# Modelling of Vacancy-Mediated Diffusion in bcc Iron-Based Dilute Alloys


***Luca Messina*** [(a)], ***Pär Olsson*** [(a)],
***Maylise Nastar*** [(b)], ***Thomas Garnier*** [(b)]
***Christophe Domain*** [(c)]

[(a)] Reactor Physics
Royal Institute of Technology (KTH)
Stockholm, Sweden

[(b)] Service de Recherches de Métallurgie Physique
(DMN-SRMP), CEA Saclay
Gyf-sur-Yvette, France

[(c)] Dpt Matériaux et Mécanique des Composants
Electricité de France, EDF Recherche et Développement
Les Renardières, Moret sur Loing, France

# Background

- Radiation-induced embrittlement of reactor pressure vessel (RPV), due to the formation of nanoclusters that hinder dislocation motion (shift of DBTT).

- Nanonclusters are solute-defect complexes caused or enhanced by the supersaturation of defects induced by radiation.

- In irradiated ferritic-martensitic alloys at 300°C, two kinds of clusters are formed:
  - Cu-rich precipitates.
  - Mn-Ni-rich precipitates (late blooming phases??).

- The solute mobilities are strictly related to their interactions with defects, which are the object of this project.

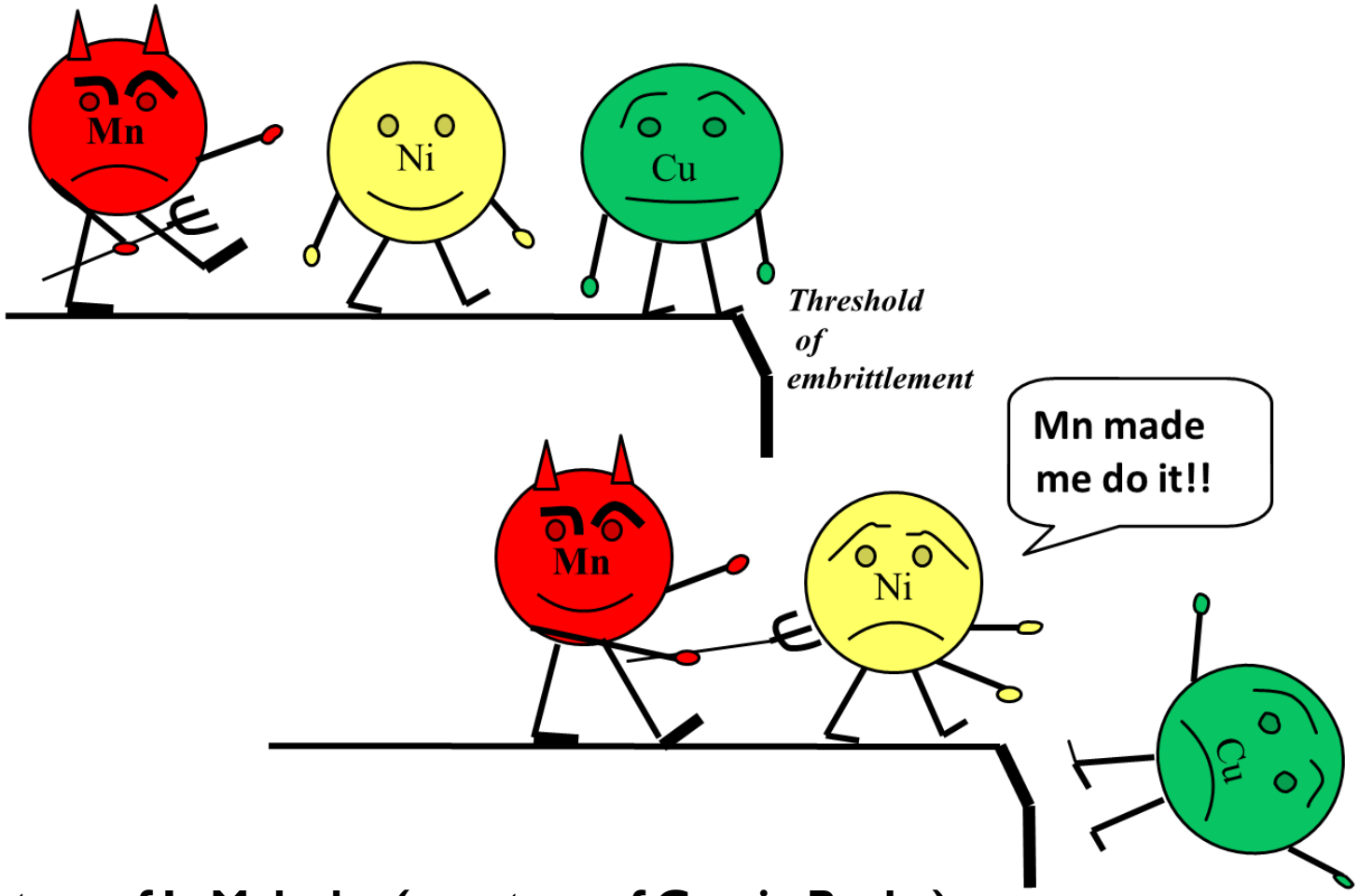
**High Mn-Ni concentration!**

| WELDS in RINGHALS 3,4 MATERIAL: SA508 cl.2 [1] | | |
|---|---|---|
| Cu | 0.08 | 0.05 |
| Mn | **1.46** | **1.35** |
| Ni | **1.58** | **1.66** |
| Si | 0.21 | 0.14 |
| P | 0.009 | 0.0015 |
| Cr | 0.07 | 0.04 |
| C | 0.052 | 0.068 |
| Mo | 0.54 | 0.50 |
| Al | 0.027 | 0.024 |
| Co | 0.015 | 0.010 |
| V | 0.002 | 0.00 |
| DBTT * | - 75°C | - 75°C |

* Ductile to Brittle Transition Temperature at Beginning of Life

[1] P. Efsing, *J. ASTM Int.* (2007)

# Who is the nasty guy here?




**Courtesy of L. Malerba (courtesy of Gracie Burke)**

*Effect of Irradiation in RPV Steels - A nanoscale perspective*
*SOTERIA, 17/09/2012*

# Onsager Matrix

FICK'S LAW → $$J_i = -\sum_{j=1}^{N} D_{ij} \nabla C_j$$

$$J_i = -\sum_{j=1}^{N} L_{ij} \nabla \mu_j \longrightarrow \begin{cases} J_A = -L_{AA}\nabla\mu_A - L_{AB}\nabla\mu_B - L_{AV}\nabla\mu_V \\ J_B = -L_{BA}\nabla\mu_A - L_{BB}\nabla\mu_B - L_{BV}\nabla\mu_V \\ J_V = -L_{AV}\nabla\mu_A - L_{BV}\nabla\mu_B - L_{VV}\nabla\mu_V \end{cases}$$

**THE MATRIX IS SYMMETRIC:** $L_{ij} = L_{ji}$

- Seperation between the kinetic properties of the system and the thermodynamical driving forces.
- The off-diagonal coefficients account for the correlation effects between fluxes of different species.
- These coefficients lead to:
  - diffusion coefficients ;
  - possible dragging mechanisms ;
  - impurity concentration profiles at defect sinks (RIS tendencies).

# The Way to the Coefficients

- A mean field approach is applied in this project to treat vacancy-mediated diffusion in terms of statistical mechanics for the following binary alloys: **FeNi**, **FeCr**, **FeCu**, **FeSi**, **FeP**, **FeMn**.
- 2 methods are used and compared + benchmark with Monte Carlo sim. (Lakimoka):
  - The approximated 9-frequency model introduced by A.D. Le Claire [1] .
  - The Self-Consistent Mean Field (SCMF) theory by M. Nastar [2], which provides an exact solution in the case of dilute binary alloys.
- The coefficients are determined by solving the master equation and determining the probability distribution of all possible configurations of the system.
- The high symmetry of the lattice allows to reduce the number of independent variables to a limited set of atom-vacancy exchange frequencies.
- The number of jump types depends on the range of the thermodynamical interaction.

$$\omega_i = \nu_i^* \exp\left(-\frac{H_i^M}{k_B T}\right) \qquad \nu_i^* = \prod_{j=-1}^{N-3} \nu_j^{init} \Big/ \prod_{j=-1}^{N-4} \nu_j^{saddle}$$

- Migration barriers and attempt frequencies were determined via ab-initio calculations (VASP).

[1] A.D. Le Claire, *J. Nucl. Mat.*. (1978)
[2] M. Nastar, *Phil. Mag.* (2005)

# From the Onsager Matrix

**VACANCY WIND**

$$G = \frac{L_{AB}}{L_{BB}} \qquad L_{vB} = -L_{BB}(G+1)$$

If G < -1, vacancy and solute flux have the same direction → **VACANCY DRAG**

**TRACER DIFFUSION COEFFICIENTS**

$$D^*_{Fe} = a^2 f_0 \omega_0 C_v (1 + b \cdot C_B)$$

$f_0$ = 0.7272 for bcc [1]

$$D^*_{sol} = a^2 f_{sol} \omega_2 \frac{\omega_{4'}}{\omega_{3'}} C_v \qquad f_{sol} = f(\omega_i)^{[1]}$$

**CONCENTRATION PROFILE AT DEFECT SINKS**

(d = partial diff.coefficients)

$$\nabla C_B = \frac{C_A C_B d_{AV} d_{AI}}{(C_B d_{BI} D_A + C_A d_{AI} D_B)} \left( \frac{d_{BV}}{d_{AV}} - \frac{d_{BI}}{d_{AI}} \right) \nabla C_V \quad [2]$$

$$d_{AV} = \frac{L^V_{AA} + L^V_{AB}}{C_A C_V} \qquad d_{BV} = \frac{L^V_{AB} + L^V_{BB}}{C_B C_V}$$

If $d_{BV} < d_{AV}$ → enrichment of solute B at grain boundaries!


