First-principles prediction of diffusion coefficients in non-dilute, multi-component solids

Anton Van der Ven
Department of Materials Science and Engineering
University of Michigan
Ann Arbor, MI

Coarse graining time
Diffusion in a crystal

Two levels of time coarse graining

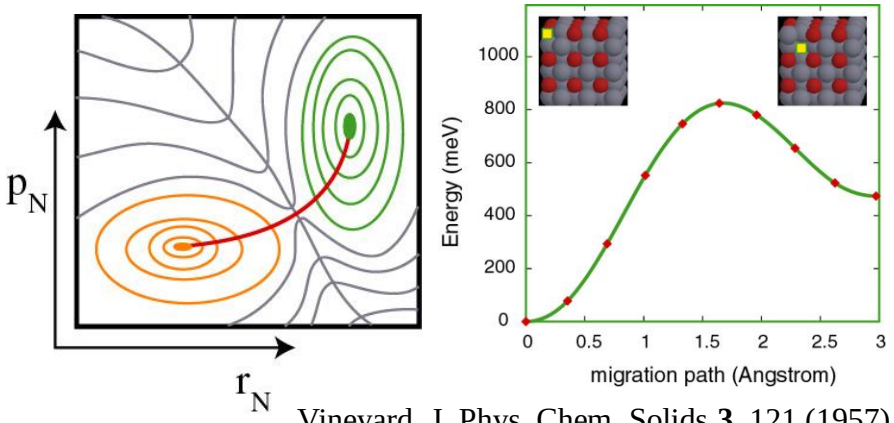
Coarse graining time
Diffusion in a crystal

Two levels of time coarse graining

Short-time coarse graining: transition state theory

$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$

- MD simulations
- Harmonic approximation



Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

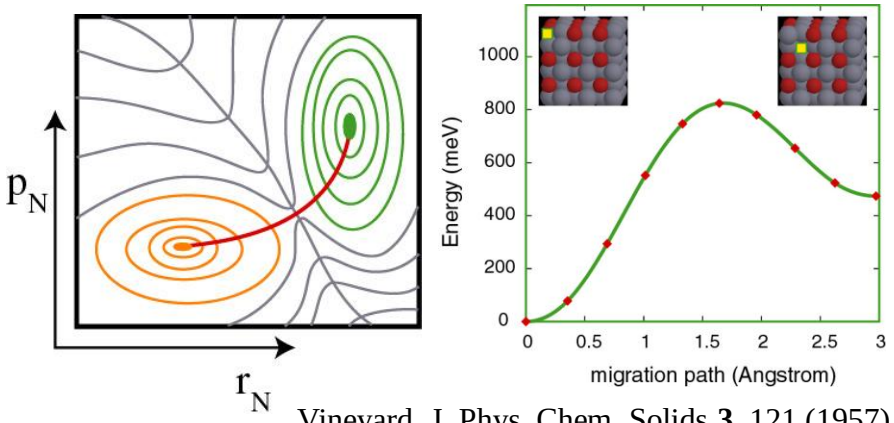
Coarse graining time
Diffusion in a crystal

Two levels of time coarse graining

Short-time coarse graining: transition state theory

$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$

- MD simulations
- Harmonic approximation



Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

A second level of coarse graining that leads to Fick's law

$$J = -D\nabla C$$

Green-Kubo

Kinetic coefficients derived from fluctuations **at equilibrium**

Zwanzig, Annu. Rev. Phys. Chem. **16**, 67 (1965).

Diffusion

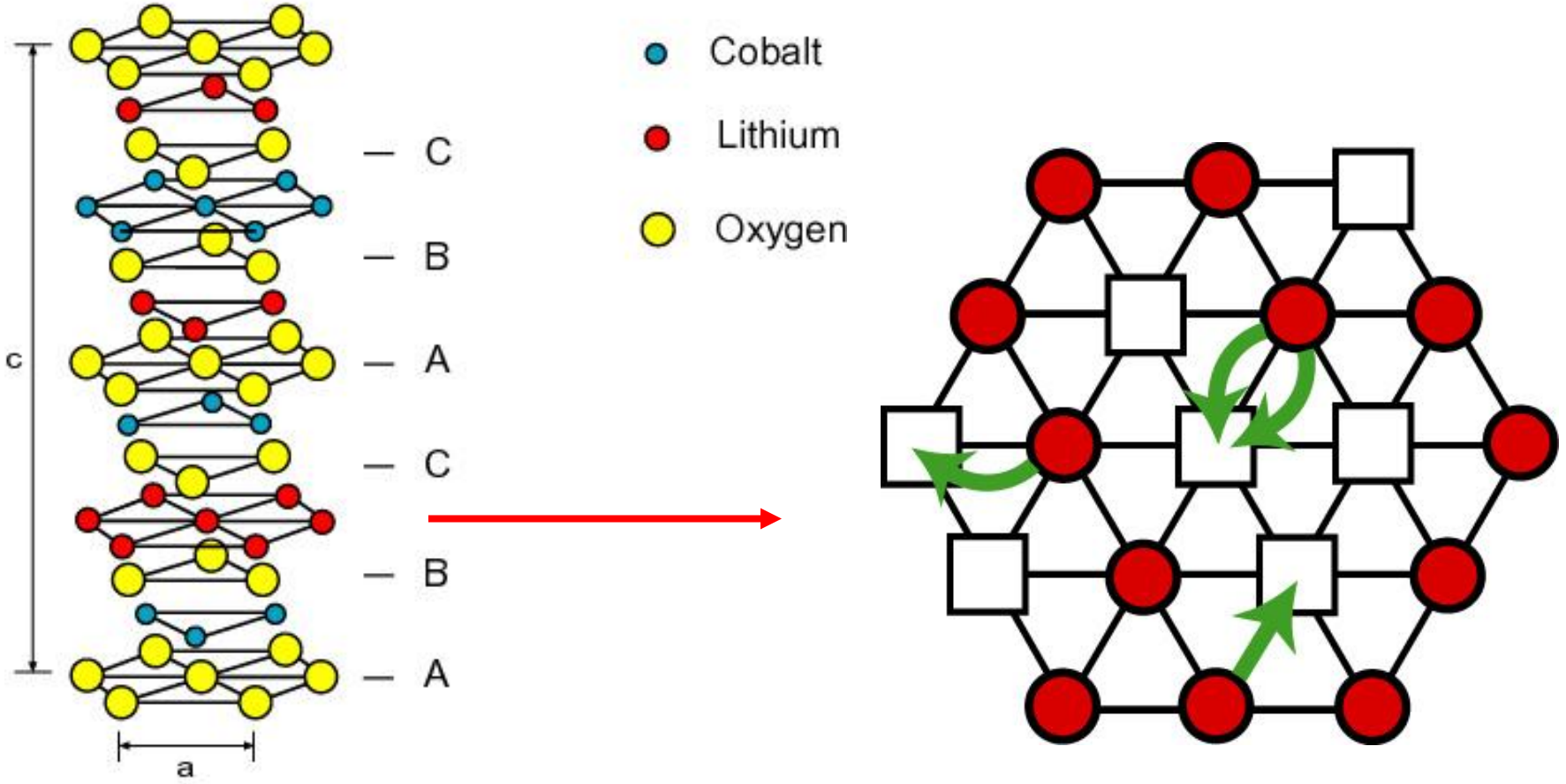
- Distinction between:
  - interstitial diffusion
  - substitutional diffusion

Interstitial diffusion

- C diffusion in bcc Iron (steel)
- Li diffusion in transition metal oxide host
- O diffusion on Pt-(111) surface

In all examples, diffusion occurs on a rigid lattice which is externally imposed by a host or substrate

