

DE LA RECHERCHE À L'INDUSTRIE



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# DIFFUSION: FROM THE ATOMIC TO THE MACROSCOPIC SCALE

MAYLISE NASTAR

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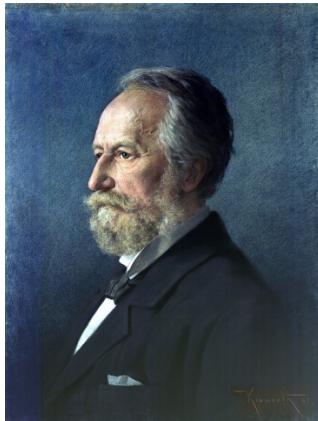
Pascal Bellon and Dallas Trinkle  
(UIUC, USA)

# TRACER DIFFUSION COEFFICIENT

## Fick's first law

(salt diffusion in liquid, 1855)

$$J_{A^*} = -D_{A^*} \nabla C_{A^*}$$



J : nb of atoms/m<sup>2</sup>/s

D : diffusion coefct m<sup>2</sup>/s

C : nb atoms/m<sup>3</sup>

Continuity equation

$$\frac{\partial c_{A^*}}{\partial t} = -\operatorname{div}(J_{A^*}) = D_{A^*} \Delta c_{A^*}$$

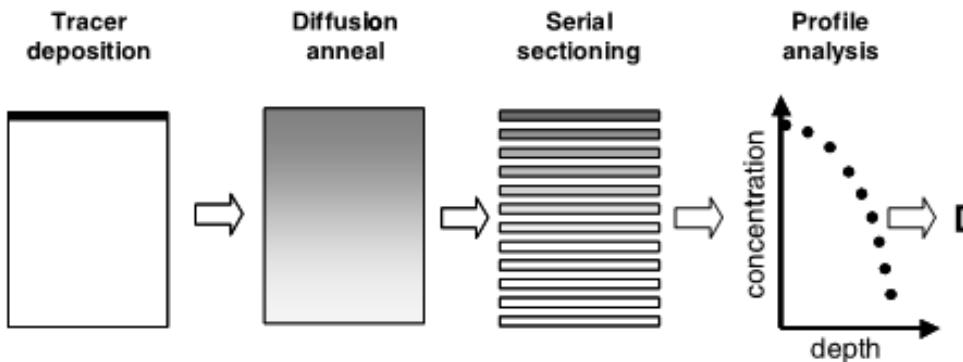
1D analytical solution

$$C_{A^*}(x, t=0) = M \delta(x)$$

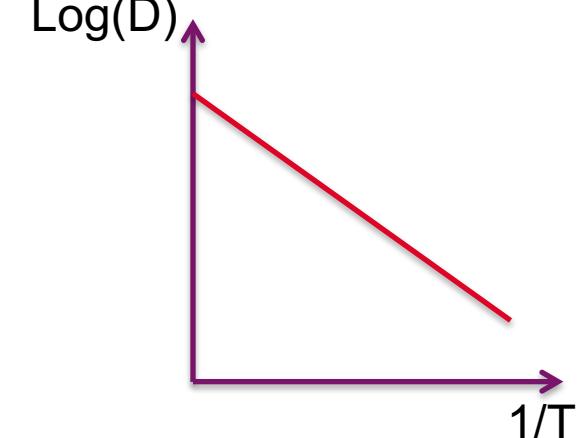
$$C_{A^*}(x, t) = \frac{M}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4 D t}\right)$$

## Diffusion experiment in solid

(\*Pb tracer, Von Hevesy, 1921)



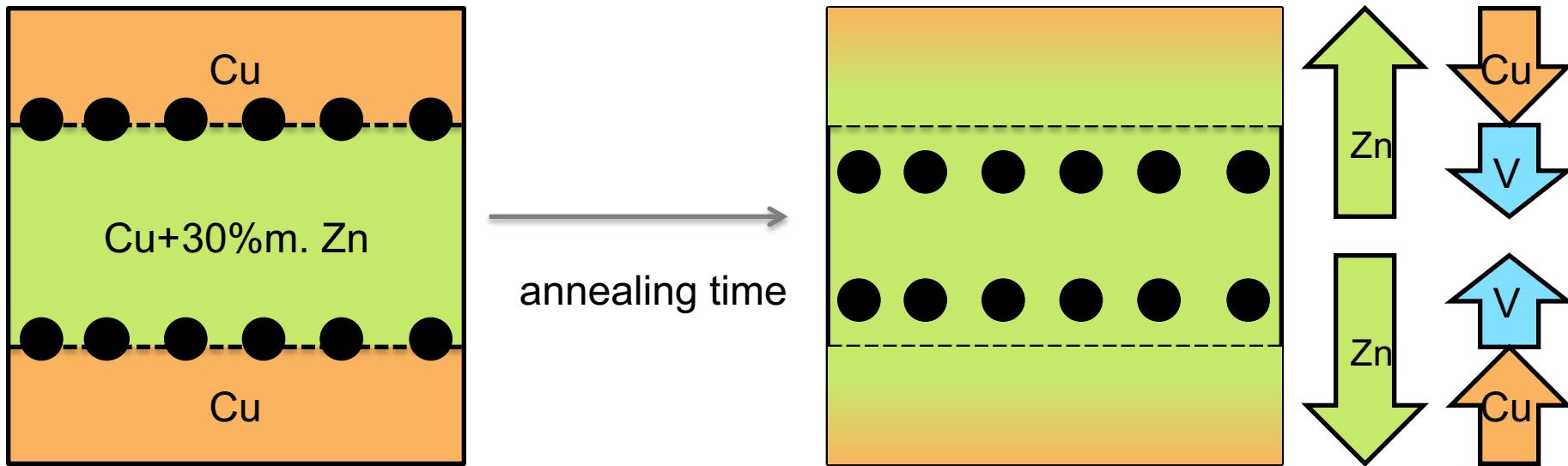
Arrhenius law  
Log(D) vs 1/T



# From macroscopic to microscopic diffusion

## Interdiffusion in Cu-Zn

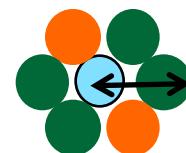
Kirkendall, 1942



Displacement of the markers during interdiffusion!

Kirkendall explained it by introducing vacancies (after his thesis defense)

Microscopic diffusion mechanism:  
Vacancy-atom exchange



Macroscopic fluxes

$$J_V = - \sum_i J_i$$

# Vacancy-atom exchange frequency

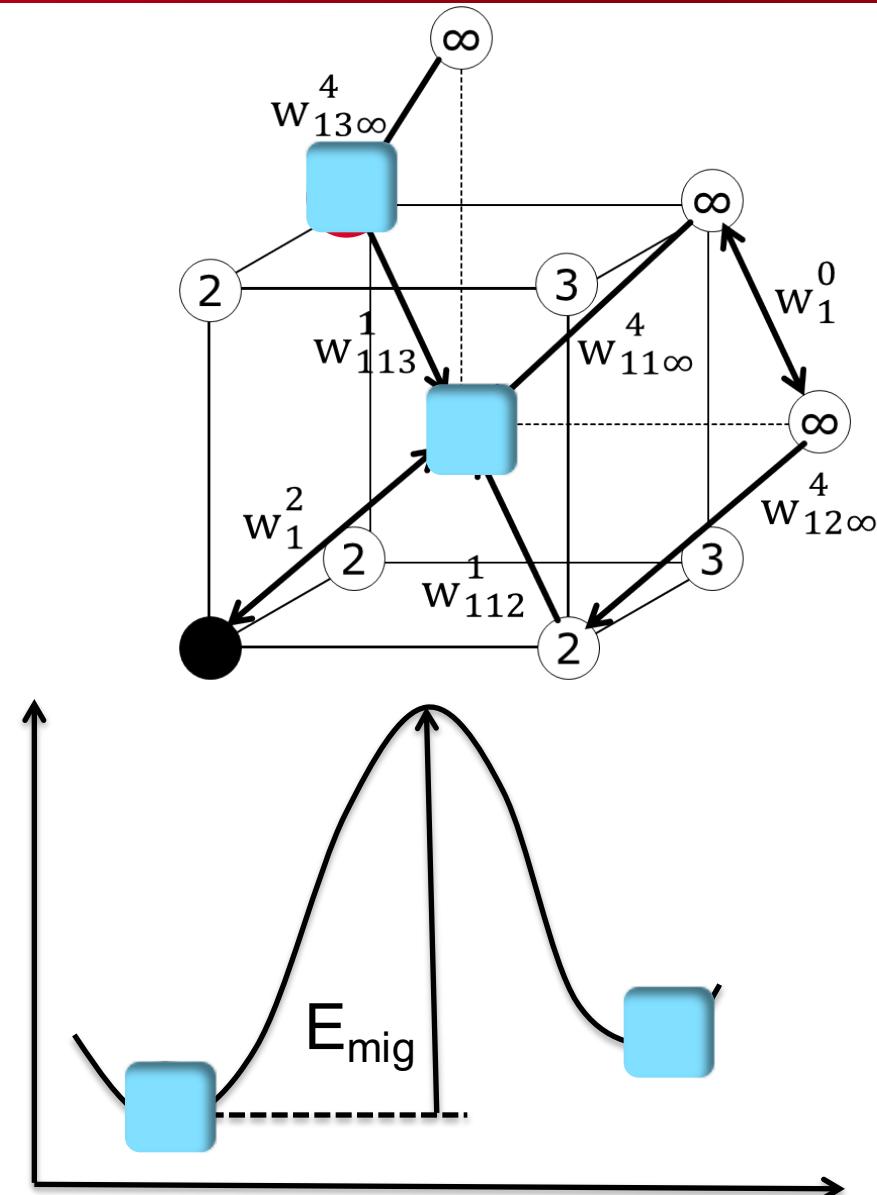
## Transition State Theory

\*H. Heyring, 1935

If  $t_{\text{vib}}, t_{\text{jump}} \ll t_{\text{residence}}$

the exchanges can be described  
on a rigid lattice using  
a thermally activated frequency

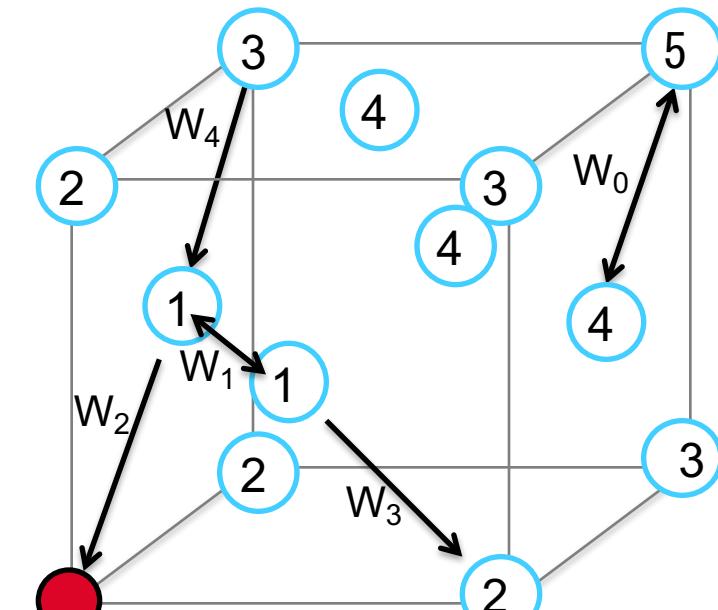
$$W_{BV} = v_B e^{-\frac{E_{\text{mig}}}{k_B T}}$$



# From microscopic to macroscopic diffusion in alloys

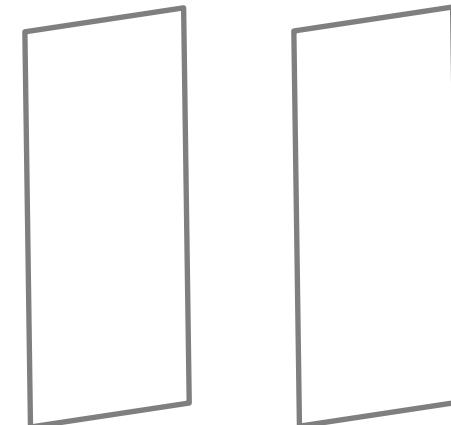
\*A.B. Lidiard. Phil. Mag., 46 (7) (1955)

## Five frequency model of Lidiard



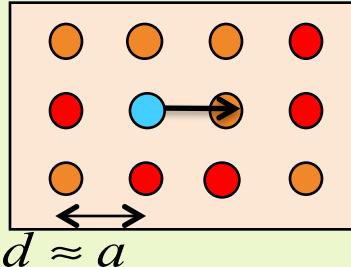
## Macroscopic fluxes

Pair method



# A multiscale approach for diffusion and phase transformations

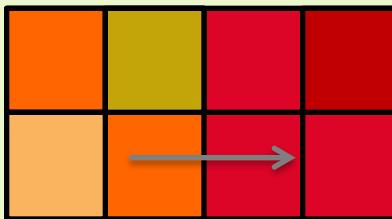
## Atomic diffusion model



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

$$\omega_{VA} = v_A \exp\left\{-\frac{E_A^{act}}{k_B T}\right\}$$

## Nanoscale diffusion Phase field method, etc.

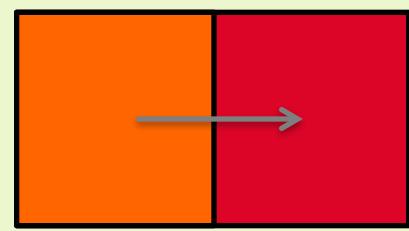


$$d \approx na$$

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

## Macroscopic

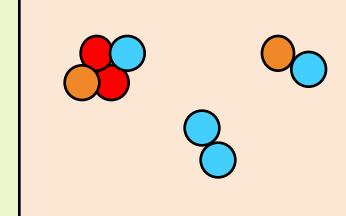
## diffusion equations From microns to meters



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

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

## Nano-clusters Cluster Dynamics, OKMC



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

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

$$\mathbf{J}_B = -D \nabla C_B$$

# OUTLINE

## 1. Diffusion: a property that can be measured at various scales

- a) Onsager formalism versus Fick's laws
- b) Interdiffusion within the Onsager formalism
- c) Nanoscale diffusion in multilayers

## 2. Modeling of diffusion and diffusion data for what?

- a) Parameterization of the Atomic Kinetic Monte Carlo
- b) Lattice rate theory for driven systems
- c) Phase Field method
- d) Cluster Dynamics

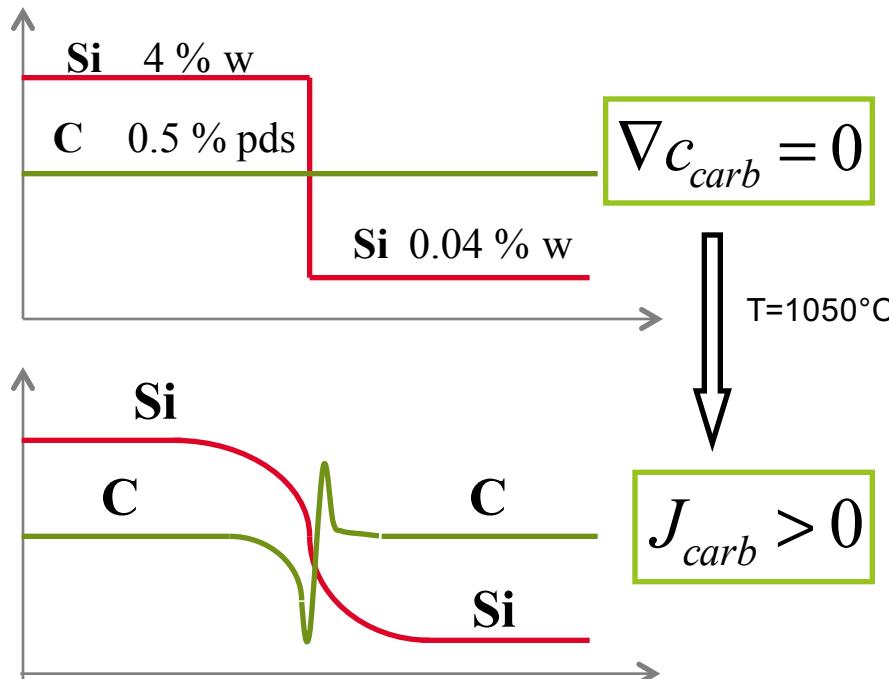
## 3. Diffusion from the microscopic diffusion processes

- a)  $Lij$  from the equilibrium fluctuations
- b) Self-consistent mean field theory: generalized diffusion equation
- c) Applications of the SCMF theory

# **ONSAGER FORMALISM**

# The needs for an Onsager formalism

Interdiffusion Fe-Si-C  
\*Darken, 1949

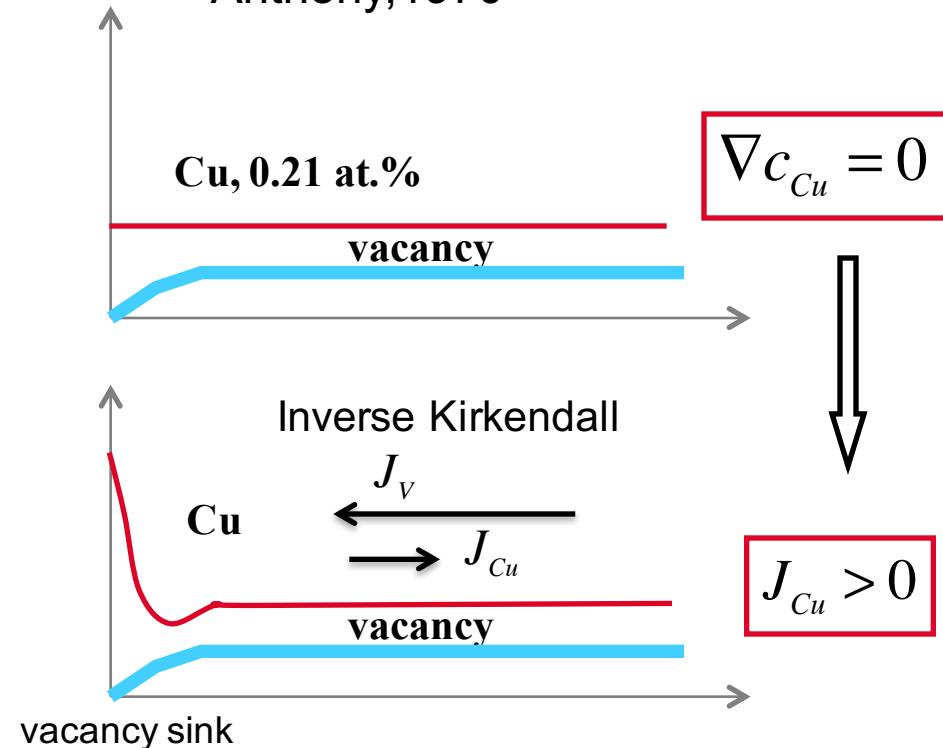


$$J_C = D_C \nabla c_{Si} = G_C J_{Si}$$

$$J_A = -D \nabla c_A$$

Fick's law is not valid

Quenching of Al-(Zn)  
\*Anthony, 1970



$$J_{Cu} = -D_{Cu} \nabla c_V = G_{Cu} J_V$$

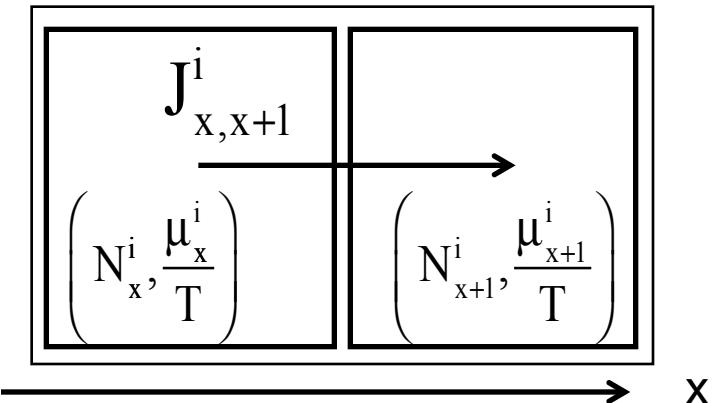
Flux couplings not reproduced by a Fick's law

# Onsager definition of fluxes

\*L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931).

$$\mu_x^i = \left. \frac{\partial F}{\partial N_x^i} \right)_{N_x^j}$$

Chemical potential as conjugate of the extensive conserved variable  $(N_x^i)$



## Flux of particles

Within the linear response theory:

$$J_i = - \sum_j L_{ij} \frac{(\mu_{x+1}^j - \mu_x^j)}{k_B T}$$

- Diffusion driving forces are gradients of chemical potentials
- $L_{ij}$  are equilibrium quantities (that do not depend on the diffusion experiment)
- Production of entropy: positive definite Onsager matrix ( $L_{ij}$ )
- Onsager-Casimir's reciprocal relation (1931):  
Microscopic time reversal (detailed balance in lattice-based diffusion) leads to symmetric Onsager matrix ( $L_{ij}$ )

# Onsager coefs versus Diffusion coefs

Fluxes in a binary alloy (ABV):

$$\begin{cases} J_A = -L_{AA} \nabla \mu_A - L_{AB} \nabla \mu_B - L_{AV} \nabla \mu_V \\ J_B = -L_{BA} \nabla \mu_A - L_{BB} \nabla \mu_B - L_{BV} \nabla \mu_V \\ J_V = -J_A - J_B \end{cases}$$

Three independent Onsager coefs  
and two driving forces

$$\begin{cases} J_A = -L_{AA} \nabla(\mu_A - \mu_V) - L_{AB} \nabla(\mu_B - \mu_V) \\ J_B = -L_{AB} \nabla(\mu_A - \mu_V) - L_{BB} \nabla(\mu_B - \mu_V) \\ L_{AV} = -L_{AA} - L_{AB} \\ L_{BV} = -L_{BB} - L_{AB} \end{cases}$$

Diffusion coefficients

$$J_i = -L_{ij} \frac{\partial(\mu_j - \mu_v)}{\partial C_A} \nabla C_A - L_{ij} \frac{\partial(\mu_j - \mu_v)}{\partial C_V} \nabla C_V$$

