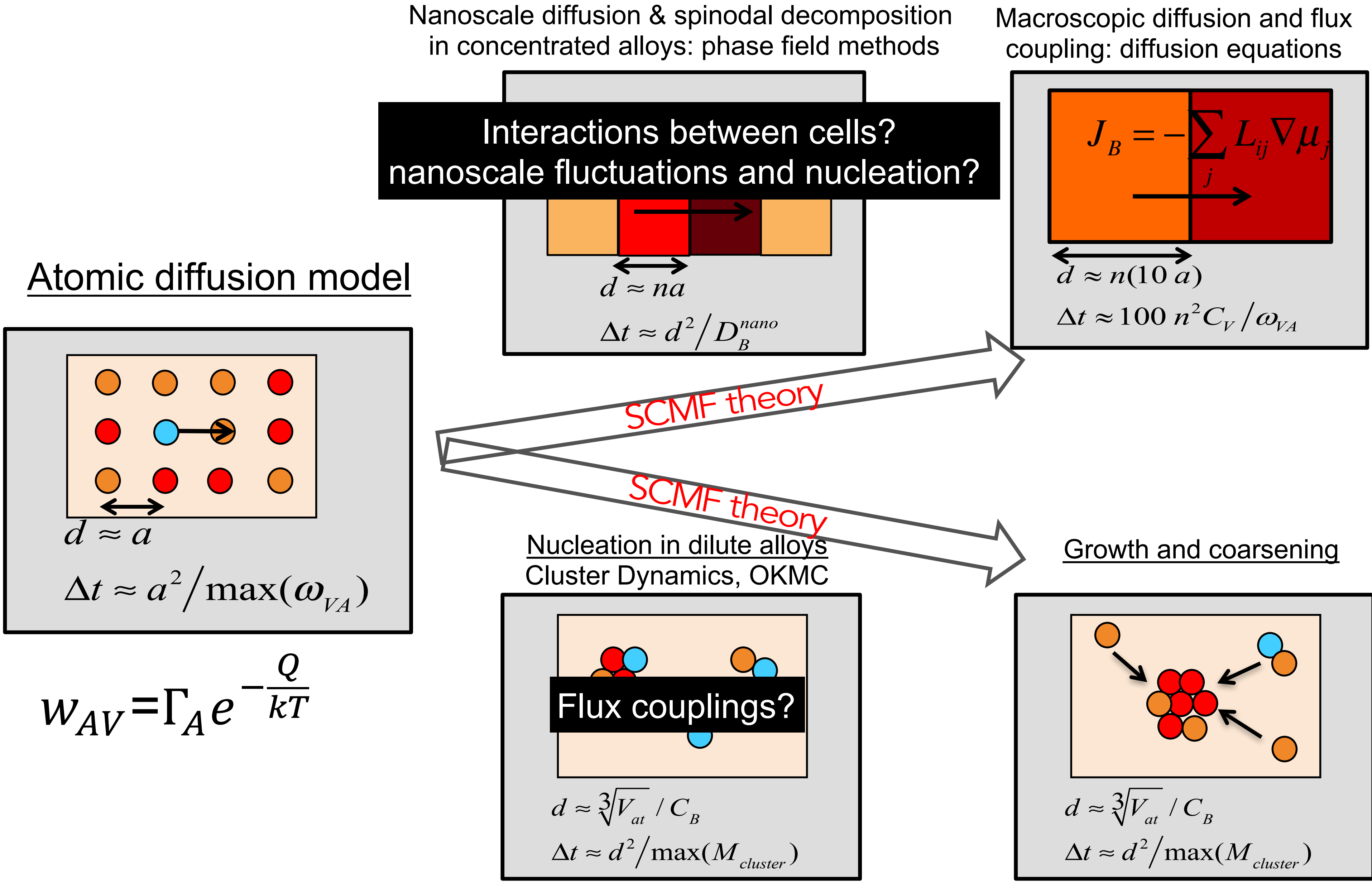
$$\Delta t \approx d^2 / \max(M_{cluster})$$

Growth and coarsening

$$d \approx \sqrt[3]{V_{at}} / C_B$$

$$\Delta t \approx d^2 / \max(M_{cluster})$$

A multiscale approach for diffusion and phase transformations



Atomic diffusion model

$d \approx a$

$\Delta t \approx a^2 / \max(\omega_{VA})$

$$w_{AV} = \Gamma_A e^{-\frac{Q}{kT}}$$

SCMF theory

SCMF theory

Nanoscale diffusion & spinodal decomposition in concentrated alloys: phase field methods

Interactions between cells?
nanoscale fluctuations and nucleation?

$d \approx na$

$\Delta t \approx d^2 / D_B^{nano}$

Macroscopic diffusion and flux coupling: diffusion equations

$J_B = -\sum_j L_{ij} \nabla \mu_j$

$d \approx n(10\ a)$

$\Delta t \approx 100\ n^2 C_V / \omega_{VA}$

Nucleation in dilute alloys
Cluster Dynamics, OKMC

Flux couplings?

$d \approx \sqrt[3]{V_{at}} / C_B$

$\Delta t \approx d^2 / \max(M_{cluster})$

Growth and coarsening

$d \approx \sqrt[3]{V_{at}} / C_B$

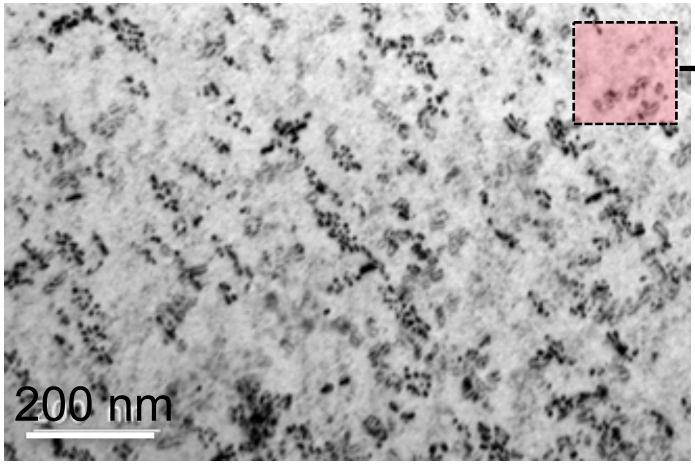
$\Delta t \approx d^2 / \max(M_{cluster})$

A typical phenomenon involving both Point defect-solute cluster reactions and flux coupling

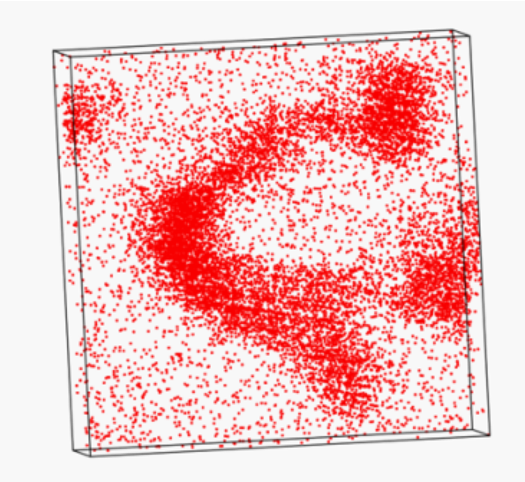
Irradiation of Fe-15 % Cr by e^- 1MeV (THT)
T=773 K, Φ=3.9x10^{-5} dpa/s, dose=0.2 dpa
O. Tissot, E. Meslin et al. (CEA-SRMP & Univ. de Rouen)

Microstructure of point defects
Interstitial loops a<100>

Radiation Induced Segregation (RIS)
of Cr at loops due to flux couplings



TEM – Bright field (CEA Saclay)



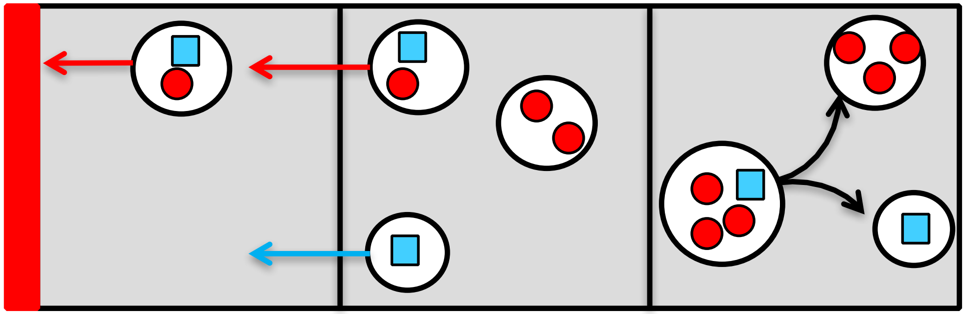
Atom Probe Tomography
(GPM,Rouen)

what is the effect of point-defect microstructure on RIS?
what is the effect of RIS on the point defect microstructure?