Example of interstitial diffusion



Irreversible thermodynamics: interstitial diffusion of one component

$$J = -L\nabla\mu$$

$$D = L\frac{d\mu}{dC}$$

$$J = -D\nabla C$$

Notation

M = number of lattice sites

N = number of diffusing atoms

v_s = volume per lattice site

x = N/M

$C=x/v_s$

Interstitial diffusion: one component

Kubo-Green relations
(linear response statistical mechanics)

$$D = L \cdot \Theta$$

Thermodynamic factor

$$\Theta = \frac{\partial \mu}{\partial C}$$

Kinetic coefficient

$$L = \frac{1}{(2d)tMv_s kT} \left\langle \left(\sum_{i=1}^{N} \Delta \vec{R}_i(t) \right)^2 \right\rangle$$

R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

A. Van der Ven, G. Ceder, Handbook of Materials Modeling, chapt. 1.17, Ed. S. Yip, Springer (2005).

More familiar form

$$J = -D\nabla C$$

$$D = D_J \cdot \tilde{\Theta}$$

Thermodynamic factor

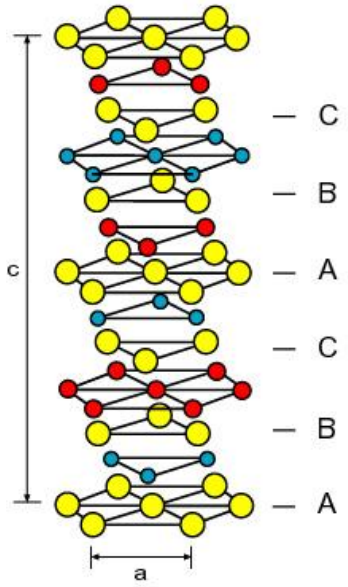
$$\tilde{\Theta} = \frac{\partial\left(\frac{\mu}{kT}\right)}{\partial \ln x}$$

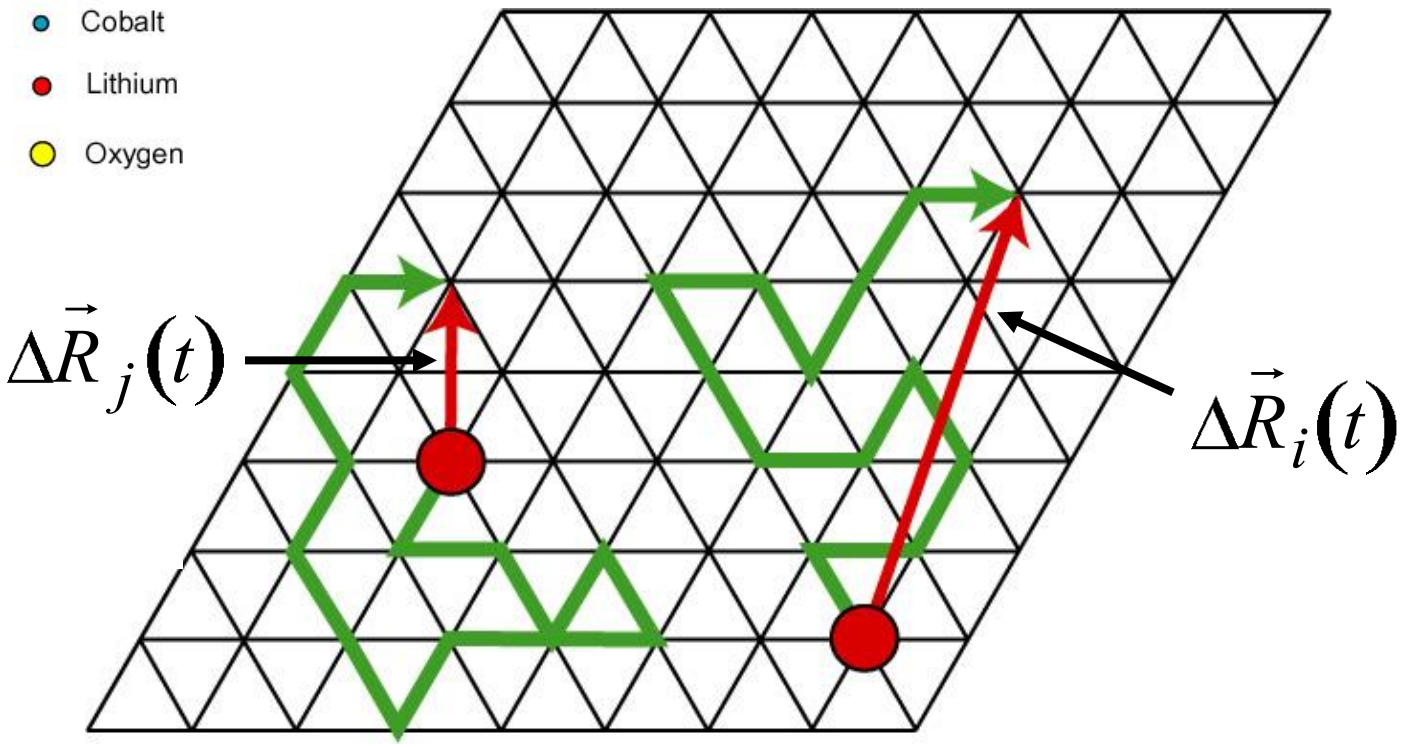
Self diffusion coefficient

$$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N}\Delta\vec{R}_i(t)\right)^2 \right\rangle$$

R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

Trajectories can be sampled with kinetic Monte Carlo simulations





$$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N}\Delta\vec{R}_i(t)\right)^2\right\rangle$$

Common approximation

$$D = D^* \cdot \tilde{\Theta}$$

Thermodynamic factor

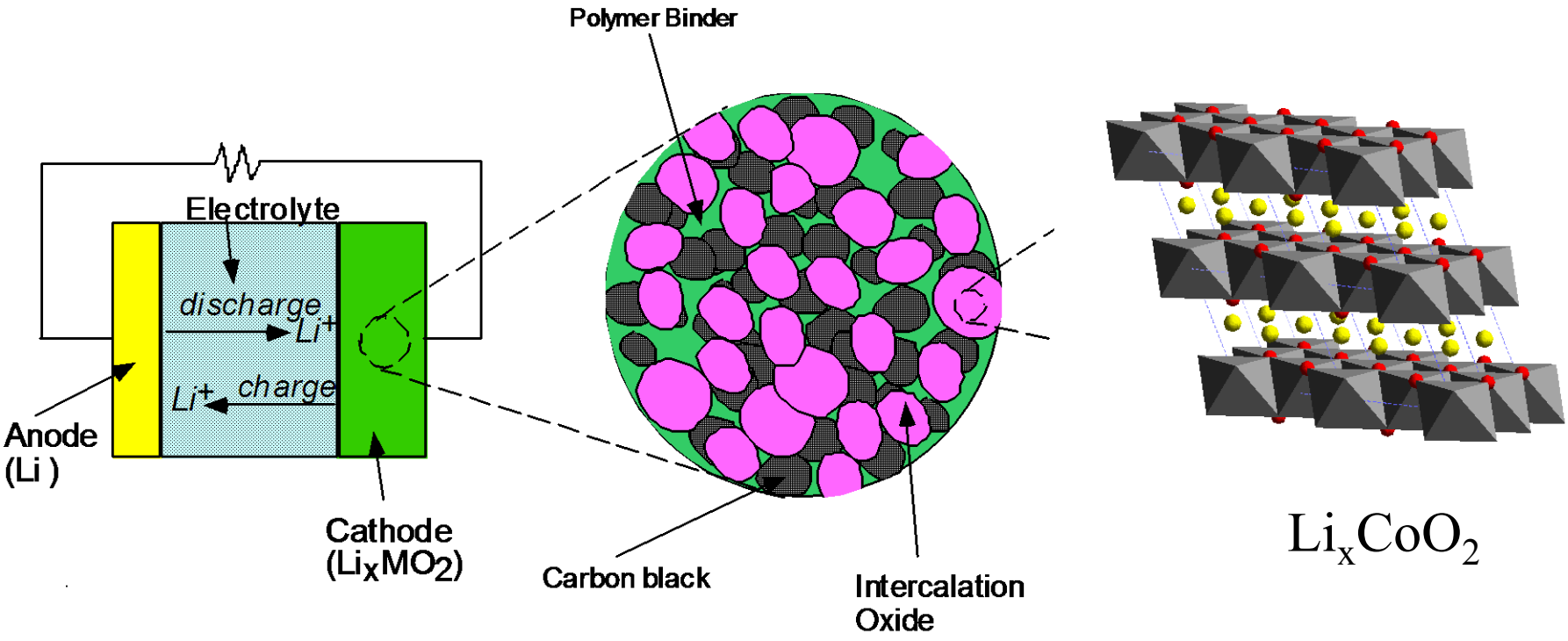
$$\tilde{\Theta} = \frac{\partial\left(\frac{\mu}{kT}\right)}{\partial \ln x}$$