 Diffusion coefft

Experimental diffusion coefs

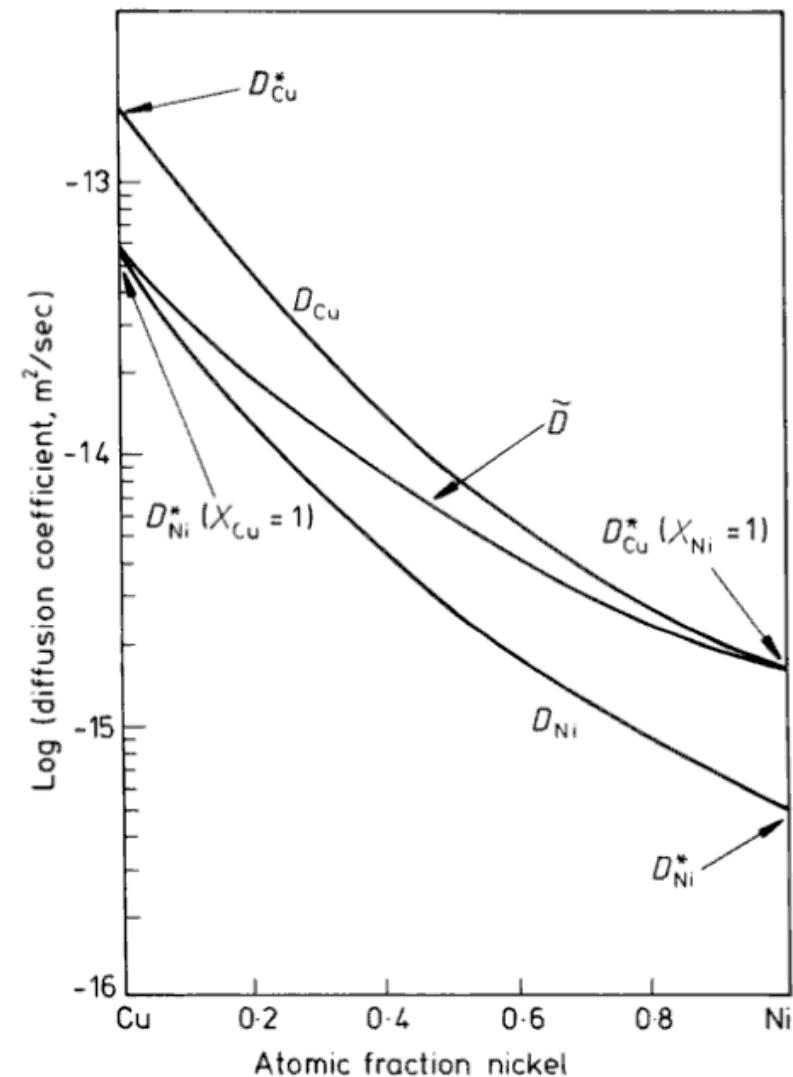
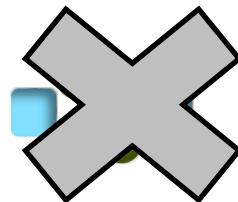


Fig. 2.21 The relationship between the various diffusion coefficients in the Cu-Ni system at 1000 °C (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

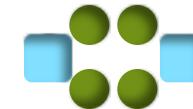
# The vacancy: both a magical concept and a nightmare

Introduces a second time-scale, off diagonal  $L_{AB}$  and correlations

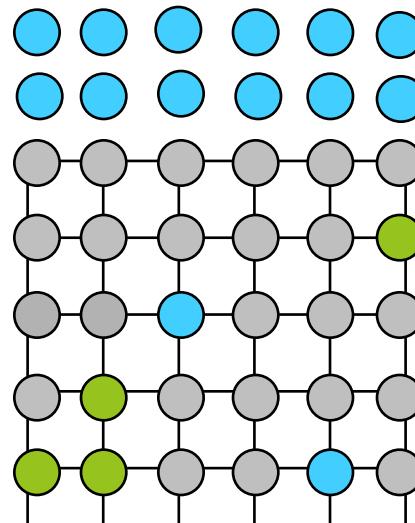
## the correlation effects



very rare event



Vacancy: an equilibrium structural defect



Vacancy in most solid systems is a non conservative species:  
the vacancy number  $N_V$  is deduced  
from the minimization of the free  
enthalpy with respect to  $N_V$

# Gibbs-Duheim relationship

Extensive variables: free energy ( $F$ )  
number of atoms of species  $i$  ( $N_i$ )

$$dF = \sum_i \mu_i dN_i$$

Variation of  $F$  depends on the variation of the extensive  $N_i$  variables

Conjugate variable of  $N_i$ : intensive variable  
that depends on intensive variables only

$$\mu_i = \left. \frac{\partial F}{\partial N_i} \right)_{V,T,N_j}$$

Free energy  $F$  deduced from  
a virtual experiment

$$F = \int_0^N \sum_i \mu_i dN_i = N \int_0^N \sum_i \mu_i dC_i = N \sum_i \mu_i C_i = \sum_i \mu_i N_i$$

At equilibrium:

$$dF = 0 \Rightarrow dF = \sum_i N_i d\mu_i + \mu_i dN_i = 0 \Rightarrow \sum_i N_i d\mu_i = 0$$

Gibbs-Duheim relationship in alloy ABV

$$C_A \nabla \mu_A + C_B \nabla \mu_B + C_V \nabla \mu_V = 0$$

# Diffusion driving forces in terms of alloy & vacancy chemical potentials

Gibbs-Duheim:  $C_A \nabla \mu_A + C_B \nabla \mu_B + C_V \nabla \mu_V = 0$

$$\nabla(\mu_A - \mu_V) = -\frac{C_B}{C_A + C_B} \nabla(\mu_B - \mu_A) - \frac{1}{C_A + C_B} \nabla \mu_V$$

Alloy driving force
vacancy driving force

## Definition of the thermodynamic factor $\Phi$

$$\nabla C_V \ll \nabla C_B \quad \frac{\nabla(\mu_B - \mu_A)}{k_B T} = \frac{\Phi}{C_A C_B} \nabla C_B$$

A Bragg-Williams mean field expression:  $\Phi_{BW} = 1 - 4C_B(1 - C_B) \frac{T_c}{T}$

# **INTERDIFFUSION WITHIN THE ONSAGER FORMALISM**

# Interdiffusion in binary alloys

nonconservative vacancy:  $\nabla \mu_v = 0$

Diffusion driving forces

Thermodynamic factor  $\Phi$

$$\nabla(\mu_A - \mu_V) = -C_B \frac{\Phi}{C_A C_B} \nabla C_B$$

$$\nabla(\mu_B - \mu_V) = C_A \frac{\Phi}{C_A C_B} \nabla C_B$$

Fluxes in the frame of the cristal lattice

Intrinsic diffusion coefft  $D_i$

Kirkendall speed  $v_k$

$$\begin{cases} J_A = -\left( \frac{L_{AA}}{C_A} - \frac{L_{AB}}{C_B} \right) \Phi \nabla C_A = -D_A \nabla C_A \\ J_B = -D_B \nabla C_B \end{cases} \quad J_V = -(J_A + J_B) = v_K$$

Fluxes in the frame of the laboratory  
displacement of the lattice

$$J_A^0 = J_A + C_A v_K = -(C_A D_B + C_B D_A) \nabla C_A$$

Interdiffusion coefficient D

$$\frac{dC_A^0}{dt} = D \nabla^2 C_A^0 \quad \text{with} \quad D = C_A D_B + C_B D_A$$

# Interdiffusion in binary alloys

conservative vacancy

$$\nabla \mu_v \neq 0$$

$$\begin{cases} J_A = +M_{CV} \frac{\nabla(\mu_B - \mu_A)}{k_B T} - \frac{L_{BB} + L_{AB}}{L_{AA} + L_{BB} + 2L_{AB}} J_v \\ J_B = -M_{CV} \frac{\nabla(\mu_B - \mu_A)}{k_B T} - \frac{L_{AA} + L_{AB}}{L_{AA} + L_{BB} + 2L_{AB}} J_v \end{cases}$$

Adiabaticity of V:  $\frac{dC_v}{dt} = 0$

$$\frac{dC_A}{dt} = -\nabla J_A = M_{CV} \frac{\Phi}{C_A C_B} \nabla^2 C_A$$

$$\text{Mobility: } M_{CV} = \frac{L_{AA} L_{BB} - L_{AB}^2}{L_{AA} + 2L_{AB} + L_{BB}}$$

$$\text{Conservative interdiffusion coefficient: } D = M_{CV} \frac{\Phi}{C_A C_B}$$

# Two interdiffusion mobilities

Non Conservative vacancy mobility

$$M_{\tilde{D}} = C_A [C_B L_{AA} - C_A L_{AB}] + C_B [C_A L_{BB} - C_B L_{AB}]$$

Conservative vacancy mobility

$$M_{CV} = \frac{L_{AA} L_{BB} - L_{AB}^2}{L_{AA} + 2L_{AB} + L_{BB}}$$

Mobility taking into account the second driving force produced by Kirkendall induced vacancies

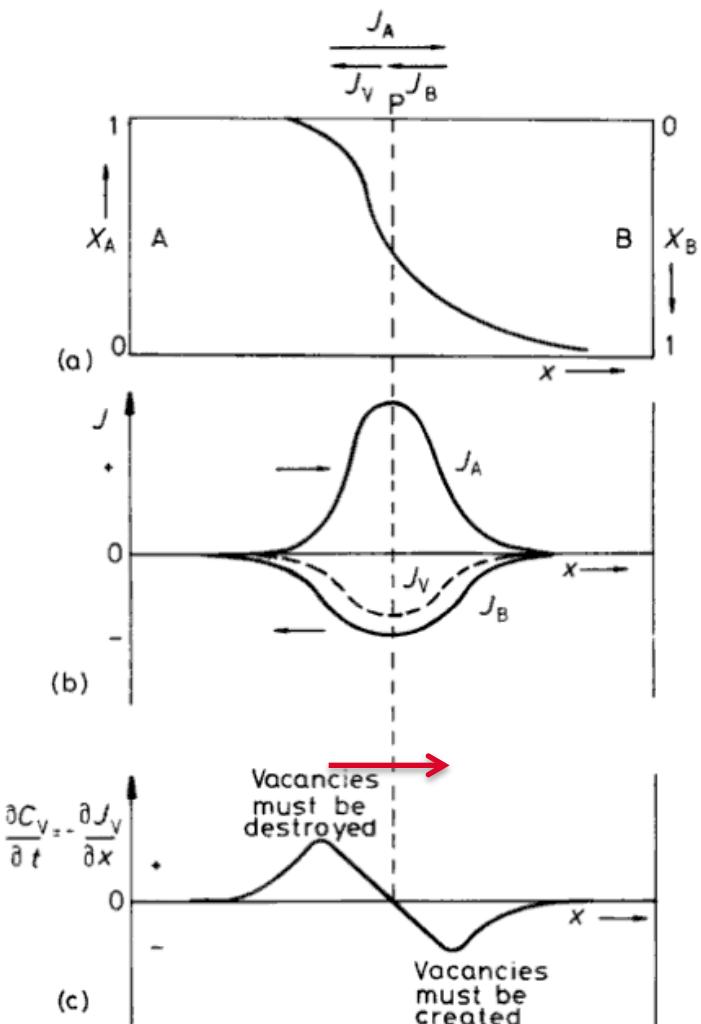
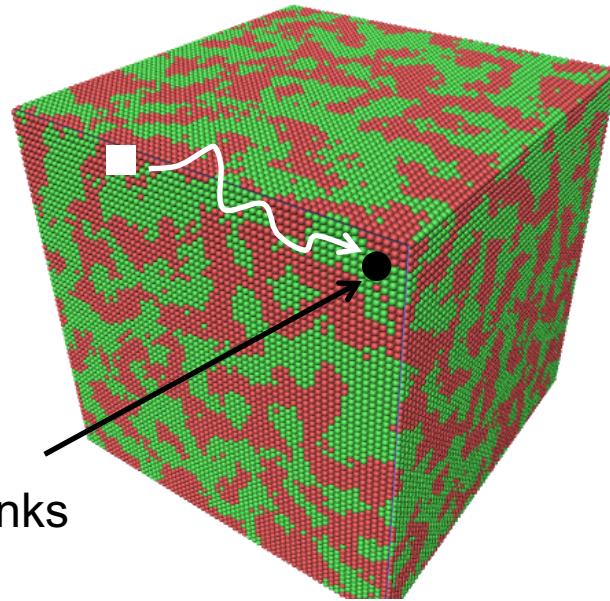


Fig. 2.15 Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position  $x$ . (c) The rate at which the vacancy concentration would increase or decrease if vacancies were not created or destroyed by dislocation climb.

# A mobility that depends on the microstructure

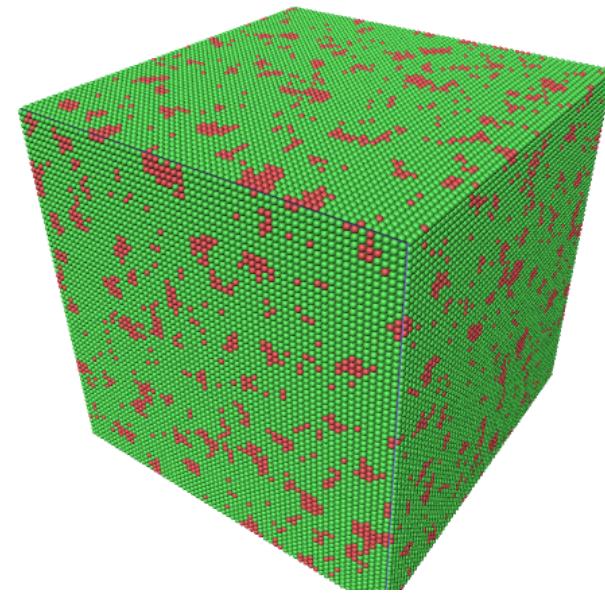
$C_B=0.5$



Point defect sinks

Percolated microstructure

$C_B=0.15$



Non percolated microstructure

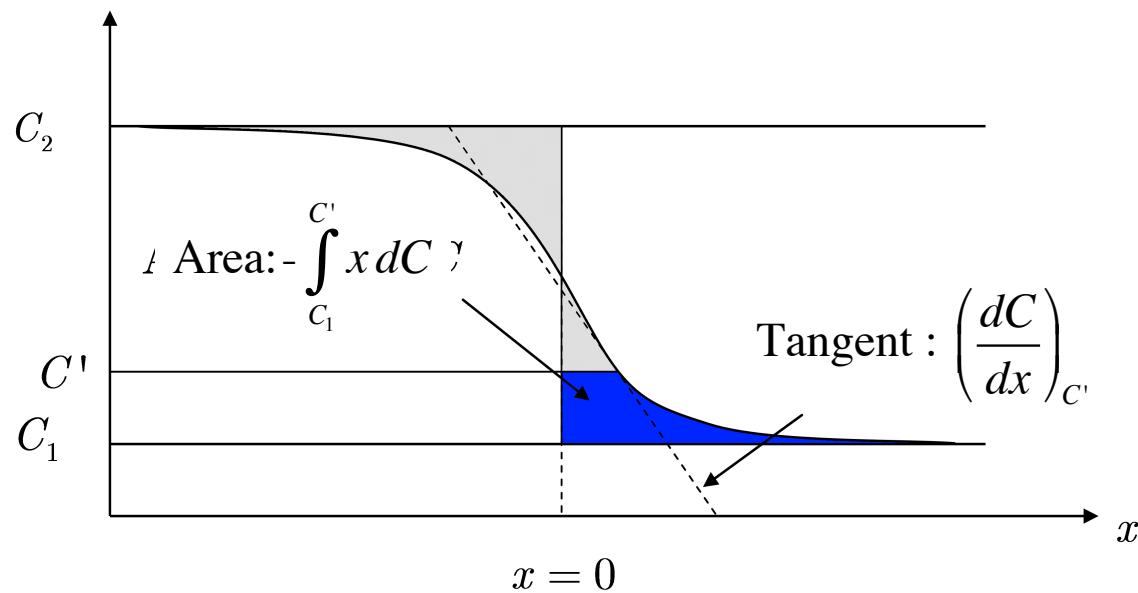
$M_{\tilde{D}}$  ?

$M_V$  ?

# The measurement of concentration dependent D

## The Matano's method

- Graphic solution  $D(C') := \frac{-\int_{C_1}^{C'} x dC}{2t \left( \frac{\partial C}{\partial x} \right)_{C'}}$
- The Matano's plane ( $x = 0$ ) is defined by :  $\Rightarrow \int_{C_1}^{C_2} x dC = 0$



# Classical diffusion experiments

Tracer A\* in A

$$\nabla \mu_B = 0 \nabla \mu_{A^*} = -(c_A / c_{A^*}) \nabla \mu_A$$

$$J_{A^*} = -L_{A^*A^*} \left( \frac{1}{C_{A^*}} - \frac{L_{A^*A}}{C_A L_{A^*A^*}} \right) \nabla C_A^*$$

Intrinsic diffusion coefficients

$$\nabla \mu_B = -(c_A / c_B) \nabla \mu_A$$

$$\begin{cases} J_A = -\left( \frac{L_{AA}}{C_A} - \frac{L_{AB}}{C_B} \right) \Phi \nabla C_A = -D_A \nabla C_A \\ J_B = -D_B \nabla C_B \end{cases}$$

Interdiffusion coefficients

$$\tilde{D} = C_B D_A + C_A D_B$$

Wind factor: not easily measured

$$\nabla \mu_V$$

$$G = \frac{L_{BV}}{L_{BB}}$$

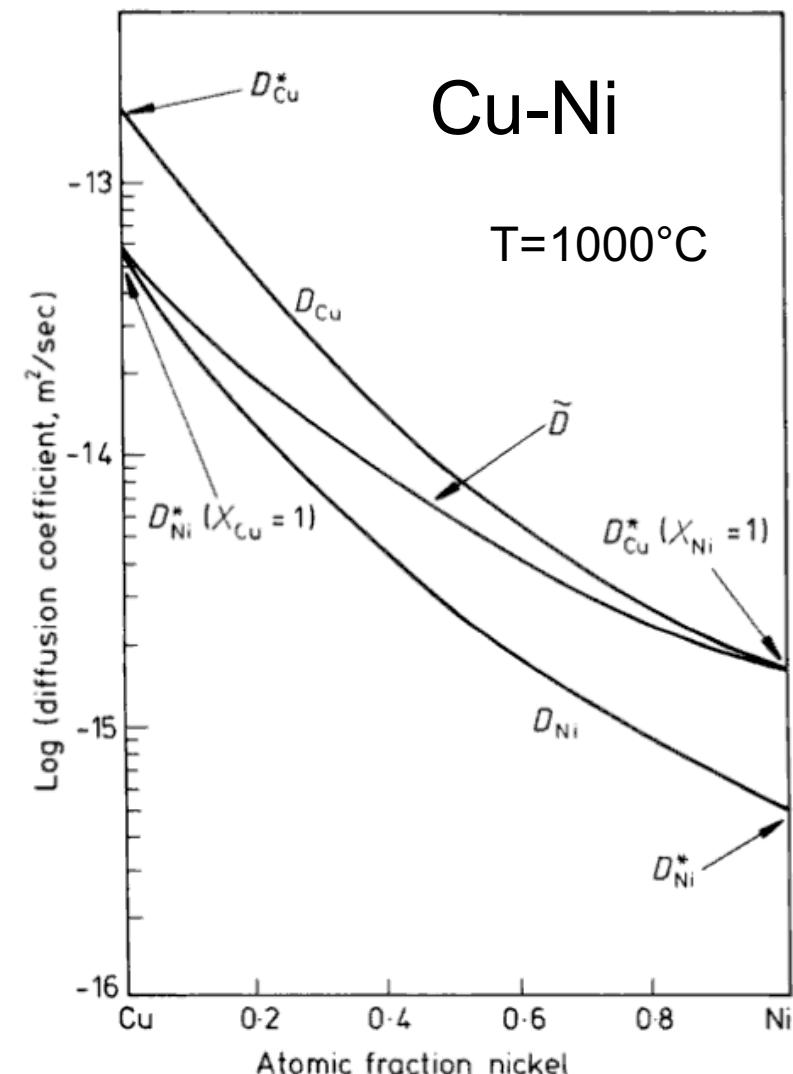


Fig. 2.21 The relationship between the various diffusion coefficients in the Cu-Ni system at 1000 °C (After A.G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1971.)

# A lack of experimental data

Partial characterization of diffusion properties in binary alloys:

- two intrinsic diffusion coefficients only for the determination of 3 Onsager coefficients
- Even for steels, diffusion coefficients have been measured for a narrow range of composition and temperature (high temperature)

Some phenomenological approximations

Darken:  $D_i = D_i^* \Phi$

CALPHAD-DICTRA:

$$L_{ij} = 0 \text{ if } i \neq j$$

Manning's relations

$$L_{ij} = \frac{C_i D_i^*}{k_B T} \left[ \delta_{ij} + \frac{1-f_0}{f_0} \sum_k C_k D_k^* \right]$$

does not produce negative off-diagonal  $L_{ij}$

- Can we extrapolate low-T diffusion properties from high T?
- No data for diffusion mechanisms occurring under irradiation only (split interstitial)
- Is the possible change of sign of the off-diagonal  $L_{ij}$  affecting kinetics?

