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KINETIC EFFECTS ON THE THERMODYNAMICS OF IRRADIATED MATERIALS

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OUTLINE

Materials under irradiation: a variety of phenomena

- Point defects supersaturation
- Phase diagrams under irradiation
- Ballistic mixing and patterning
- Radiation induced segregation and precipitation

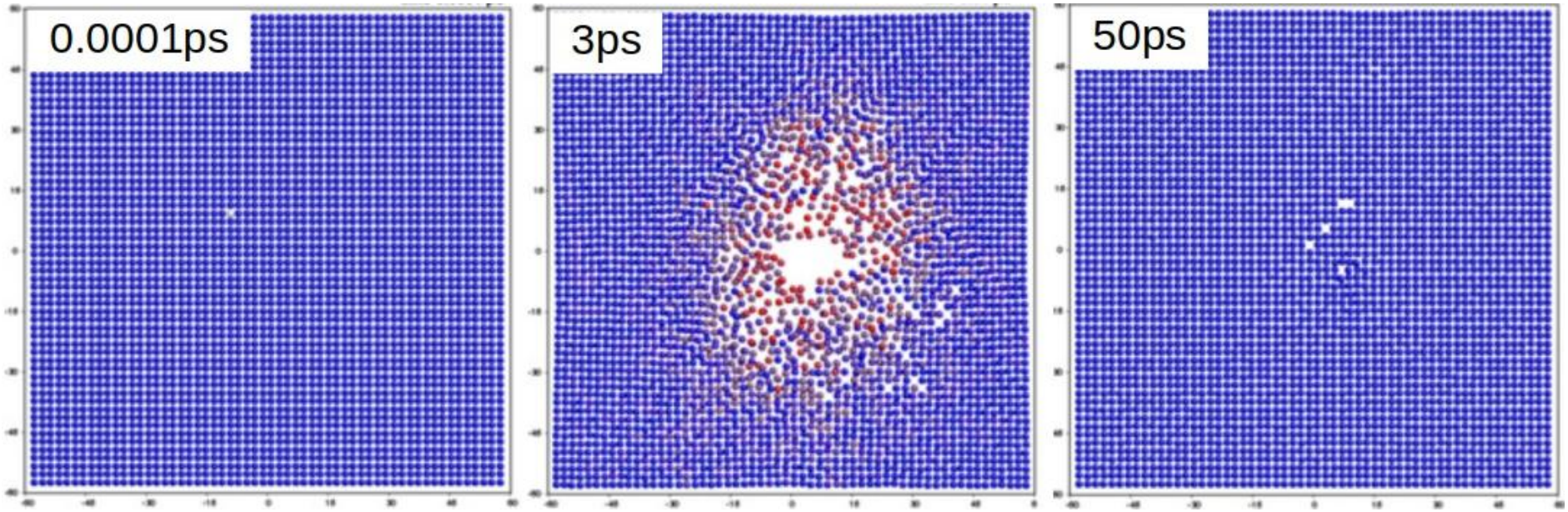
Computation of transport properties from the atomic scale

- Multi-scale modeling of materials
- The kinetic cluster expansion formalism for dilute systems
- Self-consistent mean field formulation of transport coefficients
- Example calculations
- Changing the reference state of a system with ballistic relocations

Current questions

POINT DEFECTS SUPERSATURATION UNDER IRRADIATION

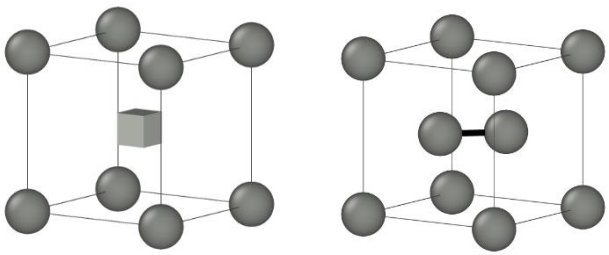
Primary damage in irradiated materials: displacement cascade



Nordlund et al. (2015) OECD / Nuclear Science, NEA/NSC/DOC(2015)9.

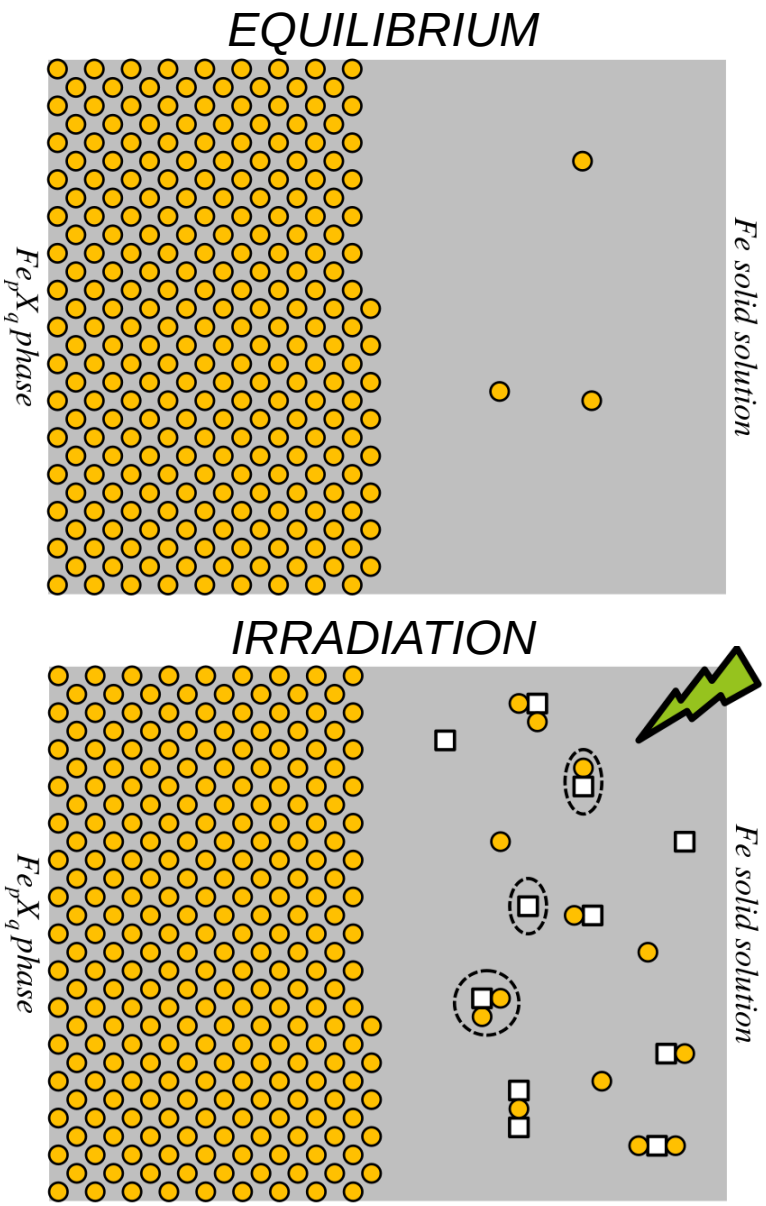
Driving force : supersaturation with respect to equilibrium concentration $[PD]^{eq} \simeq \exp\left(-\frac{E^f_{PD}}{k_B T}\right)$

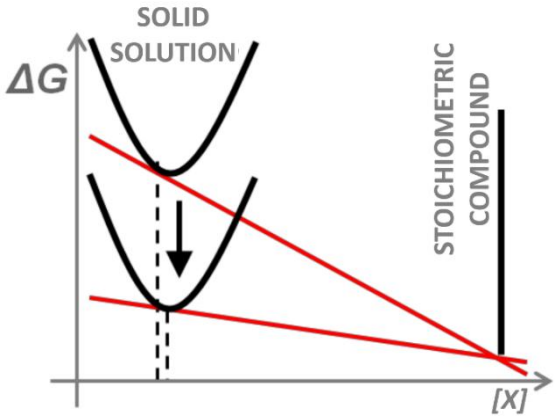
- Vacancy-self-interstitial atom recombination
- Elimination at point defects sinks (interfaces, dislocations, point defect clusters)