Tracer diffusion coefficient

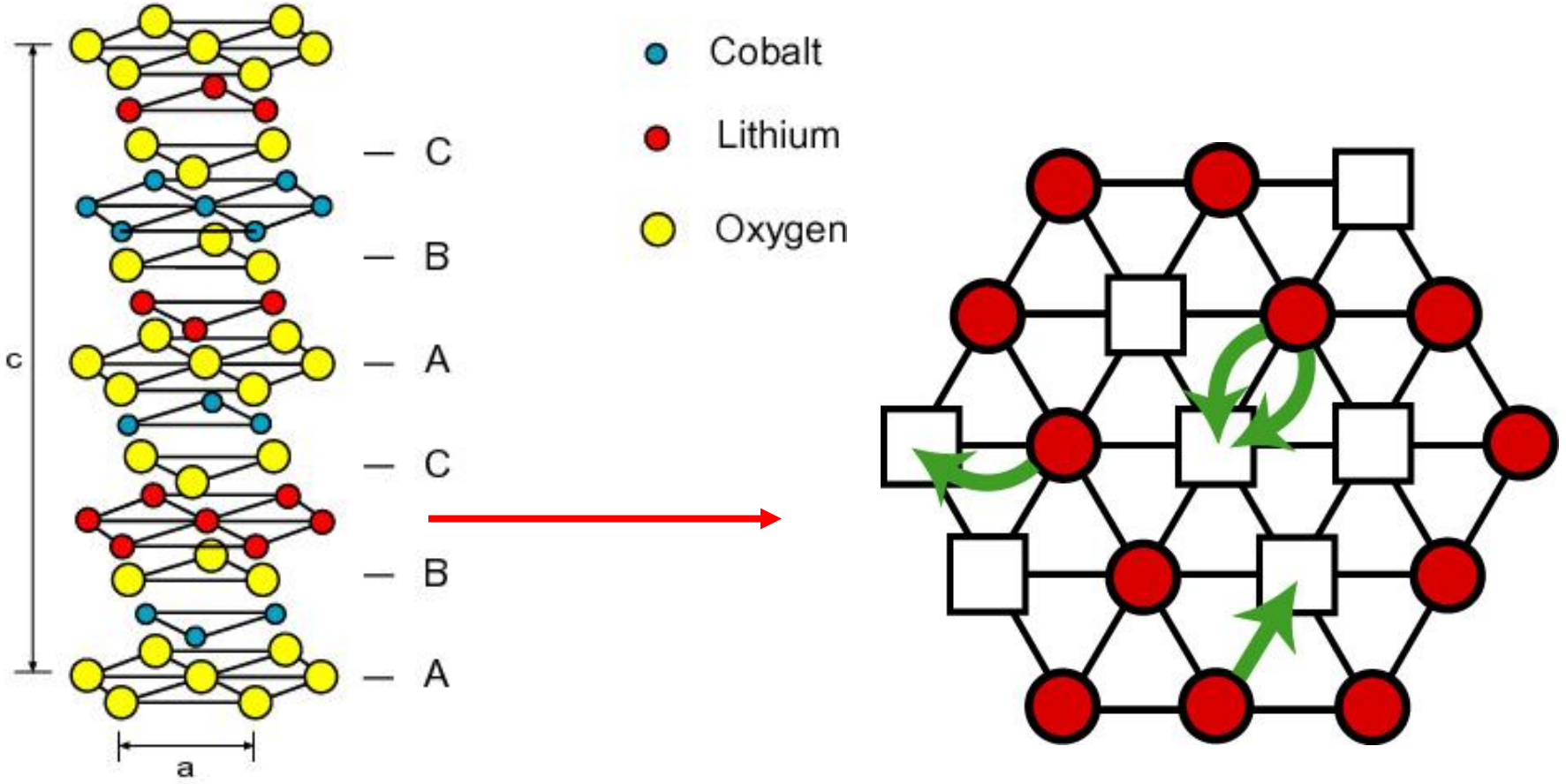
$$D^* = \frac{\left\langle \left(\Delta R_i(t)\right)^2 \right\rangle}{(2d)t}$$

R. Gomer, Rep. Prog. Phys. **53**, 917 (1990)/

Intercalation Oxide as Cathode in Rechargeable Lithium Battery



Example: Li_xCoO_2



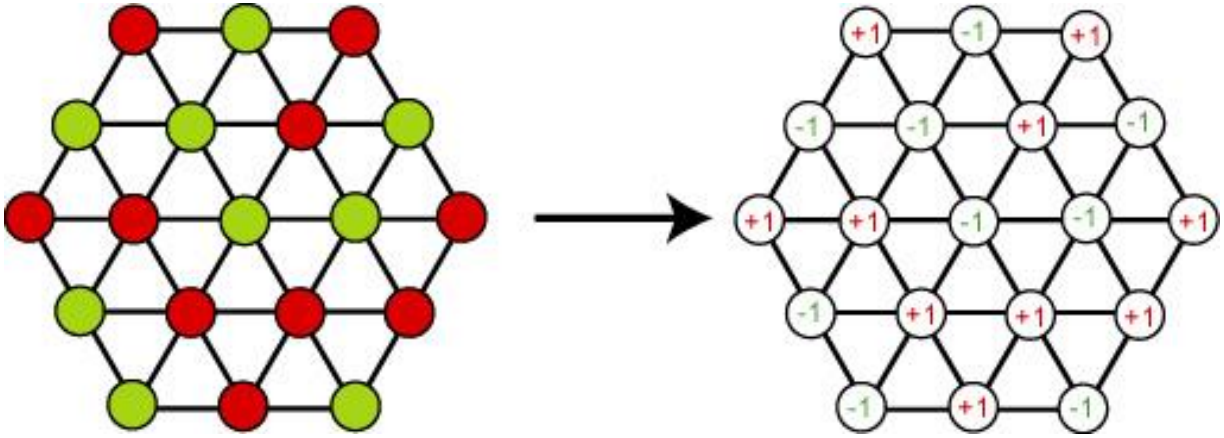
Configurational Variables

Binary system alloy (A, B atoms)