[1] A.D. Le Claire, *Physical Chemistry, an advanced treatise* (1970)
[2] M. Nastar, F. Soisson, *Compr. Nucl. Mat.* (2012)

# MODELS

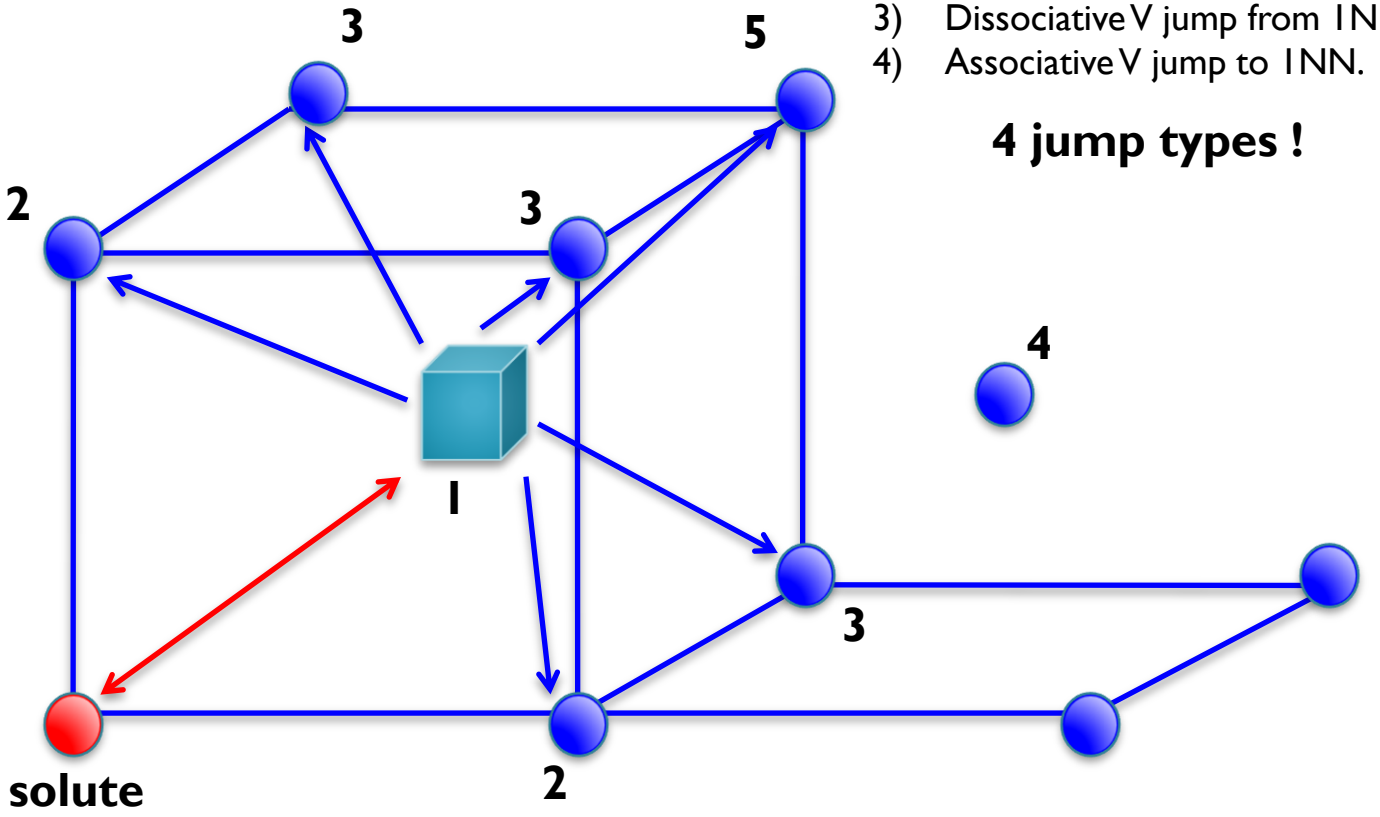
# Interaction range: 1st NN

The interaction range defines the distance beyond which the Sol-V interaction vanishes.

Jumping rates to be distinguished.

1) Unperturbed Fe-V exchange.
2) Sol-V exchange.
3) Dissociative V jump from 1NN.
4) Associative V jump to 1NN.

**4 jump types !**




The number of hopping rates to be included in the model depends upon the range of the thermodynamic interactions.

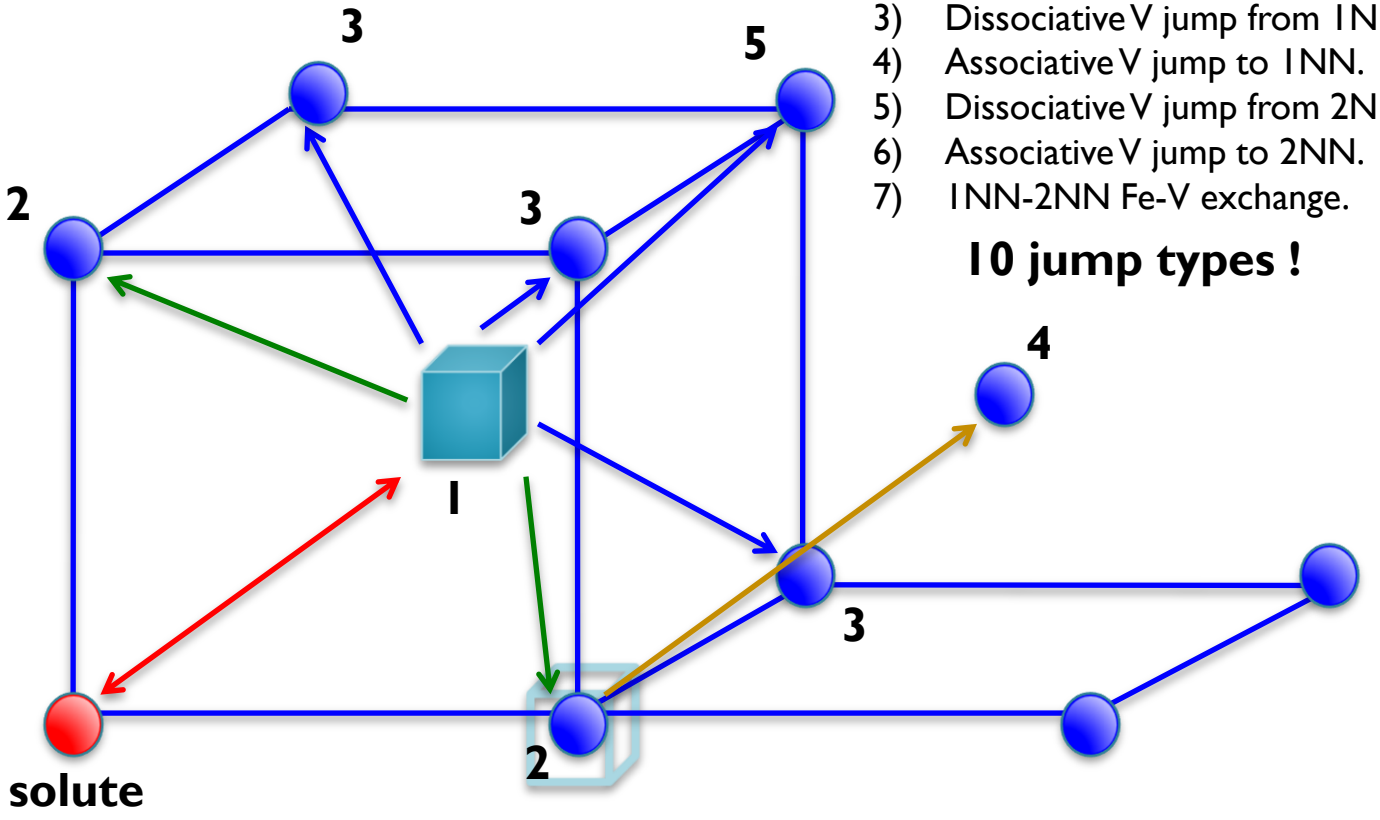
# Interaction range: 2nd NN

The interaction range defines the distance beyond which the Sol-V interaction vanishes.

Jumping rates to be distinguished.

1) Unperturbed Fe-V exchange.
2) Sol-V exchange.
3) Dissociative V jump from 1NN.
4) Associative V jump to 1NN.
5) Dissociative V jump from 2NN.
6) Associative V jump to 2NN.
7) 1NN-2NN Fe-V exchange.