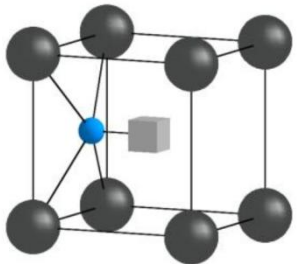


Point-defect mediated solute diffusion introduces two diffusion time scales

PHASE DIAGRAMS UNDER IRRADIATION



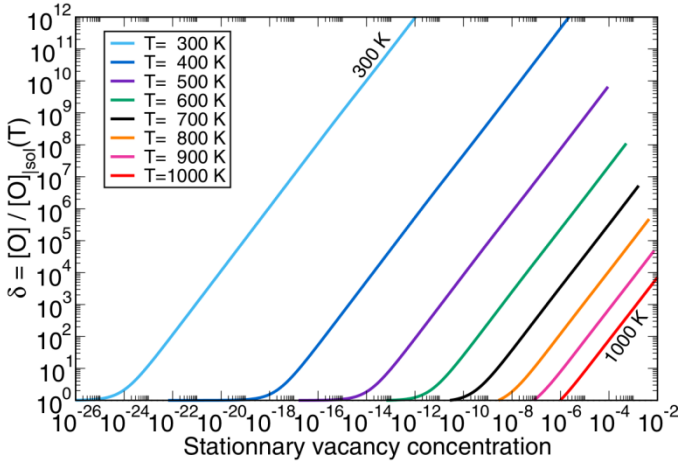




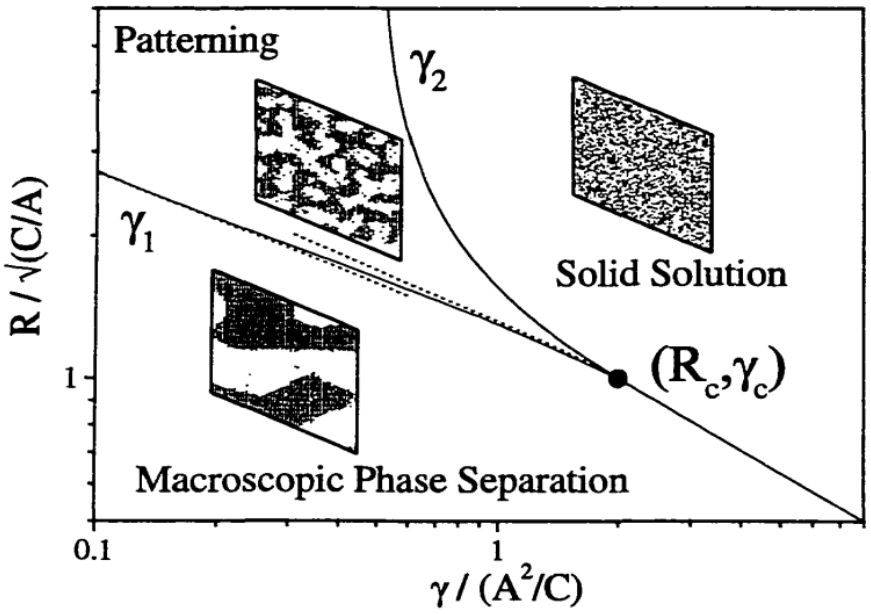
Vacancy-oxygen binding energy in Fe : 1.43 eV

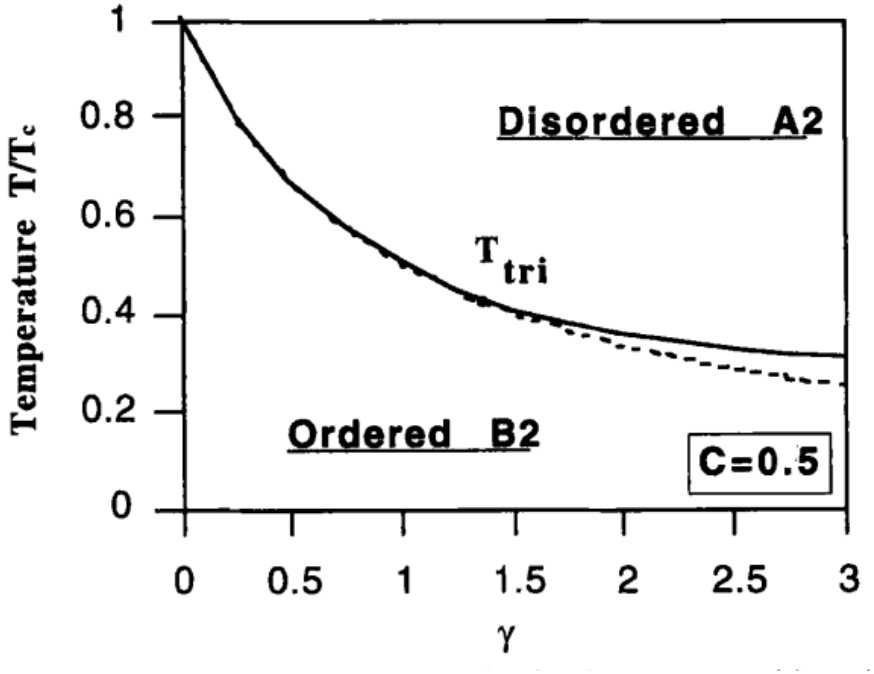
Computing the point-defect induced solubility limit increase with a **low-temperature expansion of the grand-canonical partition function**

*Schuler et al. Phys. Rev. B **95** 014113 (2017)*



BALLISTIC MIXING AND PATTERNING UNDER IRRADIATION

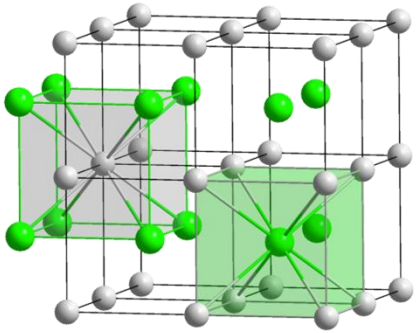




Enrique, Bellon Phys. Rev. Lett. ***84*** *2885 (2000)*

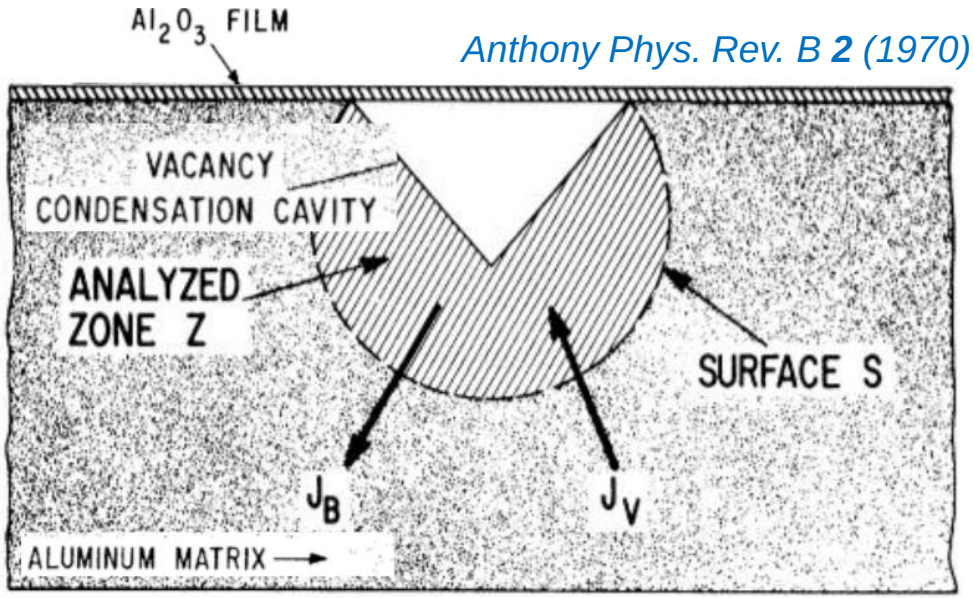
Martin, Bellon Solid State Phys. ***50*** *189 (1997)*

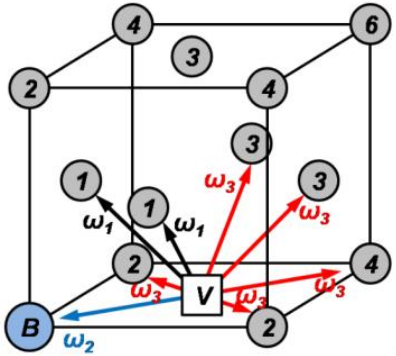
Competition between athermal relocation events and thermally-activated jumps

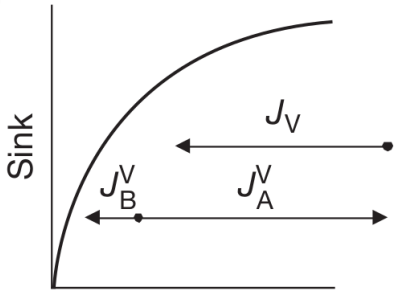


RADIATION-INDUCED SEGREGATION AND PRECIPITATION

*Anthony Phys. Rev. B **2** (1970)*







$$\frac{J_B}{J_V} = \frac{C_B D_B}{D_A + C_B D_B} \quad \frac{W_1 - \frac{13}{2} W_3}{W_1 + \frac{7}{2} W_3}$$