A typical phenomenon involving both cluster reactions and flux coupling

Spatial cluster dynamics (Crescendo)
Object kinetic Monte Carlo

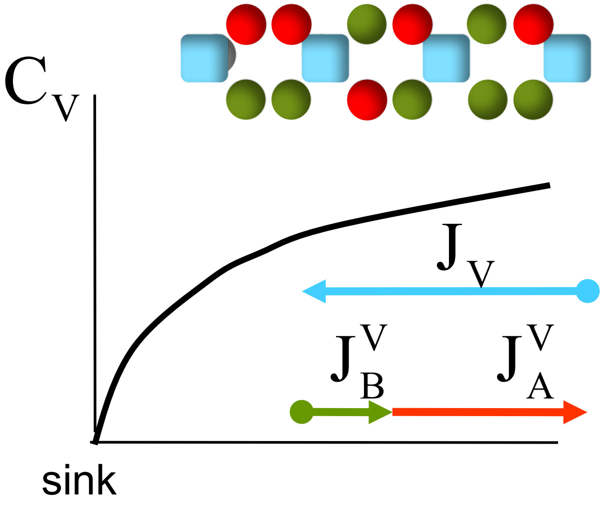
Continuous diffusion equations



Cluster mobility
(positive flux coupling)

Dissociation

Negative flux coupling

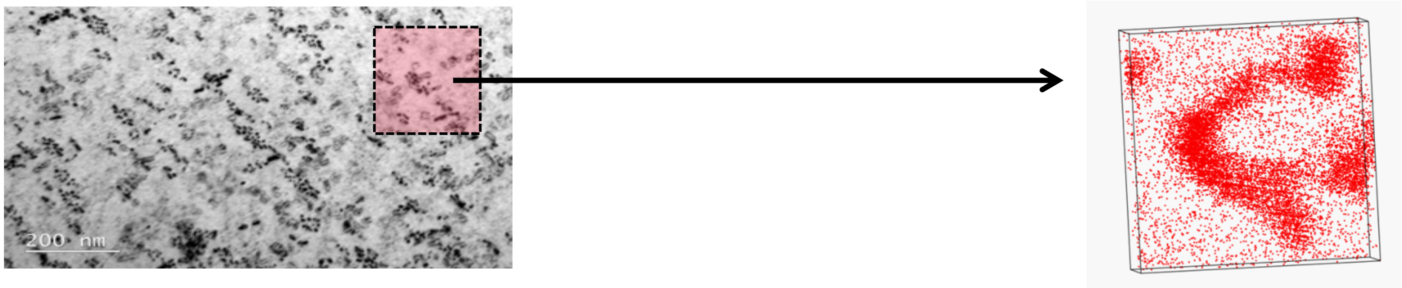


Clouet, E. ASM Handbook 2009, 22A, 203–219 .
Jourdan, T. *et al.* Acta Mater. 2010, 58, 3295–3302.
M. Nastar & F. Soisson, Comprehensive…

Onsager: positive & negative flux coupling

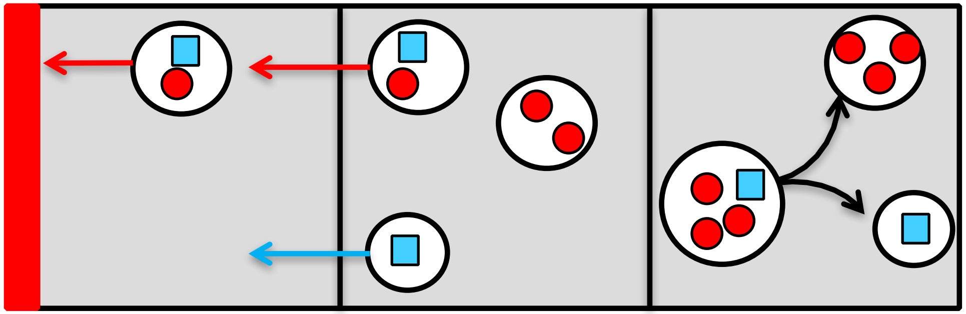
$$J_A^V = -\frac{C_V^{irr}}{C_V^{eq}}(L_{AV}\nabla\mu_V + L_{AA}^V\nabla\mu_A + L_{AB}^V\nabla\mu_B)$$

A typical phenomenon involving both cluster reactions and flux coupling



Spatial cluster dynamics (Crescendo)
Object kinetic Monte Carlo

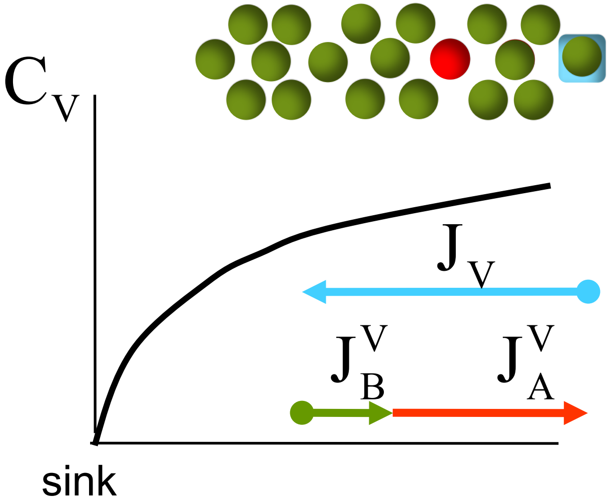
Continuous diffusion equations



Cluster mobility
(positive flux coupling)

Dissociation

Positive flux coupling



Clouet, E. ASM Handbook 2009, 22A, 203–219 .
Jourdan, T. *et al.* Acta Mater. 2010, 58, 3295–3302.
M. Nastar & F. Soisson, Comprehensive…

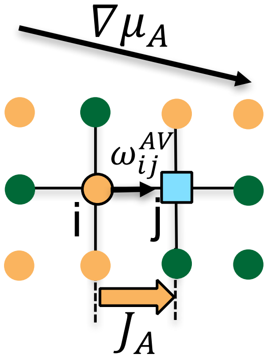
Onsager: positive & negative flux coupling

$$J_A^V = -\frac{C_V^{irr}}{C_V^{eq}}(L_{AV}\nabla\mu_V + L_{AA}^V\nabla\mu_A + L_{AB}^V\nabla\mu_B)$$

Outline

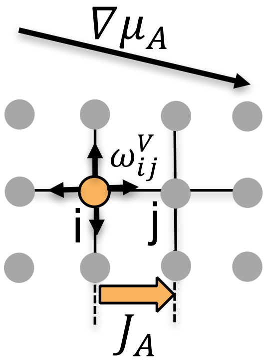
- Principles of the self-consistent mean field theory (SCMF)
- Kinetic characterization of clusters from the atomic scale
- SCMF based - Cluster Dynamics extended to heterogeneous systems
- SCMF based - Phase Field Equations

Principles of the Self-Consistent Mean Field theory (SCMF)



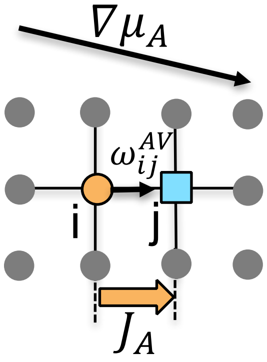
Atomic diffusion model on a rigid lattice

Application of a driving force



A mean field theory:

diffusion of particle A within a mean field



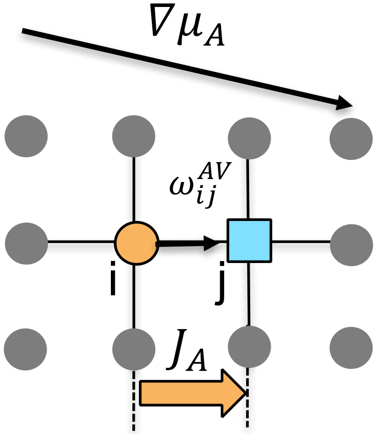
Non-equilibrium pair variables AV
Computation of the coresponding fluxes
Identification of the Lij coefficients

*Nastar et al. Phil. Mag. A 2000, 80, 155–184.