Assign occupation variables to each position in crystal

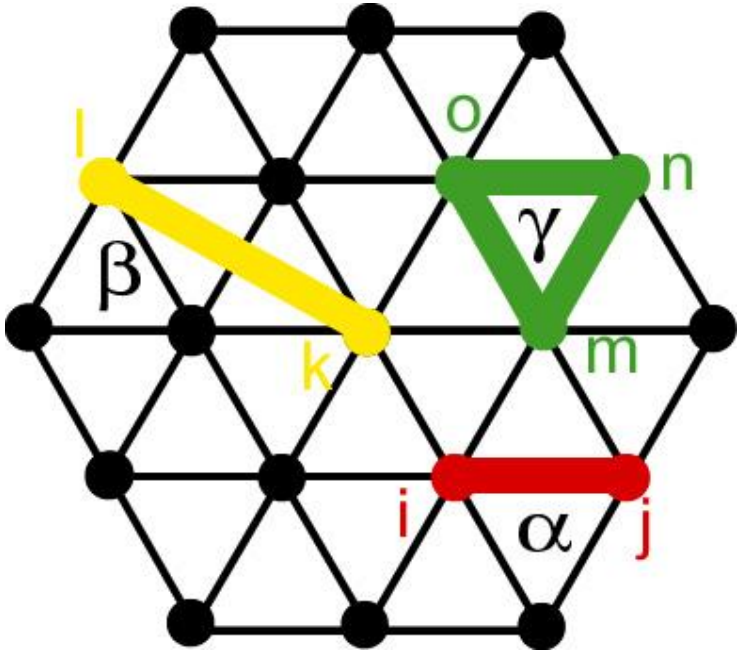
$\sigma_i = +1$ if atom **A** occupies site i

$\sigma_i = -1$ if atom **B** occupies site i



Total of 2^N configurations

Polynomials of occupation variables form a basis in configuration space



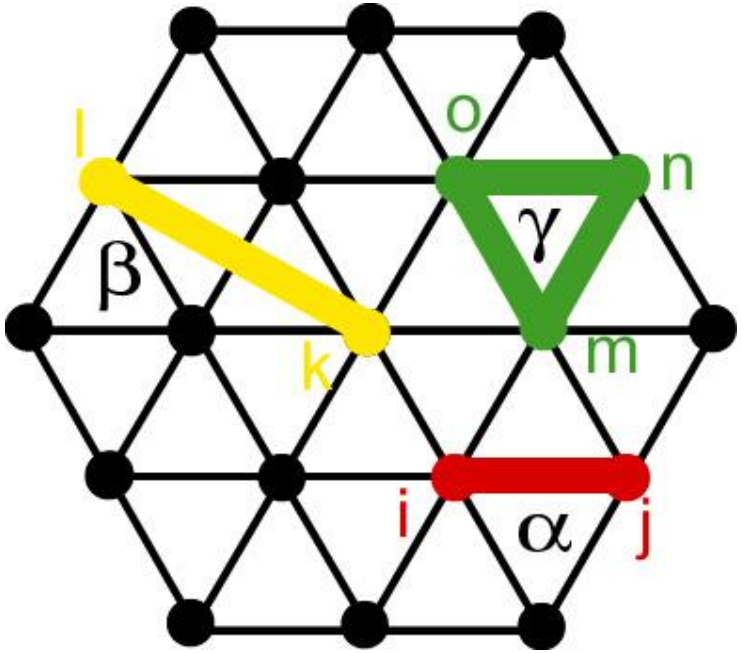
$$\Phi_\alpha = \sigma_i \sigma_j$$

$$\Phi_\beta = \sigma_l \sigma_k$$

$$\Phi_\gamma = \sigma_m \sigma_n \sigma_o$$

J. M. Sanchez et al Physica A128, 334, 1984

Polynomials of occupation variables form a basis in configuration space



$$\Phi_\alpha = \sigma_i \sigma_j$$

$$\Phi_\beta = \sigma_l \sigma_k$$

$$\Phi_\gamma = \sigma_m \sigma_n \sigma_o$$

$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

J. M. Sanchez et al Physica A128, 334, 1984

First-principles energies of
a "few" excitations

$$H = \sum_{i=1}^{N_e} -\nabla_i^2 + V_{nuc}(r_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|r_i - r_j|} + E_{nuc}(R)$$

Lattice Model Hamiltonian

$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

Extrapolate to
all other excitations

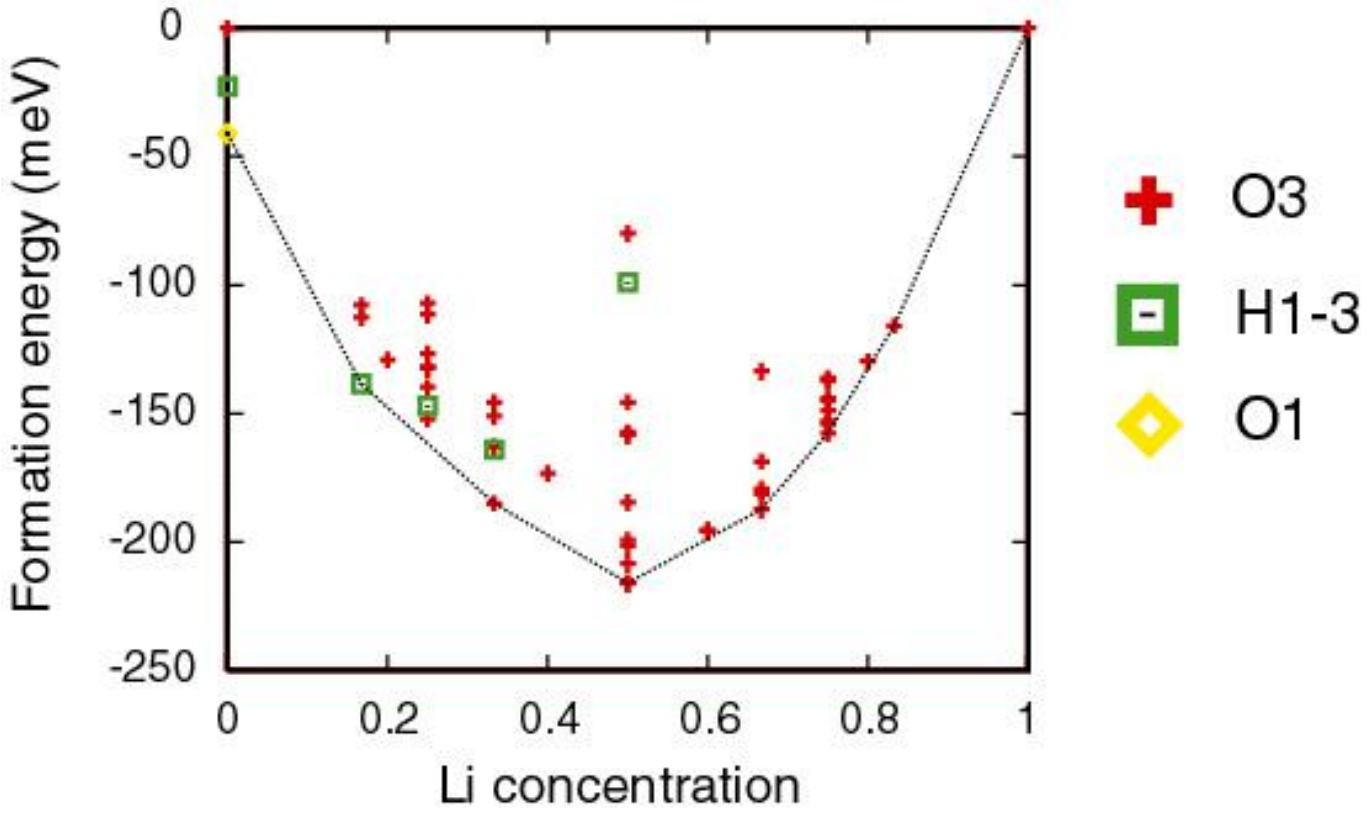
Monte Carlo

$$Z = \sum_{\vec{\sigma}} \exp\left(-\frac{E(\vec{\sigma})}{k_B T}\right)$$

$$F = -k_B T \ln(Z)$$

Thermodynamics

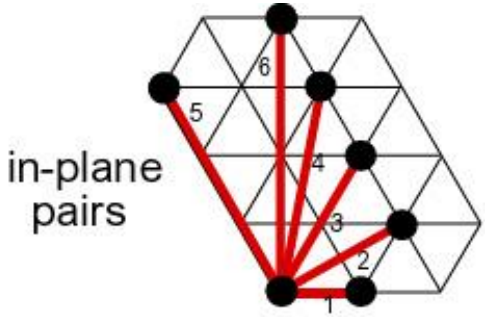
First principles energies (LDA) of different lithium-vacancy configurations