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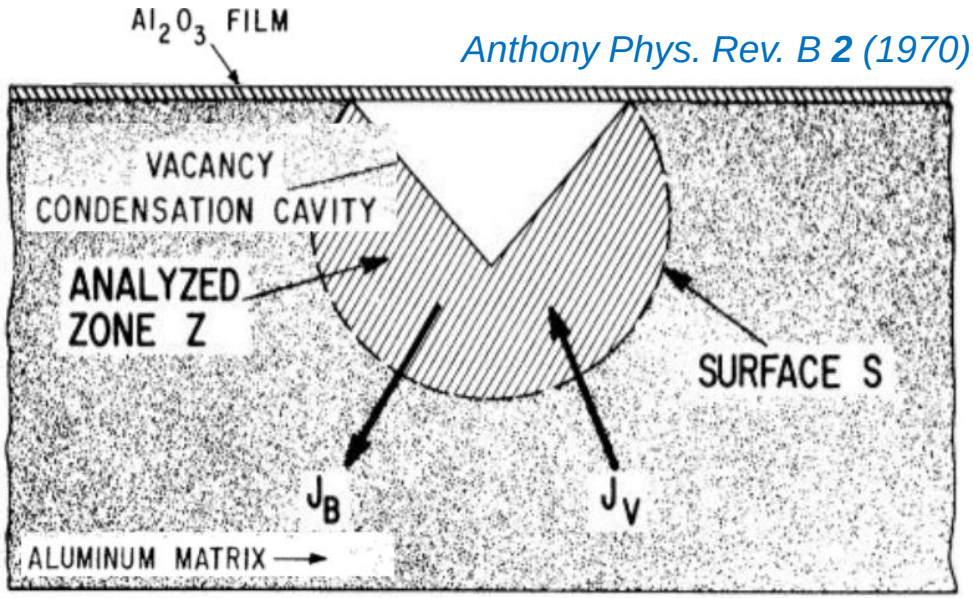

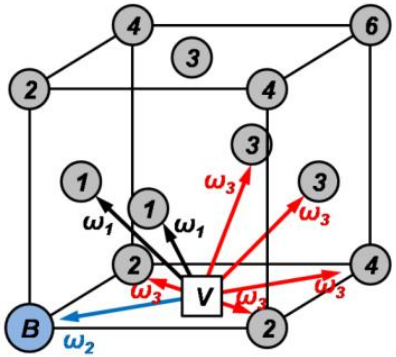

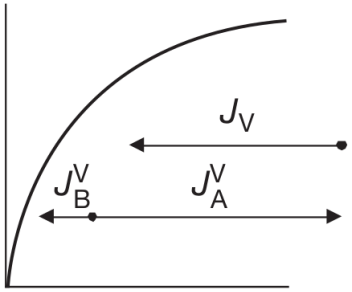

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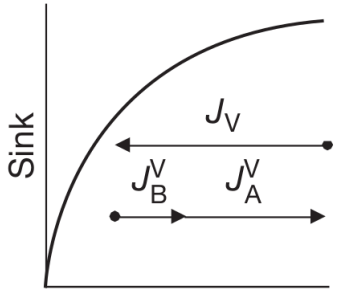
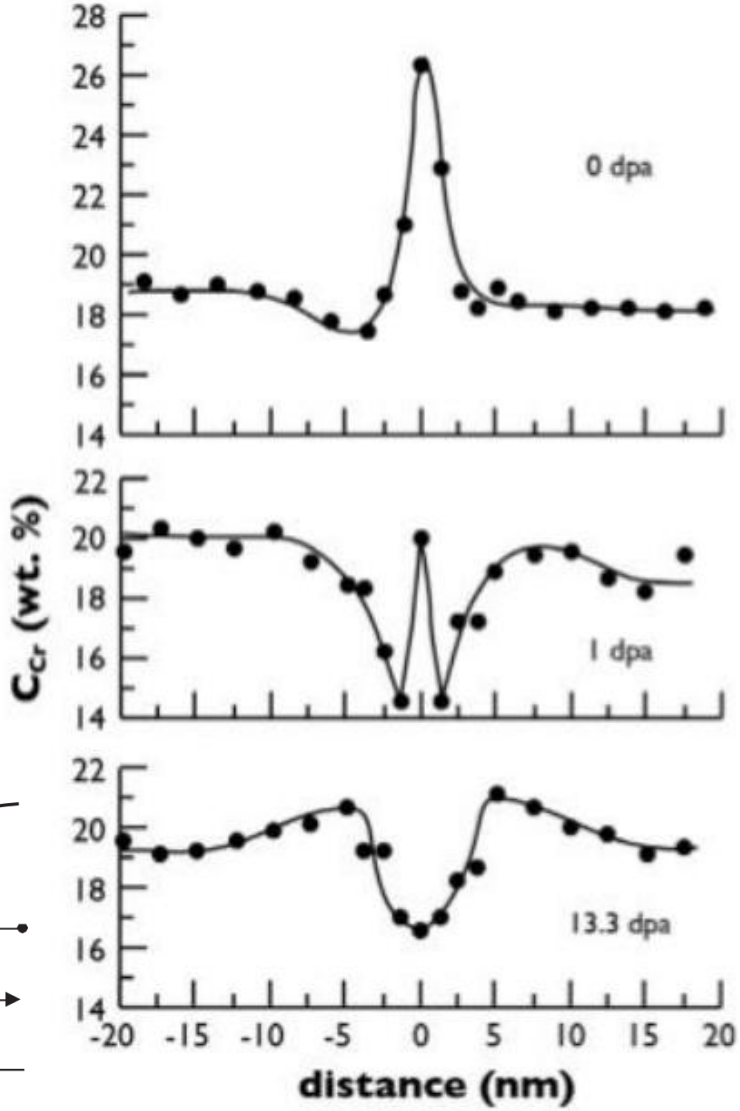
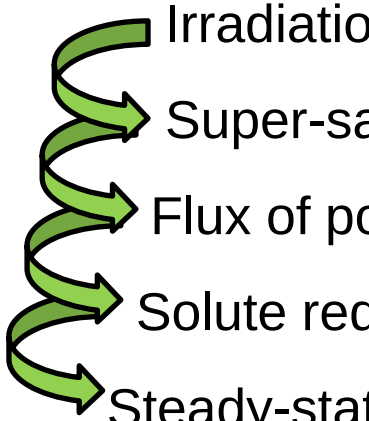


*Ardell and Bellon, Current Opinion in Solid State and Materials Science **20** 115 (2016)*



SUMMARY



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Super-saturation of point defects wrt respect to equilibrium

Flux of point defects towards point defect sinks

Solute redistribution due to flux coupling

Steady-state depending on both thermodynamic and kinetic properties

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Super-saturation of point defects wrt respect to equilibrium

Flux of point defects towards point defect sinks

Solute redistribution due to flux coupling

Steady-state depending on both thermodynamic and kinetic properties

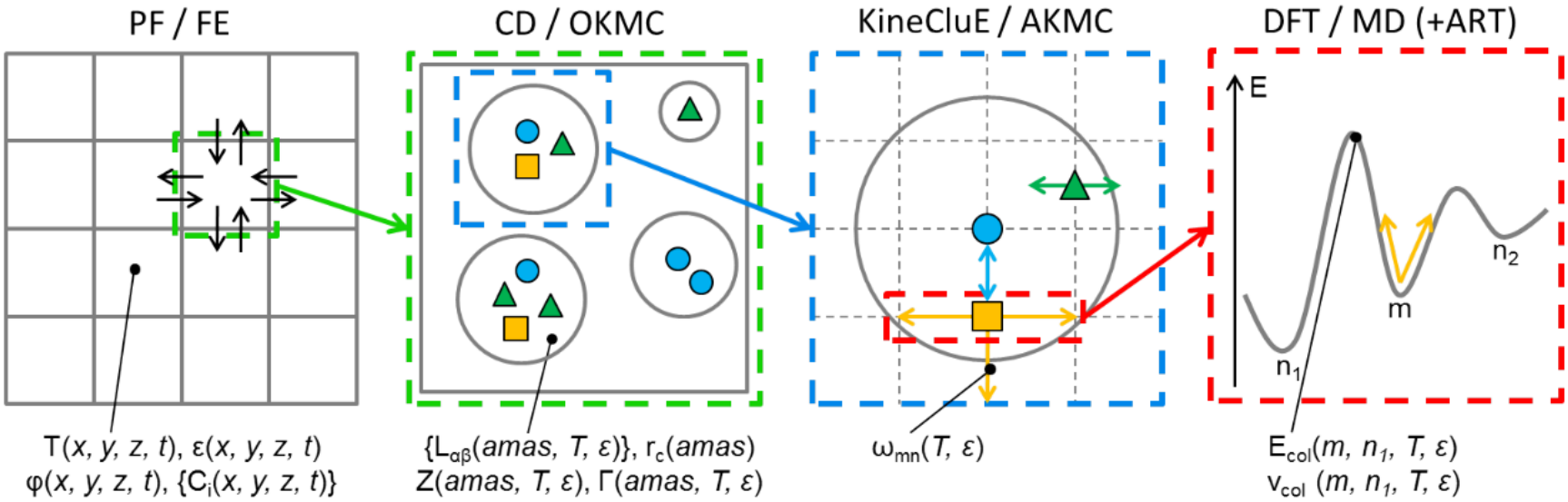
We need transport coefficients !