SCMF theory: introduction of a non equilibrium distribution function

Equilibrium distribution function

$$P^{(0)}(n) = \exp\left[\left(\Omega + \sum_{\alpha} \mu_{\alpha} \sum_{i} n_i^{\alpha} - H(n)\right)\Big/ k_B T\right]$$



$$n_i^{\alpha} = 1 \,,\, n_i^{V} = 0$$

$$n_j^{V} = 1 \,,\, n_j^{\alpha} = 0$$

Non equilibrium distribution function

$$P(n,t) = P^{(0)}(n) P^{(1)}(n,t)$$

$$P^{(1)}(n,t) = \exp\left[\left(\delta\Omega + \sum_{i,\alpha} \delta\mu_i^{\alpha} n_i^{\alpha} - \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} v_{ij}^{\alpha\beta}(t) n_i^{\alpha} n_j^{\beta}\right)\Big/ k_B T\right]$$

Pair correlators versus effective interactions

$$\left\langle n_i^{\alpha} \right\rangle = \sum_{n} n_i^{\alpha} P(n,t)$$

$$\left\langle n_i^{\alpha} n_j^{\beta} \right\rangle = \sum_{n} n_i^{\alpha} n_j^{\beta} P(n,t)$$

$$K_{ij}^{\alpha\beta} = \left\langle n_i^{\alpha} n_j^{\beta} \right\rangle - \left\langle n_i^{\alpha} \right\rangle \left\langle n_j^{\beta} \right\rangle$$

$$K_{ij}^{\alpha\beta} - K_{ij}^{\beta\alpha} = \left\langle n_i^{\alpha} n_j^{\beta} \right\rangle^{(0)} \left(v_{ij}^{\alpha\beta} - v_{ij}^{\beta\alpha} \right)$$

SCMF Kinetic equations from the Master equation

Master equation

$$\frac{dP(n,t)}{dt} = \sum_{n'}\left[W(n'\to n)P(n') - W(n\to n')P(n)\right]$$

Atomic fluxes

$$\frac{d\langle n_i^B\rangle}{dt} = -\nabla_i J_B \quad \Rightarrow J_B = -z\left\langle \omega_{i,i+1}^{BV} n_i^B n_{i+1}^V\right\rangle \beta\left[\nabla_i(\mu_B-\mu_V) + v_{i,i+1}^{VB} - v_{i,i+1}^{BV}\right]$$

$v_{ij}^{V\alpha}$ solution of the pair kinetic equations

$$\frac{d\langle n_i^B n_{i+1}^V\rangle}{dt} = \left\langle \omega_{i,i+1}^{BV} n_i^B n_{i+1}^V\right\rangle^{(0)} \nabla_i(\mu_B-\mu_V) - \left\langle n_i^B \omega_{i+1,i+2}^{VA} n_{i+1}^V n_{i+2}^A\right\rangle^{(0)} \nabla_{i+1}(\mu_A-\mu_V)$$

$$+q_1(v_{i,i+1}^{AV} - v_{i,i+1}^{VA}) + q_2(v_{i,i+2}^{AB} - v_{i,i+2}^{VB})$$

Identification with Onsager's flux and computation of $L\alpha\beta$

$$J_A = -\sum_{\beta} L_{\alpha\beta}\beta\nabla(\mu_\beta - \mu_V)$$

$$L_{\alpha\beta} = \sum_{i,j,\gamma} g_{ij} W_{ij}^{\gamma} \left(1 + \underbrace{f_{\alpha\beta}\left(\{W_{kl}^{\gamma}\}\right)}_{\textit{Kinetic correlations = jump efficiency}}\right)$$

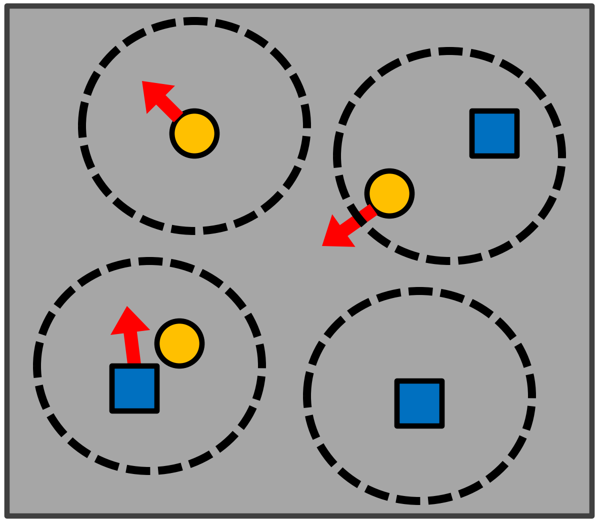
$$W_{ij}^{\alpha} = p_i\omega_{ij}^{\alpha} = p_j\omega_{ji}^{\alpha}$$

KINETIC CHARACTERIZATION OF CLUSTERS FROM THE ATOMIC SCALE

*T. SCHULER and M. NASTAR, PRB 93 (22), 224101

Breakdown of the Onsager matrix for a dilute alloy

*T. Schuler & M. Nastar, PRB 93 (22), 224101



Dilute alloy

From the SCMF theory:

$$L_{\alpha\beta} = \sum_{i,j,\gamma} g_{ij} W_{ij}^{\gamma} \left(1 + \underbrace{f_{\alpha\beta}\left(\left\{W_{kl}^{\gamma}\right\}\right)}_{\text{Kinetic correlations = jump efficiency}}\right)$$

Non equilibrium Onsager transport coefficient

$$L_{\alpha\beta} = \sum_{i} \left[c_i\right] L_{\alpha\beta}^{eq}(c_i)$$

Equilibrium cluster Transport coefficients

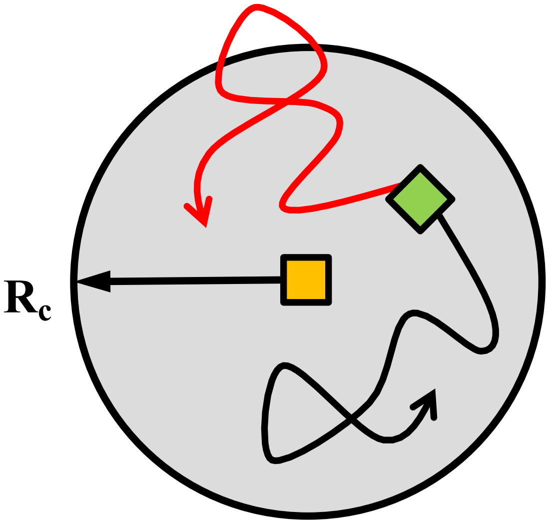
Cluster reactions

$$L_{\alpha\beta} = \sum_{c_i} [c_i] \left\{ \underbrace{L_{\alpha\beta}^{eq}(c_i)_{|M}}_{\text{Mobility without dissociation}} + \underbrace{L_{\alpha\beta}^{eq}(c_i)_{|A} + L_{\alpha\beta}^{eq}(c_i)_{|D}}_{\text{Equal because of detailed balance}} \right\}$$