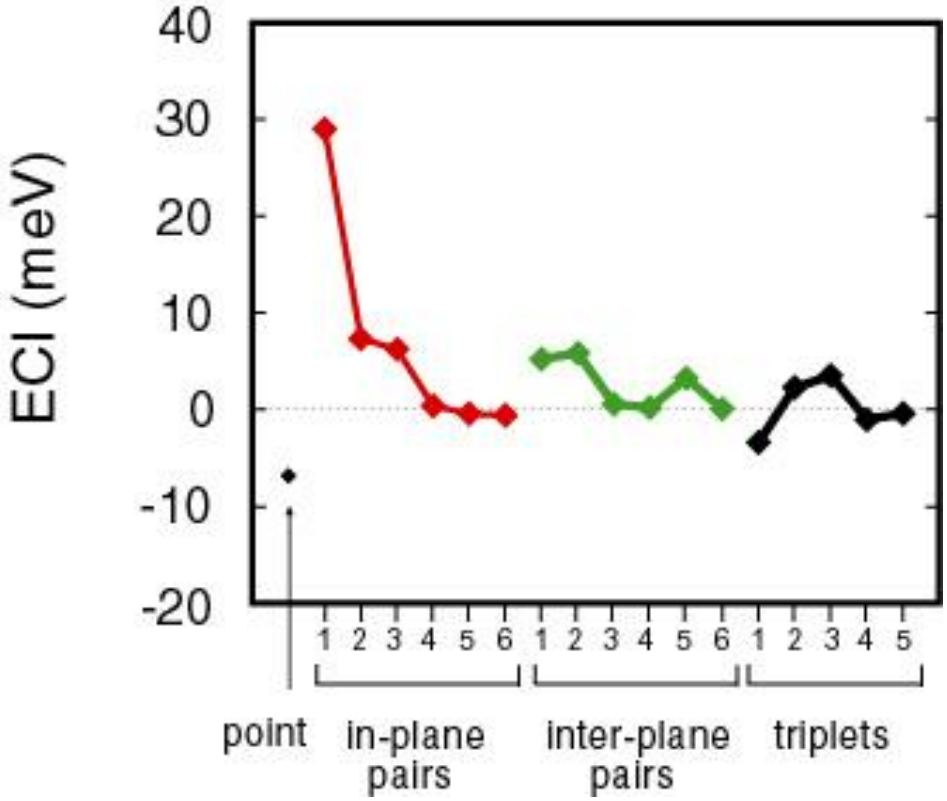


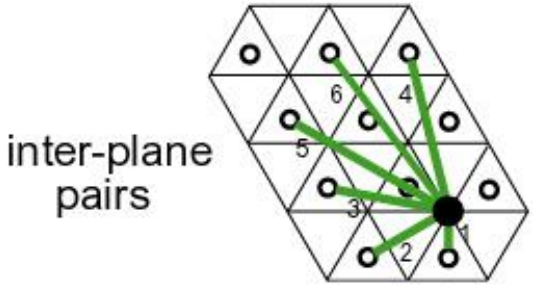
A. Van der Ven, et al, Phys. Rev. B 58 (6), p. 2975-87 (1998).