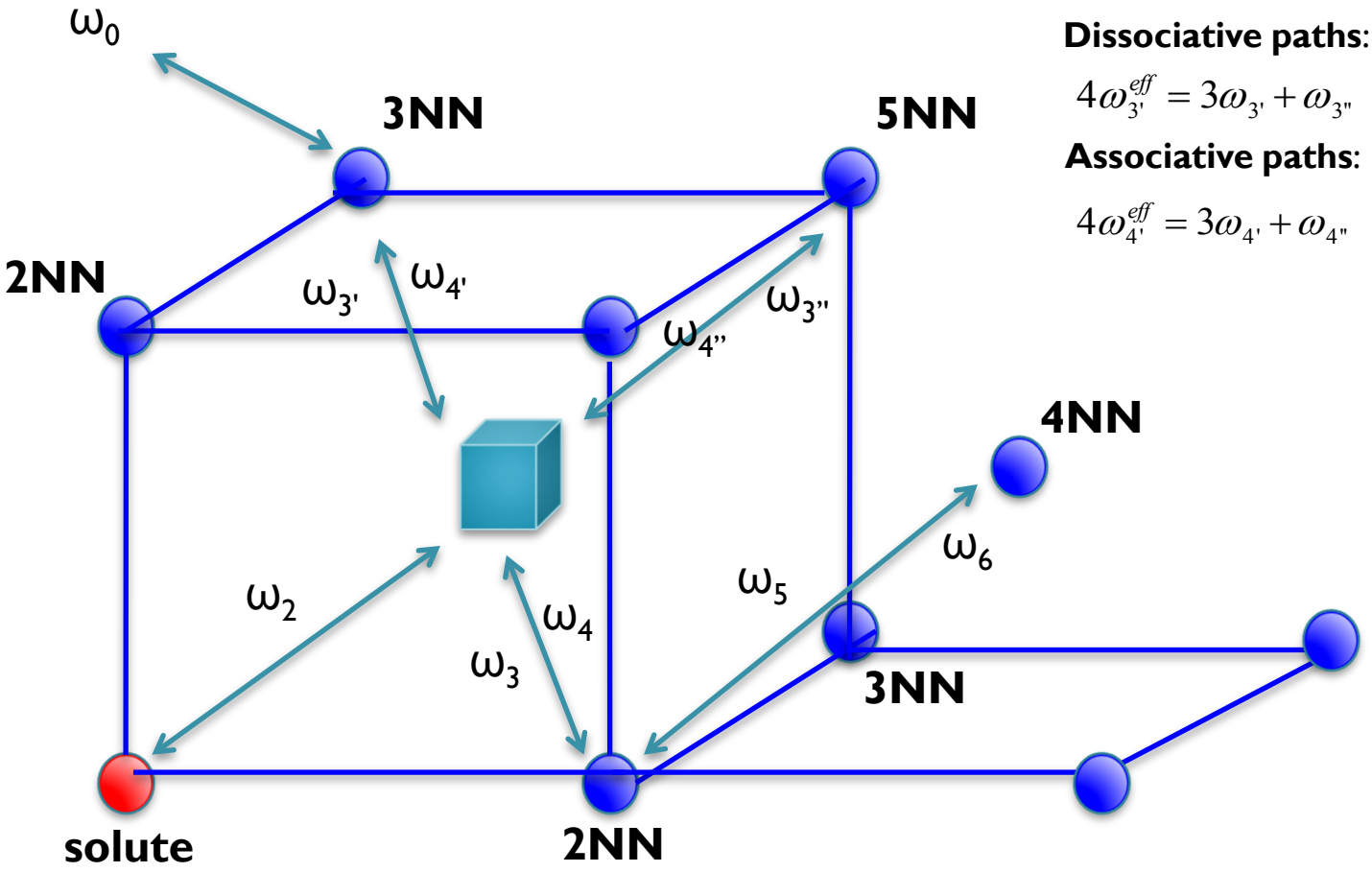
**10 jump types !**




In BCC crystals, the 2-NN interaction is part of the dragging path!

# (9+1)-Frequency model

## LeClaire's nomenclature




**Dissociative paths:**

$$4\omega_{3'}^{eff} = 3\omega_{3'} + \omega_{3''}$$

**Associative paths:**

$$4\omega_{4'}^{eff} = 3\omega_{4'} + \omega_{4''}$$

# Lij:s from Monte Carlo

- Follow evolution of the alloy with Kinetic Monte Carlo (KMC) simulations.
- At each step all possible events (vacancy jumps) are given a probability proportional to the jump frequency.
- The residence time algorithm is the most common way to estimate the time passed between two subsequent events.
- From ref.[1] :

$$L_{ij} = \frac{< \Delta\vec{R}_i \cdot \Delta\vec{R}_j >}{6VkT\tau} \quad , \quad \Delta\vec{R}_i = \sum_m \Delta\vec{r}_i(m)$$

$$G = \frac{L_{12}}{L_{22}} = \frac{< \Delta\vec{R}_i \cdot \Delta\vec{R}_j >}{< \Delta\vec{R}_j \cdot \Delta\vec{R}_j >}$$

[1] A.R. Allnatt and E.R. Allnatt, *Phil.Mag.A.* (1984)

# Self Consistent Mean Field theory

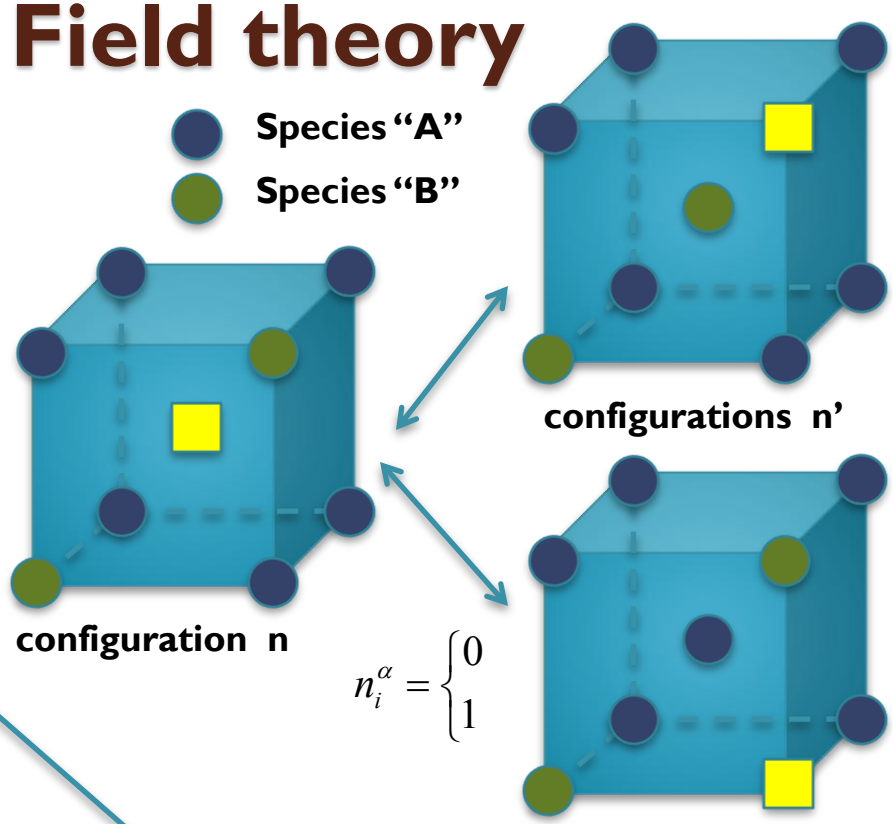
**CONFIGURATION = ENSEMBLE OF OCCUPATION NUMBERS**

$$n = \{n_1^A, n_1^B, \mathrm{L}\ n_1^v, n_2^A, n_2^B, \mathrm{L}\ , n_2^v, \mathrm{L}\ \}$$

**MASTER EQUATION**

$$\frac{dP(n)}{dt} = \sum_{n'} \left[ W(n' \to n) P(n') - W(n \to n') P(n) \right]$$

$$P(n) = P_0(n) \cdot P_1(n)$$




**EQUILIBRIUM**

The probability for a state to occur depends on the energy of the state according to the Boltzmann factor.

$$P_0(n) \propto \exp\left( -\frac{E_0(n)}{k_B T} \right)$$

**$E_0(n)$ : some of pair interactions (possibly multi-body) THERMODYNAMIC INTERACTIONS**

**NON EQUILIBRIUM**

Small perturbation from equilibrium state.
The variation of energy of the system is given by pair (possibly multi-body) interactions with the same mathematical structure.

**KINETIC INTERACTIONS**

**UNKNOWNS TO BE FOUND!**

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

[1] M. Nastar, *Phil. Mag.* (2005)

# Linear non-equilibrium thermodynamics

- Difference betweeen the two methods is how to express the non-equilibrium distribution.
- Lidiard and Allnatt started from the master equation and applied the linear response theory of the Kubo type.
- It worked well as long as random alloys were concerned. In order to introduce interactions, a more rigourous approach has to be undertaken.
- Configurational thermodynamic: the atoms occupy sites in a lattice and interact through a configurational hamiltonian (which includes the thermodynamic interactions).
- First attempted solution was to describe non equilibrium by introducing a time-dependent single particle field, but yielded wrong results.
- Nastar's novelty is to express non-equilibrium through an effective hamiltonian where kinetic interactions (null at equilibrium) are expressed in terms of an hamiltonian field.