# NANOSCALE DIFFUSION IN MULTILAYERS

# Nanoscale interdiffusion

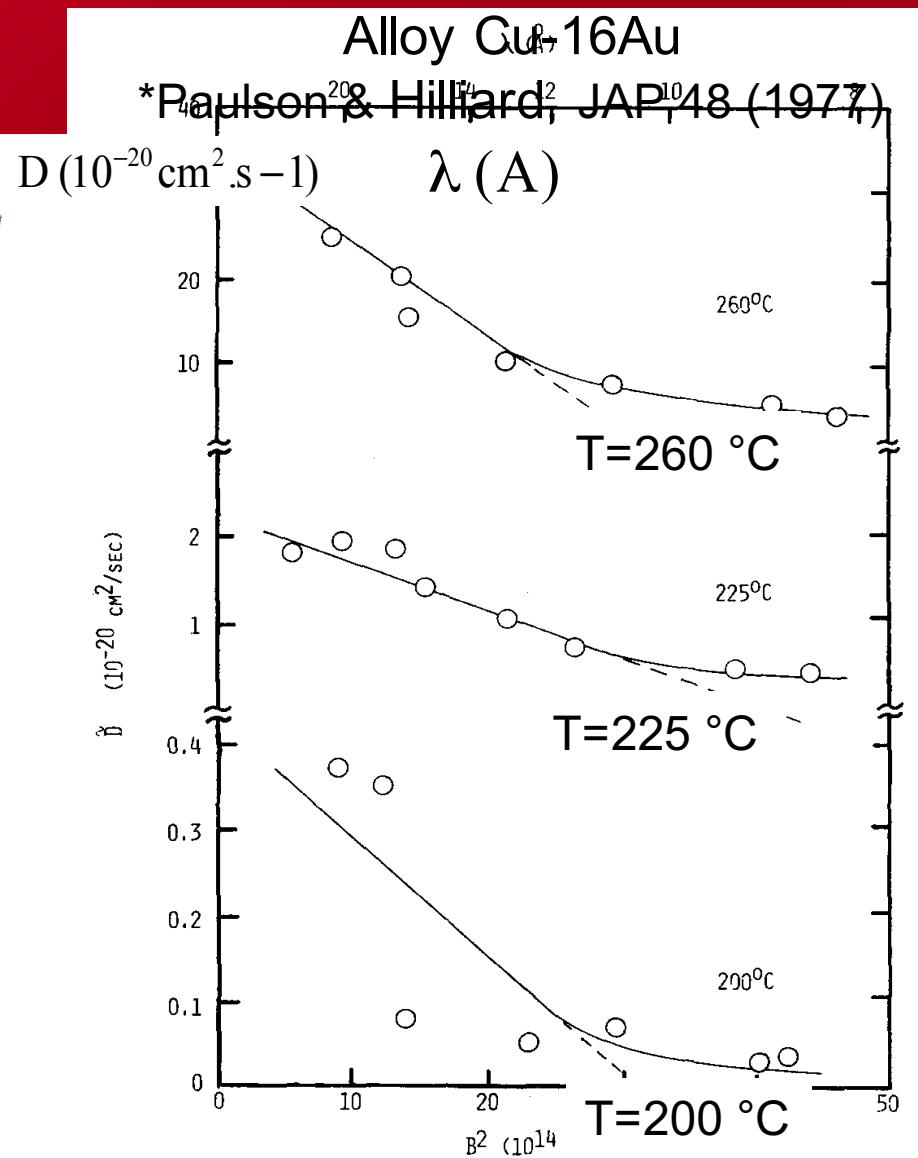
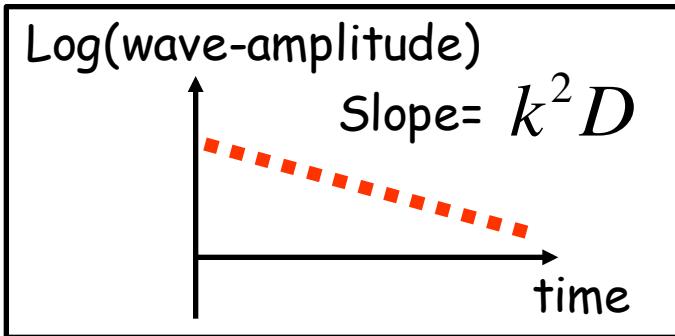
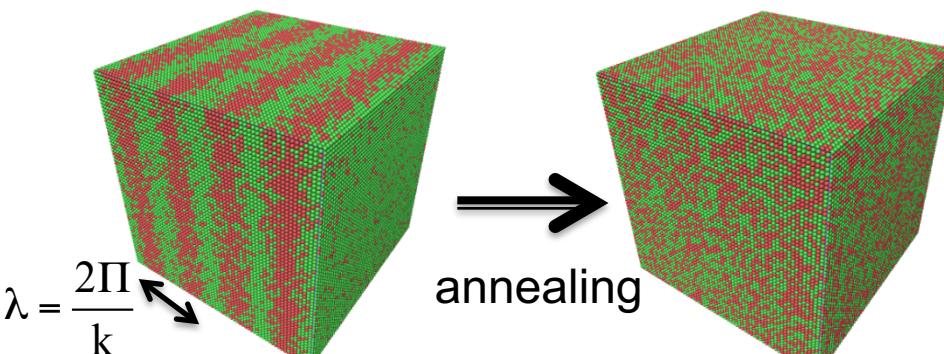


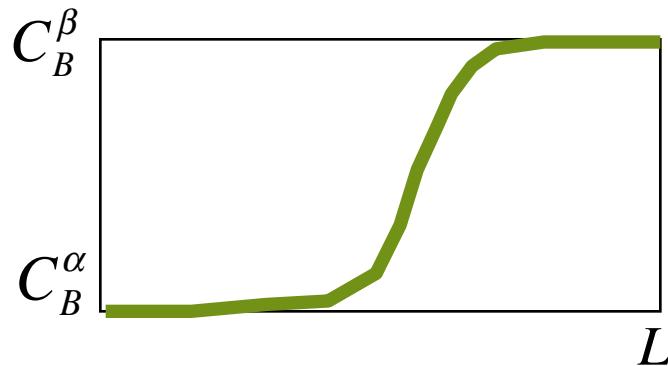
FIG. 5. The effective diffusion coefficient  $\tilde{D}_\lambda$  as a function of  $B^2$  at 200, 225, and 260 °C.

$$k^2 (10^{14} \text{ cm}^{-2})$$

# Cahn-Hilliard model of the driving force

## Free energy of an inhomogeneous system

\*Cahn and Hilliard, 1958



$$F = AN_V \int_L \left( f + \frac{1}{2} \kappa \left( \frac{dC_B}{dx} \right)^2 \right) dx$$

A: surface and V: total volum  $V=A*L$   
 $N_V$ : nbr of atoms per unit volum

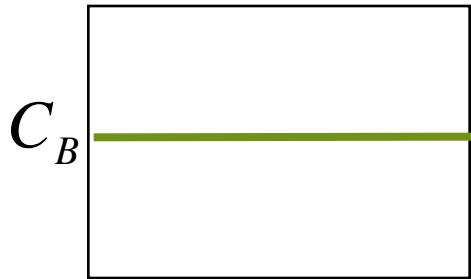
## A phase field kinetic equation (\*Cahn, 1965)

$$\frac{dC_B}{dt} = M \nabla^2 \frac{\delta F}{\delta C_B(x)} = M \nabla^2 \left( \frac{\partial f}{\partial C_B} - \kappa \frac{d^2 C_B}{dx^2} \right) \quad M = \frac{\tilde{D}}{\partial^2 f / \partial C_B^2}$$

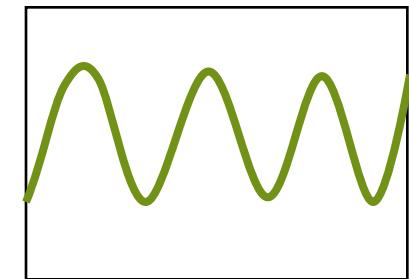
It is assumed that a similar expression of the free energy can be used in non equilibrium systems and the mobility is related to the interdiffusion coeff D

# Expansion of the alloy chemical potential around a homogeneous solid solution

$$\mu_B - \mu_A = (\mu_B - \mu_A)_{k=0} + \left( \frac{\partial^2 f}{\partial C_B^2} + \kappa k^2 \right) \delta C_B$$



+ sinusoïdal composition fluctuation  
with wavevector  $k$



Composition gradient parameter  $\kappa$  deduced from the equilibrium composition fluctuations

$$S(k) = \delta C_B(k) \delta C_B(-k) = \frac{1}{\frac{\partial^2 f}{\partial C_B^2} + \kappa k^2}$$

# THE CAHN-HILLIARD LINEAR STABILITY ANALYSIS (1958-65)

Composition modulation

$$R_{CH}(k) \quad C_B(x,t) = C_B^{(0)} \exp[i k \cdot x + R(k)t]$$

**Cahn-Hilliard**

$$\frac{dC_B}{dt} = M \left( \frac{\partial^2 f}{\partial C^2} \nabla^2 C_B - \kappa \nabla^4 C_B \right)$$

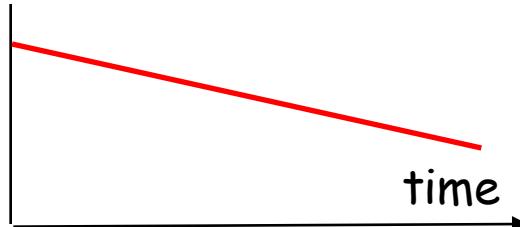
1st order in  $\delta C_B$   
+ Fourier transf.

**Dispersion relation  $R(k)$**

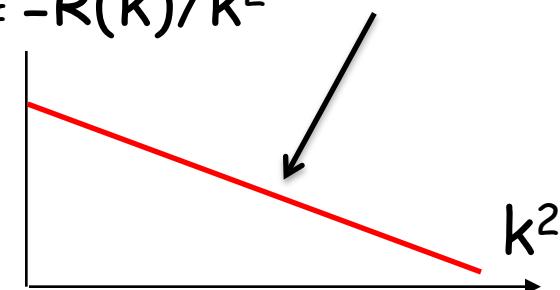
$$R_{CH}(k) = -k^2 M \left[ \frac{\partial^2 f}{\partial C^2} + \kappa k^2 \right]$$

$$S(k,t) = S(k,0) \exp(2R(k)t)$$

$\ln(S(k))$

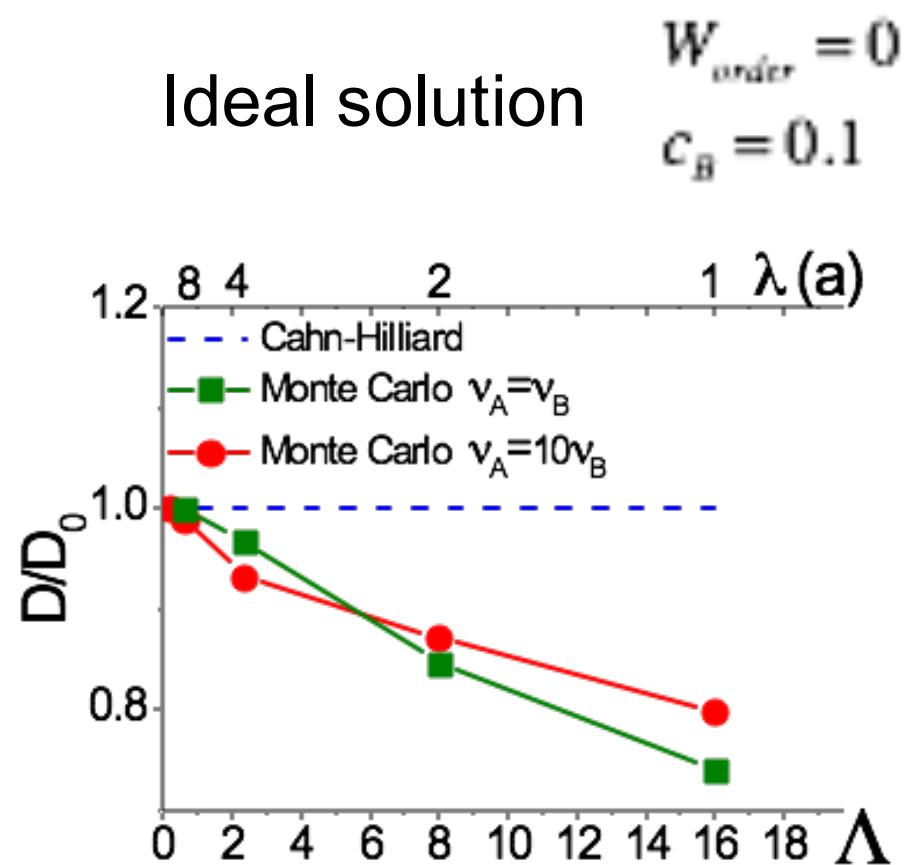
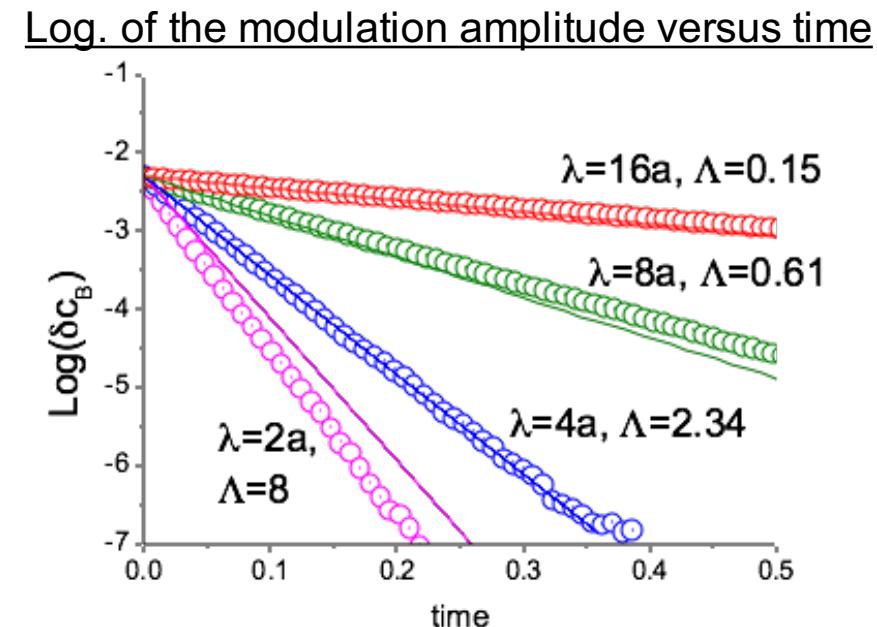
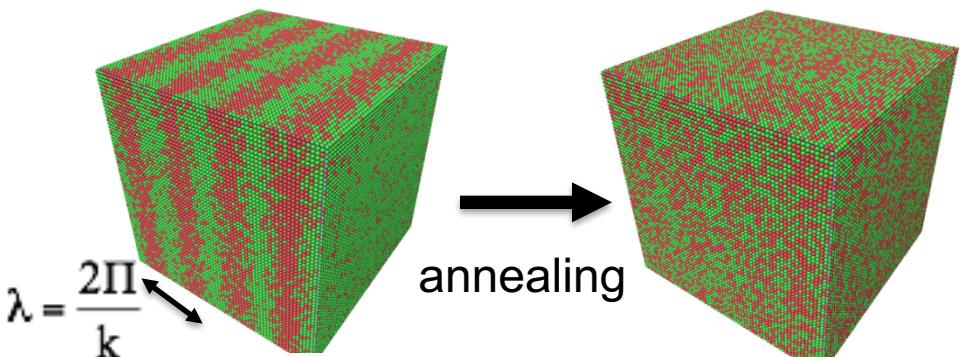


$$D_{eff} = R(k)/k^2 \quad \text{Slope=stiffness } K$$



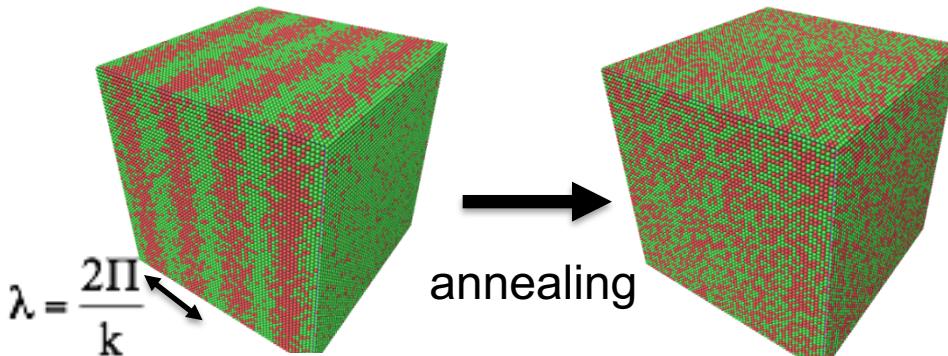
# Atomic Kinetic Monte Carlo simulations of nanoscale diffusion in ideal alloys

\*M. Nastar, Phys. Rev. B (2014)



Non zero composition gradient  
and non linear D  
in a non interacting system!

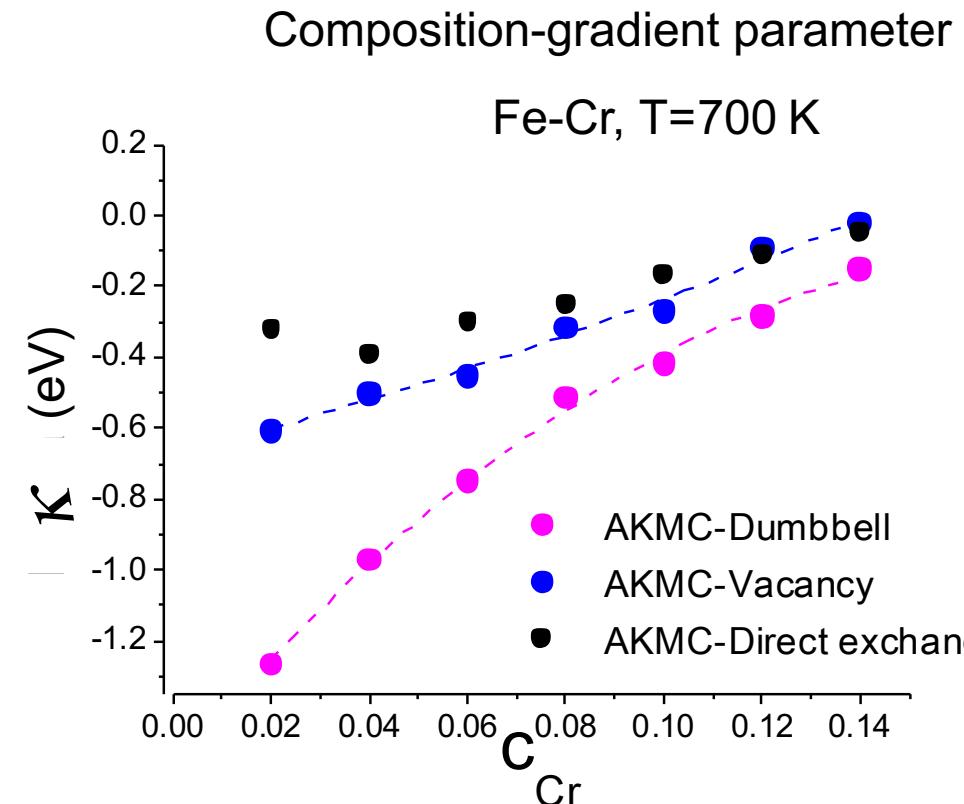
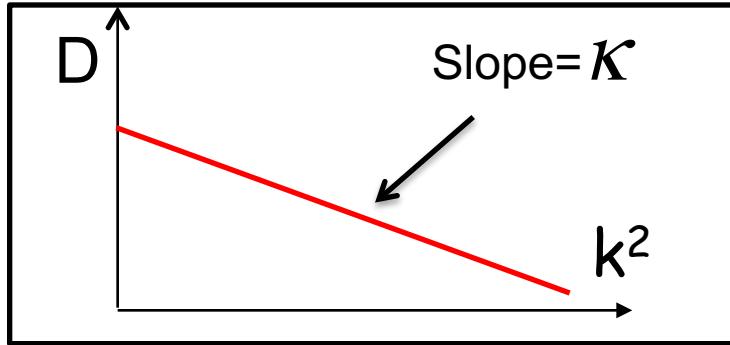
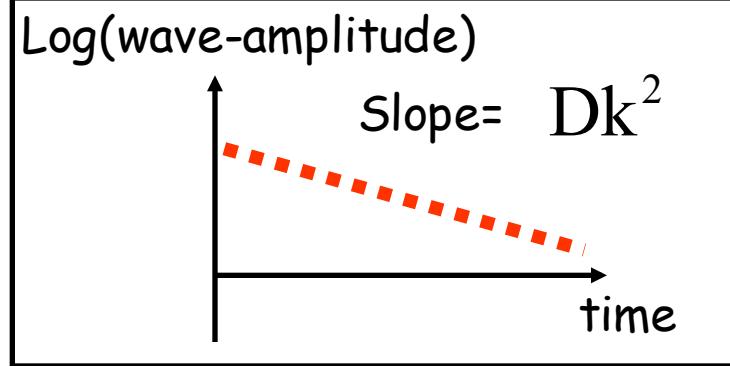
# ATOMIC KINETIC MONTE CARLO SIMULATIONS OF NANOSCALE DIFFUSION IN Fe-Cr



$$\lambda = \frac{2\pi}{k}$$

annealing

Vacancy and interstitial diffusion model fitted on DFT jump frequencies and diffusion data, \*F. Soisson et al. SRMP



➤ The composition-gradient parameter depends on the diffusion mechanism!

# OUTLINE

## 1. Diffusion: a property that can be measured at various scales

- a) Onsager formalism versus Fick's laws
- b) Interdiffusion within the Onsager formalism
- c) Nanoscale diffusion in multilayers

## 2. Modeling of diffusion and diffusion data for what?

- a) Parameterization of the Atomic Kinetic Monte Carlo
- b) Lattice rate theory for driven systems
- c) Phase Field method for spinodal decomposition
- d) Cluster Dynamics

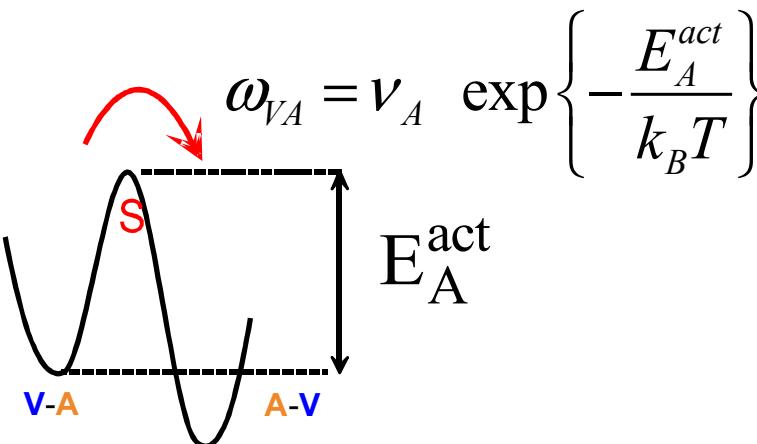
## 3. Diffusion from the microscopic diffusion processes

- a)  $Lij$  from the equilibrium fluctuations
- b) Self-consistent mean field theory: generalized diffusion equation
- c) Applications of the SCMF theory

# **PARAMETERIZATION OF THE AKMC SIMULATIONS**

# Monte Carlo simulation with a Residence time algorithm

## Activated jump frequency

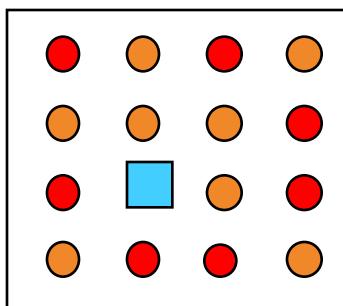


## Broken bond model of the activation energy

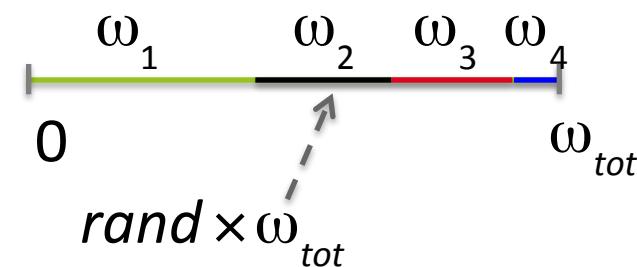
$$E_A^{act} = E_A^{saddlepoint} - \underbrace{\sum V_{Aj} + \sum V_{iV}}_{\text{broken bonds}}$$

## Master Equation of a Markov process

$$\frac{dP}{dt} = \sum_{l \neq n} B_{nl} P_l(t) - B_{ln} P_n(t)$$



## Residence time algorithm



$$t_{MC} = \frac{1}{\omega_{tot}}$$

# PHYSICAL TIME SCALE AND POINT DEFECT CONCENTRATIONS IN MONTE CARLO SIMULATIONS

$\langle C_v^{MC} \rangle = 1/N$  in a Monte Carlo box versus  $\langle C_v^{eq} \rangle$  in an alloy

If diffusion coefficient linear with Cv then

time rescaling:  $t = t_{MC} \langle C_v^{MC} \rangle / \langle C_v^{eq} \rangle$        $\langle C_v^{eq} \rangle$  evolves with time

If vacancy is at equilibrium then for any local environment  $\alpha$

$$t = t_{MC} \frac{C_v^{MC}(\alpha)}{C_v^{eq}(\alpha)}$$

possible reference environments: pure A and pure B

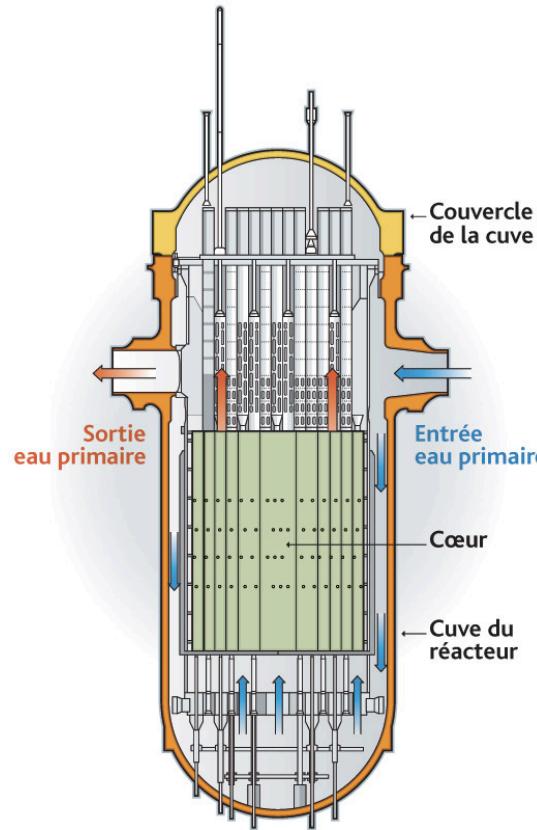
Estimation of total and local vacancy concentrations:

$$\langle C_v^{eq} \rangle = \langle C_v^{MC} \rangle \frac{C_v^{eq}(\alpha)}{C_v^{MC}(\alpha)}$$