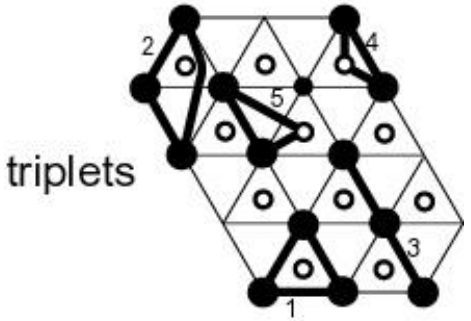
Cluster expansion for Li_xCoO_2

$$E\ \sigma = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$



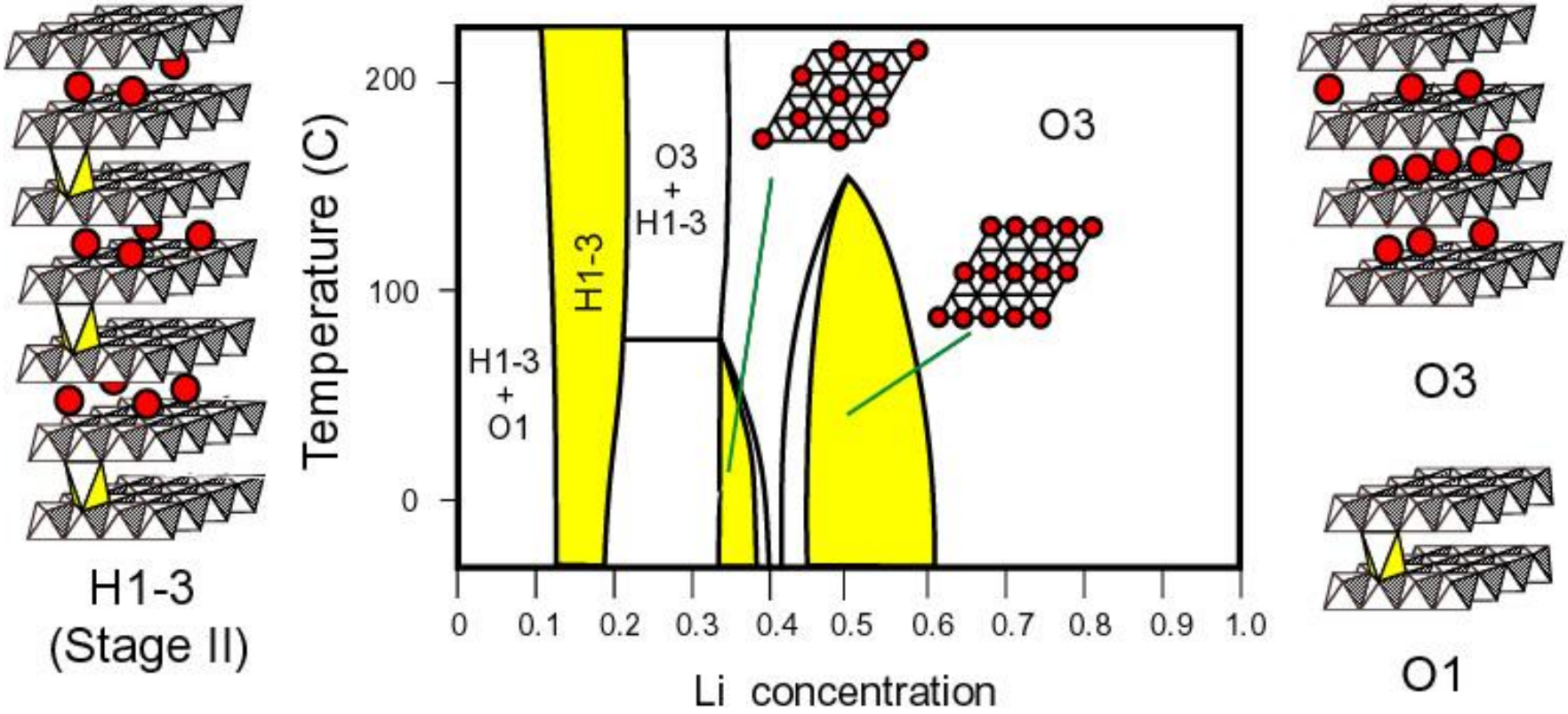






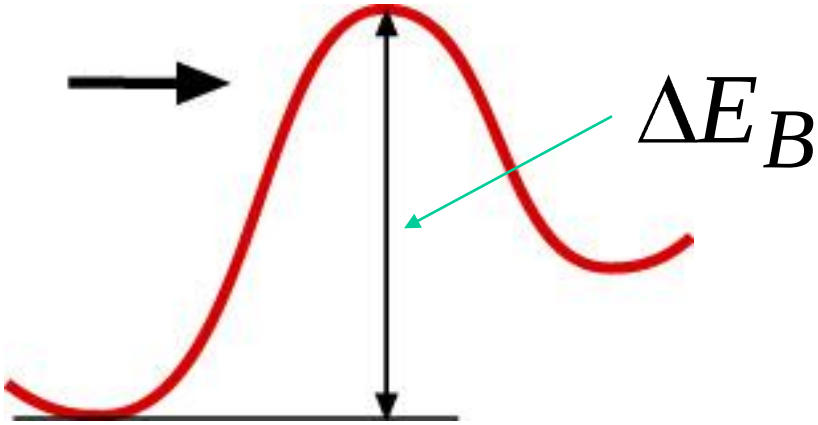
A. Van der Ven, et al, Phys. Rev. B 58 (6), p. 2975-87 (1998).

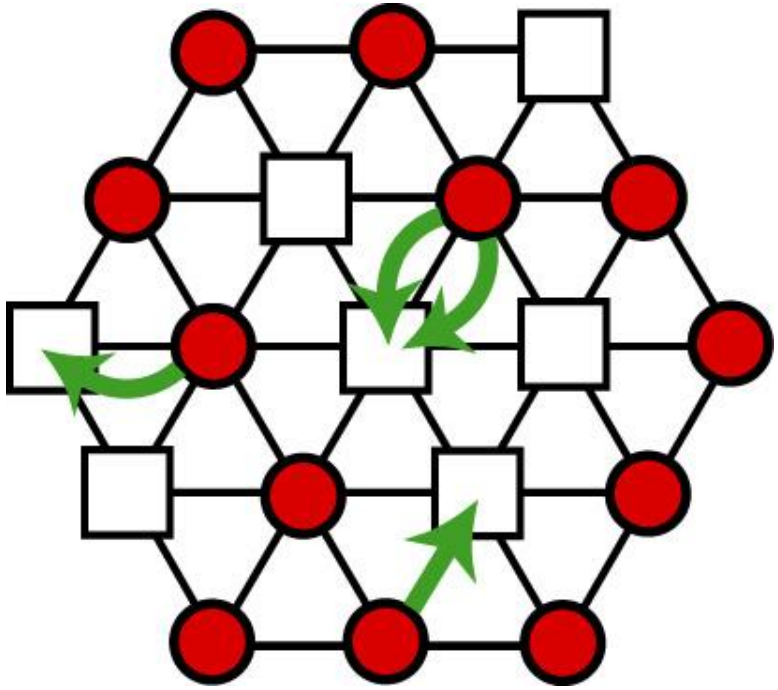
Calculated Li_xCoO_2 phase diagram



A. Van der Ven, et al, Phys. Rev. B 58 (6), p. 2975-87 (1998).

Individual hops: Transition state theory

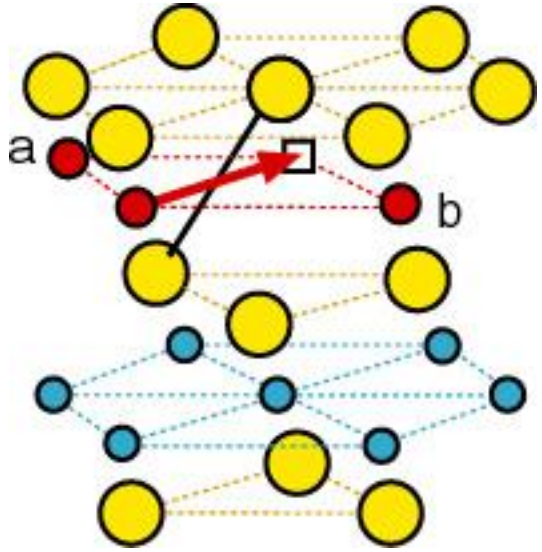




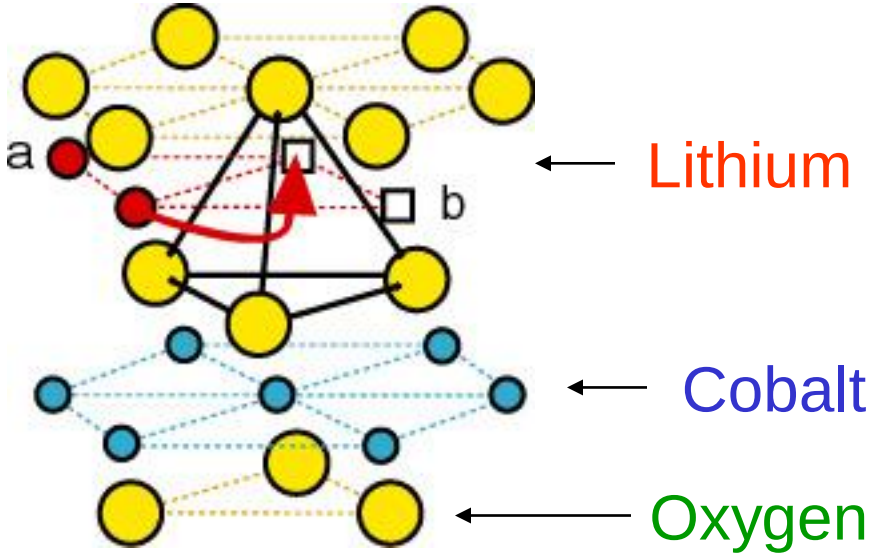
$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$