# (9+1)-Frequency model

## Serruys [1]

$$L_{AA} = \frac{4\alpha^2 C_v \omega_0 N}{k_B T}\left(1 + bC_B\right)$$

$$L_{AB} = L_{BA} = \frac{8\alpha^2 C_v \omega_2}{k_B T}\frac{\omega_0}{\omega_3'}\frac{(y-2)B_1 + (y-1)B_2}{B_4}\frac{n_B}{\psi}$$

$$L_{BB} = \frac{4\alpha^2 C_v \omega_2}{k_B T}\frac{\omega_0}{\omega_3'}\frac{B_4 + 2zB_1}{B_4}\frac{n_B}{\psi}$$

**ASSUMPTION:**

$$\omega_{4'} = \omega_{4''} = \omega_6 = \omega_0$$

**(weak 2NN interaction)**

$$b = -58 + \frac{1}{\psi}\left[(2y-4)\frac{587\cdot(y-1)B_4 + B_1B_3}{B_2B_4} + 2(y-1)\frac{B_3}{B_4} + 6y + 51\right]$$

$$B_1 = 587y + 507$$

$$B_2 = 587y + 53$$

$$B_3 = (6-7y)B_2 + 587(y-1)(2z+11y+4)$$

$$B_4 = (9y+7)B_2 - (2z+11y+4)B_1$$

$$\psi = 1 + C_v\left(44 + 8\frac{\omega_0}{\omega_3'} + 6\frac{\omega_0}{\omega_5}\right)$$

$$y = \frac{\omega_3}{\omega_3'} \qquad z = \frac{\omega_2}{\omega_3'}$$

[1] P.Y. Serruys et al. *Phil. Mag. A* (1982)

# Kinetic Equations - Vacancies

$$\frac{d\left\langle n_i^{\alpha} n_j^{\beta}\right\rangle}{dt} = \beta \sum_{s\neq i\neq j} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} \hat{\omega}_{is}^{\alpha\nu} \right\rangle (\mu_s^{\alpha} - \mu_i^{\alpha}) + \sum_{s\neq i\neq j} \left\langle n_i^{\alpha} n_j^{\beta} n_s^{\nu} \hat{\omega}_{js}^{\beta\nu} \right\rangle (\mu_s^{\beta} - \mu_i^{\beta}) +$$

$$-\beta \sum_{s\neq i\neq j} \left( \sum_{k\neq i,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{is}^{\alpha\nu} v_{ik}^{\alpha\gamma} \right\rangle - \sum_{k\neq s,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{is}^{\alpha\nu} v_{sk}^{\alpha\gamma} \right\rangle \right) +$$

1st

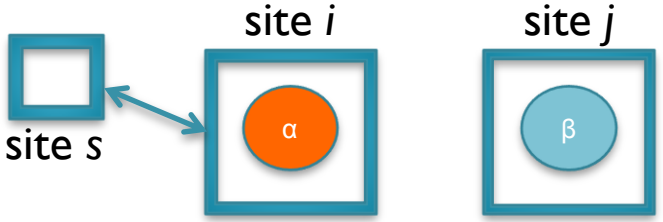
$$-\beta \sum_{s\neq i\neq j} \left( \sum_{k\neq j,\gamma} \left\langle n_i^{\alpha} n_j^{\beta} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{js}^{\beta\nu} v_{ik}^{\beta\gamma} \right\rangle - \sum_{k\neq s,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{js}^{\beta\nu} v_{sk}^{\beta\gamma} \right\rangle \right)$$

2nd

1st : Configuration n can change when atom α jump from site i to a neighboring site s occupied by a vacancy.

2nd : Configuration n can change when atom β jump from site j to a neighboring site s occupied by a vacancy.

$$\overline{T} \cdot \vec{V} = \vec{b}$$




One kinetic equation for each **relevant** site couple, for each combination of species.

# Kinetic Equations - Vacancies

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$$-\beta \sum_{s\neq i\neq j} \left( \sum_{k\neq i,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{is}^{\alpha\nu} v_{ik}^{\alpha\gamma} \right\rangle - \sum_{k\neq s,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{is}^{\alpha\nu} v_{sk}^{\alpha\gamma} \right\rangle \right) +$$

**1st**

$$-\beta \sum_{s\neq i\neq j} \left( \sum_{k\neq j,\gamma} \left\langle n_i^{\alpha} n_j^{\beta} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{js}^{\beta\nu} v_{ik}^{\beta\gamma} \right\rangle - \sum_{k\neq s,\gamma} \left\langle n_j^{\beta} n_i^{\alpha} n_s^{\nu} n_k^{\gamma} \hat{\omega}_{js}^{\beta\nu} v_{sk}^{\beta\gamma} \right\rangle \right)$$

**2nd**

1st : Configuration n can change when atom α jump from site i to a neighboring site s occupied by a vacancy.

2nd : Configuration n can change when atom β jump from site j to a neighboring site s occupied by a vacancy.

$$\overline{T} \cdot \vec{V} = \vec{b}$$


One kinetic equation for each **relevant** site couple, for each combination of species.

# Kinetic Equations – Dumbbells!

$$\frac{1}{\beta}\frac{d\left\langle n_i^{AB_\alpha}\right\rangle}{dt}=\sum_{s\neq i,\,\beta,\,\sigma}\left\langle n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}\right\rangle\left(\mu_s^A-\mu_i^A\right)+\beta\sum_{s\neq i,\,\beta,\,\sigma}\left\langle n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}\right\rangle\left(\mu_s^B-\mu_i^B\right)$$

$$+\sum_{s\neq i,\,\beta,\,\sigma}\left\{\left\langle n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{AB_\alpha}\right\rangle-\left\langle n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{\sigma A_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_s^{\sigma A_\beta}n_i^B n_k^\gamma y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq s,\,\gamma}\left\langle n_s^{\sigma A_\beta}n_i^B n_k^\gamma y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{sk}^{\sigma A_\beta\gamma}\right\rangle\right\}$$

$$+\sum_{s\neq i,\,\beta,\,\sigma}\left\{\left\langle n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{AB_\alpha}\right\rangle-\left\langle n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{\sigma B_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_s^{\sigma B_\beta}n_i^A n_k^\gamma y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq s,\,\gamma}\left\langle n_s^{\sigma B_\beta}n_i^A n_k^\gamma y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{sk}^{\sigma B_\beta\gamma}\right\rangle\right\}$$

$$+\sum_{\beta\neq\alpha}\left\{\left\langle n_i^{AB_\beta}y_R^{\beta\alpha}\omega_R^{AB}v_{AB_\alpha}\right\rangle-\left\langle n_i^{AB_\beta}y_R^{\beta\alpha}\omega_R^{AB}v_{AB_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_i^{AB_\beta}n_k^\gamma y_R^{\beta\alpha}\omega_R^{AB}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq i,\,\gamma}\left\langle n_i^{AB_\beta}n_k^\gamma y_R^{\beta\alpha}\omega_R^{AB}v_{ik}^{AB_\beta\gamma}\right\rangle\right\}=0$$

$$\frac{1}{\beta}\frac{d\left\langle n_i^{AB_\alpha}n_j^C\right\rangle}{dt}=\sum_{s\neq i\neq j,\,\beta,\,\sigma}\left\langle n_j^C n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}\right\rangle\left(\mu_s^A-\mu_i^A\right)+\sum_{s\neq i\neq j,\,\beta,\,\sigma}\left\langle n_j^C n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}\right\rangle\left(\mu_s^B-\mu_i^B\right)$$

$$+\sum_{\beta}\left\langle n_j^{CA_\beta}n_i^B y_{ji}^{\beta\alpha}\omega_{CA/B}^{\beta\alpha}\right\rangle\left(\mu_j^A-\mu_i^A\right)+\sum_{\beta}\left\langle n_j^{CB_\beta}n_i^A y_{ji}^{\beta\bar{\alpha}}\omega_{CB/A}^{\beta\bar{\alpha}}\right\rangle\left(\mu_j^B-\mu_i^B\right)$$

$$+\sum_{s\neq i\neq j,\,\beta,\,\sigma}\left\{\left\langle n_j^C n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{AB_\alpha}\right\rangle-\left\langle n_j^C n_s^{\sigma A_\beta}n_i^B y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{\sigma A_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_j^C n_s^{\sigma A_\beta}n_i^B n_k^\gamma y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq s,\,\gamma}\left\langle n_j^C n_s^{\sigma A_\beta}n_i^B n_k^\gamma y_{si}^{\beta\alpha}\omega_{\sigma A/B}^{\beta\alpha}v_{sk}^{\sigma A_\beta\gamma}\right\rangle\right\}$$

$$+\sum_{s\neq i\neq j,\,\beta,\,\sigma}\left\{\left\langle n_j^C n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{AB_\alpha}\right\rangle-\left\langle n_j^C n_s^{\sigma B_\beta}n_i^A y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{\sigma B_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_j^C n_s^{\sigma B_\beta}n_i^A n_k^\gamma y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq s,\,\gamma}\left\langle n_j^C n_s^{\sigma B_\beta}n_i^A n_k^\gamma y_{si}^{\beta\bar{\alpha}}\omega_{\sigma B/A}^{\beta\bar{\alpha}}v_{sk}^{\sigma B_\beta\gamma}\right\rangle\right\}$$