The mobility of a cluster

*T. Schuler & M. Nastar, PRB 93 (22), 224101

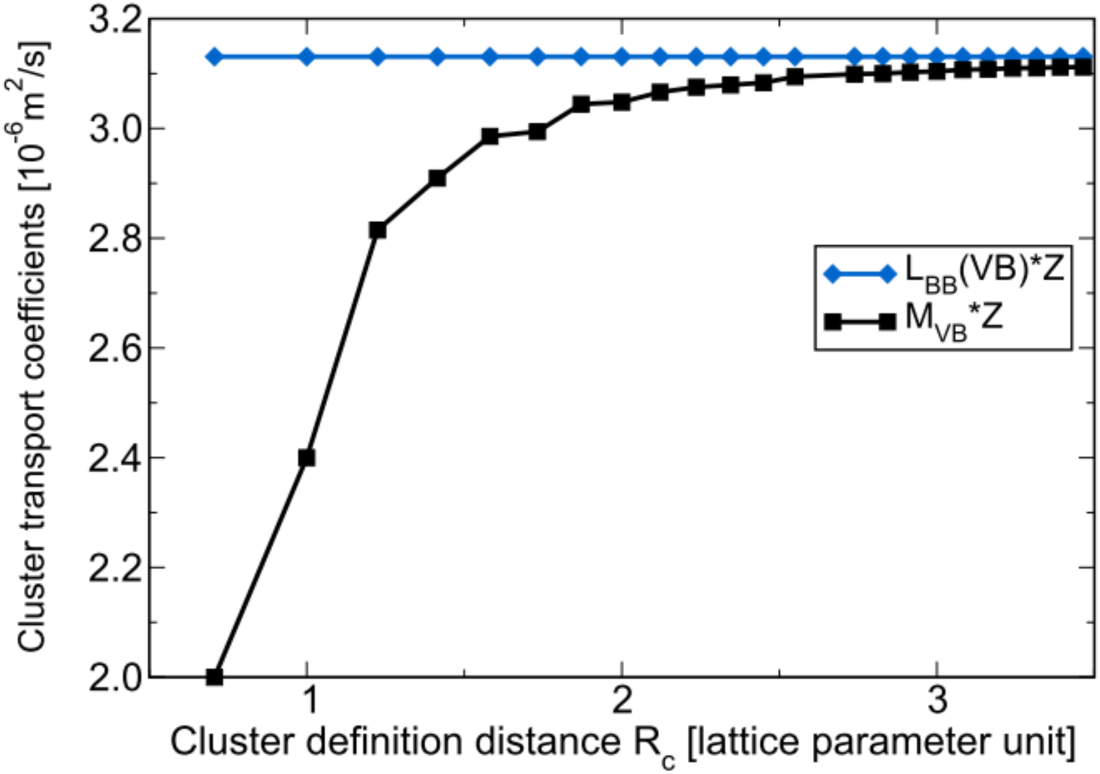
Mobility without dissociation



A consistent definition of the cluster radius (R_c) is not only thermodynamic, but also depends on kinetic correlations

SCMF in the cluster volume
(no association/dissociation jumps) :

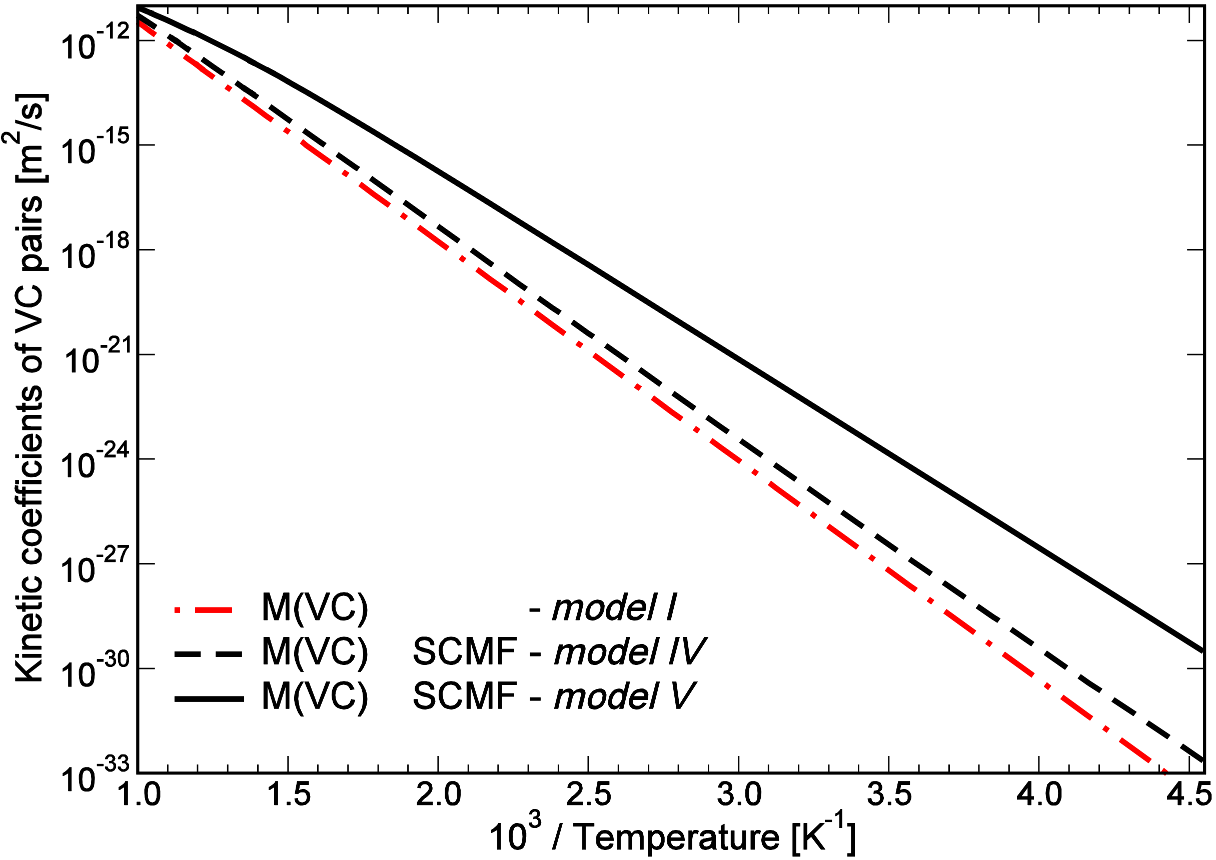
$$\begin{pmatrix} L^{eq}_{\alpha\alpha}(c_i)_{|M} & L^{eq}_{\alpha\beta}(c_i)_{|M} \\ L^{eq}_{\beta\alpha}(c_i)_{|M} & L^{eq}_{\beta\beta}(c_i)_{|M} \end{pmatrix} = M^{eq}_{c_i} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$



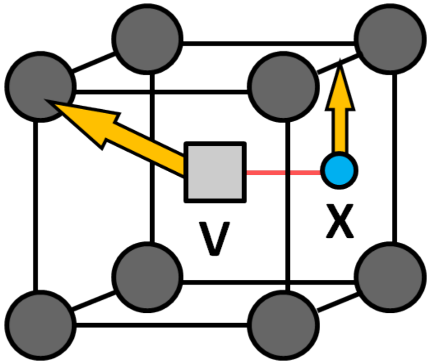
SCMF mobility compared to the highest barrier model

*T. Schuler & M. Nastar, PRB 93 (22), 224101

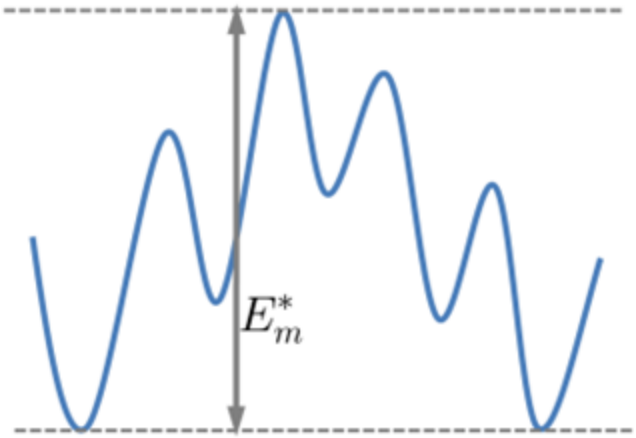
Mobility of VC pairs in Fe



Fe(C)



Model I



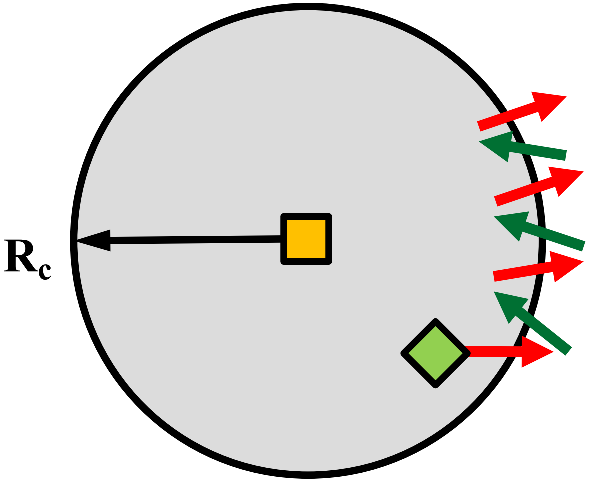
Model I: Highest barrier model

Model IV: $R=R_{th}=1.23$ a

Model V: $R=3.2$ a

The association-dissociation term

Dissociation - Association



$$\underbrace{L_{\alpha\beta}^{eq}\left(c_i\right)_{|A} = L_{\alpha\beta}^{eq}\left(c_i\right)_{|D}}_{\text{Equal because of detailed balance}} = \frac{1}{2}L_{\alpha\beta}^{eq}\left(c_i\right)_{|AD}$$