Thermodynamics of irreversible processes :

*Onsager Phys. Rev. B **38** 2265 (1931)*

$$\vec{J}_\alpha = -\sum_\beta L_{\alpha\beta} \vec{\nabla} \frac{\mu_\beta}{k_B T}$$

MULTI-SCALE MODELING OF MATERIALS



Homogeneous cells | *Local equilibrium* | *Thermalized states*

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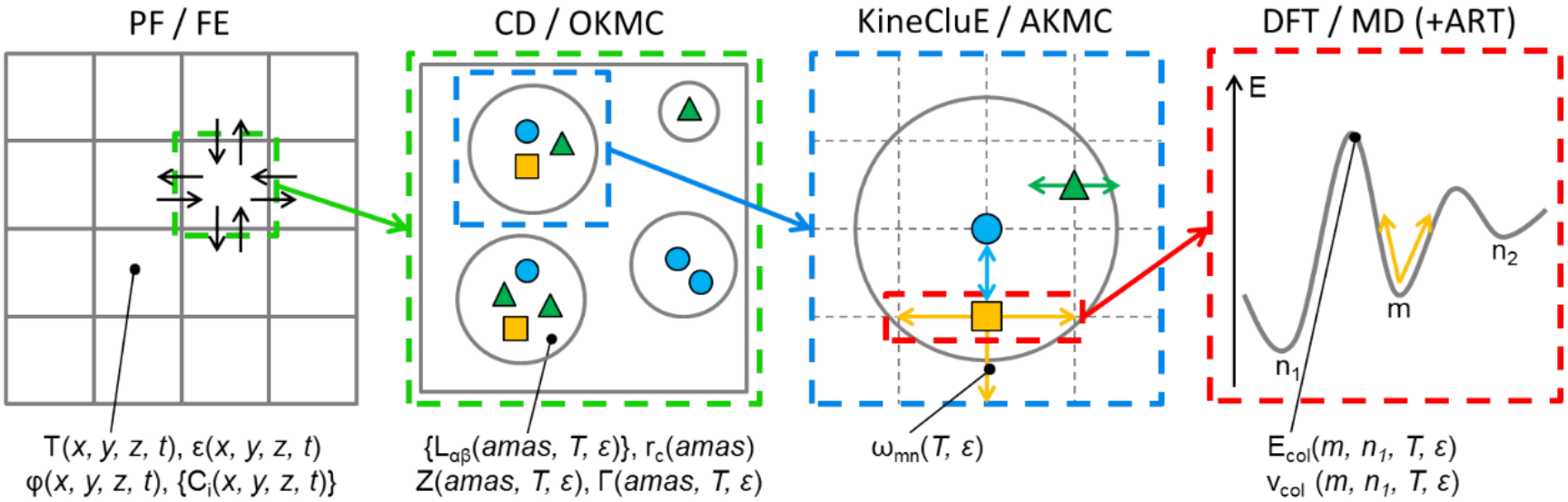

Several issues with atomic kinetic Monte Carlo simulations:

- Kinetic trapping
- Result is concentration and temperature dependent
- Off-diagonal coefficients are often difficult to measure precisely

Analytical models ?

- Dilute models *Lidiard Phil. Mag.* ***46*** *1218 (1955)*
- Concentrated models *Kikuchi J. Chem. Phys.* ***51*** *161 (1969), Manning Phys. Rev. B* ***4*** *1111 (1971)*

KINECTIC CLUSTER EXPANSION FORMALISM FOR DILUTE SYSTEMS

Thermodynamic cluster expansion:

*Sanchez Phys. A **128** 334 (1984)*

$$H(\mathbf{n}) = \sum_i \sum_\alpha n_i^\alpha \varepsilon_i^\alpha + \frac{1}{2!} \sum_{i,j} \sum_{\alpha,\beta} n_i^\alpha n_j^\beta \varepsilon_{\lambda(ij)}^{\alpha\beta} + \frac{1}{3!} \sum_{i,j,k} \sum_{\alpha,\beta,\gamma} n_i^\alpha n_j^\beta n_k^\gamma \varepsilon_{\lambda(ijk)}^{\alpha\beta\gamma} + \cdots,$$

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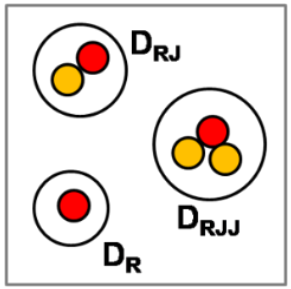
Kinetic cluster expansion:

Schuler Comp. Phys. Comm. submitted (2018)

- Configuration space is split into **independent sub-spaces called cluster**, defined by a kinetic radius



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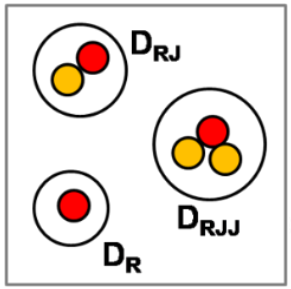

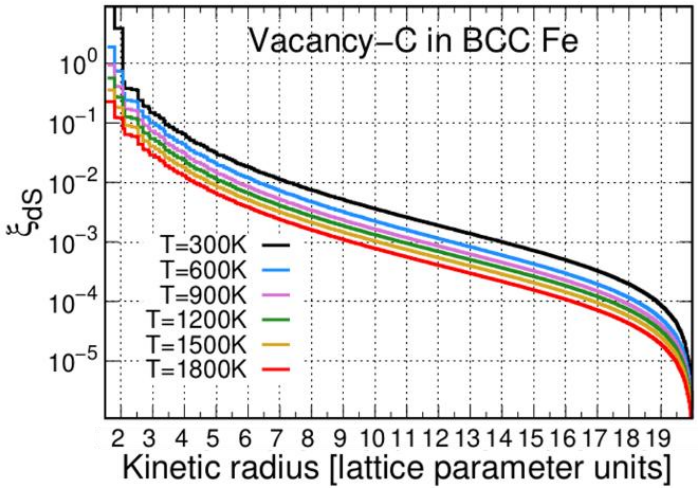

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- Configuration space is split into **independent sub-spaces called cluster**, defined by a kinetic radius
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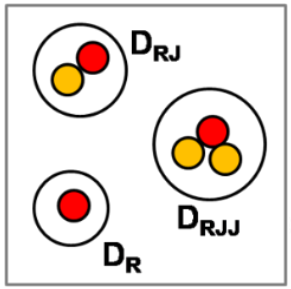
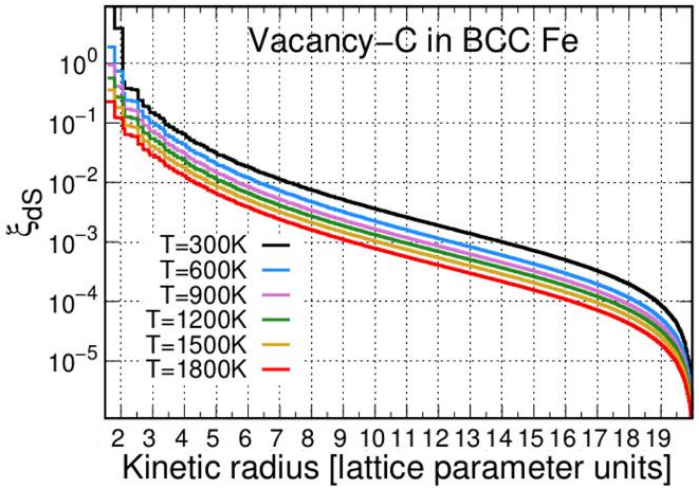
- This way, cluster transport coefficients are **intrinsic equilibrium properties** of each cluster
- We are thus able to define **transport coefficients for out of equilibrium systems** (not feasible with AKMC)