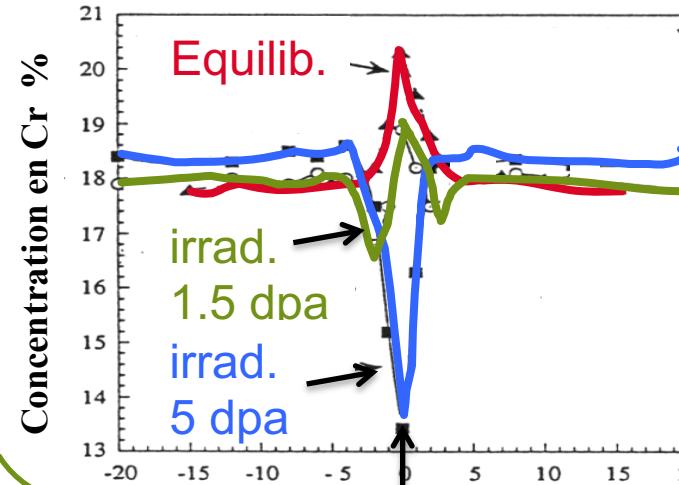
$$\langle C_i^v \rangle_\tau = \langle C_v^{eq} \rangle \frac{\tau_i^v}{\tau}$$

# LATTICE RATE THEORY FOR DRIVEN SYSTEMS

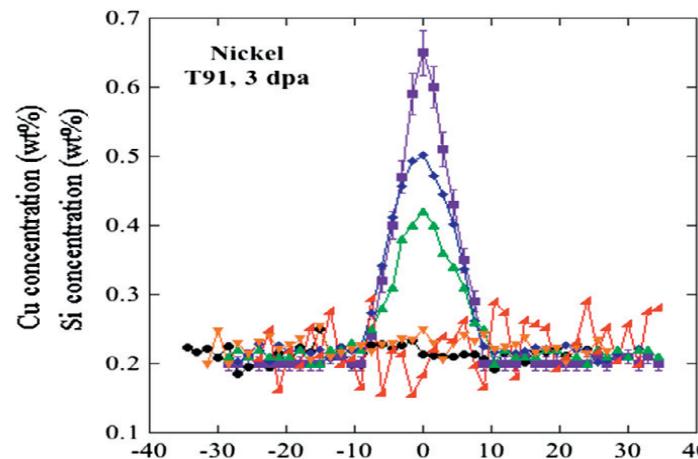
# Radiation Induced Segregation (RIS) in steels



## Austenitic steels (316)



## Ferritic steels (T91)

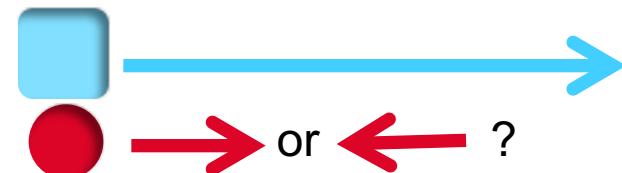
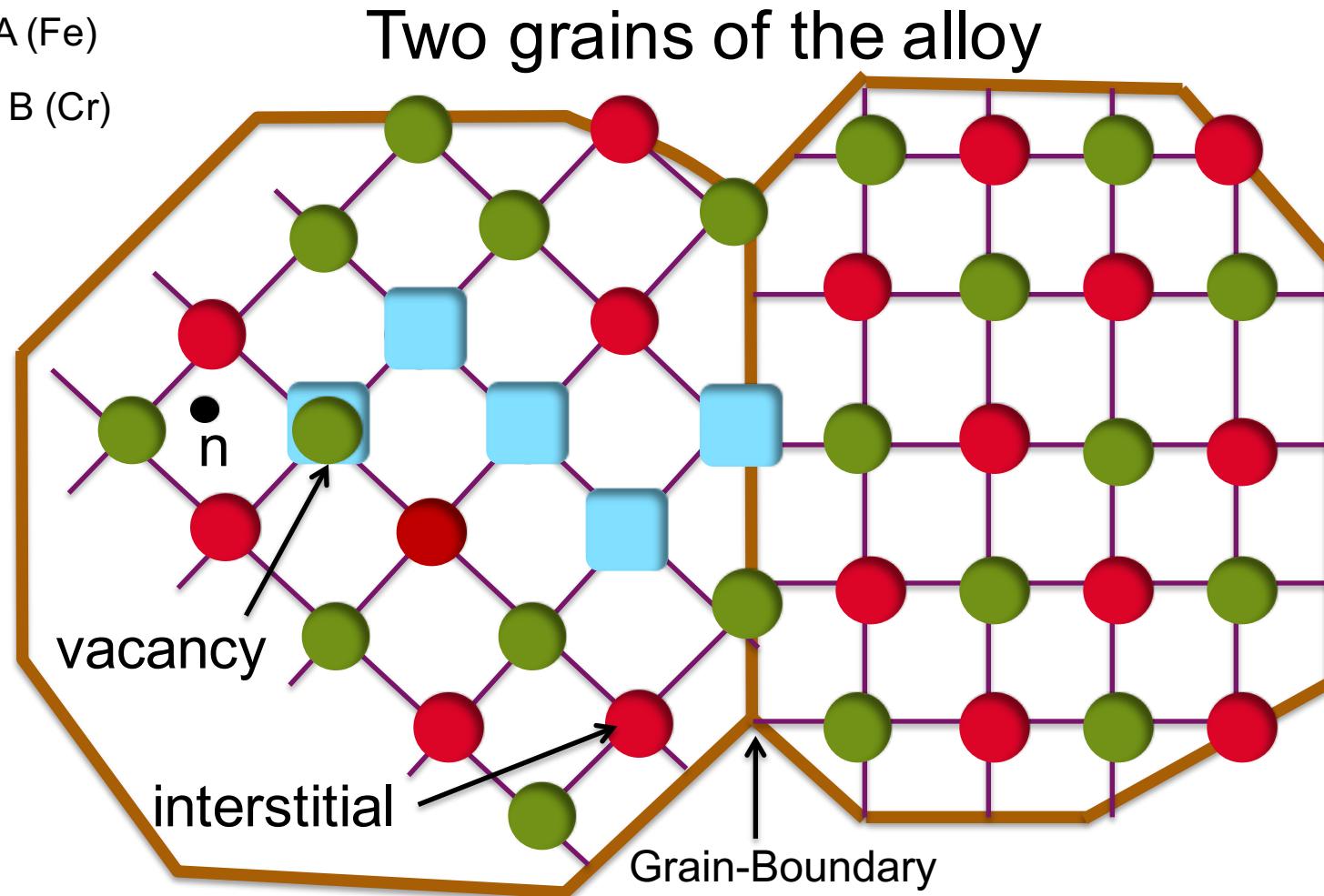


\*Busby, Was, Bruemmer, Edwards, Kenik,  
MRS Symp. Proc., 1999, **540**, 451

\*Wharry, Was , JNM 442 (2013)

# RIS at the atomic scale

atom A (Fe)  
atom B (Cr)



$$J_B = (L_{BB}^V + L_{AB}^V) \nabla \mu_V = -L_{BV}^V \nabla \mu_V$$

# Fluxes in binary alloys

$$\begin{cases} J_A^V = -L_{AA}^V \nabla \mu_A - L_{AB}^V \nabla \mu_B - L_{AV}^V \nabla \mu_V \\ J_B^V = -L_{AB}^V \nabla \mu_A - L_{BB}^V \nabla \mu_B - L_{BV}^V \nabla \mu_V \\ J_V = -(J_A^V + J_B^V) \\ J_A^I = -L_{AA}^I \nabla \mu_A - L_{AB}^I \nabla \mu_B - L_{AI}^I \nabla \mu_I \\ J_B^I = -L_{AB}^I \nabla \mu_A - L_{BB}^I \nabla \mu_B - L_{BI}^I \nabla \mu_I \\ J_I = +(J_A^I + J_B^I) \end{cases}$$

2x3 independant Lij coefcts

$$\begin{cases} L_{AV} = -(L_{AA}^V + L_{AB}^V) \\ L_{BV} = -(L_{BB}^V + L_{AB}^V) \\ L_{AI} = +(L_{AA}^I + L_{AB}^I) \\ L_{BI} = +(L_{BB}^I + L_{AB}^I) \end{cases}$$

## Driving forces in binary alloys

Chemical driving force

$$\frac{\nabla \mu_A}{k_B T} = \frac{\Phi}{C_A} \nabla C_A \quad \frac{\nabla \mu_B}{k_B T} = \frac{\Phi}{C_B} \nabla C_B$$

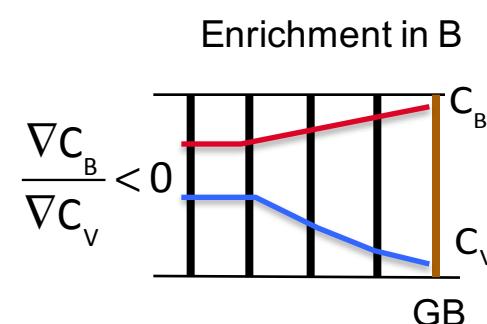
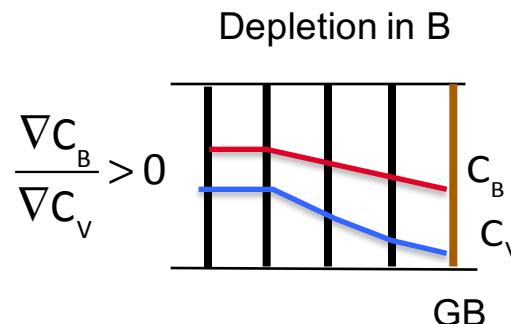
Quenching or irradiation driving force

$$\begin{aligned} \frac{\nabla \mu_V}{k_B T} &= \frac{1}{C_V} \nabla C_V - \frac{1}{C_A} \frac{\partial \ln C_V^{eq}}{\partial \ln C_A} \nabla C_A \\ \frac{\nabla \mu_I}{k_B T} &= \frac{1}{C_I} \nabla C_I - \frac{1}{C_A} \frac{\partial \ln C_I^{eq}}{\partial \ln C_A} \nabla C_A \end{aligned}$$

# Diffusion rate theory for Radiation Induced Seg.

$$\begin{cases} \frac{dC_V}{dt} = K_0 - RC_I C_V - \text{div}(J_V) \\ \frac{dC_I}{dt} = K_0 - RC_I C_V - \text{div}(J_I) \\ \frac{dC_A}{dt} = -\text{div}(J_A^V + J_A^I) \\ \frac{dC_B}{dt} = -\text{div}(J_B^V + J_B^I) \end{cases}$$

$$J_A^V = -L_{AA}^V \nabla \mu_A - L_{AB}^V \nabla \mu_B - L_{AV} \nabla \mu_V$$



## Steady state profile

$$\begin{cases} J_A = 0 \\ J_B = 0 \\ J_V = J_I \end{cases}$$

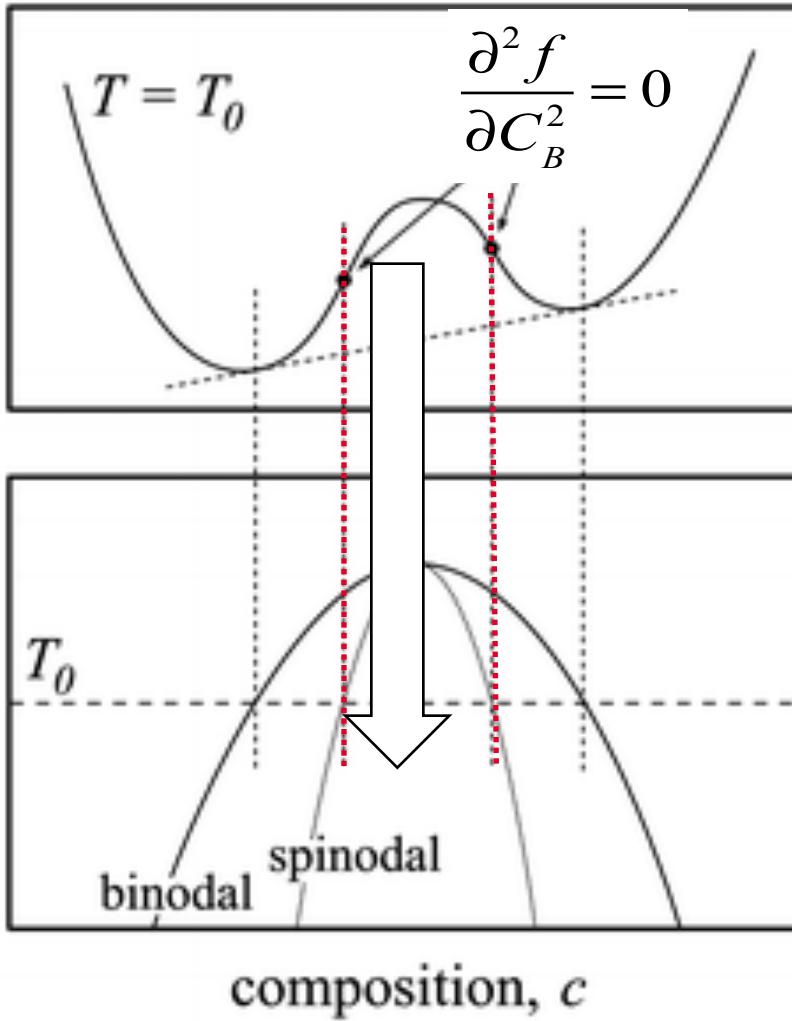
## Wiedersich formulae

$$\frac{\nabla C_B}{\nabla C_V} \propto - \left( \frac{L_{BV}}{L_{AV}} - \frac{L_{BI}}{L_{AI}} \right)$$

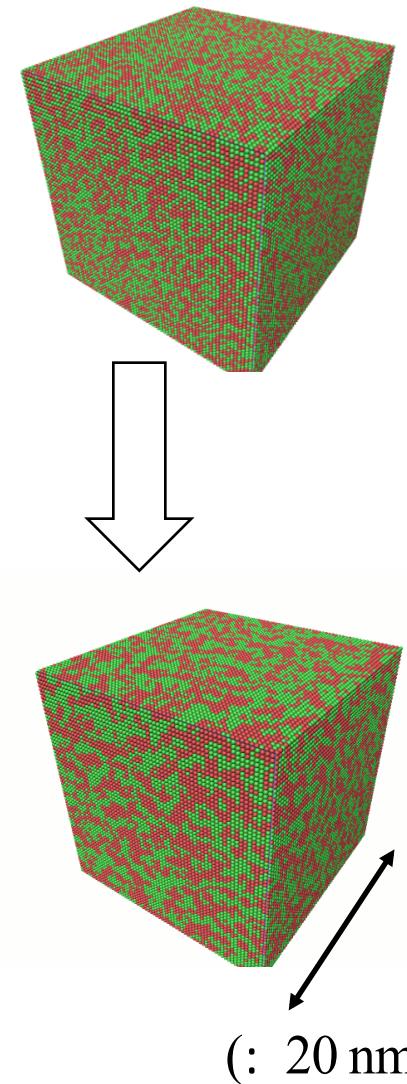
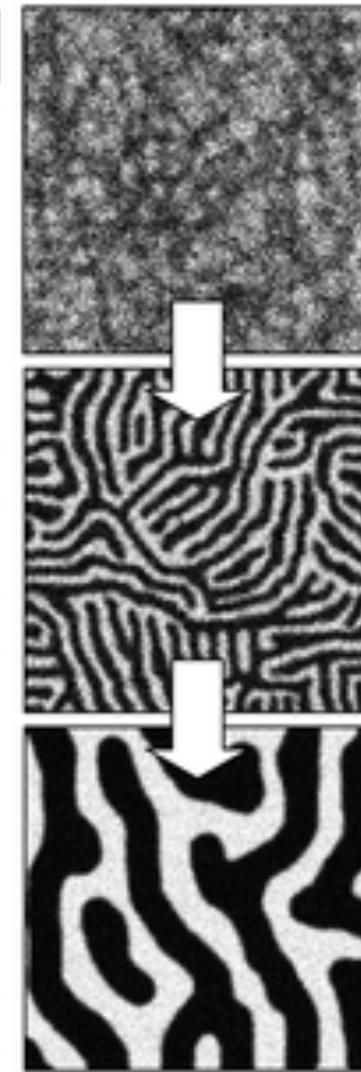
# PHASE FIELD METHOD FOR SPINODAL DECOMPOSITION

**SPINODAL REGIME: A MEAN FIELD CONCEPT**

(a)



(b)



# THE CAHN-HILLIARD LINEAR STABILITY ANALYSIS (1958-65)



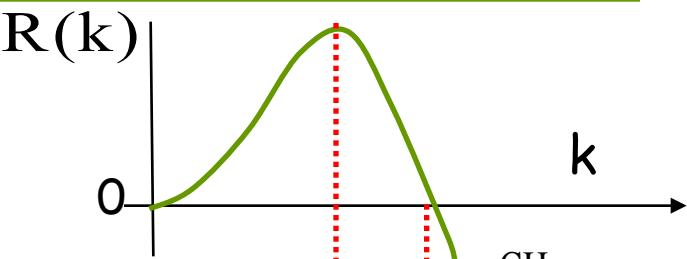
$$\delta C_B(x, t) = \delta C_B^{(0)} \exp[ik.x + R(k)t]$$

$$\frac{dC_B}{dt} = M \left( \frac{\partial^2 f}{\partial C_B^2} \nabla^2 C_B - \kappa \nabla^4 C_B \right)$$

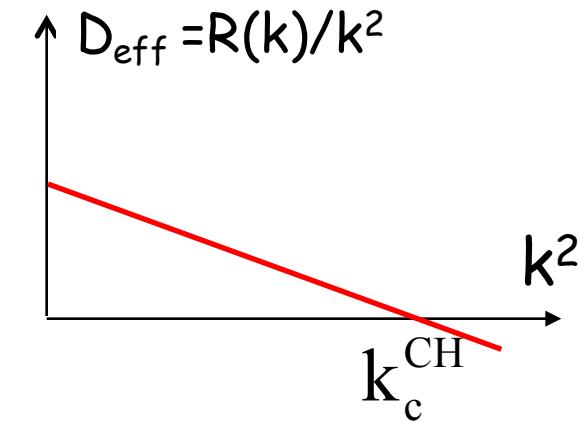
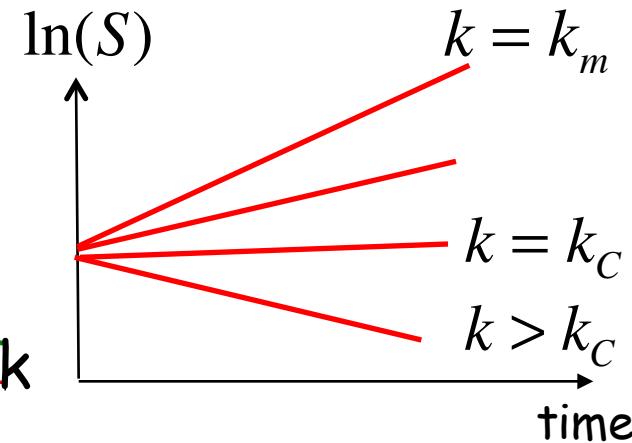
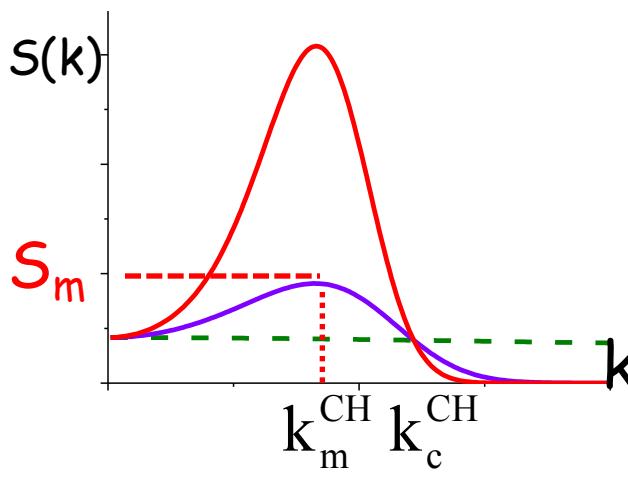
1st order in  $\delta C_B$   
+ Fourier transf.