$$+\sum_{\beta}\left\{\left\langle n_j^{CA_\beta}n_i^B y_{ji}^{\beta\alpha}\omega_{CA/B}^{\beta\alpha}v_{AB_\alpha}\right\rangle-\left\langle n_j^{CA_\beta}n_i^B y_{ji}^{\beta\alpha}\omega_{CA/B}^{\beta\alpha}v_{CA_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_j^{CA_\beta}n_i^B n_k^\gamma y_{ji}^{\beta\alpha}\omega_{CA/B}^{\beta\alpha}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq j,\,\gamma}\left\langle n_j^{CA_\beta}n_i^B n_k^\gamma y_{ji}^{\beta\alpha}\omega_{CA/B}^{\beta\alpha}v_{jk}^{CA_\beta\gamma}\right\rangle\right\}$$

$$+\sum_{\beta}\left\{\left\langle n_j^{CB_\beta}n_i^A y_{ji}^{\beta\bar{\alpha}}\omega_{CB/A}^{\beta\bar{\alpha}}v_{AB_\alpha}\right\rangle-\left\langle n_j^{CB_\beta}n_i^A y_{ji}^{\beta\bar{\alpha}}\omega_{CB/A}^{\beta\bar{\alpha}}v_{CB_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_j^{CB_\beta}n_i^A n_k^\gamma y_{ji}^{\beta\bar{\alpha}}\omega_{CB/A}^{\beta\bar{\alpha}}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq j,\,\gamma}\left\langle n_j^{CB_\beta}n_i^A n_k^\gamma y_{ji}^{\beta\bar{\alpha}}\omega_{CB/A}^{\beta\bar{\alpha}}v_{jk}^{CB_\beta\gamma}\right\rangle\right\}$$

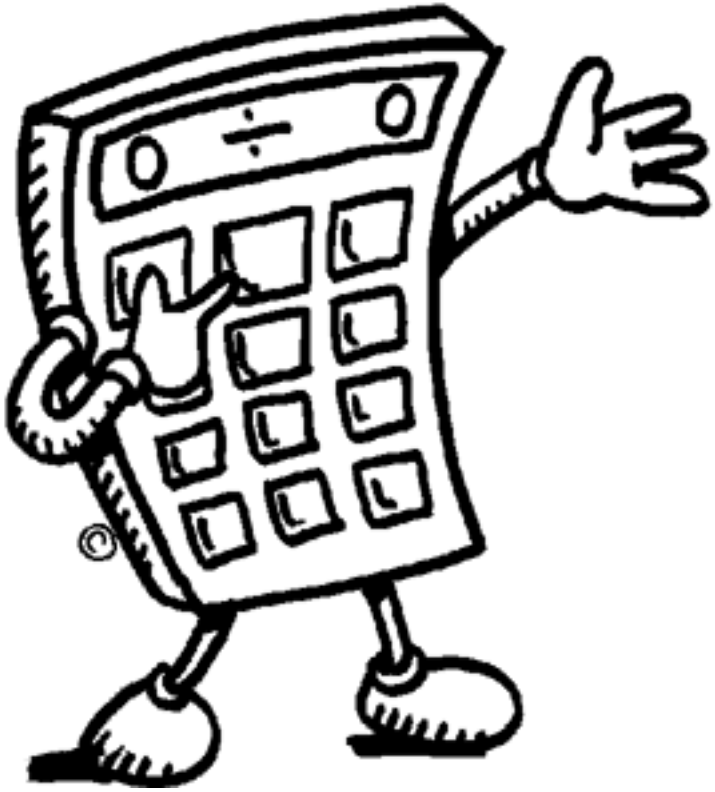
$$+\sum_{\beta\neq\alpha}\left\{\left\langle n_j^C n_i^{AB_\beta}y_R^{\beta\alpha}\omega_R^{AB}v_{AB_\alpha}\right\rangle-\left\langle n_j^C n_i^{AB_\beta}y_R^{\beta\alpha}\omega_R^{AB}v_{AB_\beta}\right\rangle+\sum_{k\neq i,\,\gamma}\left\langle n_j^C n_i^{AB_\beta}n_k^\gamma y_R^{\beta\alpha}\omega_R^{AB}v_{ik}^{AB_\alpha\gamma}\right\rangle-\sum_{k\neq i,\,\gamma}\left\langle n_j^C n_i^{AB_\beta}n_k^\gamma y_R^{\beta\alpha}\omega_R^{AB}v_{ik}^{AB_\beta\gamma}\right\rangle\right\}=0$$

# Why is the dumbbell case so complicated?

- Internal dumbbell interaction.
  - More equations and more complicated structure of the T matrix.
  - Application of the symmetry condition involves also the dumbbell inversion.
- Several dumbbell orientations.
  - "Combined" symmetry.
  - For each orientation there is a change of
    - accessible sites.
    - symmetry classes.
    - vanishing interactions.
- More paths for configuration change.
  - The defect is made of two atoms.
  - Possibility of "i-j" exchange.
  - Dumbbell on-site rotation.
  - Rotation-translation jumps.

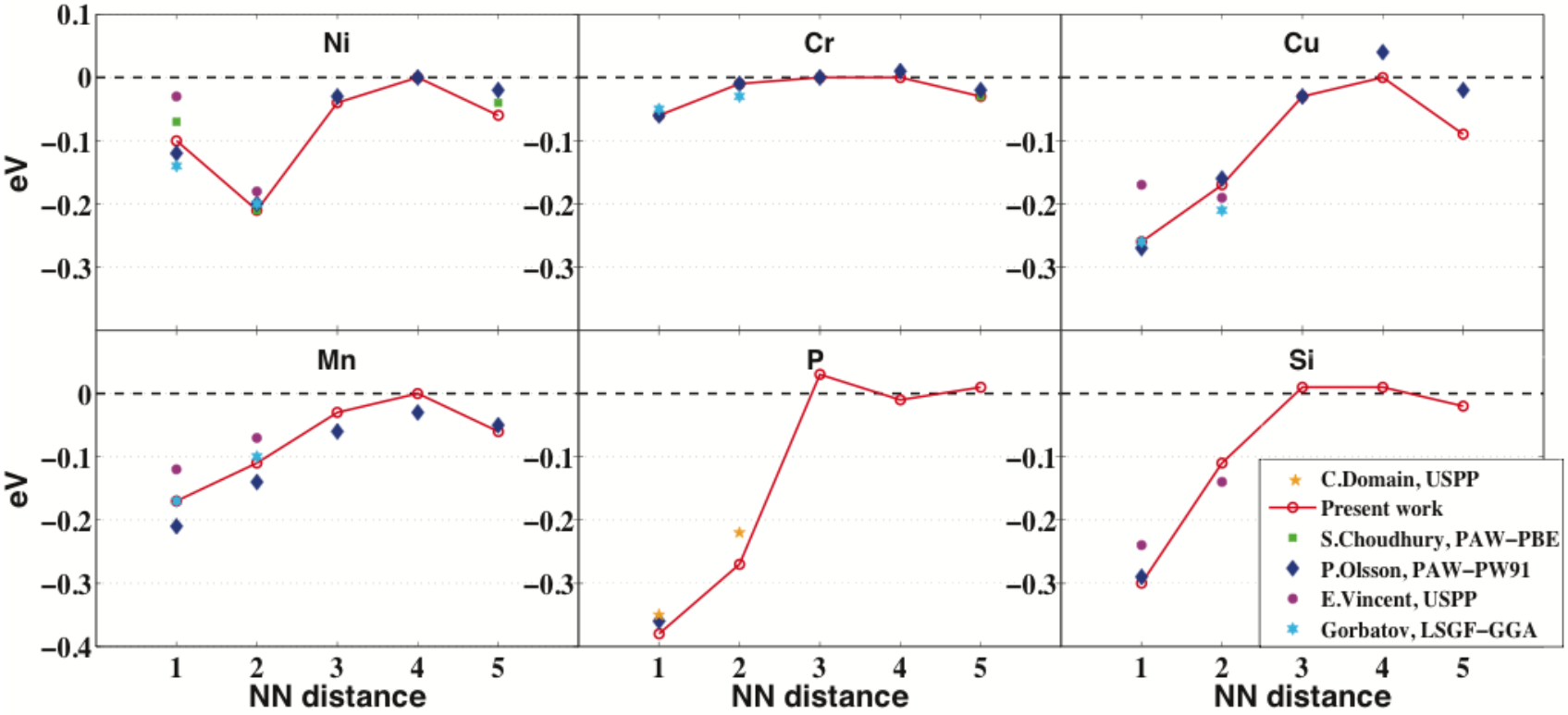
**Code in progress!**

# RESULTS



# Solute-Vacancy Binding Energies

Ab-initio solute-vacancy binding energies computed with the PAW-PBE method in VASP and comparison with previous works. Negative energy stands for attractive interaction.




- Cr is almost transparent to vacancies!
- Large disagreement with previous calculations only for binding energies computed with Ultra-Soft Pseudopotentials (USPP) [1].