$$L_{\alpha\beta} = \sum_c [c]^{\mathrm{oe}} L_{\alpha\beta}^{\mathrm{eq}}(c)$$

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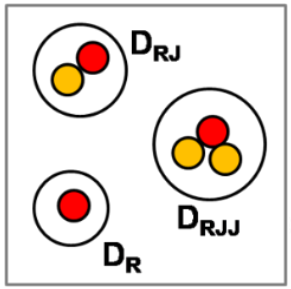
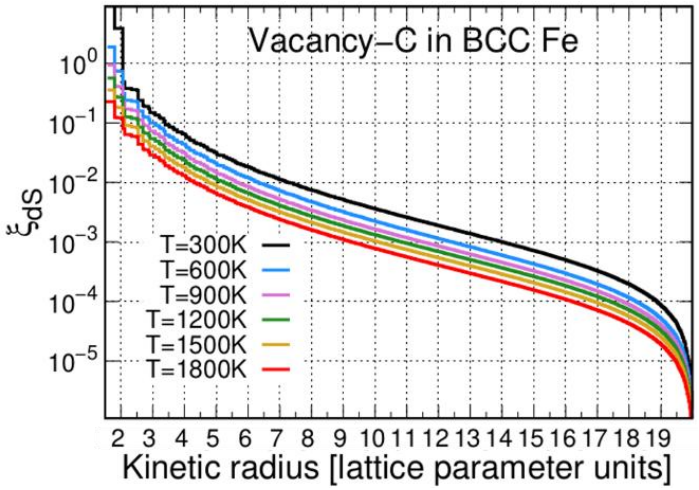




$$L_{\alpha\beta} = \sum_c [c]^{oe} L_{\alpha\beta}^{eq}(c)$$

Open-source code KineCluE

COARSE-GRAINING PROCESS

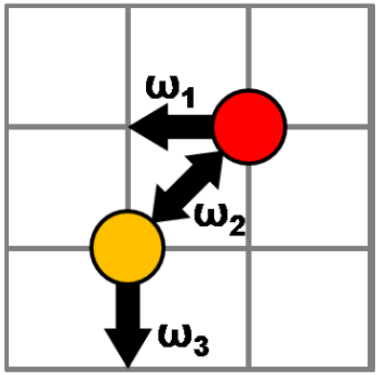
$\{\omega_{p\to q}\}$

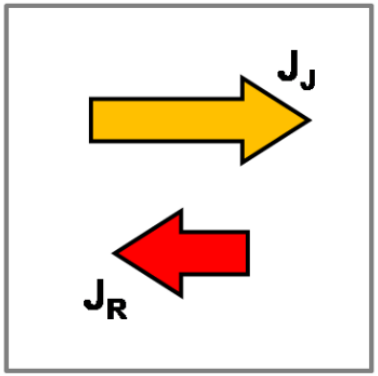
$$\begin{pmatrix} L_{VV} & L_{VX} \\ L_{XV} & L_{XX} \end{pmatrix}$$

Atomic jump frequencies

DFT+SCMF

Continuous description (TIP)

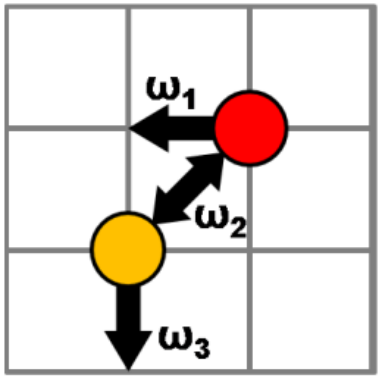


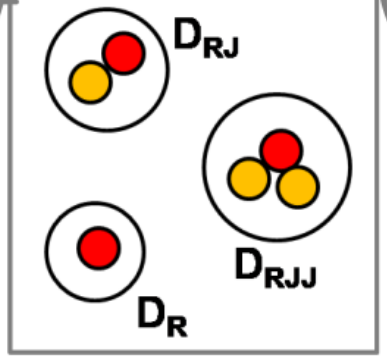


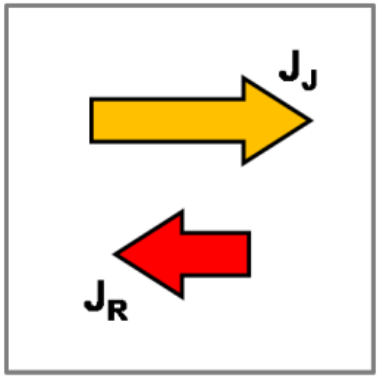
COARSE-GRAINING PROCESS

$\{\omega_{p\to q}\}$ $\left(\begin{array}{cc} L^{eq}_{VV}(c_i) & L^{eq}_{VX}(c_i) \\ L^{eq}_{XV}(c_i) & L^{eq}_{XX}(c_i) \end{array} \right)$ $\left(\begin{array}{cc} L_{VV} & L_{VX} \\ L_{XV} & L_{XX} \end{array} \right)$

Atomic jump frequencies → **Cluster transport coefficients** → **Continuous description (TIP)**







DFT+SCMF

$$L_{\alpha\beta} = \sum_{c_i} [c_i]\, L^{eq}_{\alpha\beta}(c_i)$$

Local equilibrium within a cluster is assumed

TRANSPORT COEFFICIENTS

Fluctuations point of view

Kinetic Monte Carlo, Molecular Dynamics

Allnatt J. Phys. C: Solid State Phys. ***15*** *5605 (1982)*

$$L_{\alpha\beta} = \lim_{\tau\to\infty} \frac{\left\langle \Delta\vec{R}_\alpha(\tau)\,\Delta\vec{R}_\beta(\tau)\right\rangle}{6V\tau}$$

Thermodynamics of irreversible processes

Analytical models

Onsager Phys. Rev. B ***38*** *2265 (1931)*

$$\vec{J}_\alpha = -\sum_\beta L_{\alpha\beta}\vec{\nabla}\frac{\mu_\beta}{k_B T}$$

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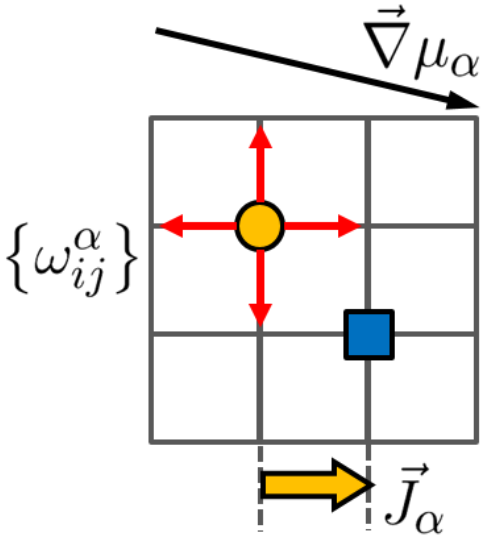
SCMF in brief:

- Rigid lattice
- Atomic jump mechanisms
- Application of a driving force (small)
- Computation of the resulting flux
- Identification of transport coefficients

Nastar et al. Phil. Mag. A, 80 155 (2000)



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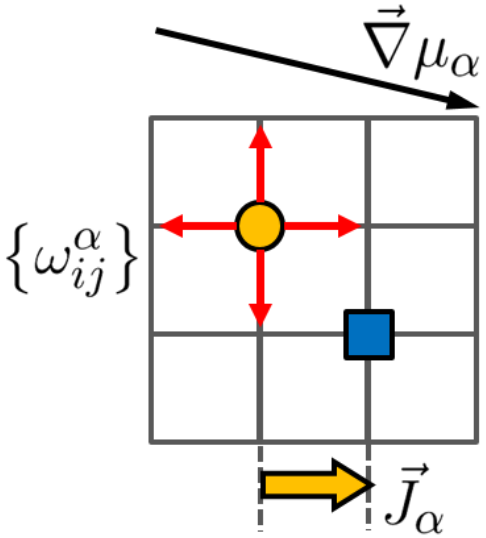

Can we use our transport coefficient formalism to obtain equilibrium fluctuations, and hence study nucleation phenomena ?