There are different dissociation paths
=> the AD matrix does not reduce to a scalar

Systems Fe(X): Monte Carlo versus SCMF

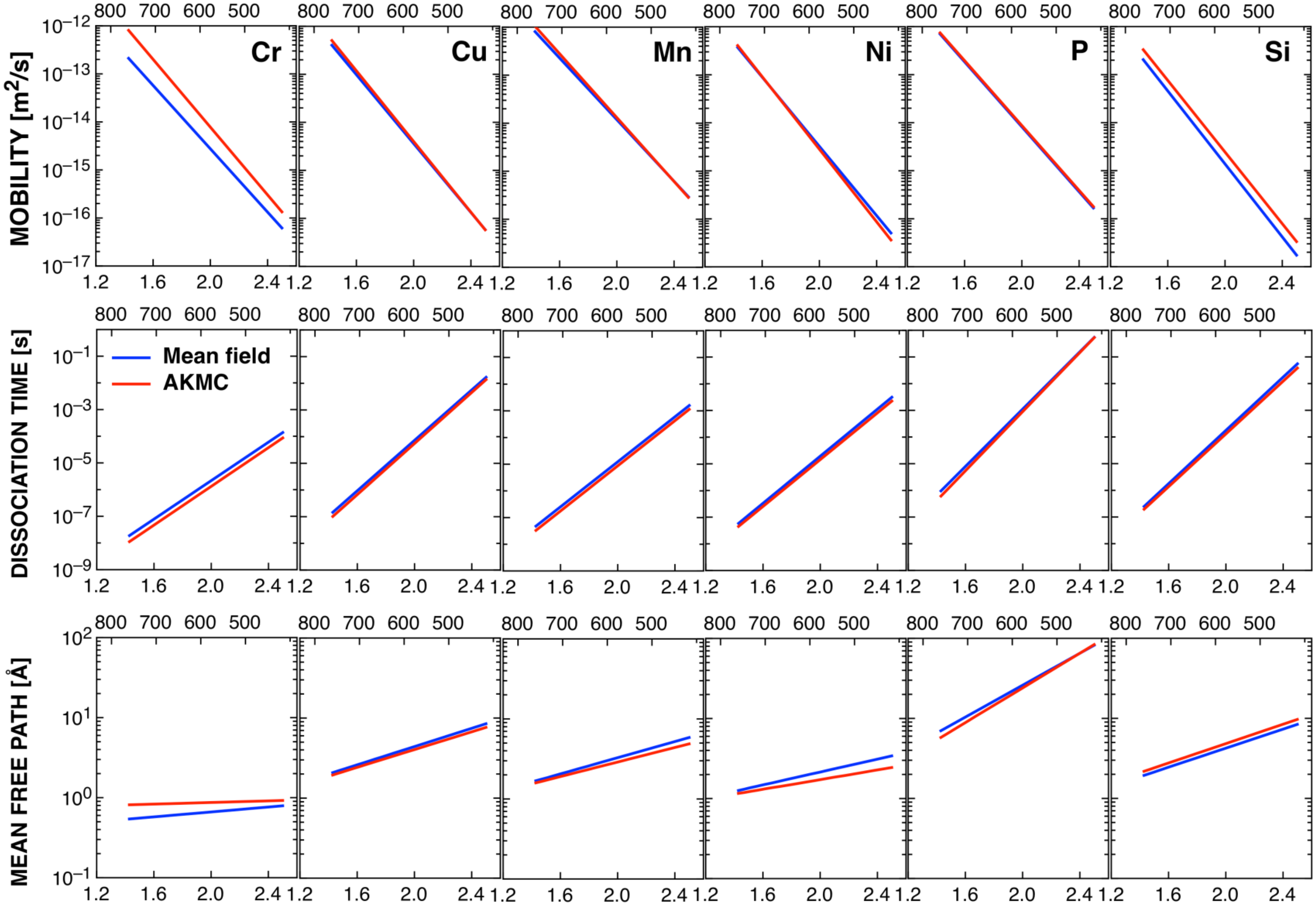
*L. Messina, T. Schuler, P. Olsson, M. Nastar

Monte Carlo simulations: in coll. with M. Chiapetto et al. (SCK, Belgium)

$$M_{XV}$$

$$\tau = \frac{a^2}{L_{VV}(XV)_{|AD}}$$

$$l = \sqrt{M_{XV}\tau}$$

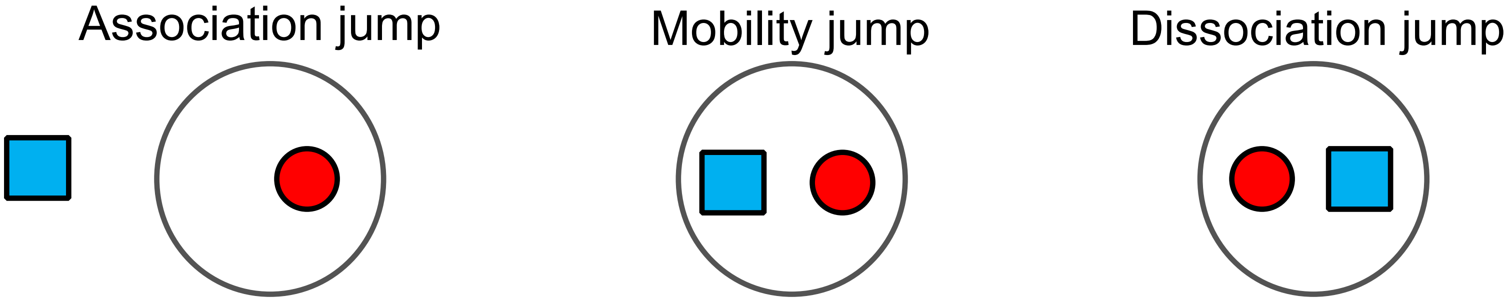


Physics of flux coupling within cluster dynamics

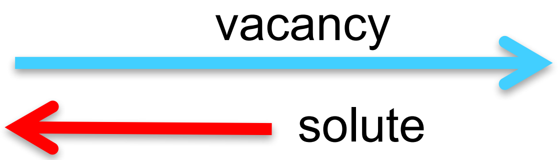
Breakdown of the Onsager matrix into cluster contributions for dilute systems

$$\begin{pmatrix} L_{\alpha\alpha} & L_{\alpha\beta} \\ L_{\beta\alpha} & L_{\beta\beta} \end{pmatrix} = \sum_{c_i} [c_i] \left\{ M_{c_i}^{eq} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \begin{pmatrix} L_{\alpha\alpha}^{eq}(c_i)_{|AD} & 0 \\ 0 & L_{\beta\beta}^{eq}(c_i)_{|AD} \end{pmatrix} + \boxed{\begin{pmatrix} L_{\alpha\alpha}^{eq}(c_i)_{|E} & L_{\alpha\beta}^{eq}(c_i)_{|E} \\ L_{\beta\alpha}^{eq}(c_i)_{|E} & L_{\beta\beta}^{eq}(c_i)_{|E} \end{pmatrix}} \right\}$$

- Exchange Correlations between A/D and M jumps
- Contains the physics of negative flux coupling