**Dispersion relation  $R(k)$**

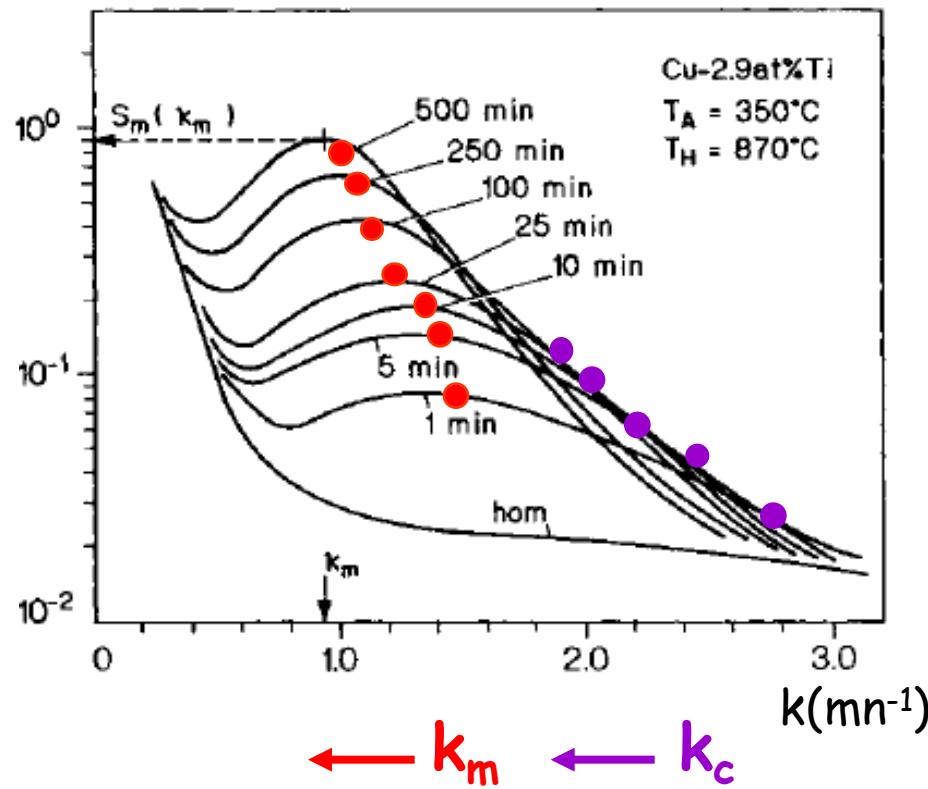
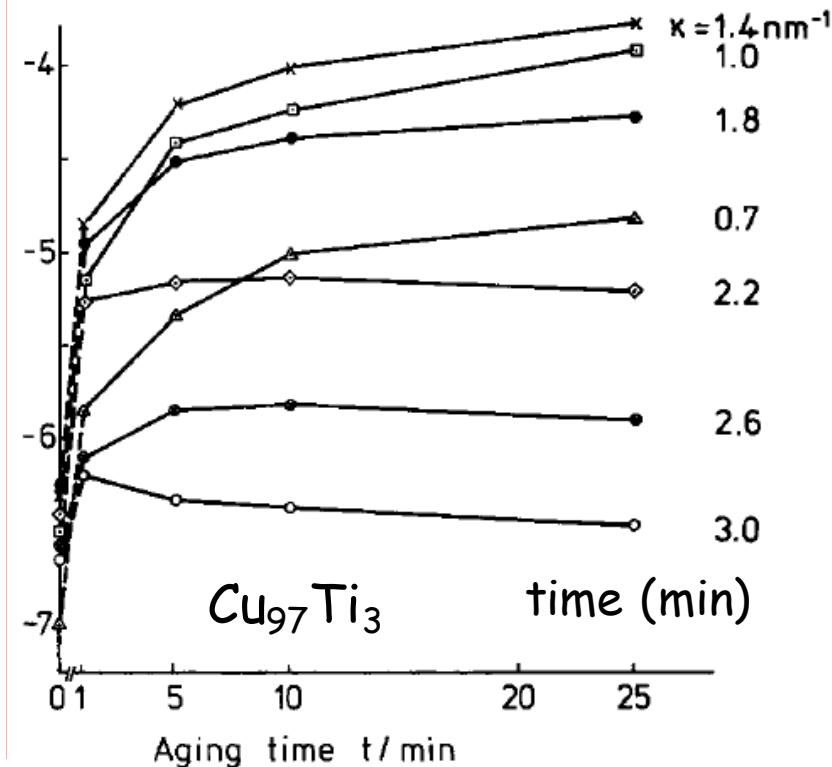
$$R_{CH}(k) = -k^2 M \left[ \frac{\partial^2 f}{\partial C_B^2} + \kappa k^2 \right]$$



$$S(k, t) = S(k, 0) \exp(2R(k)t)$$



## EXPERIMENTAL KINETICS: S AND LOG(S)

Decomposition of  $\text{Cu}_{97}\text{Ti}_3$  $T_H = 870^\circ \text{ C}$     $T_A = 350^\circ \text{ C}$ Structure function  $S(k, t)$ Temporal evolution of  $\ln(S(k))$ 

\*Eckerlebe et al., Springer (1986)

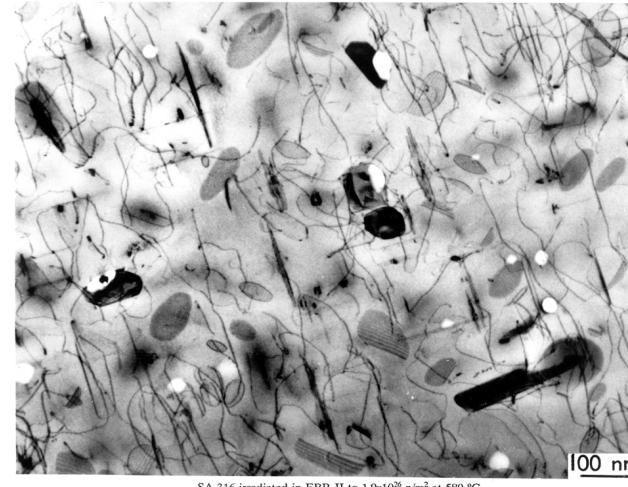
- The early stage effective diffusion coefficient is positive and not varying so much with  $k$

# **CLUSTER DYNAMICS**

# Microstructural evolution under irradiation

\*after slides of T. Jourdan

Formation of cavities, second phases, dislocation loops



Rate theory:

$$\begin{cases} \frac{dC_v}{dt} = G - K_{iv} C_i C_v - \sum_j k_{j,v}^2 D_v (C_v - C_{v,j}^{eq}) \\ \frac{dC_i}{dt} = G - K_{iv} C_i C_v - \sum_j k_{j,i}^2 D_i (C_i - C_{i,j}^{eq}) \end{cases}$$

Ex: a divacancy  $V_2$  should be treated as a sink, in  $k_{V_2,V}^2$  but  $C_{V_2}$  can also evolve

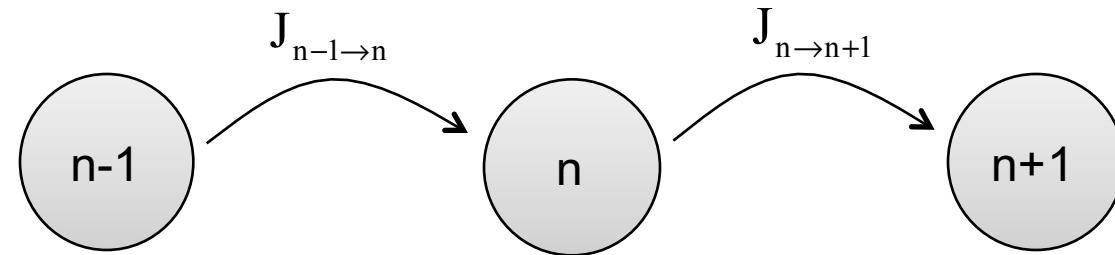
→ Simulate the whole clustering process:  $\frac{dC_v}{dt}, \frac{dC_{V_2}}{dt}, \frac{dC_{V_3}}{dt}, \dots, \frac{dC_{V_n}}{dt}$

# Cluster Dynamics

\*E. Clouet, *Modeling of Nucleation Processes, ASM handbook 22A (2009)*

## Master equation

$$\begin{cases} \frac{dC_n}{dt} = G_n + J_{n-1 \rightarrow n} - J_{n \rightarrow n+1} & n \geq 2 \\ \frac{dC_1}{dt} = G_1 - 2J_{1 \rightarrow 2} - \sum_{n \geq 2} J_{n \rightarrow n+1} - \sum_j k_{j,V}^2 D_V (C_V - C_{V,j}^{eq}) \end{cases}$$



## Flux in terms of V mobility

- Absorption coefficients  $\beta_{n,V}$ :

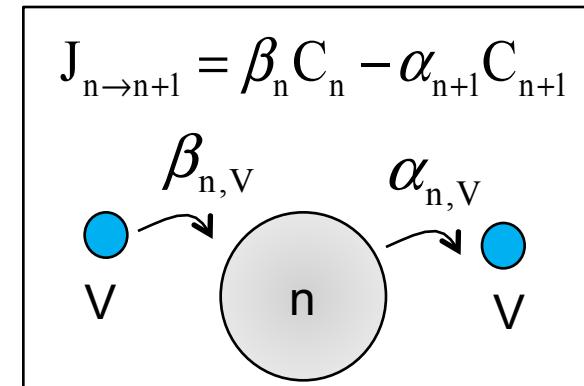
$$\beta_{n,V} = 4\pi r_n \frac{D_V}{\Omega} C_V$$

Asumption of a steady state profile:  $\Delta C_V = 0$

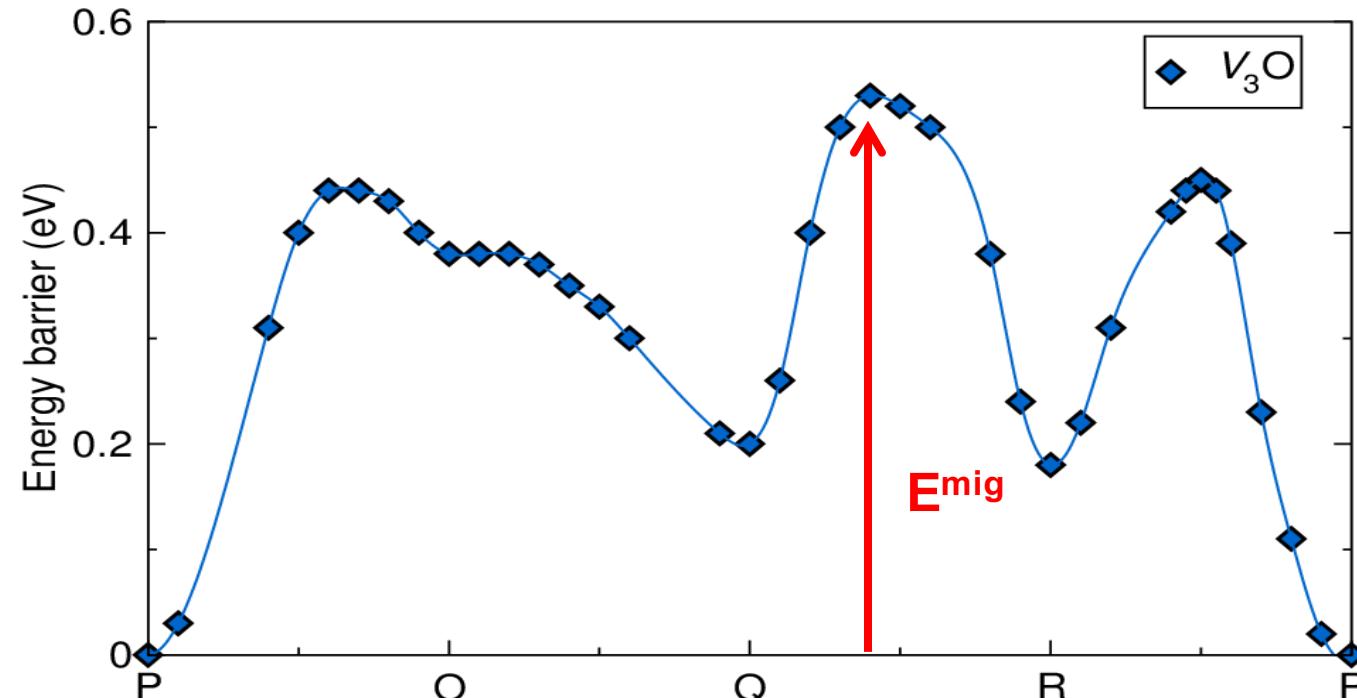
- Emission coefficients  $\alpha_{n,V}$  :

$$J_{n \rightarrow n+1} = 0 \Rightarrow \alpha_{n,V}^{eq} = f(\beta_n)$$

Asumption:  $\alpha_{n,V} = \alpha_{n,V}^{eq}$



# Cluster migration of clusters V<sub>3</sub>O in Fe

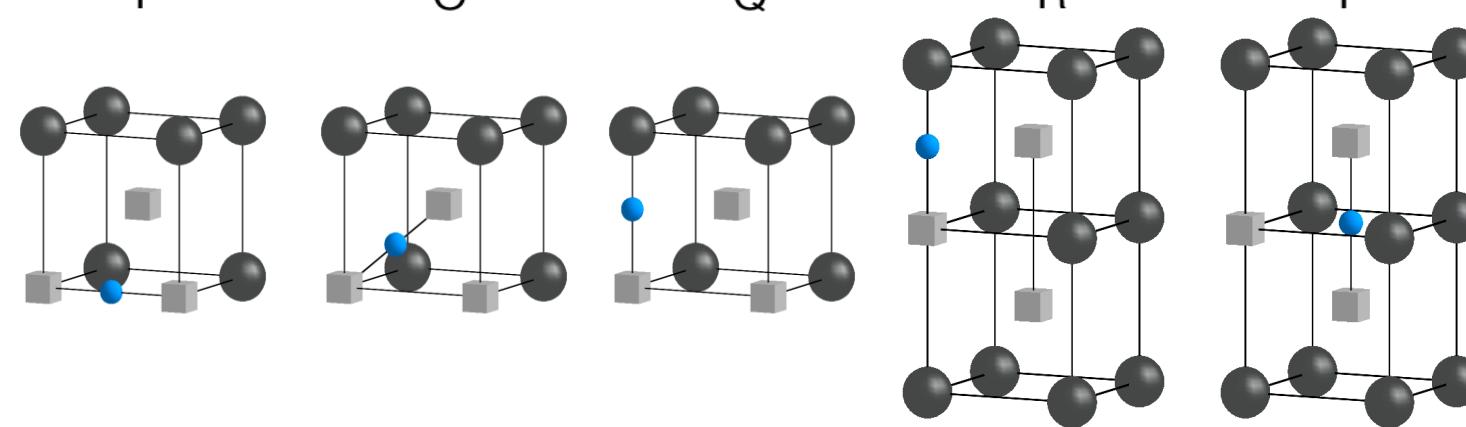


Centaine de sauts explorés

Approximation:

$$E^{\text{mig}}(\text{amas})$$

= largest barrier



# Conclusions on kinetic methods

## -Driven systems:

Not only the path but also steady states depend on  $L_{ij}$

## -Phase Field method

What is the spinodal diffusion coefficient?

Is the Cahn-Hilliard kinetic law valid for spinodal decomposition?

## -Cluster Dynamics

Needs for a statistical definition of  
atom-based mobilities, association and dissociation rates

# OUTLINE

## 1. Diffusion: a property that can be measured at various scales

- a) Onsager formalism versus Fick's laws
- b) Interdiffusion within the Onsager formalism
- c) Nanoscale diffusion in multilayers

## 2. Modeling of diffusion and diffusion data for what?

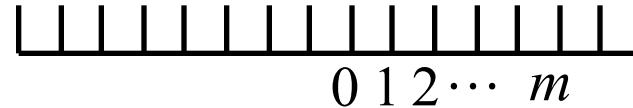
- a) Parameterization of the Atomic Kinetic Monte Carlo
- b) Lattice rate theory for driven systems
- c) Phase Field method for spinodal decomposition
- d) Cluster Dynamics

## 3. Diffusion from the microscopic diffusion processes

- a)  $Lij$  from the equilibrium fluctuations
- b) Self-consistent mean field theory: generalized diffusion equation
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$L_{ij}$  FROM THE EQUILIBRIUM  
FLUCTUATIONS

# Diffusion of a random walker (vacancy)



Probability of being at m after N jumps :  $P(m, N) = \left(\frac{1}{2}\right)^N \frac{N!}{m! (N-m)!}$

Continuous limit:  
 $m/N \ll 1$ ,

$$P(m, N) \approx \sqrt{\frac{2}{\pi N}} \exp \frac{-m^2}{2N}$$

Fick's solution

$$P(x, t) = \sqrt{\frac{1}{4\pi D t}} \exp \frac{-x^2}{4Dt}$$

Einstein relation (1905):

$$D = \frac{\langle x^2 \rangle}{2t}$$

Mean free path

$$\langle x^2 \rangle = \sum_{i=1}^N \langle x_i^2 \rangle + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle x_i x_j \rangle$$

Diffusion coefficient of a random walker

Jump frequency:  $W_0$

Jump distance:  $l_x$

Coordination number:  $Z$

Averaged number of jumps:  $\langle n_{jp} \rangle = Z \Gamma t$

$$\langle x^2 \rangle = \sum_{i=1}^N \langle x_i^2 \rangle = \langle n_{jp} \rangle l_x^2$$

$$D_x = \frac{\langle n_{jp} \rangle l_x^2}{2t} = \frac{1}{2} Z W_0 l_x^2$$

BCC cristal

$$\begin{cases} l_x = a/2 \\ Z = 8 \end{cases} \longrightarrow$$

$$D_x = \frac{1}{2} 8 W_0 \frac{a^2}{4} = W_0 a^2$$

# Tracer A\* is not a random walker

\*Bardeen and Herring, ASM, (1951)

Vacancy in pure metal A

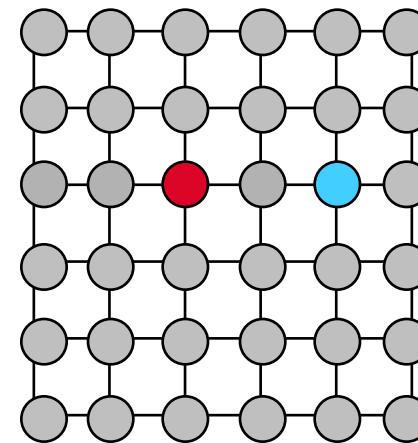
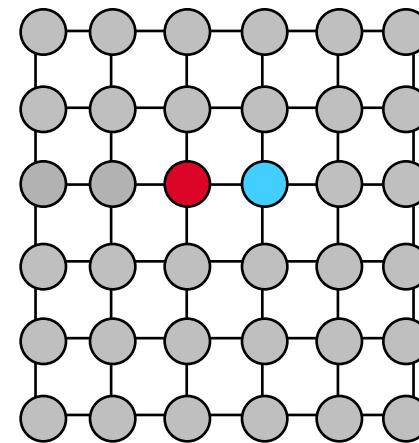
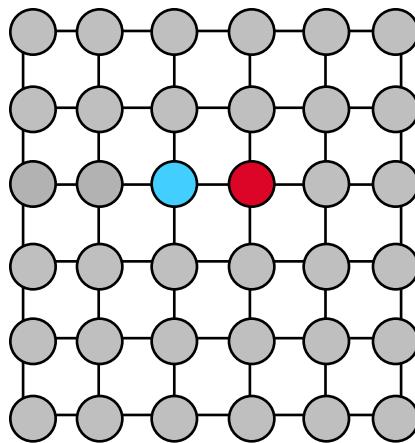
$$D_V = \frac{\langle n_{jp}^V \rangle l^2}{6t}$$

A chosen atom in pure metal A = tracer A\* (red atom)

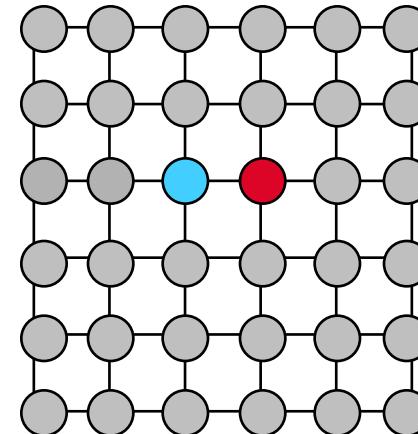
$$D_{A^*} = C_V \frac{\langle (R^{A^*})^2 \rangle}{6t} = C_V \frac{\langle n_{jp}^{A^*} \rangle l^2}{6t} f_0 \quad \text{with} \quad f_0 = \frac{\langle (R^{A^*})^2 \rangle}{\langle n_{jp}^{A^*} \rangle l^2}$$

# Estimation of the self-diffusion factor

$$f_0 = \left\langle (R^{A*})^2 \right\rangle / \left\langle n_{jp}^{A*} \right\rangle l^2$$



**✗ (Z-1)**



**✗ (1)**

$$\left\langle n_{jp}^{A*} \right\rangle = [2 + (Z - 1)] / Z$$

$$\left\langle (R^{A*})^2 \right\rangle = (Z - 1)l^2 / Z$$

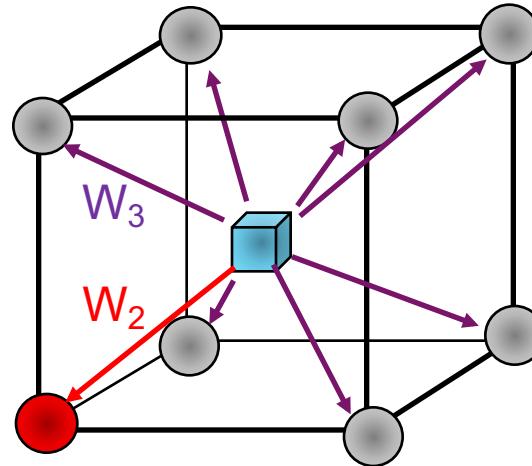
= Z jump sequences

$$f_0 = \frac{Z - 1}{1 + Z} = \frac{H}{2 + H} \quad \text{with} \quad H = Z - 1$$

H: nbre of vacancy escape paths

# BCC dilute alloy: correlation factor

Body centered cubic cristal



Pure metal

$$f_0 = \frac{H}{2+H} \quad \text{avec} \quad H = Z - 1$$

First shell approximation of the correlation factor

$$H = 7W_3 \quad \text{Number of exit ways to leave the first shell of B}$$

$$f_B = \frac{7W_3}{2W_2 + 7W_3}$$

\*Manning (1964)

Leclaire (1970)

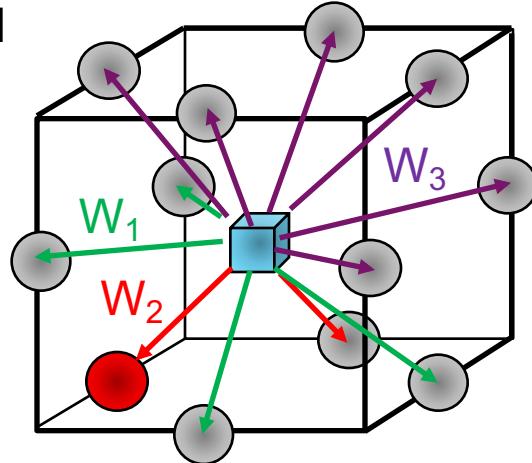
Serruys and Brebec (1982)

Garnier et al., Phys. Rev. B (2014)

# FCC dilute alloy: correlation factor

\*A. B. Lidiard, Phil. Mag. 46, 1218 (1955)

Face cubic centered cristal



First shell approximation of the correlation factor

$$f_B = \frac{H}{2W_2 + H} = \frac{2W_1 + 7W_3}{2W_2 + 2W_1 + 7W_3}$$

How do we calculate the correlation factor?

How do we calculate the whole Onsager matrix?

Definition of the  $L_{ij}$  in terms of displacement fluctuations?

# Lij from equilibrium fluctuations

## Tracer diffusion coefficient from Einstein relation

\*A. Einstein, Ann. Phys. Lpz. 17, 549 (1905)

\*A. D. Le Claire, Phil. Mag. 3,921 (1958)

$$D_{A^*} = \frac{\langle r^2 \rangle}{6t} \quad r: \text{displ. of a tracer A* in time t}$$

## Phenomenological coefficients

Kubo's linear response theory applied to transport in alloys

\*A. R. Allnatt, J. of Chem. Phys. 43, 1855 (1965):

$$L_{ij} = \frac{\langle R_i R_j \rangle}{6Vt} \quad R_i: \text{collective displacement of species i in time t}$$

## Calculation methods based on fluctuations:

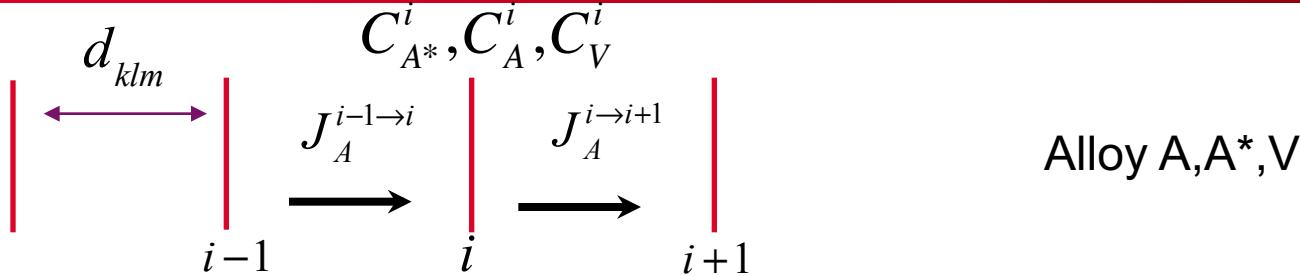
-Analytical approach (Bardeen and Herring, 1951 ; Manning 59, ; random lattice gas models (Manning 69) ,transition Matrix (Moleko)

-Computational approach: Atomic Kinetic Monte Carlo

# $L_{IJ}$ FROM DISSIPATION PROCESSES

First pair mean field calculation of the  $L_{ij}$  in concentrated alloys  
\*R. Kikuchi, Ann. Phys. N. Y. II, 306 (1961);  
J. Phys. Chem. Solids 20, 17, 35 (1961).