[1] A.V. Barashev et al., *Phil. Mag. Lett. (2006)*

# Migration barriers

| ΔG [eV] | Ni | Cr | Cu | Mn | Si | P |
|---|---|---|---|---|---|---|
| $w_0$ | | | 0.70 | | | |
| $w_2$ | 0.63 | 0.55 | 0.51 | 0.41 | 0.51 | 0.40 |
| $w_3$ | 0.59 | 0.70 | 0.72 | 0.66 | 0.74 | 0.68 |
| $w_4$ | 0.69 | 0.66 (0.64) | 0.64 | 0.70 | 0.55 | 0.57 |
| $w_{3'}$ | 0.72 | 0.69 | 0.74 | 0.70 | 0.89 | 0.98 |
| $w_{4'}$ | 0.66 (0.62) | 0.64 | 0.51 (0.49) | 0.56 (0.53) | 0.58 (0.59) | 0.58 (0.61) |
| $w_{3''}$ | 0.66 | 0.67 | 0.67 | 0.66 | 0.82 | 0.86 |
| $w_{4''}$ | 0.62 (0.56) | 0.65 (0.62) | 0.50 (0.41) | 0.56 (0.49) | 0.55 (0.52) | 0.47 (0.48) |
| $w_5$ | 0.80 | 0.72 | 0.75 | 0.76 | 0.71 | 0.74 |
| $w_6$ | 0.59 | 0.70 | 0.57 | 0.64 | 0.58 (0.59) | 0.48(0.47) |

Values in red: modified migration barriers in order to fulfill detailed balance.

# Detailed balance

- In absence of irradiation, the equilibrium vacancy concentration must be conserved, locally and globally.
- This condition reduces the number of independent hopping rates.

$$\frac{\omega_4}{\omega_3} = \frac{\nu_4^*}{\nu_3^*} \exp\left\{ -\frac{(H_4^m - H_3^m)}{k_B T} \right\}$$

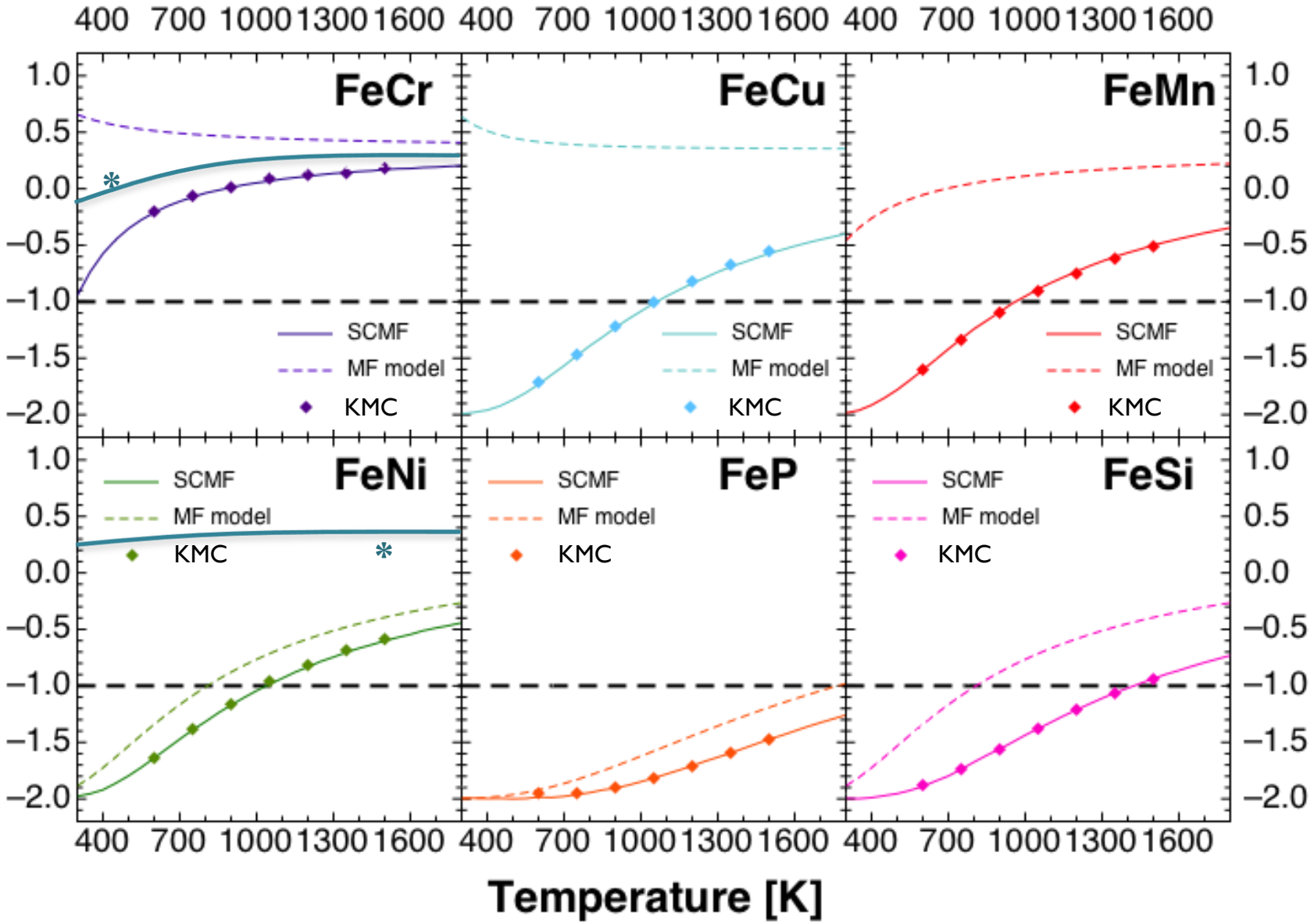
$$\boxed{\frac{\omega_4}{\omega_3} = \exp\left( -\frac{(H_{1NN}^b - H_{2NN}^b)}{k_B T} \right)}$$

- Attempt frequencies contain the migration entropy term. If their ratio is equal to 1

$$H_1^m - H_2^m = H_{1NN}^b - H_{2NN}^b$$

- **If the interactions beyond the 2NN are to be neglected, the dft-computed migration barriers must be adjusted in order to respect detailed balance.**
- In other words: at equilibrium, there is no interaction between solute and vacancy beyond the fixed interaction range (2NN).