SELF-CONSISTENT MEAN FIELD FORMULATION OF TRANSPORT COEFFICIENTS (1/2)

Microscopic master equation

$$\frac{dP(\mathbf{n},t)}{dt} = \sum_{\tilde{\mathbf{n}}} \left[W(\tilde{\mathbf{n}},\mathbf{n})\, P(\tilde{\mathbf{n}},t) - W(\mathbf{n},\tilde{\mathbf{n}})\, P(\mathbf{n},t) \right]$$

Out-of-equilibrium probability distribution $P(\mathbf{n},t) = P_0(\mathbf{n})\ \delta P(\mathbf{n},t)$

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Continuity equation per crystallographic site

$$\frac{d[\alpha]_i}{dt} = -\oiint_S \vec{J}_i^{\alpha}.d\vec{S} \qquad [\alpha]_i = \langle n_i^{\alpha} \rangle^{\mathrm{oe}} = \sum_{\mathbf{n}} n_i^{\alpha} P(\mathbf{n},t)$$

SELF-CONSISTENT MEAN FIELD FORMULATION OF TRANSPORT COEFFICIENTS (1/2)

Microscopic master equation

$$\frac{dP(\mathbf{n},t)}{dt} = \sum_{\tilde{\mathbf{n}}} \left[W(\tilde{\mathbf{n}},\mathbf{n})\, P(\tilde{\mathbf{n}},t) - W(\mathbf{n},\tilde{\mathbf{n}})\, P(\mathbf{n},t) \right]$$

Out-of-equilibrium probability distribution $P(\mathbf{n},t) = P_0(\mathbf{n})\ \delta P(\mathbf{n},t)$

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Assumption : microscopic detailed balance

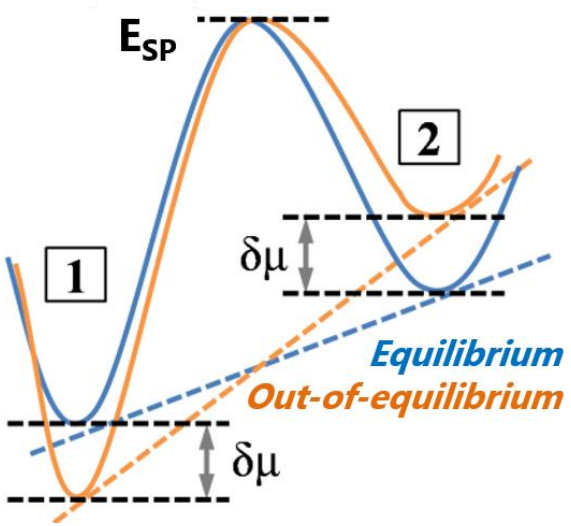
$$\frac{d\langle n_j^{\beta} \rangle^{\mathrm{oe}}}{dt} = \left\langle \sum_{\tilde{\mathbf{n}}} n_j^{\beta} W(\mathbf{n},\tilde{\mathbf{n}}) \left[\delta P(\tilde{\mathbf{n}}) - \delta P(\mathbf{n}) \right] \right\rangle$$

SELF-CONSISTENT MEAN FIELD FORMULATION OF TRANSPORT COEFFICIENTS (2/2)

Deviation from equilibrium probability distribution

$$\delta P(\mathbf{n}, t) = \exp\left(\delta\Omega + \sum_{i,\alpha} n_i^\alpha \frac{\delta\mu_i^\alpha}{k_B T} - \sum_{\sigma} n_\sigma \frac{\nu_\sigma}{k_B T} \right)$$

Assumption : small deviations from equilibrium



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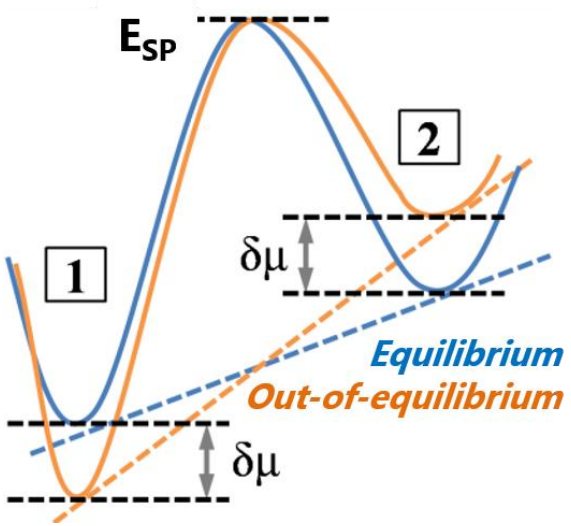

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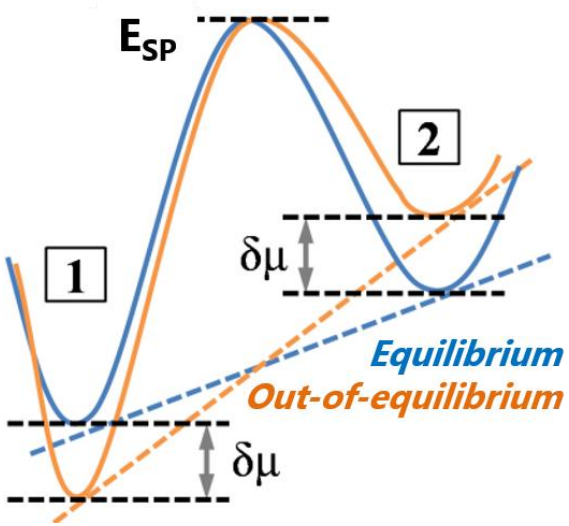
Imposing all moments of the probability distribution to be stationary, we find the values of effective interactions

$$\frac{d}{dt}\left\langle n_{i_1}^{\alpha_1} n_{i_2}^{\alpha_2} .. n_{i_n}^{\alpha_n} \right\rangle^{oe} = 0$$



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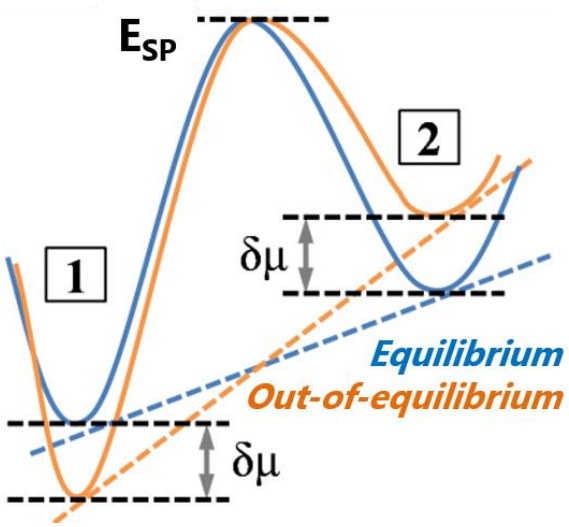


- Can we use these effective interactions to compute out-of-equilibrium phase diagrams ?
- Can we go beyond small deviations from equilibrium ?
- Boundary conditions for subcluster moments ?

EXAMPLE CALCULATION : CONCENTRATION EFFECTS IN Fe-C ALLOYS

Flux coupling between vacancy and carbon:

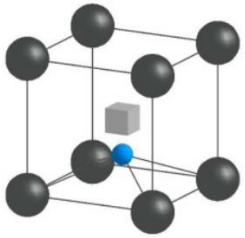
$$\vec{\nabla}\mu_V \Leftarrow$$

$$\vec{J}_V = -L_{VV}\vec{\nabla}\mu_V \Rightarrow$$

$$\vec{J}_C = \frac{L_{CV}}{L_{VV}}\vec{J}_V \Leftarrow ? \Rightarrow$$

VACANCY SINK

1. Classical « dilute » approximation : at most one vacancy interacting with one carbon atom => negative flux coupling



Schuler Phys. Rev. B 93 224101 (2016)

$$\frac{L_{CV}}{L_{VV}} = \frac{[VC]\,L_{CV}\,(VC)}{[V]\,L_{VV}\,(V) + [VC]\,L_{VV}\,(VC)}$$

DFT data from *Barouh Phys. Rev. B **92** 104102 (2015)*

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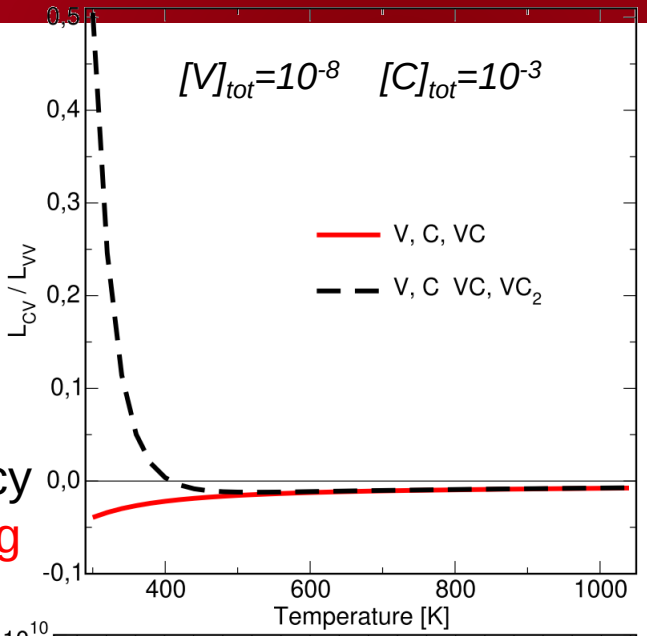