# Point mean field fluxes



Microscopic flux of A\* between two sites

$$J_{A^*}^{i \rightarrow i+1} = \omega_{A^*} C_{A^*}^i C_V^{i+1} - \omega_{A^*} C_{A^*}^{i+1} C_V^i \simeq -\omega_{A^*} C_V d_{klm} \frac{C_{A^*}^{i+1} - C_{A^*}^i}{d_{klm}} \simeq -\omega_{A^*} C_V d_{klm} \nabla_i C_{A^*}$$

Macroscopic flux

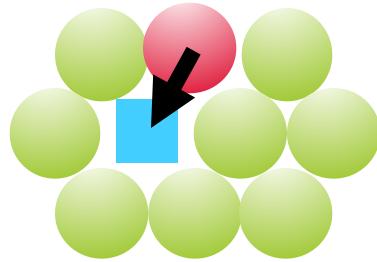
$$J_{A^*} = \frac{Z_{klm}}{S_{klm}} J_{A^*}^{i \rightarrow i+1} = -\frac{Z_{klm} d_{klm}}{S_{klm}} \omega_{A^*} C_V \nabla_i C_{A^*} = -\frac{Z_{klm} {d_{klm}}^2}{S_{klm} d_{klm}} \omega_{A^*} C_V \nabla_i C_{A^*} = -\frac{a^2}{\Omega_{at}} \omega_{A^*} C_V \nabla_i C_{A^*}$$

Tracer diffusion coefficient:  $D_{A^*} = \omega_{A^*} a^2 C_V$

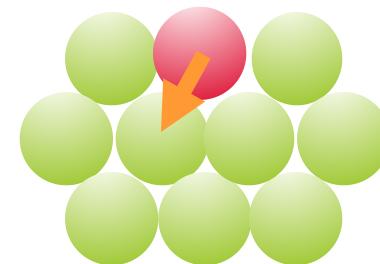
A point mean field approximation does not yield the correlations

# Kinetic correlations are in the pair probabilities

Pair probability: correlations



No pair probability: no correlation



Non equilibrium pair probabilities as state variables not deduced from local concentrations

# Non equilibrium distribution function

Occupation numbers       $n = \{n_i^\alpha, n_i^\beta, \dots, n_j^\alpha, n_j^\beta\}$

Equilibrium distribution function

$$P_0(n) = \exp \left[ \left( \Omega + \sum_{\alpha} \mu_{\alpha} \sum_i n_i^{\alpha} - H(n) \right) / k_B T \right]$$

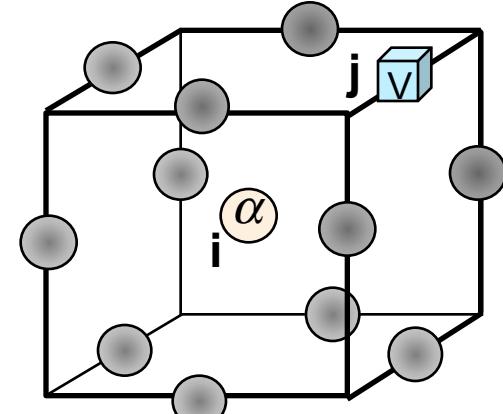
Non equilibrium distribution function

$$P(n,t) = P_0(n) P^{(1)}(n,t)$$

$$P^{(1)}(n,t) = \exp \left[ \left( \delta \Omega + \sum_{\alpha} \mu_{\alpha} \sum_i n_i^{\alpha} \delta \mu_i^{\alpha}(t) - h(n,t) \right) / k_B T \right]$$

**Effective hamiltonian**

$$h(n,t) = \frac{1}{2!} \sum_{i,j} \sum_{\alpha,\beta} v_{ij}^{\alpha\beta}(t) n_i^{\alpha} n_j^{\beta} + \frac{1}{3!} \sum_{i,j,k} \sum_{\alpha,\beta,\gamma} v_{ijk}^{\alpha\beta\gamma}(t) n_i^{\alpha} n_j^{\beta} n_k^{\gamma} + \dots$$



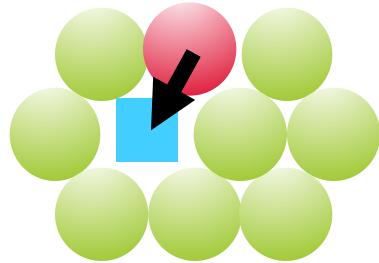
$$n_i^{\alpha} = 1, n_i^V = 0$$

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

What is the evolution of the effective interactions?

# Kinetic correlations are in the pair probabilities

Pair probability: correlations



Moments of the probability

$$\langle n_i^\alpha \rangle = \sum_n n_i^\alpha P(n,t)$$

$$\langle n_i^\alpha n_j^\beta \rangle = \sum_n n_i^\alpha n_j^\beta P(n,t)$$

Equilibrium probability

$$\langle n_i^\alpha n_j^\beta \rangle^{(0)} = \sum_n n_i^\alpha n_j^\beta P_0(n) = \langle n_i^\alpha \rangle^{(0)} \langle n_j^\beta \rangle^{(0)} y_{\alpha\beta}$$

Dilute alloy     $y_{\alpha\beta} = e^{-\frac{E_{\alpha\beta}^b}{kT}}$

$E_{\alpha\beta}^b$ : binding energy

# PAIR CORRELATORS VERSUS EFFECTIVE INTERACTIONS

Pair correlators in terms of the effective interactions

$$k_{ij}^{\alpha\beta} = \langle n_i^\alpha n_j^\beta \rangle - \langle n_i^\alpha \rangle \langle n_j^\beta \rangle$$

$$k_{ij}^{\alpha\beta} - k_{ij}^{\beta\alpha} = \langle n_i^\alpha n_j^\beta \rangle^{(0)} (v_{ij}^{\alpha\beta} - v_{ij}^{\beta\alpha}) = \langle n_i^\alpha n_j^\beta \rangle^{(0)} a_{ij}^{\alpha\beta}$$

Relationships between effective interactions due to the normalisation of pair probabilities

$$\sum_\beta k_{ij}^{\alpha\beta} = 0, \quad \forall \alpha \quad \Longrightarrow \quad a_{ij}^{AV} = -\frac{C_B}{C_V} a_{ij}^{AB} = -\frac{C_B}{C_A} y_{BV} a_{ij}^{BV}$$

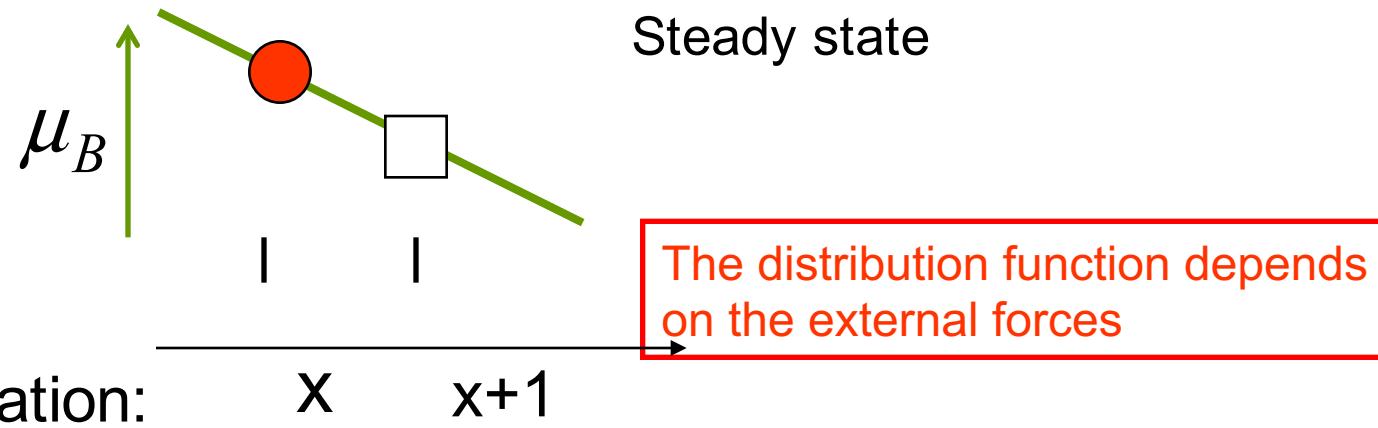
where  $y_{BV} = e^{-\frac{E_{BV}}{k_B T}}$

Low vacancy concentration:  $C_V \ll C_A, C_B \Rightarrow a_{ij}^{AB} \ll a_{ij}^{BV}$

Specific case of a dilute alloy A(B):  $C_B \ll C_A \Rightarrow a_{ij}^{AV} \ll a_{ij}^{BV}$

In sums of anti-symmetric interactions, a single interaction to be considered:  $a_{ij}^{BV}$

# Self-consistent mean field theory (SCMF)



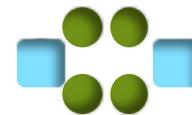
$$\frac{d}{dt} P = \sum \pm P^{(0)} P^{(1)}(V_{x,y}^{\alpha\beta}(t), V_{x,y,z}^{\alpha\beta\gamma}(t)) \times W$$

$$\frac{d\langle n_x^\alpha \rangle}{dt} = \left\langle \sum_y \left\{ \omega_{yx}^{\alpha V} n_x^V n_y^\alpha - \omega_{xy}^{\alpha V} n_x^V n_y^\alpha \right\} P^{(1)}(t) \right\rangle^{(0)} \Rightarrow J_{x,x+1}^\alpha (\nabla \mu_\alpha, V_{x,x+1}^{\alpha V})$$

First shell approximation:

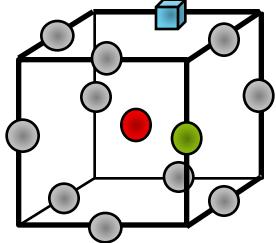
$$V_{x,x+1}^{\alpha V}(t) / \frac{d}{dt} \langle n_x^\alpha n_{x+1}^V \rangle = 0$$

# Kinetic correlations versus the range of the effective interactions



Length of vacancy loops related to the range of the effective interactions

## SCMF microscopic flux



$$J_{i \rightarrow s}^{\alpha} = \delta_{is} \left\langle n_i^{\alpha} n_s^V W_{is}^{\alpha V} \left( \delta \mu_i^{\alpha} + \delta \mu_s^V - \sum_{j,\beta} v_{ij}^{\alpha\beta} n_j^{\beta} - \sum_{j,\beta} v_{sj}^{V\beta} n_j^{\beta} + v_{is}^{\alpha V} \right) \right\rangle^{(0)} \\ - \delta_{is} \left\langle n_i^V n_s^{\alpha} W_{is}^{\alpha V} \left( \delta \mu_i^V + \delta \mu_s^{\alpha} - \sum_{j,\beta} v_{sj}^{\alpha\beta} n_j^{\beta} - \sum_{j,\beta} v_{ij}^{V\beta} n_j^{\beta} + v_{is}^{V\alpha} \right) \right\rangle^{(0)}$$

## Detailed balance:

$$\left\langle n_i^\alpha n_s^V W_{is}^{\alpha V} \right\rangle^{(0)} = \left\langle n_i^V n_s^\alpha W_{is}^{V \alpha} \right\rangle^{(0)}$$

$$\text{Non equil. Chemical potentials: } \delta\mu_i^{\alpha V} = \left( \delta\mu_i^\alpha - \sum_{j,\beta} v_{ij}^{\alpha\beta} n_j^\beta \right) - \left( \delta\mu_i^V - \sum_{j,\beta} v_{ij}^{V\beta} n_j^\beta \right)$$

$$J_{i \rightarrow s}^\alpha = -\delta_{is} \left\langle n_i^\alpha n_s^V W_{is}^{\alpha V} \left( \delta\mu_s^{\alpha V} - \delta\mu_i^{\alpha V} \right) \right\rangle^{(0)} + \delta_{is} \left\langle n_i^\alpha n_s^V W_{is}^{\alpha V} \left( v_{is}^{\alpha V} - v_{is}^{V\alpha} \right) \right\rangle^{(0)}$$

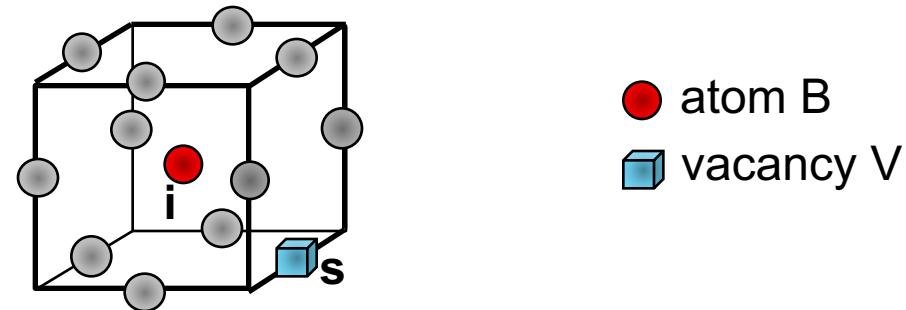
non correlated part	correlations
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# Flux of solute B in dilute alloys A(B)

$$J_{i \rightarrow s}^B = -L_{BB}^{(0)} \left( \delta\mu_s^{BV} - \delta\mu_i^{BV} \right) + L_{BB}^{(0)} \left( v_{is}^{BV} - v_{is}^{VB} \right)$$

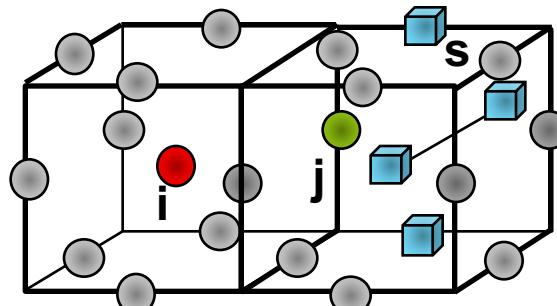
Non correlated Onsager coefficient

$$L_{BB}^{(0)} = \delta_{is} \left\langle n_i^B n_s^V W_{is}^{BV} \right\rangle^{(0)} = C_V C_B y_{BV} W_2$$

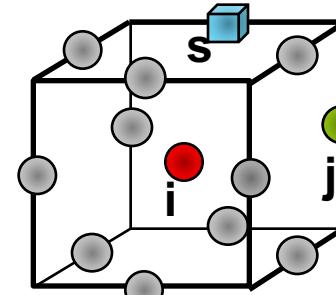


# Rate equations of pair correlations (1)

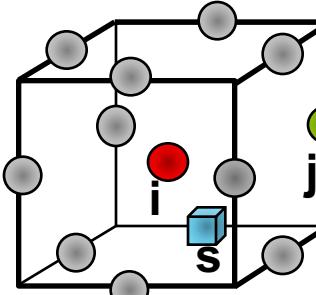
$$\begin{aligned}
 \frac{dk_{ij}^{BV}}{dt} &= \frac{d\langle n_i^B n_j^V \rangle - \langle n_i^B \rangle \langle n_j^V \rangle}{dt} \simeq \frac{d\langle n_i^B n_j^V \rangle}{dt} - \langle n_i^B \rangle \frac{d\langle n_j^V \rangle}{dt} = \delta_{ij} \left\langle n_i^B n_j^V W_{ij}^{BV} (\delta\mu_j^{BV} - \delta\mu_i^{BV} - a_{ij}^{BV}) \right\rangle^{(0)} \\
 &\quad + \sum_{s \neq j} \delta_{js} \left\langle n_i^B n_j^A n_s^V W_{js}^{AV} (\delta\mu_j^{AV} - \delta\mu_s^{AV}) \right\rangle^{(0)} + A \\
 &\quad + \left\langle n_i^B \right\rangle^{(0)} \sum_s \delta_{js} \left\langle n_j^A n_s^V W_{js}^{AV} (\delta\mu_j^{AV} - \delta\mu_s^{AV} - a_{ij}^{AV}) \right\rangle^{(0)} \\
 \frac{dk_{ij}^{BV}}{dt} &= C_B C_V y_{BV} W_2 (\delta\mu_{i+1}^{BV} - \delta\mu_i^{BV} - a_{i,i+1}^{BV}) \\
 &\quad + C_B C_V y_{BV} \left[ -4W_3 (\delta\mu_{i+2}^{AV} - \delta\mu_{i+1}^{AV}) + (2W_1 + W_3) (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV}) \right] + A \\
 &\quad + C_B C_V W_0 \left[ 4(\delta\mu_{i+2}^{AV} - 2\delta\mu_{i+1}^{AV} + \delta\mu_i^{AV}) - 4(a_{i+1,i+2}^{AV} - a_{i,i+1}^{AV}) \right]
 \end{aligned}$$



$$4W_3 (\delta\mu_{i+1}^{AV} - \delta\mu_{i+2}^{AV})$$



$$2W_1 (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV})$$



$$W_3 (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV})$$

Now we need to calculate

$$A = \sum_{s \neq j} \delta_{js} \left\langle n_i^B n_j^A n_s^V W_{js}^{AV} (v_{is}^{BV} + v_{ij}^{BA} + v_{sj}^{VA} - v_{is}^{BA} - v_{ij}^{BV} - v_{sj}^{AV}) \right\rangle^{(0)}$$

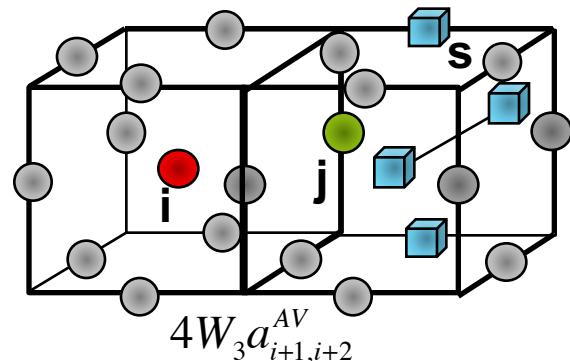
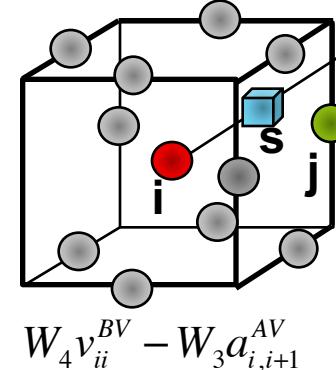
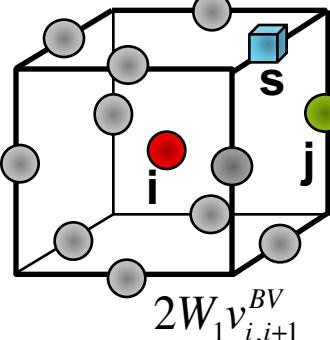
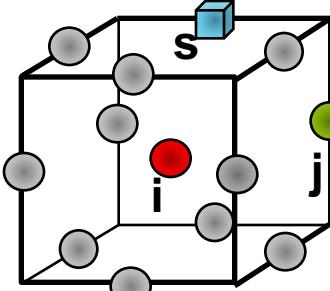
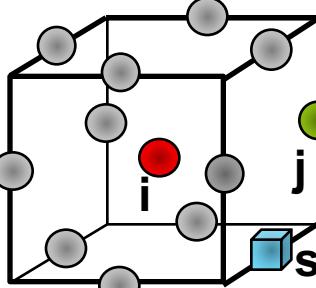
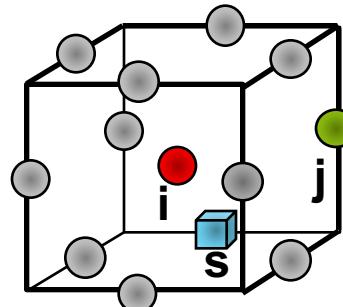
# Rate equations of pair correlations (2)

$$A = \sum_{s \neq j} \delta_{js} \left\langle n_i^B n_j^A n_s^V W_{js}^{AV} \left( v_{is}^{BV} + v_{ij}^{BA} + v_{sj}^{VA} - v_{is}^{BA} - v_{ij}^{BV} - v_{sj}^{AV} \right) \right\rangle^{(0)}$$

$$B = - \sum_{s \neq j} \delta_{js} \left\langle n_i^B n_j^A n_s^V W_{js}^{AV} \right\rangle^{(0)} \left( v_{ij}^{BV} - v_{ij}^{BA} \right) = -C_B C_V y_{BV} (7W_3 + 4W_1) \left( v_{i,i+1}^{BV} - v_{i,i+1}^{BA} \right)$$

$$C = \sum_{s \neq j} \delta_{js} \left\langle n_i^B n_j^A n_s^V W_{js}^{AV} \left( v_{is}^{BV} - v_{is}^{BA} - a_{sj}^{AV} \right) \right\rangle^{(0)} = C_B C_V y_{BV} \left[ 2W_1(v_{i,i+1}^{BV} - v_{i,i+1}^{BA}) - 2(W_1 + W_3)a_{i,i+1}^{AV} + 4W_3a_{i+1,i+2}^{AV} + 2W_1(v_{i,i}^{BV} - v_{i,i}^{BA}) \right]$$

$$A = B + C = C_B C_V y_{BV} \left[ -(7W_3 + 2W_1)(v_{i,i+1}^{BV} - v_{i,i+1}^{BA}) - 2(W_1 + W_3)a_{i,i+1}^{AV} + 4W_3a_{i+1,i+2}^{AV} + 2W_1(v_{i,i}^{BV} - v_{i,i}^{BA}) \right]$$



# Rate equations of antisymmetric pair interactions

$$\frac{1}{C_B C_V} \frac{dk_{ij}^{BV}}{dt} = y_{BV} W_2 (\delta\mu_{i+1}^{BV} - \delta\mu_i^{BV} - a_{i,i+1}^{BV}) + y_{BV} \left[ -4W_3 (\delta\mu_{i+2}^{AV} - \delta\mu_{i+1}^{AV}) + (2W_1 + W_3) (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV}) \right] \\ + W_0 \left[ 4(\delta\mu_{i+2}^{AV} - 2\delta\mu_{i+1}^{AV} + \delta\mu_i^{AV}) - 4(a_{i+1,i+2}^{AV} - a_{i,i+1}^{AV}) \right] \\ + y_{BV} \left[ -(7W_3 + 2W_1)(v_{i,i+1}^{BV} - v_{i,i+1}^{BA}) - 2(W_1 + W_3)a_{i,i+1}^{AV} + 4W_3 a_{i+1,i+2}^{AV} + 2W_1(v_{i,i}^{BV} - v_{i,i}^{BA}) \right]$$

$$a_{ij}^{AB} \ll a_{ij}^{BV}$$

$$a_{ij}^{AV} \ll a_{ij}^{BV}$$

$$\frac{da_{i,i+1}^{BV}}{dt} = \frac{1}{C_B C_V y_{BV}} \left( \frac{dk_{ij}^{BV}}{dt} - \frac{dk_{ij}^{VB}}{dt} \right)$$

$$\frac{da_{i,i+1}^{BV}}{dt} = 2W_2 (\delta\mu_{i+1}^{BV} - \delta\mu_i^{BV} - a_{i,i+1}^{BV}) + \left[ -4W_3 (\delta\mu_{i+2}^{AV} - \delta\mu_i^{AV}) + 2(2W_1 + W_3) (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV}) \right] \\ + \frac{W_0}{y_{BV}} \left[ 4(\delta\mu_{i+2}^{AV} - 3\delta\mu_{i+1}^{AV} + 3\delta\mu_i^{AV} - \delta\mu_{i-1}^{AV}) \right] \\ + \left[ -(7W_3 + 2W_1)a_{i,i+1}^{BV} + 2W_1(v_{i,i}^{BV} - v_{i+1,i+1}^{BV} - v_{i,i}^{BA} + v_{i+1,i+1}^{BA}) \right]$$