Negative flux coupling
Due to exchange correlations



SCMF-BASED CLUSTER DYNAMICS EXTENDED TO HETEROGENEOUS SYSTEMS

*T. SCHULER, T. JOURDAN, M. NASTAR

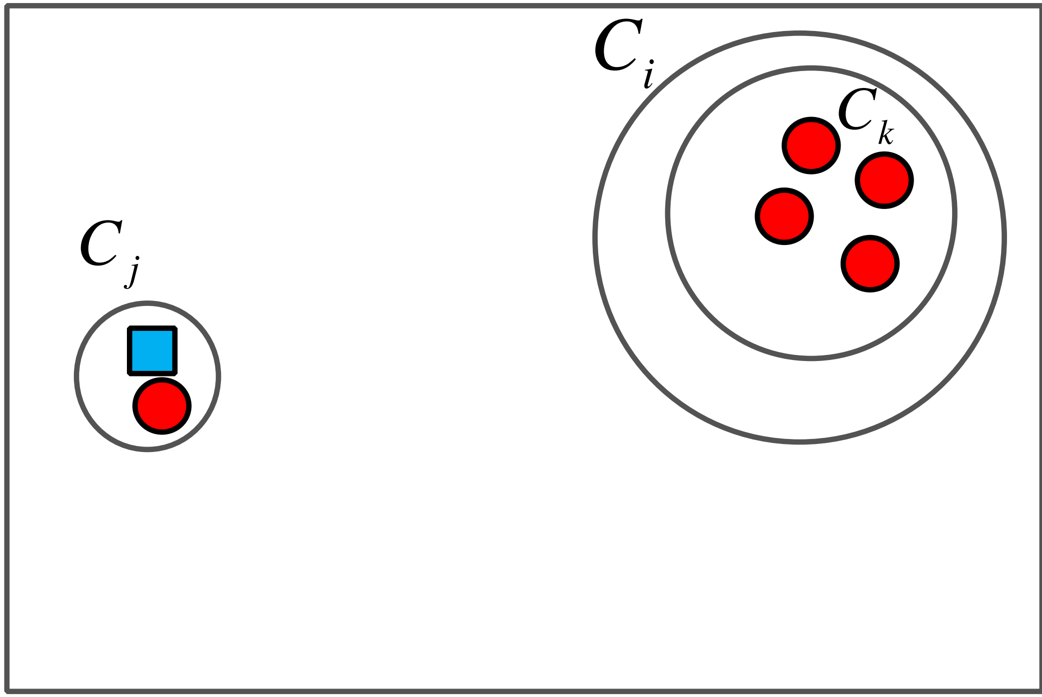
Homogeneous Cluster Dynamics

Association coefficient Γ_A

Waite formulae

$$\Gamma_A\left(C_j + C_k \rightarrow C_i\right) = \frac{4\pi R(C_k)^2 M_{C_j}}{(R(C_k)+\kappa)}$$

$$\kappa = \sum_{\gamma=\alpha,\beta} \sum_{m=j,k} \frac{2 M_{C_j} \lambda_\gamma}{L_{\gamma\gamma}(C_i, C_m)_{AD}}$$



*Clouet, E. ASM Handbook 2009, 22A, 203–219 .

*Jourdan, T. *et al.* Acta Mater. 2010, 58, 3295–3302.

Dissociation coefficient Γ_D

Global detailed balance condition

$$\Gamma_D\left(C_i \rightarrow C_j + C_k\right) = \frac{1}{\Omega_{at}} \Gamma_A\left(C_j + C_k \rightarrow C_i\right) \exp\left(\frac{F(C_j) + F(C_k) - F(C_i)}{k_B T}\right)$$

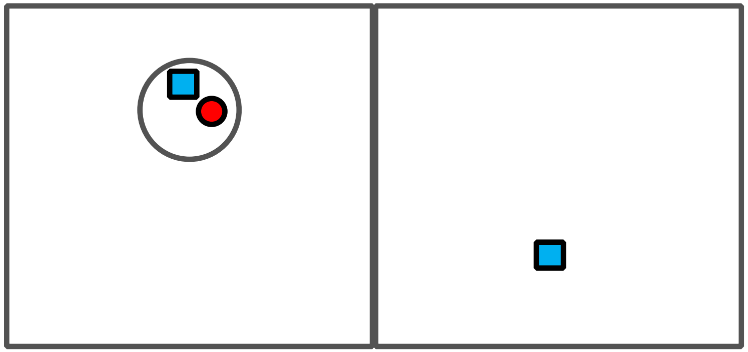
Heterogeneous Cluster Dynamics

*T. Schuler, T. Jourdan, M. Nastar

Vacancy diffusion mechanism, 3 species: monovacancy V, solute B, pair BV

$$\begin{cases} \dfrac{\partial[V]}{\partial t} = -\nabla J_V^{CD} - \Gamma_A[V][B] + \Gamma_D[VB] \\ \dfrac{\partial[B]}{\partial t} = -\nabla J_B^{CD} - \Gamma_A[V][B] + \Gamma_D[VB] \\ \dfrac{\partial[BV]}{\partial t} = -\nabla J_{BV}^{CD} + \Gamma_A[V][B] - \Gamma_D[VB] \end{cases}$$

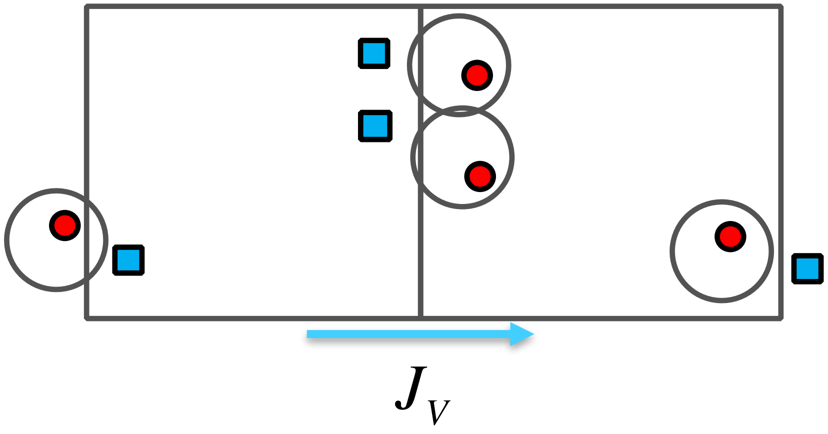
Flux – part 1: migration of clusters



$$J_V^{CD} = -M_V \nabla[V]$$

$$J_{BV}^{CD} = -M_{BV} \nabla[BV]$$

Flux – part 2: Association-Dissociation of clusters



Different cluster concentrations between two adjacent cells leads to asymmetric A-D reactions and fluxes between cells.

AD fluxes obtained from TIP

at local equilibrium,

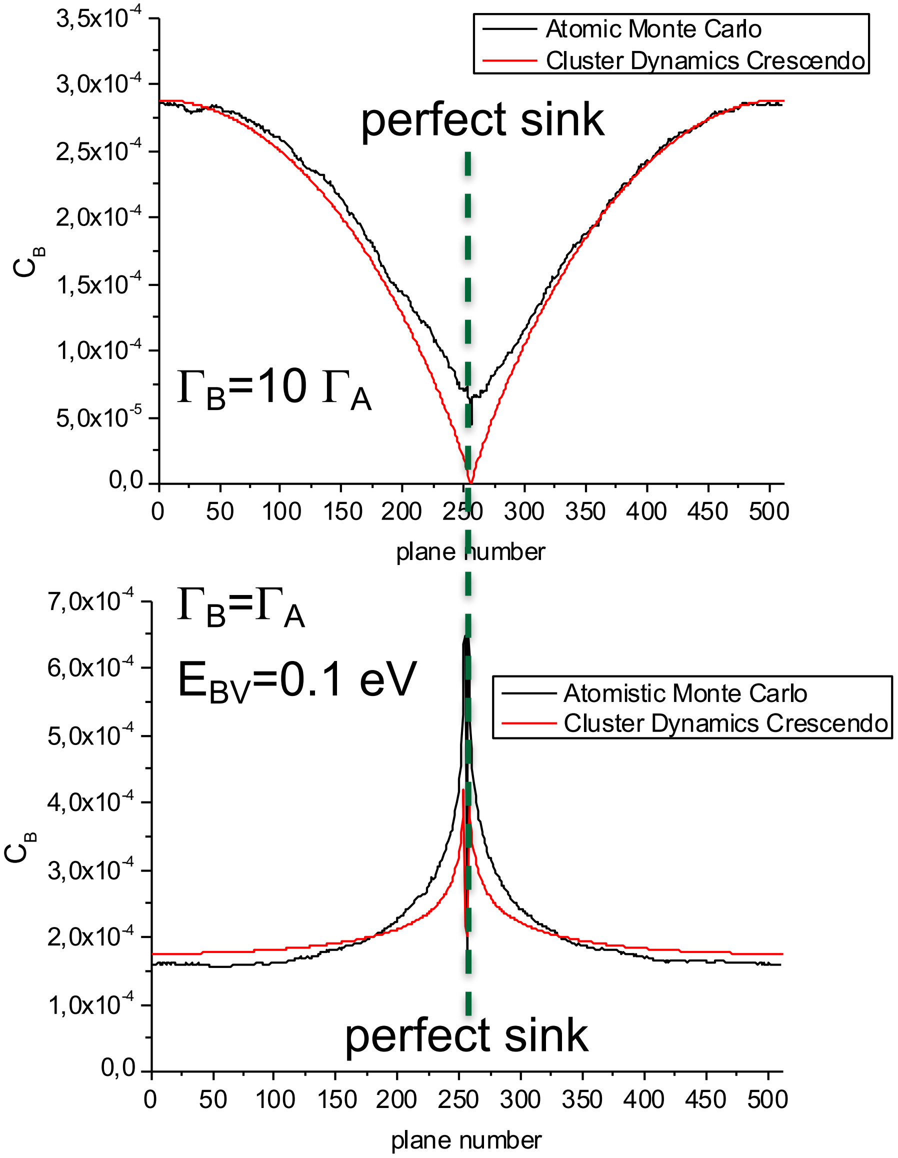
$$\begin{cases} k_B T \dfrac{\nabla[B]}{[B]} = \nabla\mu_B \\ k_B T \dfrac{\nabla[V]}{[V]} = \nabla\mu_V \\ k_B T \dfrac{\nabla[BV]}{[BV]} = \nabla\mu_B + \nabla\mu_V \end{cases}$$