Can be calculated with
First-principles
Density functional theory

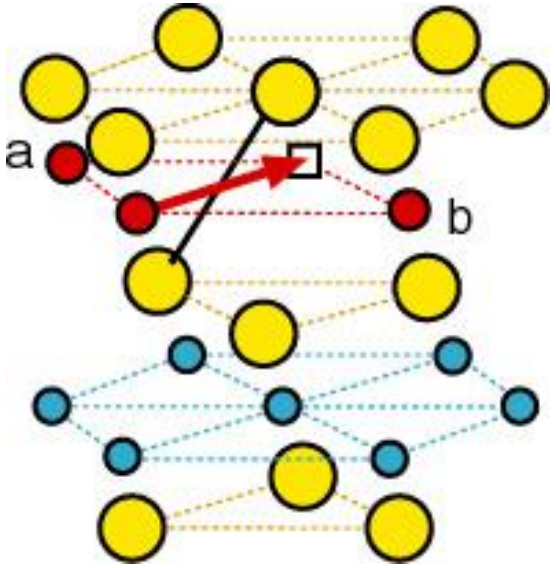
Migration mechanism in Li_xCoO_2

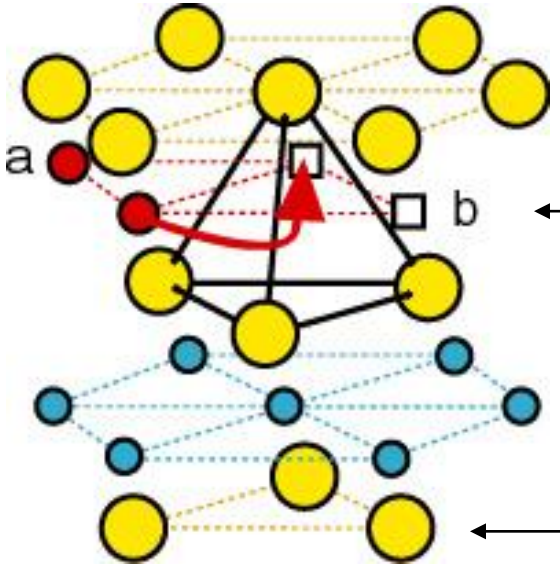


Single vacancy hop mechanism



Divacancy hop Mechanism





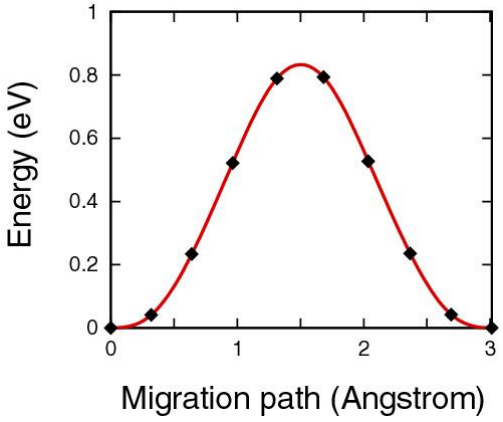
Lithium

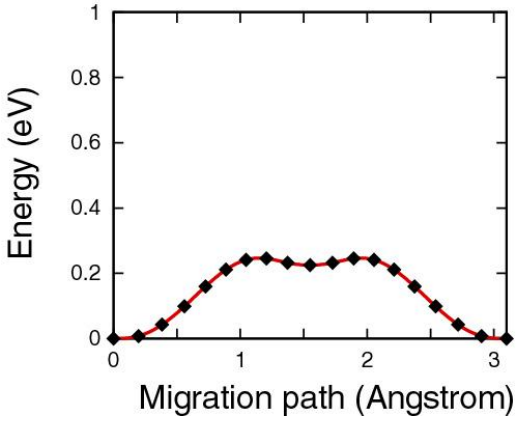
Cobalt

Oxygen

Single vacancy hop

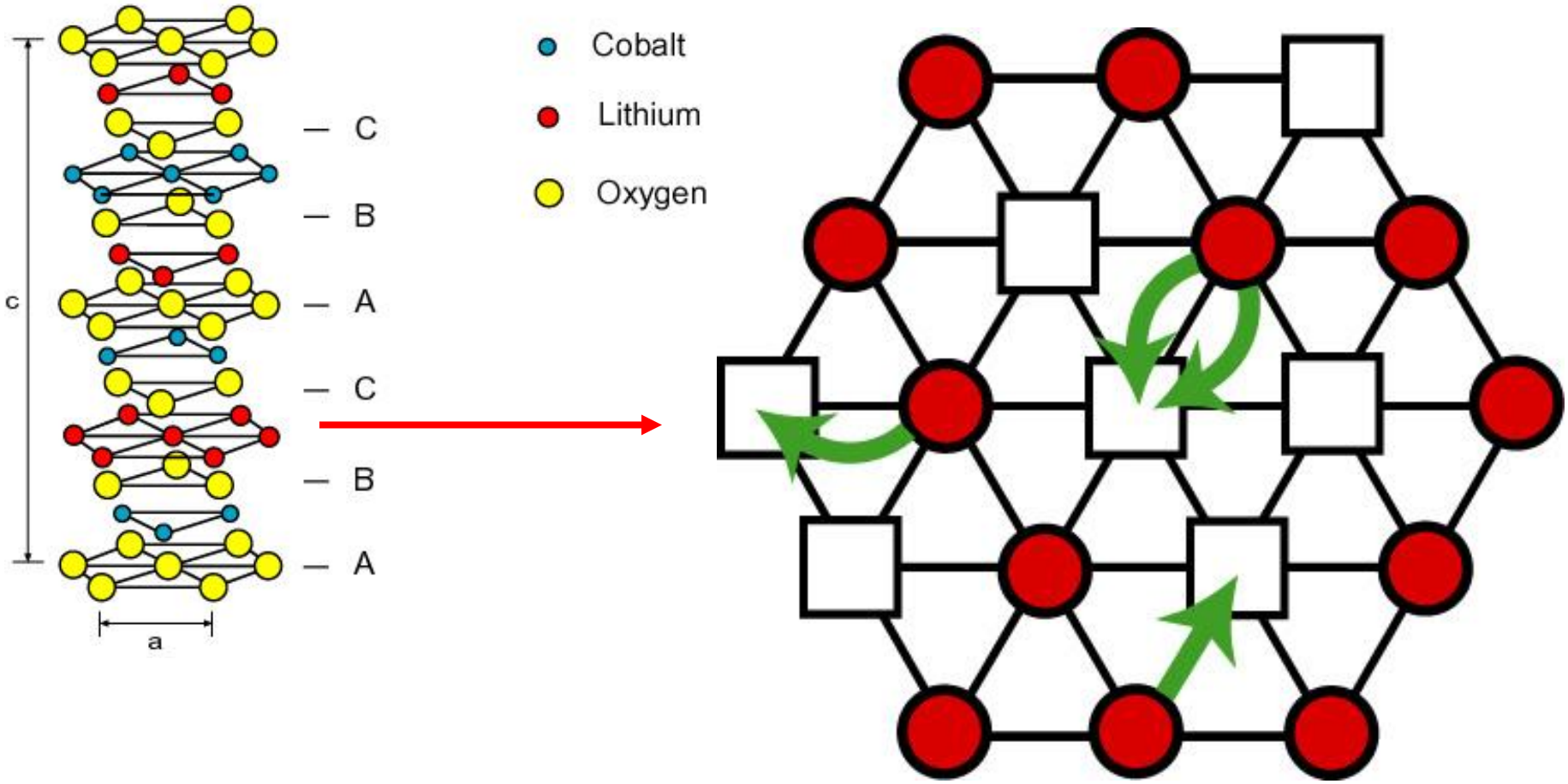
Divacancy hop



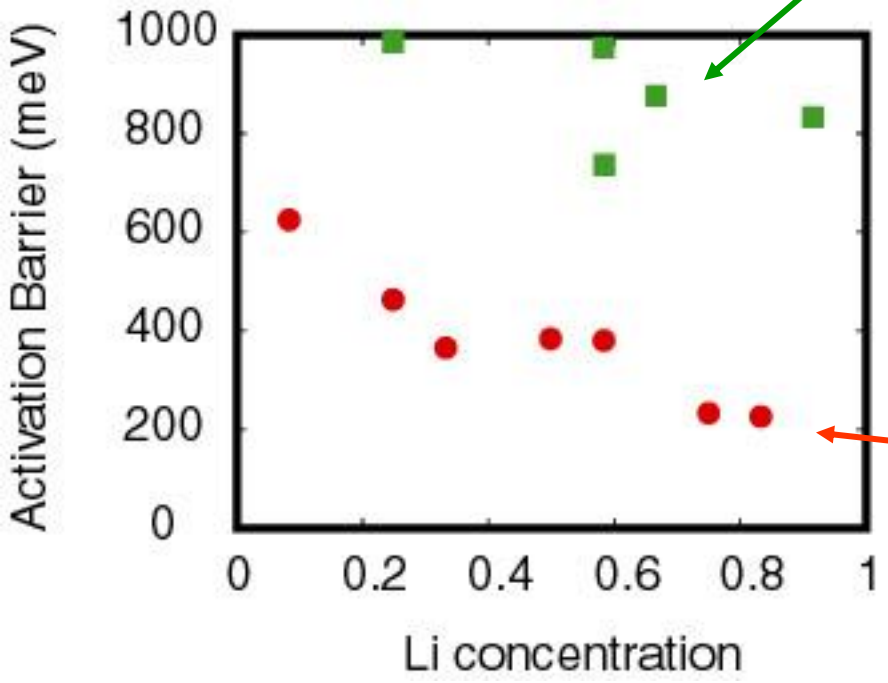


A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

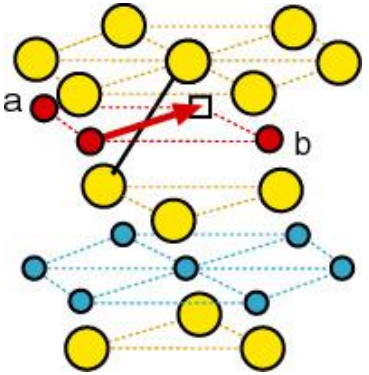
Many types of hop possibilities in the lithium plane