# The case of uniform gradients of chemical potentials

$$\begin{aligned} \frac{da_{i,i+1}^{BV}}{dt} = & 2W_2(\delta\mu_{i+1}^{BV} - \delta\mu_i^{BV} - a_{i,i+1}^{BV}) + [-4W_3(\delta\mu_{i+2}^{AV} - \delta\mu_i^{AV}) + 2(2W_1 + W_3)(\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV})] \\ & + \frac{W_0}{y_{BV}} [4(\delta\mu_{i+2}^{AV} - 3\delta\mu_{i+1}^{AV} + 3\delta\mu_i^{AV} - \delta\mu_{i-1}^{AV})] \\ & + [-(7W_3 + 2W_1)a_{i,i+1}^{BV} + 2W_1(v_{i,i}^{BV} - v_{i+1,i+1}^{BV} - v_{i,i}^{BA} + v_{i+1,i+1}^{BA})] \end{aligned}$$

Uniform gradients of chemical potentials:

$$\begin{cases} \nabla\mu_{\alpha V} = \delta\mu_{i+1}^{\alpha V} - \delta\mu_i^{\alpha V} = \delta\mu_{i+2}^{\alpha V} - \delta\mu_{i+1}^{\alpha V} = \delta\mu_i^{\alpha V} - \delta\mu_{i-1}^{\alpha V} \\ v_{i,i}^{\alpha\beta} = v_{i+1,i+1}^{\alpha\beta} \end{cases}$$

Adiabatic approximation on  $a_{i,i+1}^{BV}$  because characteristic time of  $a_{i,i+1}^{BV}$

is proportional to  $1/(7W_3 + 2W_2)$  while characteristic time of solute B is  $1/(C_V W_2)$

$$\frac{da_{ij}^{BV}}{dt} = 0 \iff a_{i,i+1}^{BV} = \frac{2W_2\nabla\mu_{BV} + 2(2W_1 - 3W_3)\nabla\mu_{AV}}{7W_3 + 2W_1 + 2W_2}$$

# SCMF calculation of the Lij in FCC

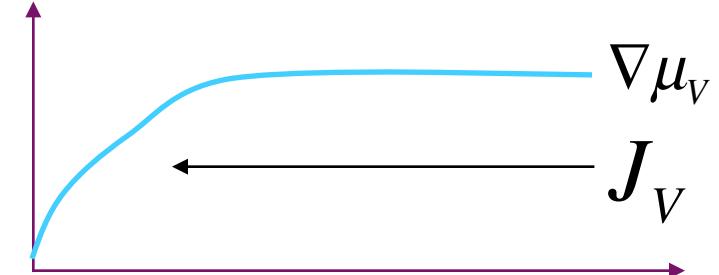
$$a_{i,i+1}^{BV} = \frac{2W_2\nabla\mu_{BV} + 2(2W_1 - 3W_3)\nabla\mu_{AV}}{7W_3 + 2W_1 + 2W_2}$$

$$J_{i \rightarrow s}^B = -y_{BV}C_B C_V W_2 \nabla\mu_{BV} + y_{BV}C_B C_V W_2 a_{i,i+1}^{BV} = -L_{BB}\nabla\mu_{BV} - L_{AB}\nabla\mu_{AV}$$

Onsager coefficients Lij

$$\begin{cases} L_{BB} = y_{BV}C_B C_V W_2 \left(1 - \frac{2W_2}{7W_3 + 2W_1 + 2W_2}\right) \\ L_{AB} = y_{BV}C_B C_V W_2 \frac{2(3W_3 - 2W_1)}{7W_3 + 2W_1 + 2W_2} \end{cases}$$

Flux coupling under irradiation



$$J_B = (L_{BB} + L_{AB})\nabla\mu_V$$

Solute drag by vacancy if  
 $(L_{BB} + L_{AB}) < 0$

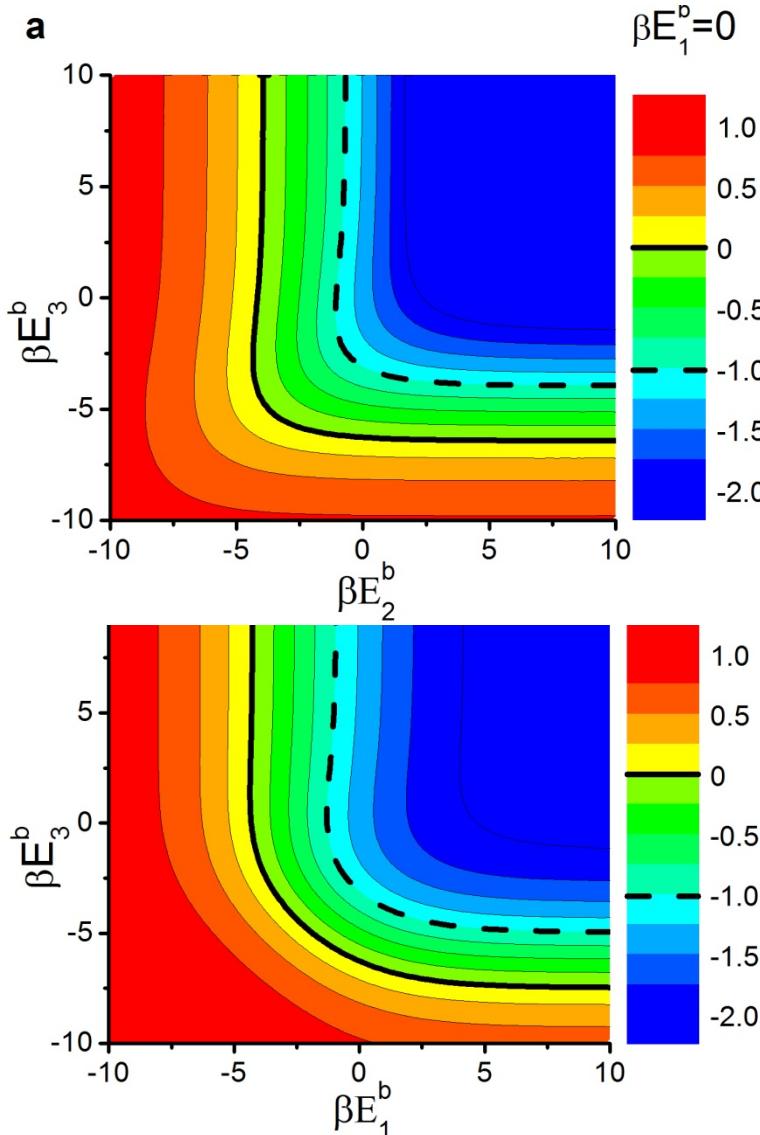
SCMF applied to dilute BCC and FCC alloys:

- In coll. with Univ. Illinois (D. Trinkle, P. Bellon): T. Garnier et al., PRB 88, 134108 (2013); PRB 88, 134201 (2013), PRB 89, 144202 (2014), PRB 90, 184301 (2014)
- In coll. with KTH (Pär Olsson and L. Messina): Messina et al. PRB 90, 104203 (2014)

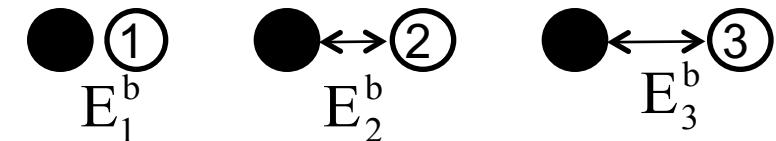
# General criteria for the solute drag

in coll. With Univ. Illinois, Garnier et al. *PRB* 88, 134201 (2013)

## Contour map of the wind factor

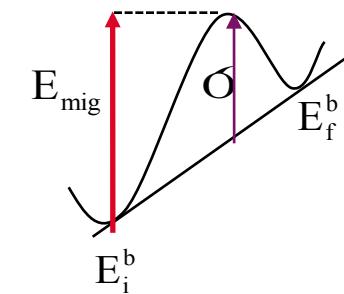


## Solute-Vacancy binding energies

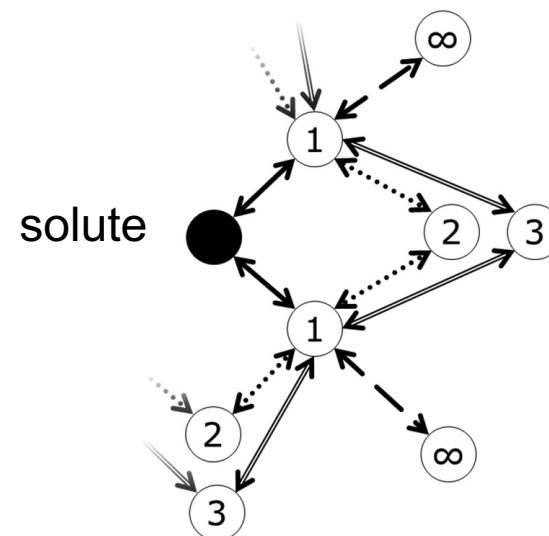


## KRA atomic diffusion model

$$E_{\text{mig}} = Q + \frac{1}{2}(E_f^b + E_i^b) - E_i^b$$



## Schematic pathway of the vacancy



# Tracer diffusion coefficients



$$D_B^* = k_B T \frac{L_{BB}}{n c_B}$$

- Magnetic transition modeled as homogeneous reduction of activation energy<sup>[5,6]</sup>.

$$Q(T) = Q(T=0) - \alpha H(T)$$

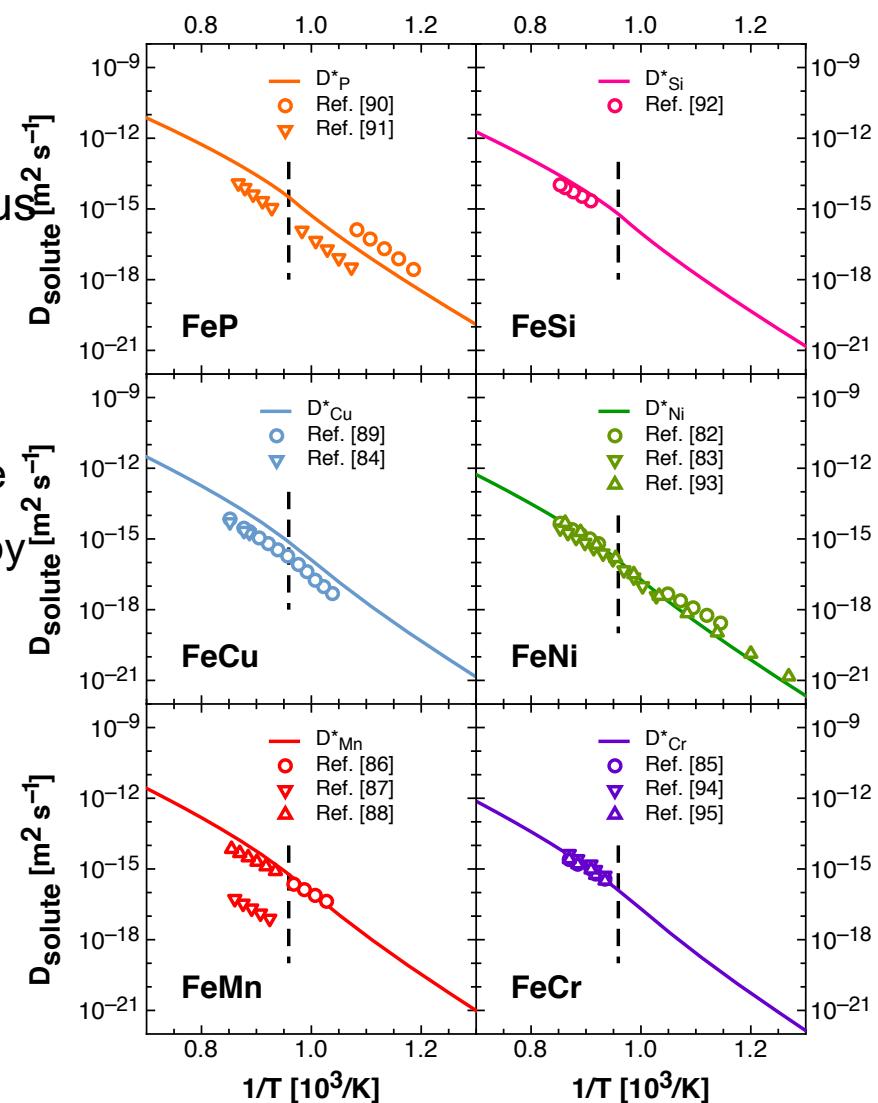
$$\alpha = Q(T=0) - Q(T_c)$$

$T_c$  = Curie temperature

$$H(T) = 1 - H^{\text{mag}}(T) / H^{\text{mag}}(T=0)$$

$H^{\text{mag}}$  = excess enthalpy

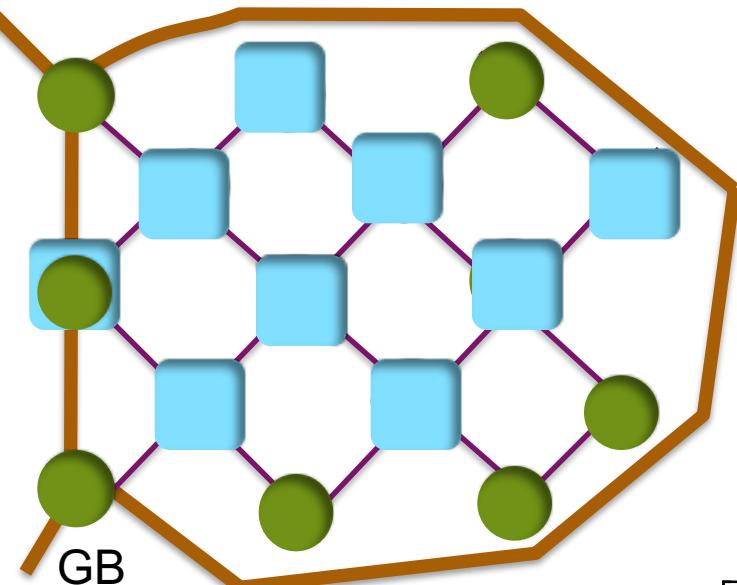
- Non-Arrhenius behavior induced by magnetic model.
- Slopes are consistent, with exception of Mn.
- Prefactors depend on attempt frequency (error bar negligible on log scale).



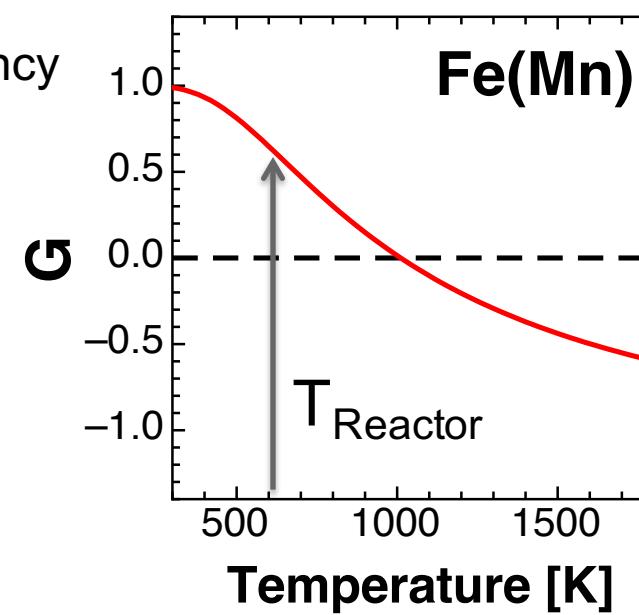
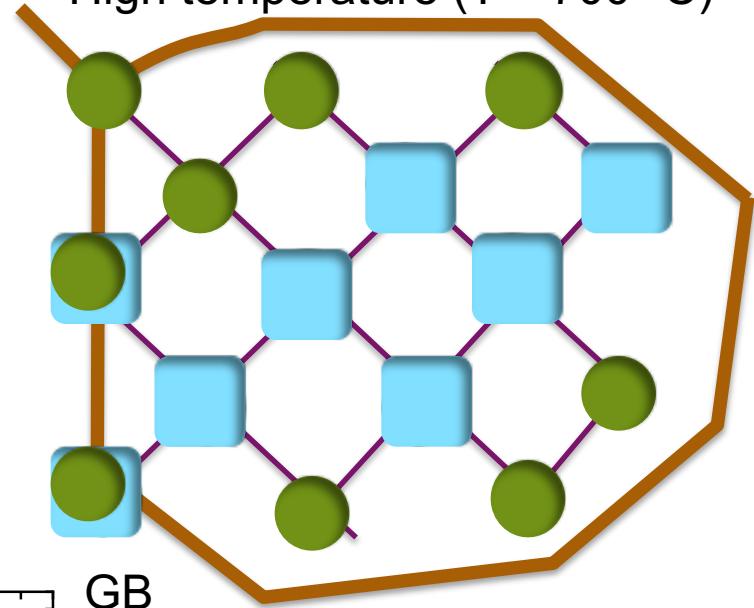
# Vacancy flux coupling in Fe(X)

in coll. with KTH, Sweden, Messina et al. PRB 90, 104203 (2014)

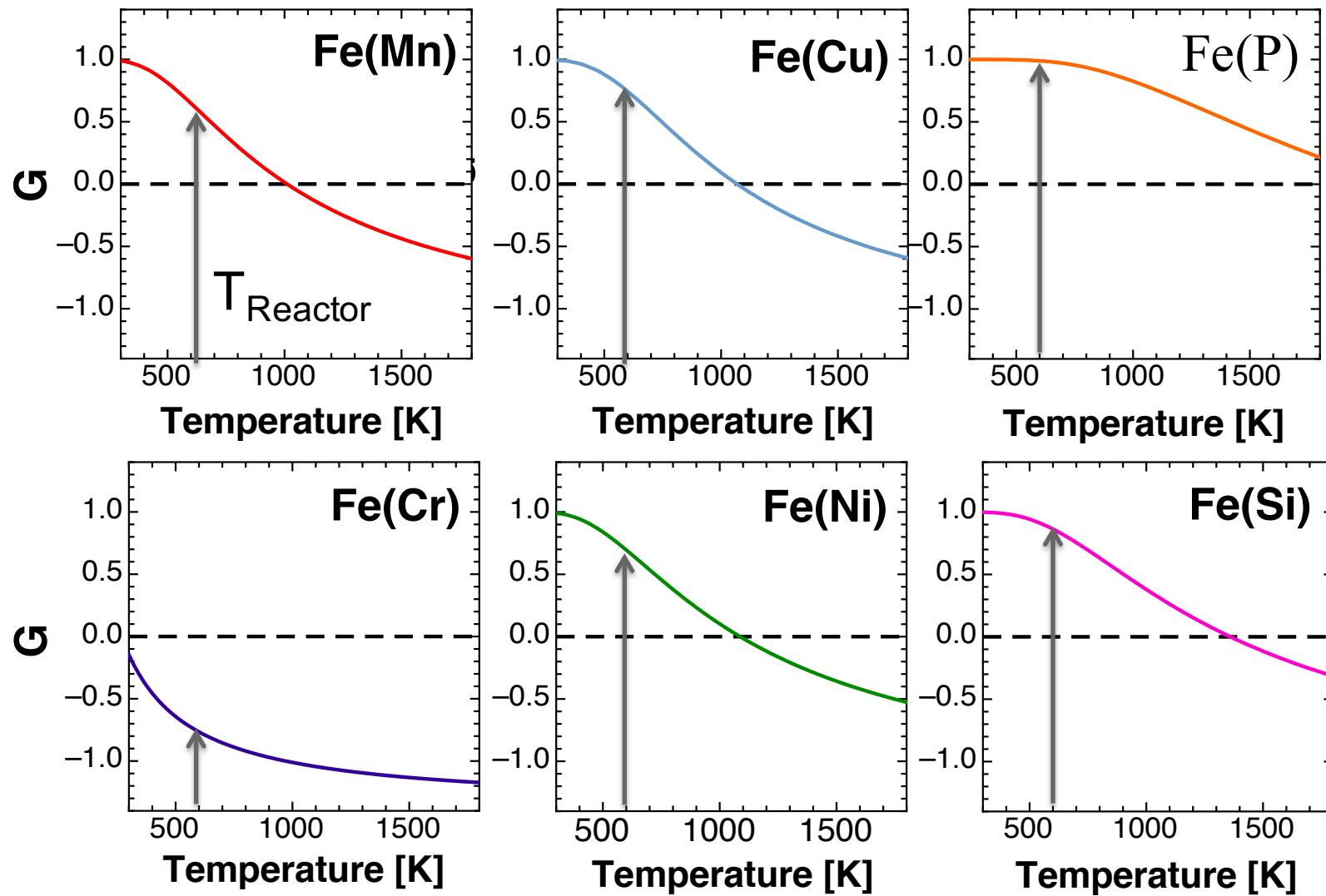
Low temperature ( $T < 700$  °C)



High temperature ( $T > 700$  °C)

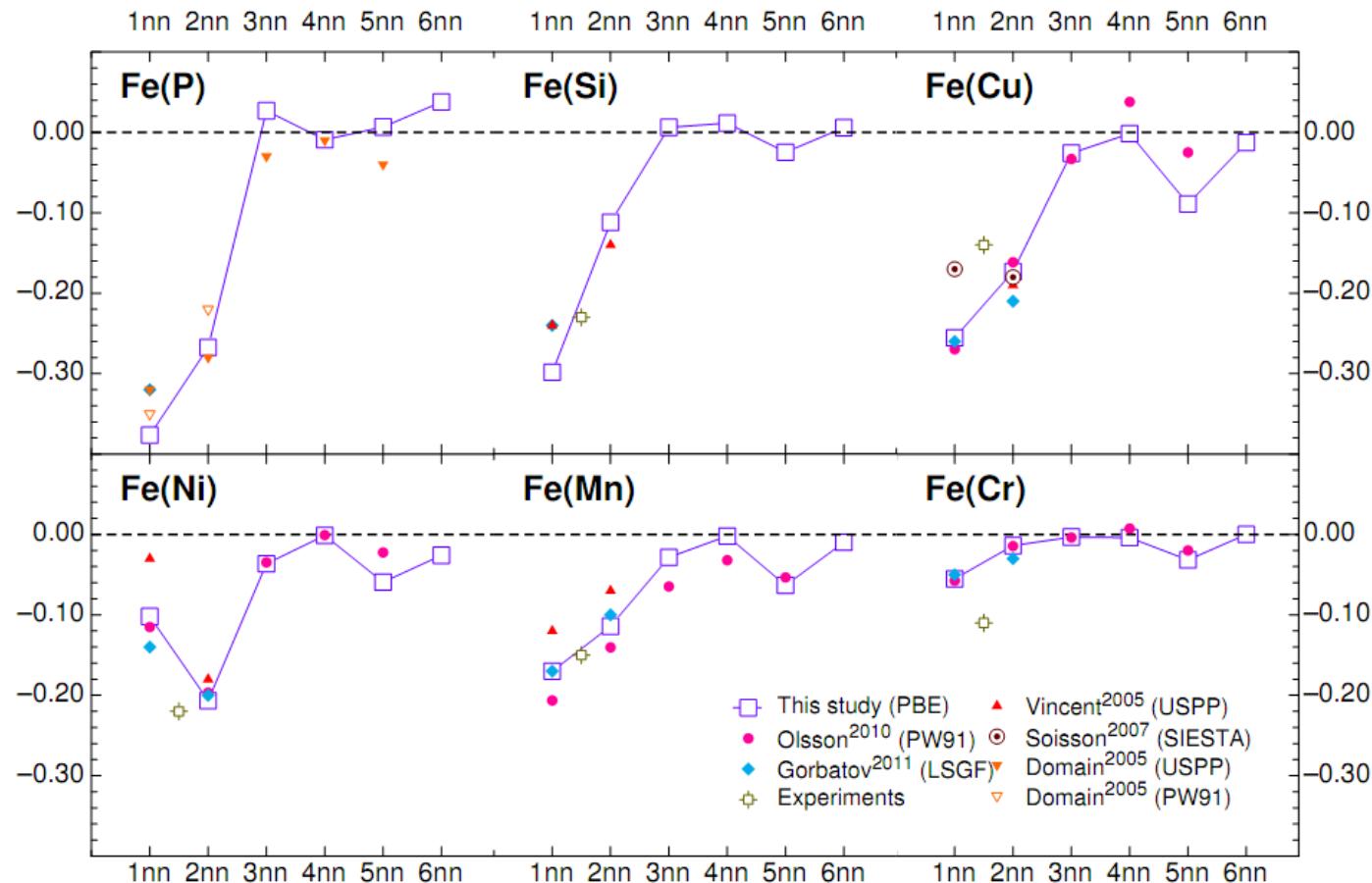


# Vacancy flux coupling in Fe(X)



L. Messina et al., *Exact ab initio transport coefficients in bcc Fe-X (X=Cr, Cu, Mn, Ni, P, Si) dilute alloys*, Phys. Rev. B **90**, 104203 (2014). Collaboration KTH et EDF.