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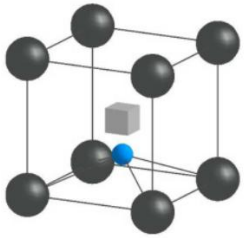
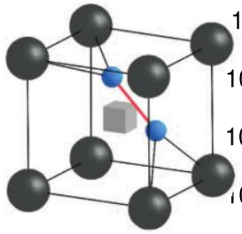
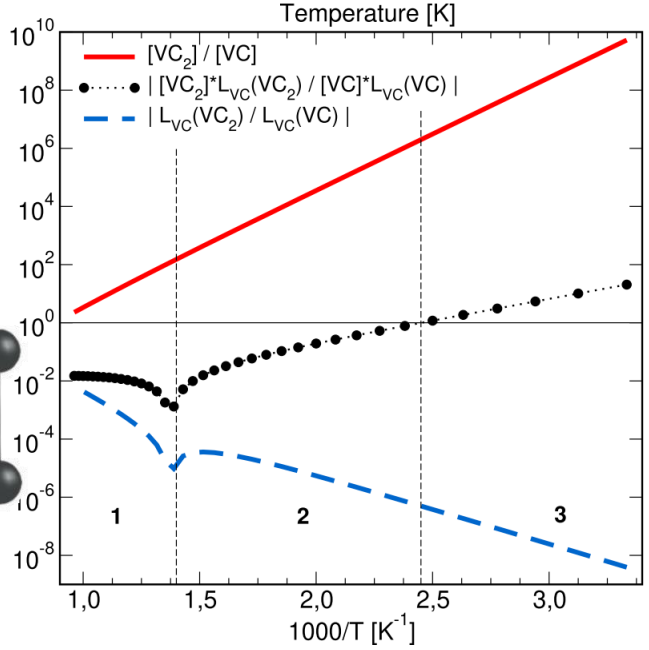


$$\frac{L_{CV}}{L_{VV}} = \frac{[VC]\,L_{CV}\,(VC)}{[V]\,L_{VV}\,(V) + [VC]\,L_{VV}\,(VC)}$$

2. First order concentration effect : allowing a second C atom around V => qualitatively different result !

$$\frac{L_{CV}}{L_{VV}} = \frac{[VC]\,L_{CV}\,(VC) + [VC_2]\,L_{CV}\,(VC_2)}{[V]\,L_{VV}\,(V) + [VC]\,L_{VV}\,(VC) + [VC_2]\,L_{VV}\,(VC_2)}$$





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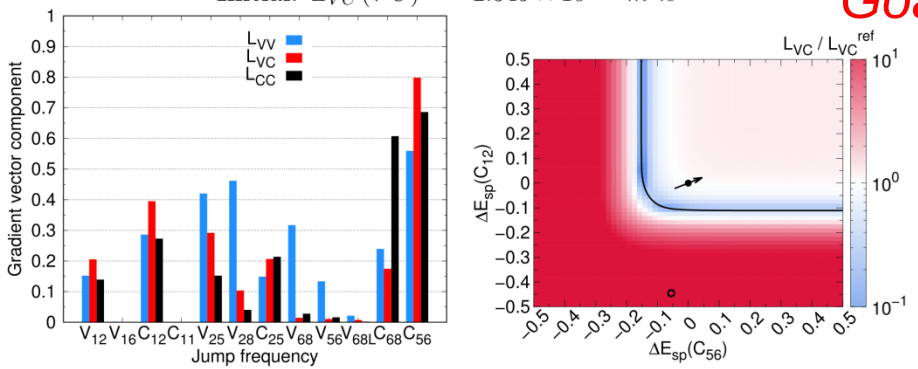
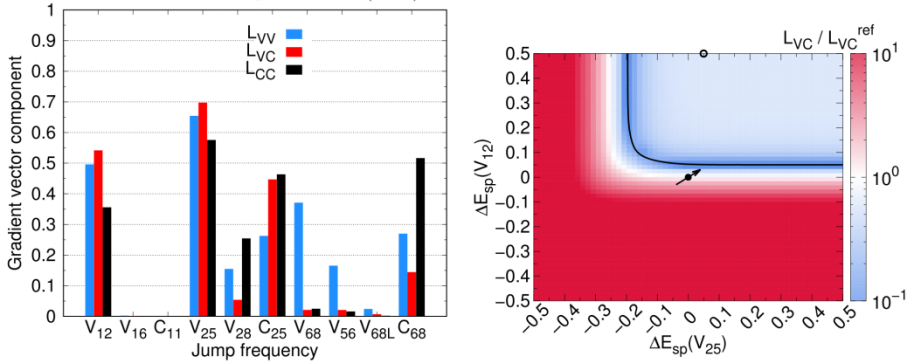
EXAMPLE CALCULATION: JUMP FREQUENCY SENSITIVITY STUDY

Goal: identification of key input parameters

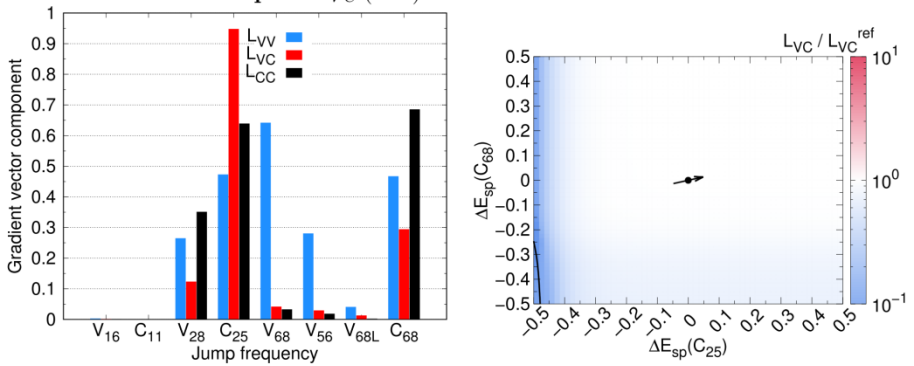
Initial: $L_{VC}(VC) = -2.345 \times 10^{-15}\ m^2.s^{-1}$



Step 1: $L_{VC}(VC) = +3.750 \times 10^{-14}\ m^2.s^{-1}$



Step 2: $L_{VC}(VC) = -2.263 \times 10^{-14}\ m^2.s^{-1}$



Final: $L_{VC}(VC) = -2.388 \times 10^{-14}\ m^2.s^{-1}$

We compute the gradient of cluster transport coefficients in jump frequency space :

$$\nabla \mathbf{L}_d = \left(\frac{\partial \mathbf{L}_d}{\partial \omega_i}\bigg|_{\mathbf{W}_0} \right)$$

We have analytic expressions for this gradient => does not cost much computation time

$$\mathbf{L}_d = \mathbf{\Lambda}_d^0 - \mathbf{\Lambda}_d \tilde{\mathbf{T}}^{-1} \mathbf{\Lambda}_\mu^t$$

$$\frac{\partial \mathbf{L}_d}{\partial \omega_i} = \frac{\partial \mathbf{\Lambda}_d^0}{\partial \omega_i} + \mathbf{\Lambda}_d \tilde{\mathbf{T}}^{-1} \frac{\partial \tilde{\mathbf{T}}}{\partial \omega_i} \tilde{\mathbf{T}}^{-1} \mathbf{\Lambda}_\mu - \frac{\partial \mathbf{\Lambda}_d}{\partial \omega_i} \tilde{\mathbf{T}}^{-1} \mathbf{\Lambda}_\mu - \mathbf{\Lambda}_d \tilde{\mathbf{T}}^{-1} \frac{\partial \mathbf{\Lambda}_\mu}{\partial \omega_i}.$$

Iterative process because the analysis is only local

CHANGING THE REFERENCE STATE OF A SYSTEM WITH BALLISTIC RELOCATIONS

Ballistic relocations introduce **new jump mechanisms** at frequencies that are not thermally activated and hence do not obey detailed balance.