# VACANCY WIND




* Choudhoury JNM 2011

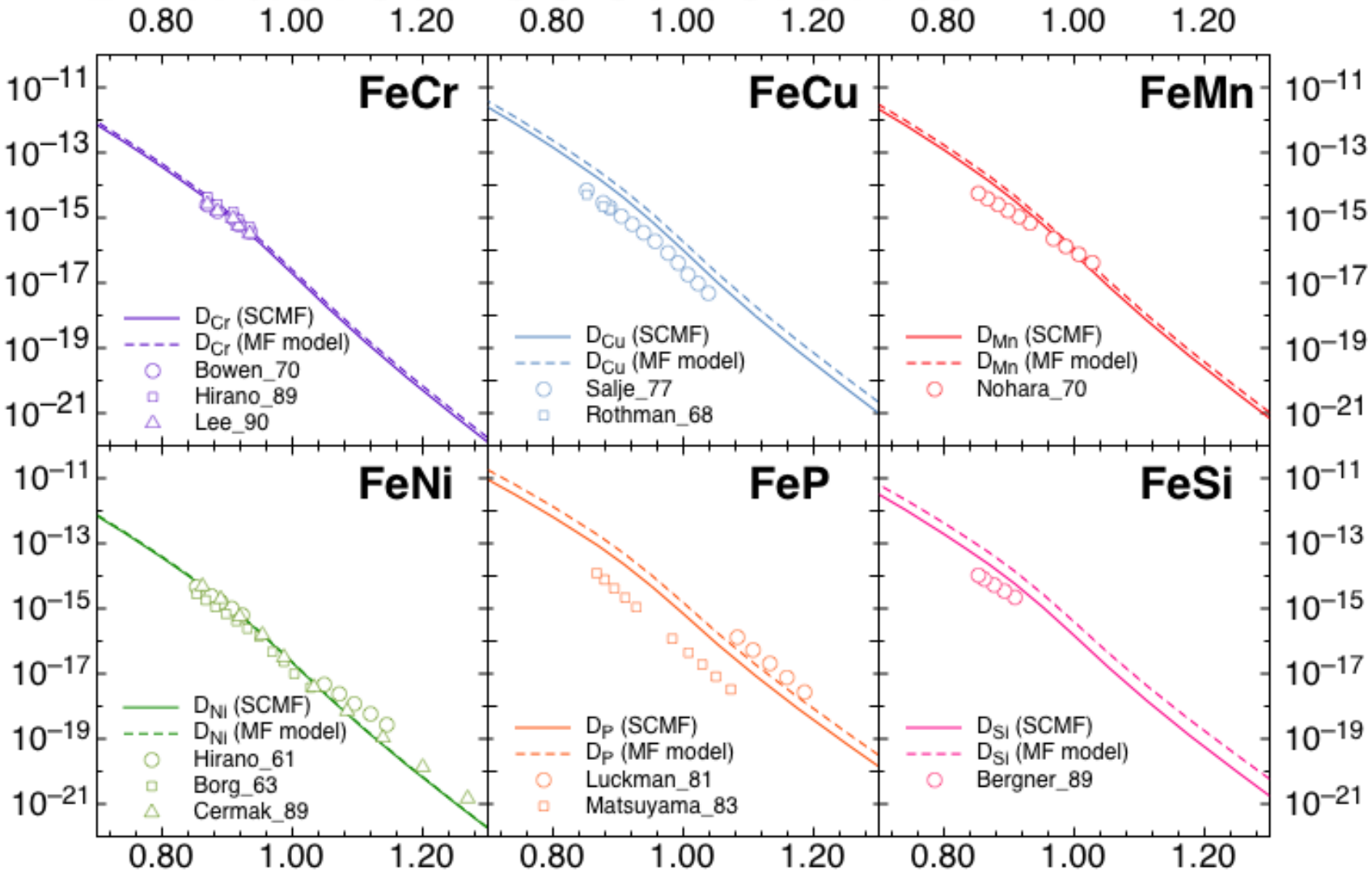
# Vacancy wind

| | P | Si | Cu | Ni | Mn | Cr |
|---|---|---|---|---|---|---|
| $E^{1nn}$ | -0.38 eV | -0.30 eV | -0.26 eV | -0.10 eV | -0.17 eV | -0.06 eV |
| $E^{2nn}$ | -0.27 eV | -0.11 eV | -0.17 eV | -0.21 eV | -0.11 eV | -0.01 eV |
| $\sum E^{Xnn}$ | -0.65 eV | -0.41 eV | -0.43 eV | -0.31 eV | -0.28 eV | -0.07 eV |
| $T_{crit}$ [K] | ➢2100 | 1424 | 1062 | 1038 | 962 | ≈290 |
| $G_{573K}$ | -1.99 | -1.91 | -1.77 | -1.68 | -1.65 | -0.25 |

- There is a clear correlation between vacancy-solute binding strength and dragging tendency.

- At RPV temperature (≈ 573 K) all solutes but Cr are expected to be dragged along.

# Diffusion coefficients



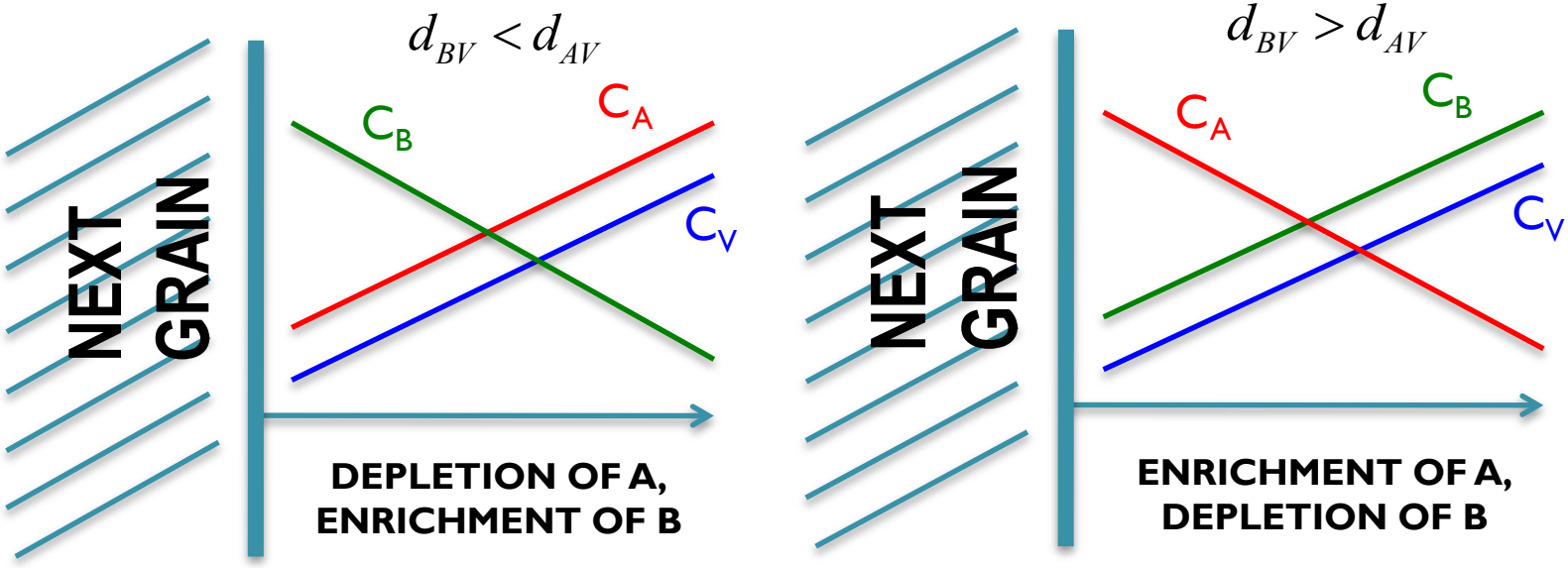
# Benchmarking with Kinetic Monte-Carlo

- Box of 432 atoms, 1 sol + 1 vacancy
- $10^6$ observations of 5000 events each, at 1500 K.

| WIND | FeCr | FeCu | FeMn | FeNi | FeP | FeSi |
|---|---|---|---|---|---|---|
| SCMF | +0.14 | -0.74 | -0.38 | -0.71 | -1.45 | -0.93 |
| KMC | +0.16 | -0.71 | -0.42 | -0.70 | -1.43 | -0.91 |
| KMC [b] | | +0.06 | +0.16 | +0.25 | -0.36 | -0.01 |
| KMC [m] | | +0.04 | +0.25 | +0.21 | -0.37 | +0.00 |

([b]) Parameters from E. Aublant (Vincent) and R. Ngayam-Happy, **binary** alloys
([m]) Parameters from E. Aublant (Vincent) and R. Ngayam-Happy, **multi-component** alloy

# RIS at grain boundaries




**CONCENTRATION GRADIENTS**

$$\frac{\nabla C_B}{\nabla C_V} = \frac{C_B C_A d_{AV} d_{AI}}{\phi\left(C_A d_{AI} D_B + C_B d_{BI} D_A\right)}\left(\frac{d_{BV}}{d_{AV}} - \frac{d_{BI}}{d_{AI}}\right)$$

$d_{BI}/d_{AI} = 1$

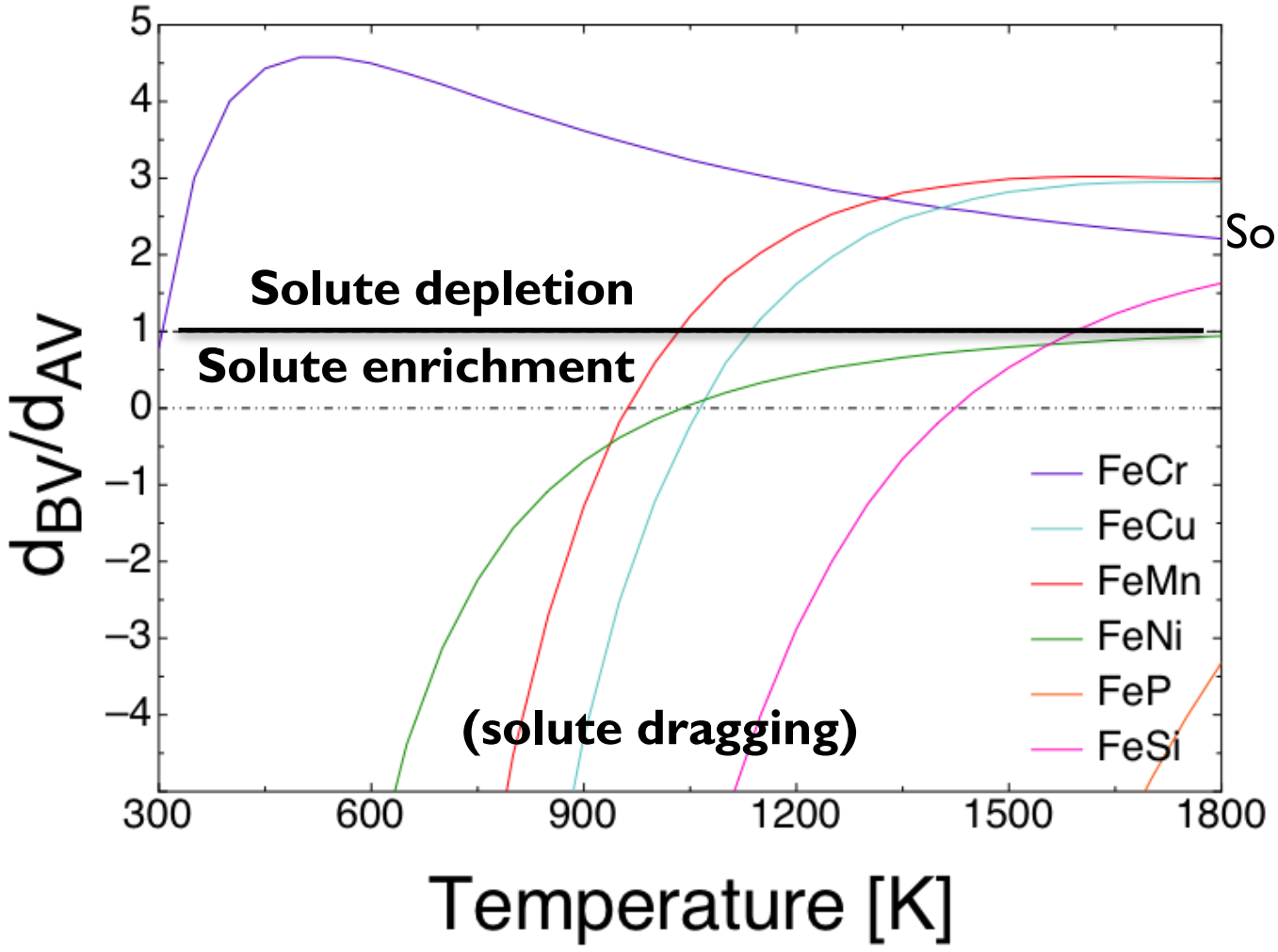
**PARTIAL DIFFUSION COEFFICIENTS**

$$d_{BV} = \frac{L^V_{BB} + L^V_{BA}}{C_B C_V} \qquad d_{AV} = \frac{L^V_{AA} + L^V_{AB}}{C_A C_V}$$

The RIS behaviour is determined by the relative diffusion velocities between Fe and solute.