# Vacancy-solute binding energies in Fe(X)



The magnitude and threshold temperature of solute drag is related to the solute-vacancy binding energy.

# Vacancy-direct interstitial flux coupling in Fe

PhD of Thomas Schuler, SRMP, CEA-Saclay

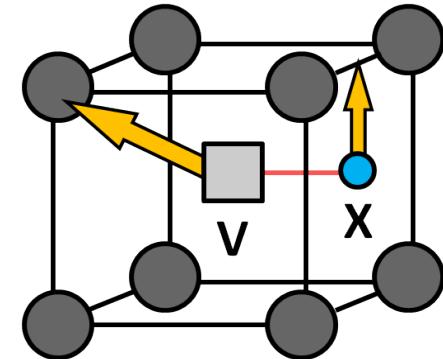
## Small solute concentrations

	X = C	X = N	X = O
max([X <sub>sol</sub> ]) (appm)	10 <sup>2</sup>	10 <sup>3</sup>	10 <sup>1</sup>

## High vacancy-solute binding energy

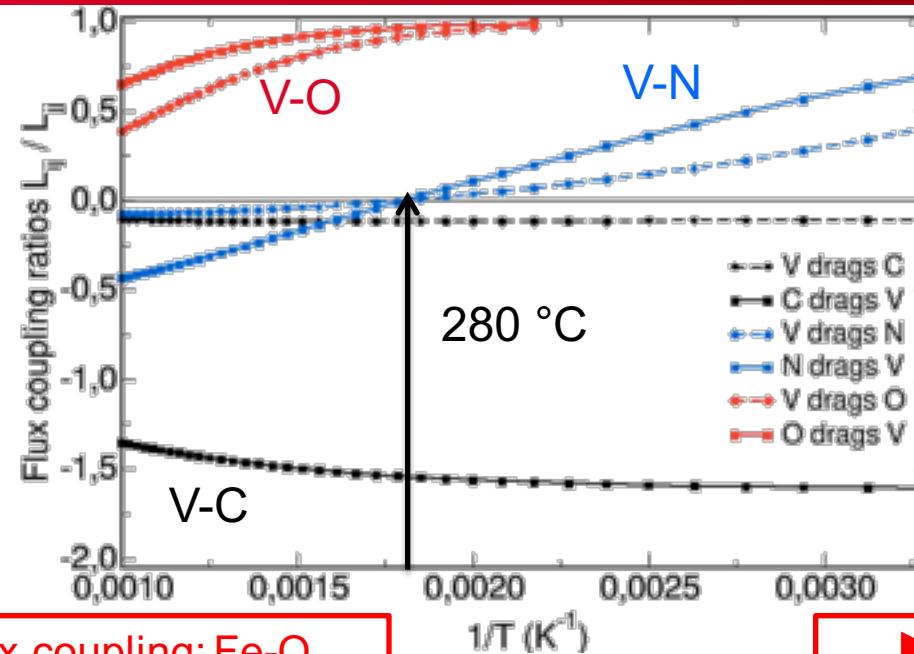
	X = C	X = N	X = O
E <sup>bt</sup> (VX) (eV)	0.41	0.73	1.43
E <sup>bt</sup> (VX <sub>2</sub> ) (eV)	1.18	1.56	2.97

## Transport coefficients ( $L_{ij}$ ): a macroscopic quantity



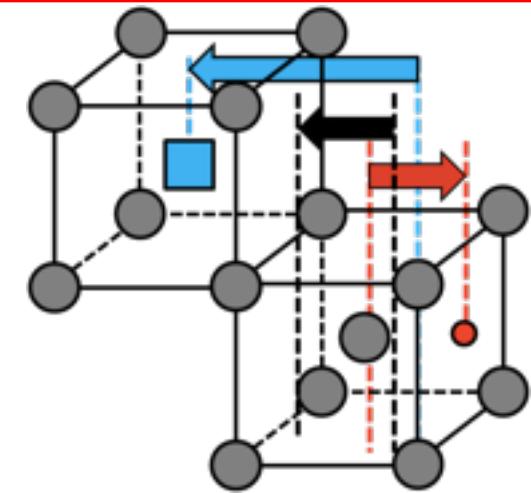
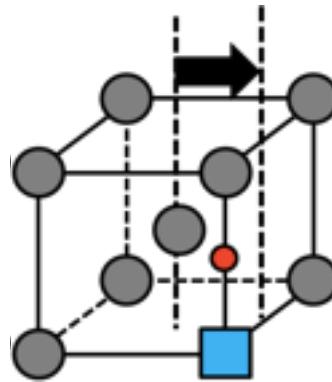
$$\begin{pmatrix} \vec{J}_V \\ \vec{J}_X \end{pmatrix} = - \begin{pmatrix} L_{VV} & L_{VX} \\ L_{XV} & L_{XX} \end{pmatrix} \begin{pmatrix} \vec{\nabla} \mu_V \\ \vec{\nabla} \mu_X \end{pmatrix}$$

# Flux coupling including paires VX



► Positive flux coupling: Fe-O  
V drags O

► Negative flux coupling: Fe-C  
V « repels » C



# Non uniform gradients of chemical potentials

\*Nastar, PRB 90, 144101 (2014)

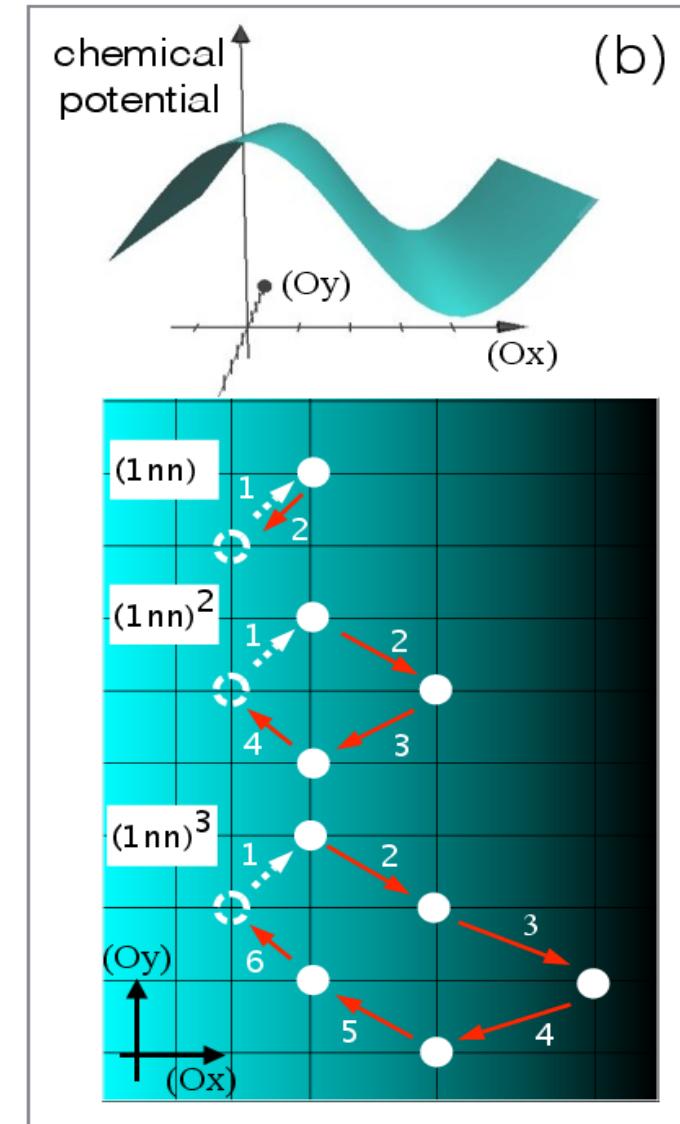
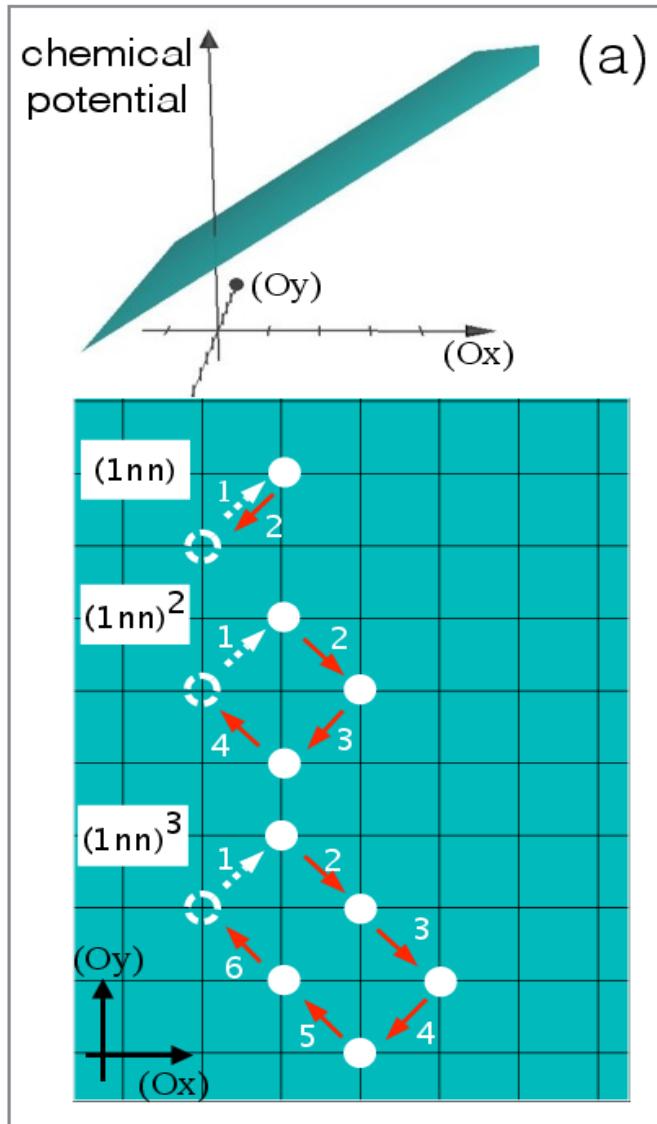
$$J_{i \rightarrow s}^B = -y_{BV} C_B C_V W_2 \nabla \mu_{BV} + y_{BV} C_B C_V W_2 a_{i,i+1}^{BV}$$

$$\begin{aligned} \frac{da_{i,i+1}^{BV}}{dt} &= 2W_2 (\delta\mu_{i+1}^{BV} - \delta\mu_i^{BV} - a_{i,i+1}^{BV}) + [-4W_3 (\delta\mu_{i+2}^{AV} - \delta\mu_i^{AV}) + 2(2W_1 + W_3) (\delta\mu_{i+1}^{AV} - \delta\mu_i^{AV})] \\ &\quad + \frac{W_0}{y_{BV}} [4(\delta\mu_{i+2}^{AV} - 3\delta\mu_{i+1}^{AV} + 3\delta\mu_i^{AV} - \delta\mu_{i-1}^{AV})] \\ &\quad + [-(7W_3 + 2W_1) a_{i,i+1}^{BV} + 2W_1 (v_{i,i}^{BV} - v_{i+1,i+1}^{BV} - v_{i,i}^{BA} + v_{i+1,i+1}^{BA})] \end{aligned}$$

Adiabatic approximation on  $a_{i,i+1}^{BV}$  because the characteristic time of  $a_{i,i+1}^{BV}$   
is proportional to  $1/(7W_3 + 2W_1)$  while characteristic time of solute B is  $1/(C_V W_2)$

$$\frac{da_{i,i+1}^{BV}}{dt} = 0 \quad \Rightarrow J_B = -L_{BB} \nabla \mu_{BV} - L_{AB} \nabla \mu_{AV} - Q_{BB} \nabla^3 \mu_{BV} - Q_{AB} \nabla^3 \mu_{AV} - \dots$$

# Vacancy kinetic correlation effects driven by non uniform driving forces



# Interdiffusion in binary alloys with non uniform driving forces

Non homogeneous linear response theory



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

$$\frac{dC_B}{dt} = -\nabla J_B = L_{BB} \nabla^2 \mu_{BV} + L_{AB} \nabla^2 \mu_{AV} + Q_{BB} \nabla^4 \mu_{BV} + Q_{AB} \nabla^4 \mu_{AV}$$

nonconservative vacancy

$$D = C_A D_B + C_B D_A$$

$$D_B = \left( \frac{L_{BB} - k^2 Q_{BB}}{C_B} - \frac{L_{AB} - k^2 Q_{AB}}{C_A} \right) (C_A C_B \Phi_{CH})$$

$$D_A = \left( \frac{L_{AA} - k^2 Q_{AA}}{C_A} - \frac{L_{AB} - k^2 Q_{AB}}{C_B} \right) (C_A C_B \Phi_{CH})$$

$$D_B = \left( \frac{L_{BB}}{C_B} - \frac{L_{AB}}{C_A} \right) C_A C_B \left[ \frac{\partial^2 f}{\partial C_B^2} + (\kappa_E + \kappa_C) k^2 \right]$$

$$D_A = \left( \frac{L_{AA}}{C_A} - \frac{L_{AB}}{C_B} \right) C_A C_B \left[ \frac{\partial^2 f}{\partial C_B^2} + (\kappa_E + \kappa_C) k^2 \right]$$

conservative vacancy

$$D = \frac{(L_{AA} - k^2 Q_{AA})(L_{BB} - k^2 Q_{BB}) - (L_{AB} - k^2 Q_{AB})^2}{L_{AA} + L_{BB} + 2L_{AB} - k^2(Q_{AA} + Q_{BB} + 2L_{AB})} \Phi_{CH}$$

$$D \approx \frac{L_{AA} L_{BB} - L_{AB}^2}{L_{AA} + L_{BB} + 2L_{AB}} \left[ \frac{\partial^2 f}{\partial C_B^2} + (\kappa_E + \kappa_C) k^2 \right]$$

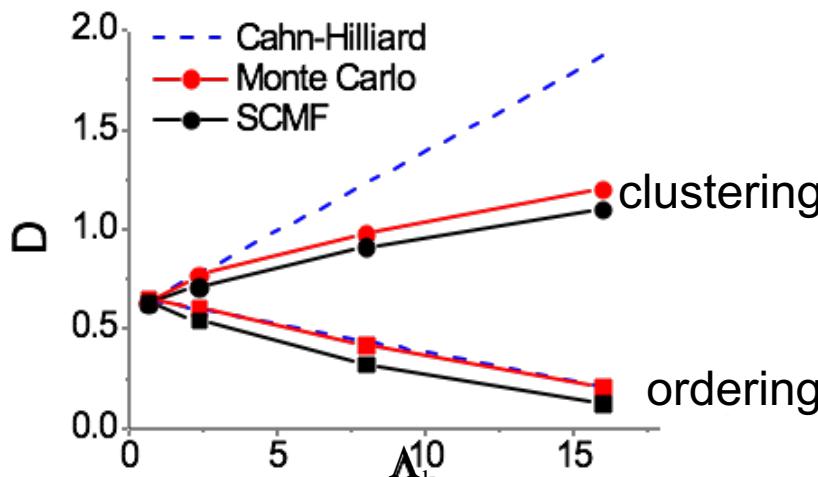
# Interdiffusion coefficient: the SCMF theory versus Monte Carlo

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## Interacting alloys

$$C_B = 0.5$$

$$\nu_A = \nu_B$$



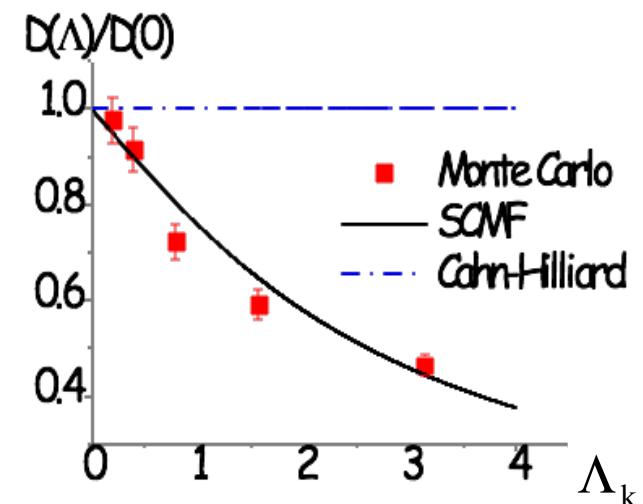
Discrete wavevector operator:  $\Lambda_k = -8 \left[ \cos\left(\frac{ka}{2}\right) - 1 \right]$

$$D_{SCMF} = M \left[ \frac{\partial^2 f}{\partial C_B^2} + (\kappa_E + \kappa_C) \Lambda_k + \kappa^{nl} \Lambda_k^2 \right]$$

## Ideal solution

$$C_B = 0.1$$

$$\nu_A = 10 \nu_B$$



SCMF in satisfying agreement with Monte Carlo: the deviation from Cahn-Hilliard comes from the heterogeneous correlation effects

# Effect of the correlations on $D(k^2)$

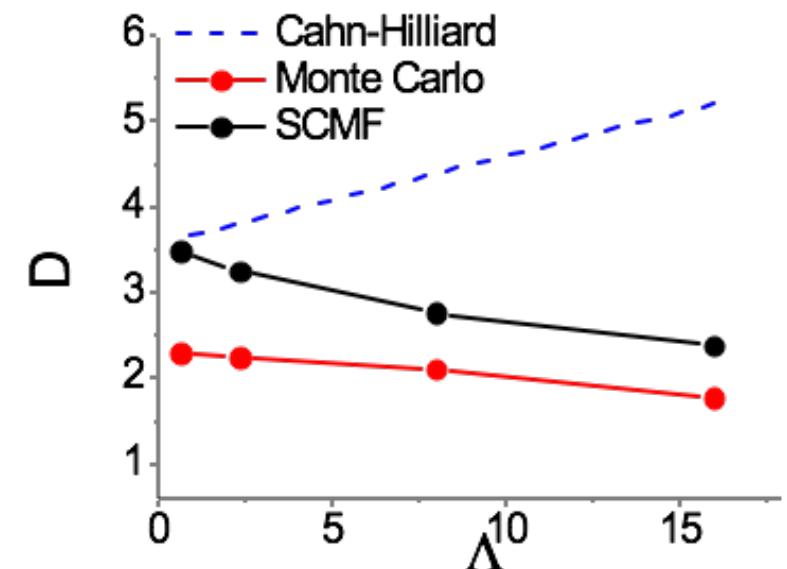
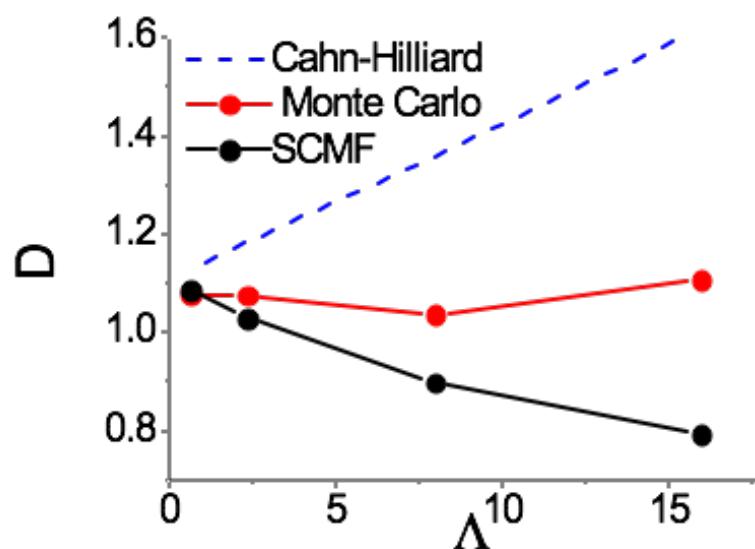
$T/T_c=2.4$  and  $C_B=0.1$

$$\nu_A = \nu_B$$

$$\kappa_E > 0$$

$$\nu_B = 10\nu_A$$

$$\kappa_C < 0$$



$$D_{SCMF} = M \left[ \frac{\partial^2 f}{\partial C_B^2} + (\kappa_E + \kappa_C) \Lambda_k + \kappa^{nl} \Lambda_k^2 \right]$$

SCMF prediction of a possible change of sign of the composition gradient parameter due to correlations is verified

# CONCLUSION

## Diffusion

A multi-scale phenomenon that can be characterized at various scales (from nm to microns).

However there is a crucial lack of diffusion data: diffusion experiments do not catch the large variety of point defect behaviors, they are mostly measured at high Temperature.

## SCMF theory

An atomic diffusion theory that integrates kinetic correlations produced by a point defect diffusion mechanism.

It gives a clear definition of the mesoscopic and macroscopic thermodynamic and kinetic parameters and in this way facilitates a step by step multiscale approach.

Moreover, it yields new kinetic laws challenging the phenomenological models such as the Cahn-Hilliard method.

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