Three things we need to do beforehand :

- Add ballistic relocation mechanisms
- Find the **steady state** (global detailed balance)

$$\frac{dP_i}{dt} = 0 = \sum_j \tilde{P}_j \left(\omega_{ji}^{th} + \Gamma_{ij}^{bal}\right) - \tilde{P}_i \left(\omega_{ij}^{th} + \Gamma_{ij}^{bal}\right)$$

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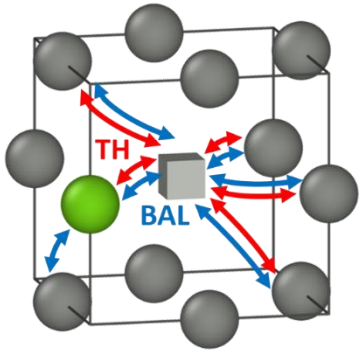

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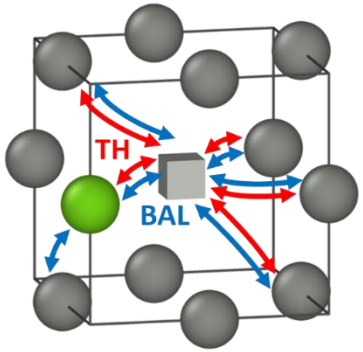

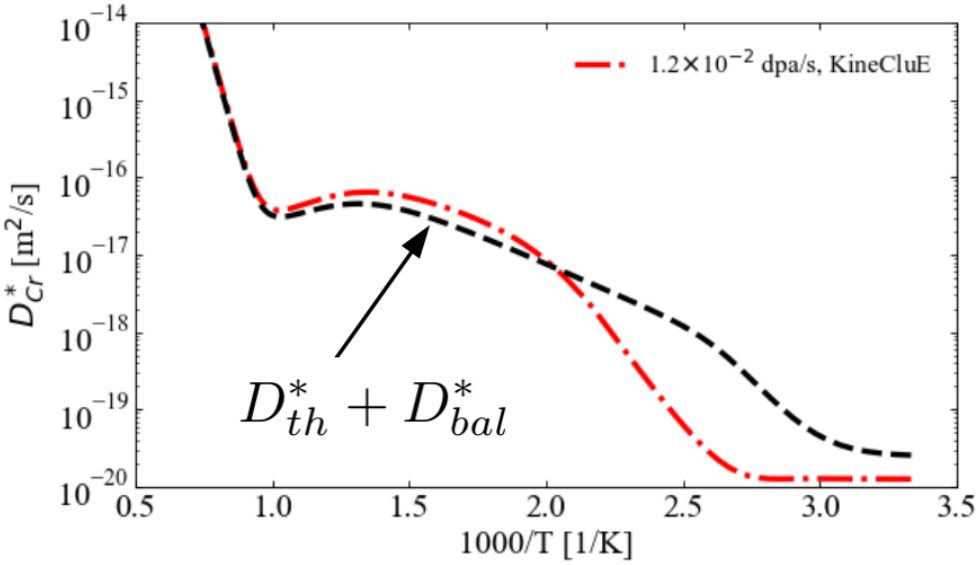

Example: Cr tracer diffusion coefficient in FCC Ni.
Because of correlations between thermal and ballistic jumps,

$$D^* \neq D^*_{th} + D^*_{bal}$$

Huang Phys. Rev. B *submitted (2018)*

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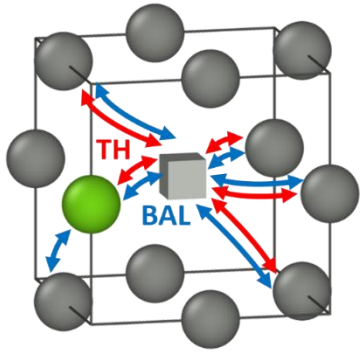
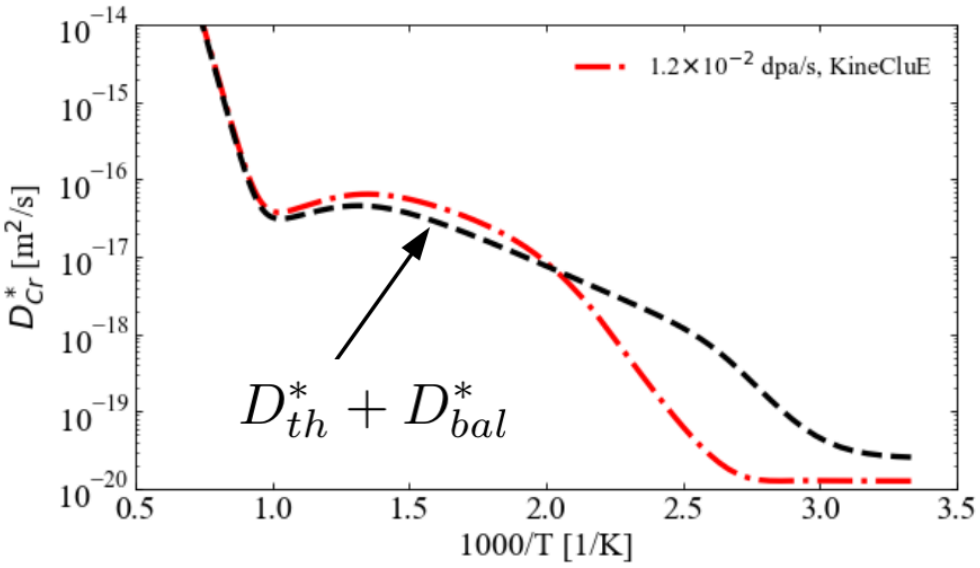


Is this a good way to approach systems far from equilibrium ?



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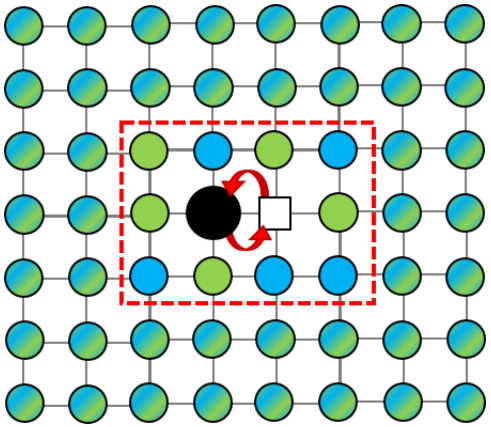
   - Parallelization
   - Thermodynamic sampling
2. Concentrated alloys
   - Matrix effect on jump frequencies and kinetic correlations
   - Embedding the cluster in some effective matrix (mean-field)
   - Boundary condition ?



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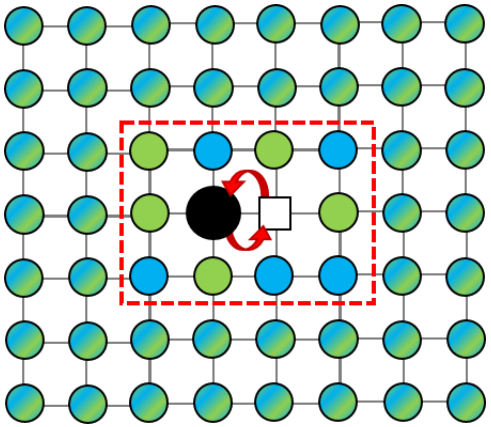
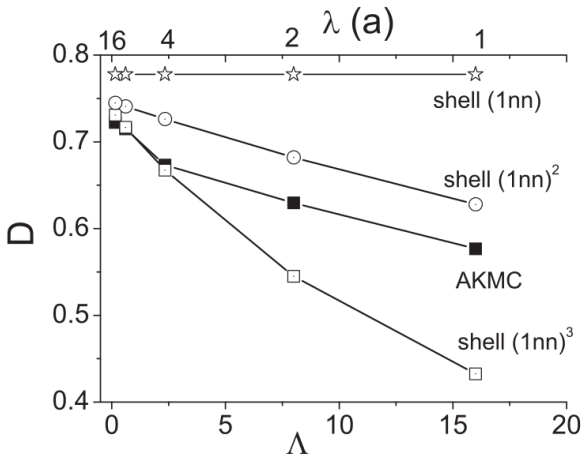
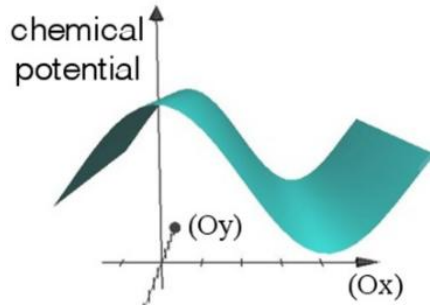
3. Inhomogeneous driving forces
   - Beyond the thermodynamic formulation of Onsager
   - Importance of the different diffusion time scales between point defects and solutes







*astar Phys. Rev. B **90** 144101 (2014)*

Thank you for your attention
Any questions ?

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