CD and TIP fluxes are put equal

$$\begin{cases} J_V^{CD} + J_{BV}^{CD} = J_V^{TIP} \\ J_B^{CD} + J_{BV}^{CD} = J_B^{TIP} \end{cases}$$

Cluster Dynamics versus Monte Carlo

Steady state profiles of solute



Simulation of vacancy irradiation segregation

T=500 K, C_B=2.10-4, Φ=5. 10^{-10} dpa.s^{-1}

Monte Carlo simulations N=512*256*256/4

Monte Carlo events

Random replacement of an atom by a vacancy

$at\ rate\ \Phi * N$

Exchange of a vacancy with an atom (A or B)

$with\ frequency : w_{AV}=\Gamma_A e^{-\frac{(E_{AV})}{kT}}\ and\ W_{BV}$

Boundary conditions

Vacancy at sinks is removed and randomly replaced by atom A or B with the constraint of constant solute concentration.

ClusterDynamics

Boundary conditions

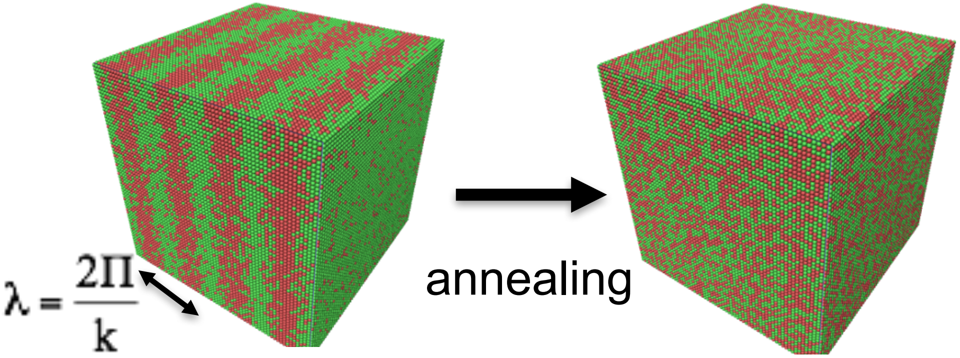
$C_B=C_{BV}=0$ at sinks

SCMF-BASED PHASE FIELD EQUATIONS

*M. NASTAR, PRB 90 (14), 144101

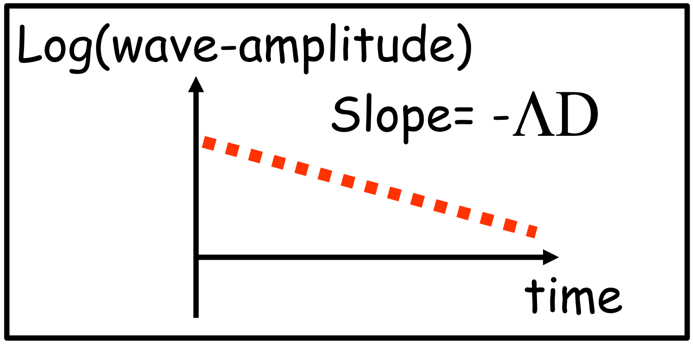
Nanoscale interdiffusion experiments

*O Senninger, F Soisson, E Martínez, M Nastar, CC Fu, Y Bréchet, Acta Materialia 103, 1-11

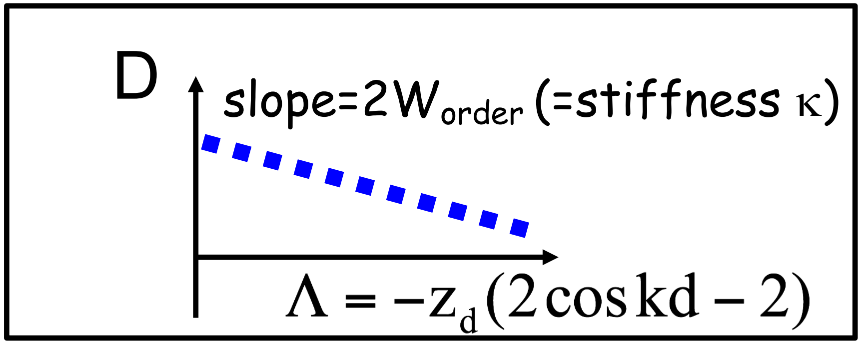


Multilayers of isotopic atoms

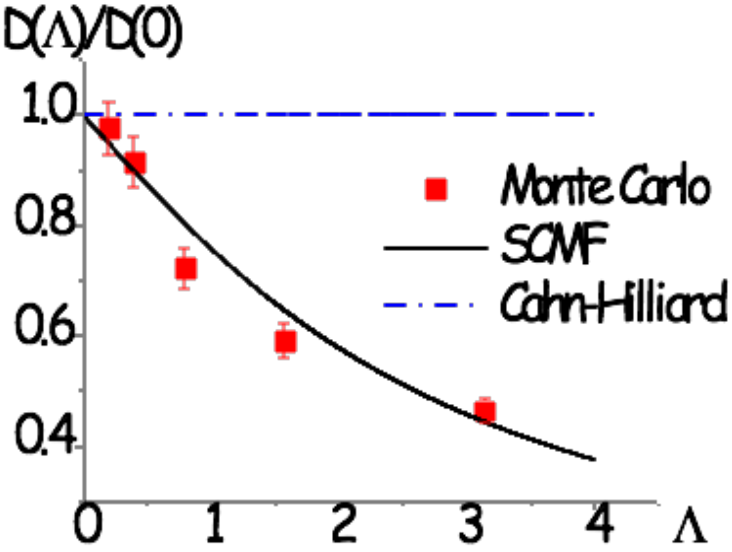
$$W_{order} = 0 \quad \Rightarrow D(\Lambda) = D(0)\,?$$