Hitherto the contribution of vacancy mediated diffusion was analyzed ($d_{BV}$, $d_{AV}$).

# RIS at grain boundaries




Solute dragging for

$$\frac{d_{BV}}{d_{AV}} < 0$$

# Conclusions

- A complete set of Lij coefficients was computed.
  - P and Si have the strongest interaction with vacancies. The interaction vac-Ni is particularly strong at the 2NN.
  - All solutes (with the exception of Cr) are expected to undergo vacancy dragging. In the case of Mn, the effect is weak.
  - As opposed to the approximated Serruy's model, SCMF is able to predict dragging of Cu in bcc iron, as expected from experimental evidence, and for Mn at low temperatures.
  - At low temperatures, all solutes are expected to enrich at grain boundaries **with the exception of Cr**, which is expected to deplete (as far as only the interaction with vacancies is concerned).

- Perspectives:
  - DFT calculation of interstitial migration barriers for the 6 alloys.
  - Calculation of Lij:s for interstitial-mediated diffusion, consequences on dragging and RIS behaviour.
  - Multi-component dilute alloys
  - Concentrated alloys (Fe-Cr based)

KTH VETENSKAP OCH KONST

# THANKS FOR YOUR ATTENTION!

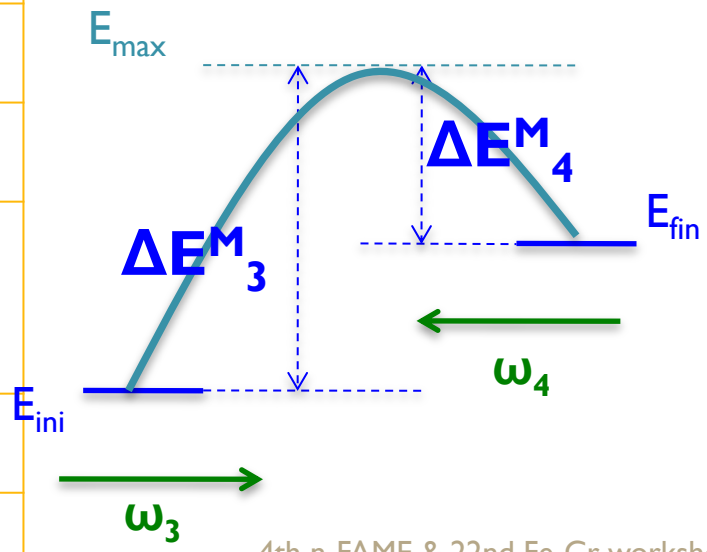
# Ab-initio calculations

| VASP SETTINGS |
| --- |
| PAW-PBE method |
| Spin-polarized calculations |
| Full-core PAW potentials for Fe, Cu, Ni, Si, P, Mn<br>Semi-core PAW potential for Cr |
| Supercell: 4x4x4 (128 atoms) |
| K-point mesh: 3x3x3 |
| Cutoff energy: 300 eV |
| Refinement of mixing tags to prevent the simulation from getting trapped into a wrong magnetic state (Mn, Si). |
| Nudged Elastic Band (NEB) method |
| Molecular statics simulation for frozen phonons. |

**ATTEMPT FREQUENCY (only in pure Fe at the moment):**

$$\nu_i^* = \prod_{j=-1}^{N} \nu_j^{init} \Big/ \prod_{j=-1}^{N-1} \nu_j^{saddle}$$

**MIGRATION BARRIERS:**



# Magnetic Models

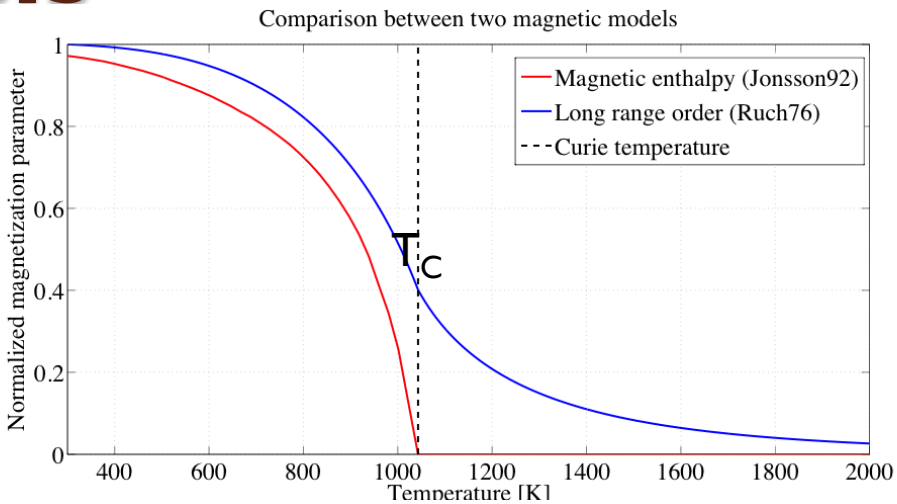
Activation energy: $Q = H^f + H^m$

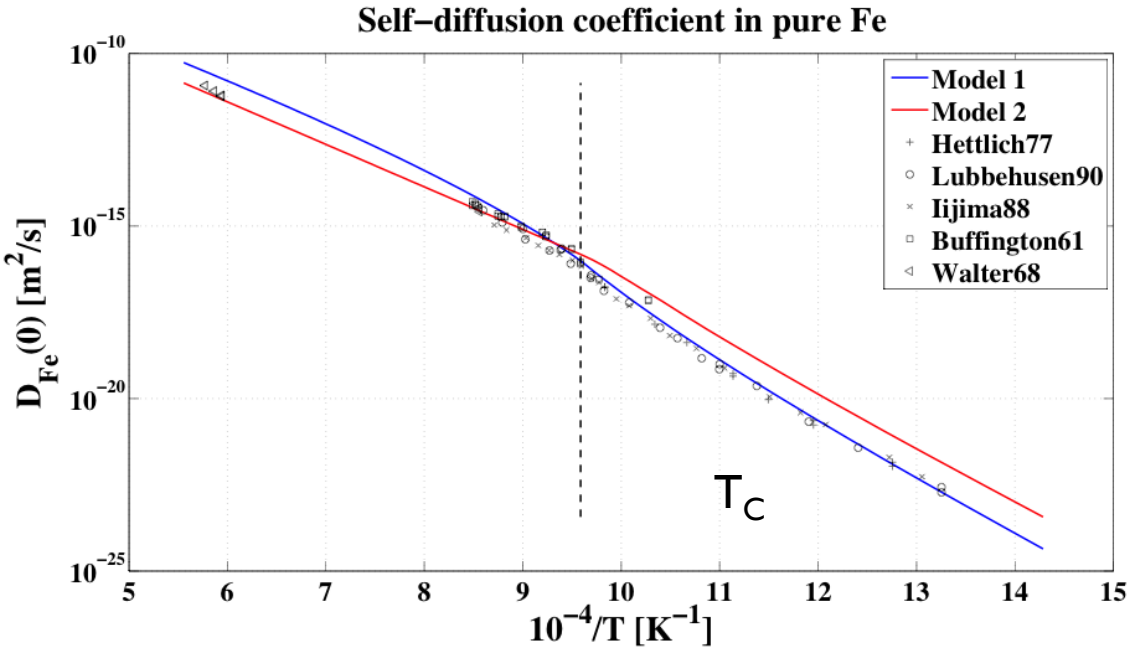
- B. Jönsson, *Z. Metallkd.* (1992)

$$Q(T) = Q^F_{T=0} - \alpha h$$

- L. Ruch, *J. Phys. Chem. Solids* (1976)

$$Q(T) = Q^P(1 + \beta M^2)$$




Ab-initio computed self-diffusion coefficient in pure Fe ($C_B$=0) by applying Jönsson's and Ruch's magnetic models, and comparison with experimental measurements (α=0.62 eV, β= 0.156[1] ).

[1] S. Takemoto et al., *Phil. Mag.* (2007)

# Sensitivity to binding energies