Phenomenological Cahn-Hilliard theory

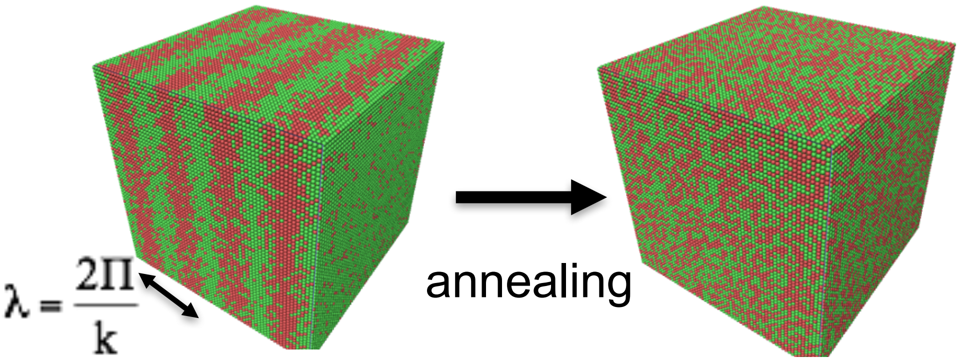


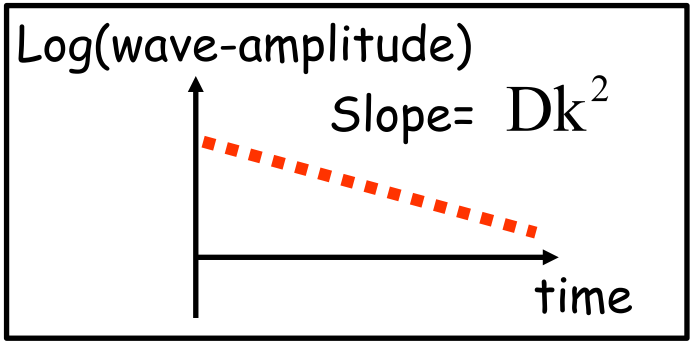
$$\Lambda = -z_d(2\cos kd - 2)$$



Something is missing in the Cahn-Hilliard theory

A kinetic stiffness parameter challenging the Cahn-Hilliard phenomenological equation



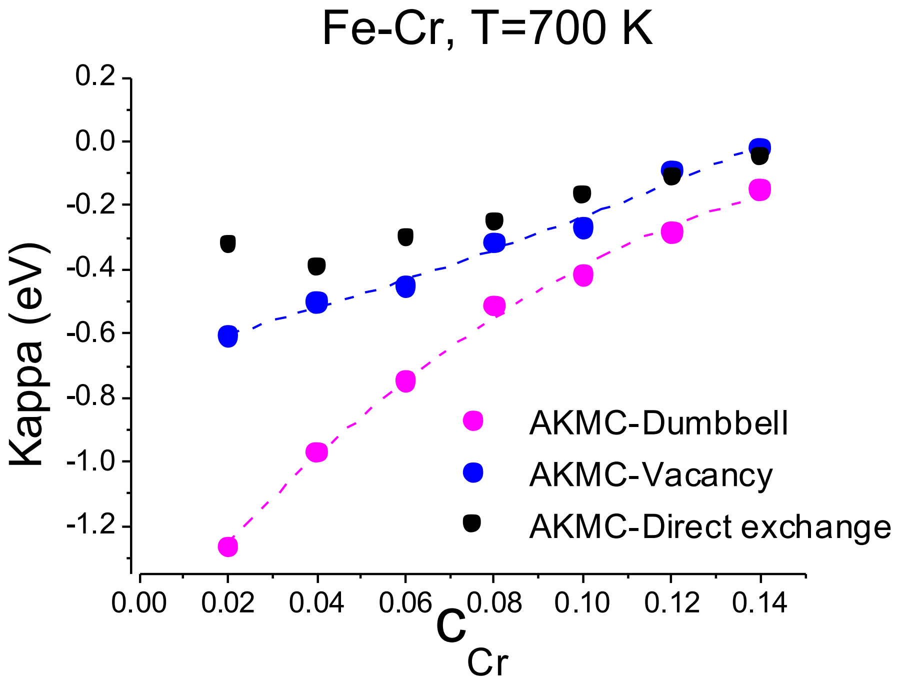


Interdiffusion coefficient as a function of k

$$D = M\left[f'' + (\kappa_{th} + \kappa_{kin})k^2 \right]$$

κ_E : Composition gradient-energy

κ_C : Composition gradient-correlation



*M. Nastar, PRB 90 (2014), 144101

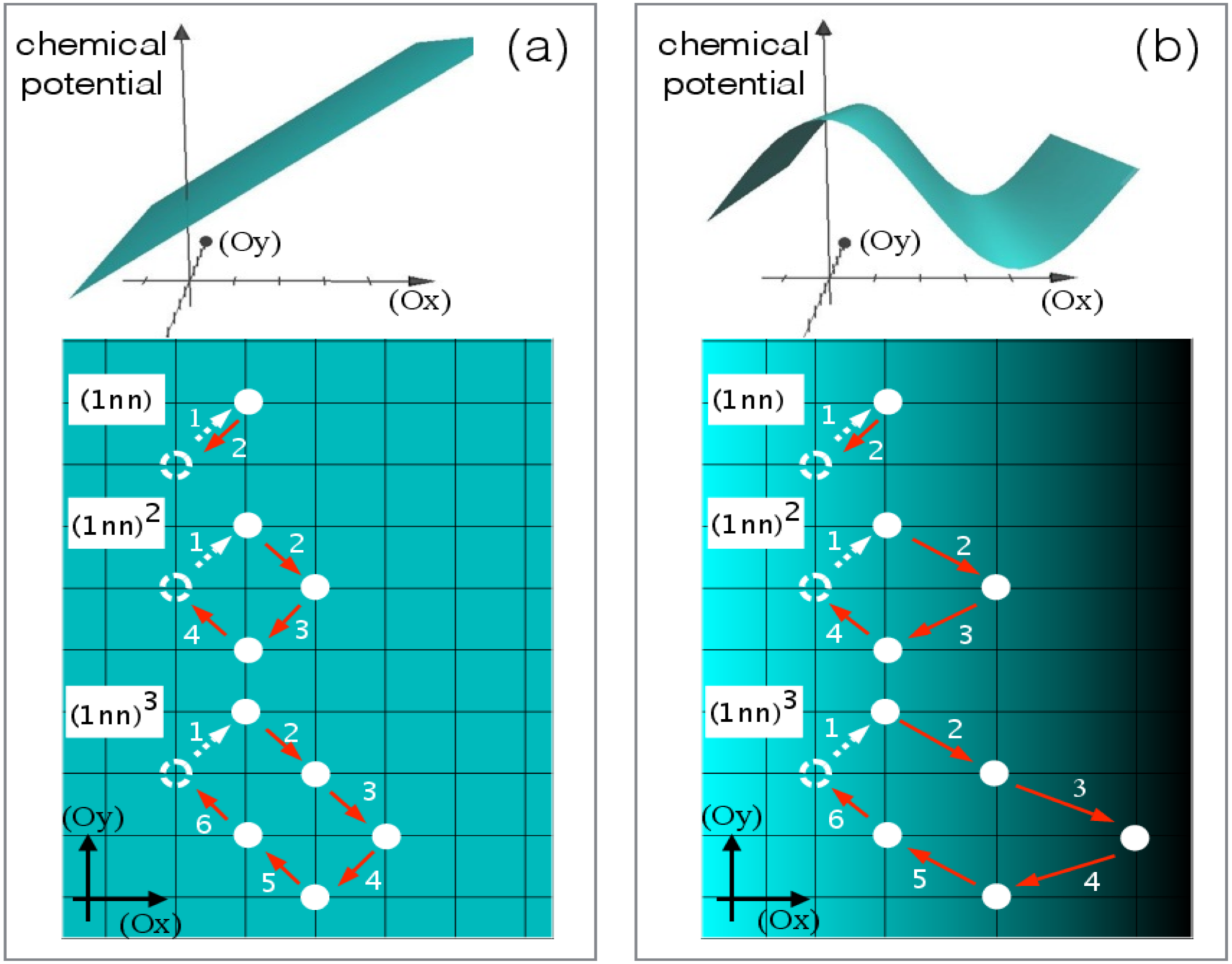
Interdiffusion in binary alloys with non uniform driving forces

Beyond the Onsager coefficients

$$J_B = -L_{BB}\nabla\mu_{BV} - L_{AB}\nabla\mu_{AV} - Q_{BB}\nabla^3\mu_{BV} - Q_{AB}\nabla^3\mu_{AV}$$

Uniform driving force

Non uniform driving force



Conclusion and perspectives

Atomic diffusion theory SCMF could be used to properly bridge space-time scales in diffusion controlled phenomena

-Heterogeneous object oriented simulation methods

  -A rigourous definition of cluster kinetic properties

  -Modeling of flux coupling phenomena

-New diffusion equation for the phase field method

  -Nanoscale diffusion experiments: a way to get detailed information on the alloy diffusion properties

-Perspectives:

Off-lattice modeling: a network specific to each cluster