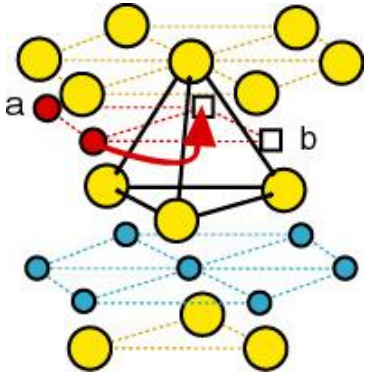
Migration barriers depend configuration and concentration



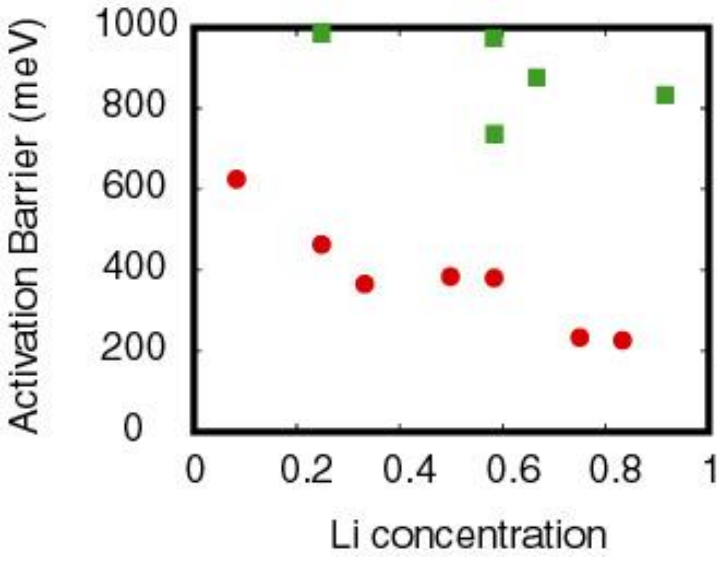
Single-vacancy mechanism

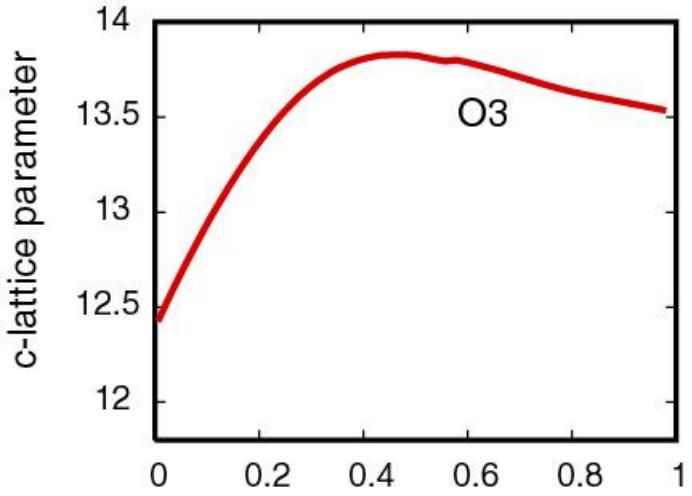


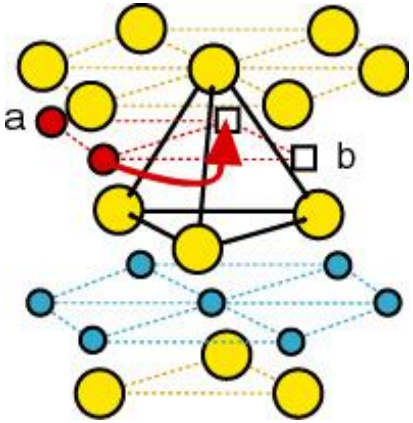
Divacancy mechanism



Barrier dependence on concentration







$Co^{3+} \longrightarrow Co^{4+}$

as lithium is removed:

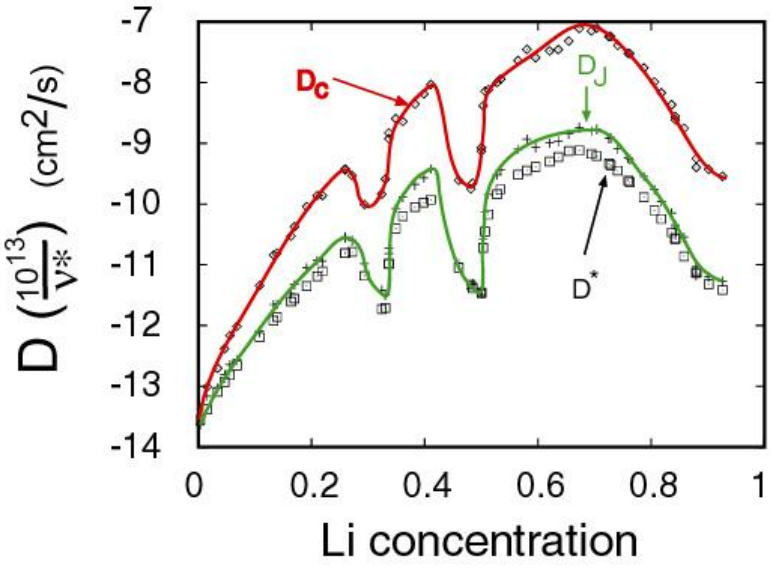
increased electrostatic repulsion for

Li^{+} in the activated state

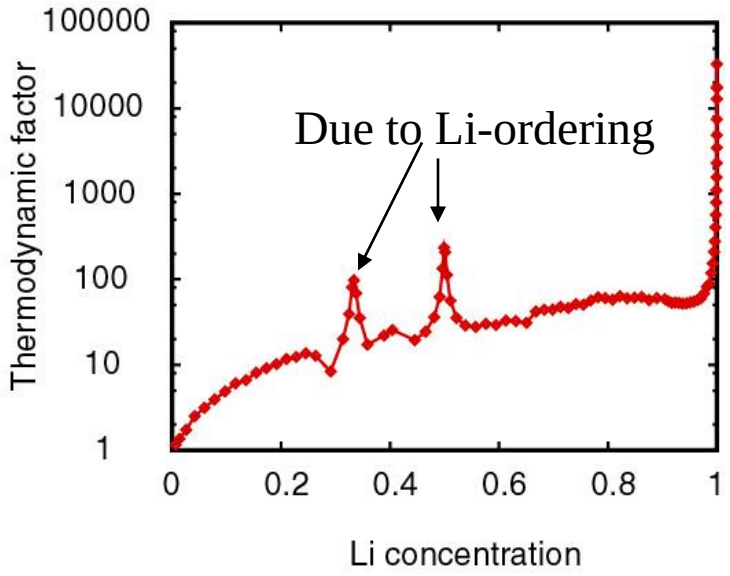
Calculated diffusion coefficient
(First Principles cluster expansion + kinetic Monte Carlo)

$$D = \Theta \cdot D_J$$

Diffusion coefficient at 300 K

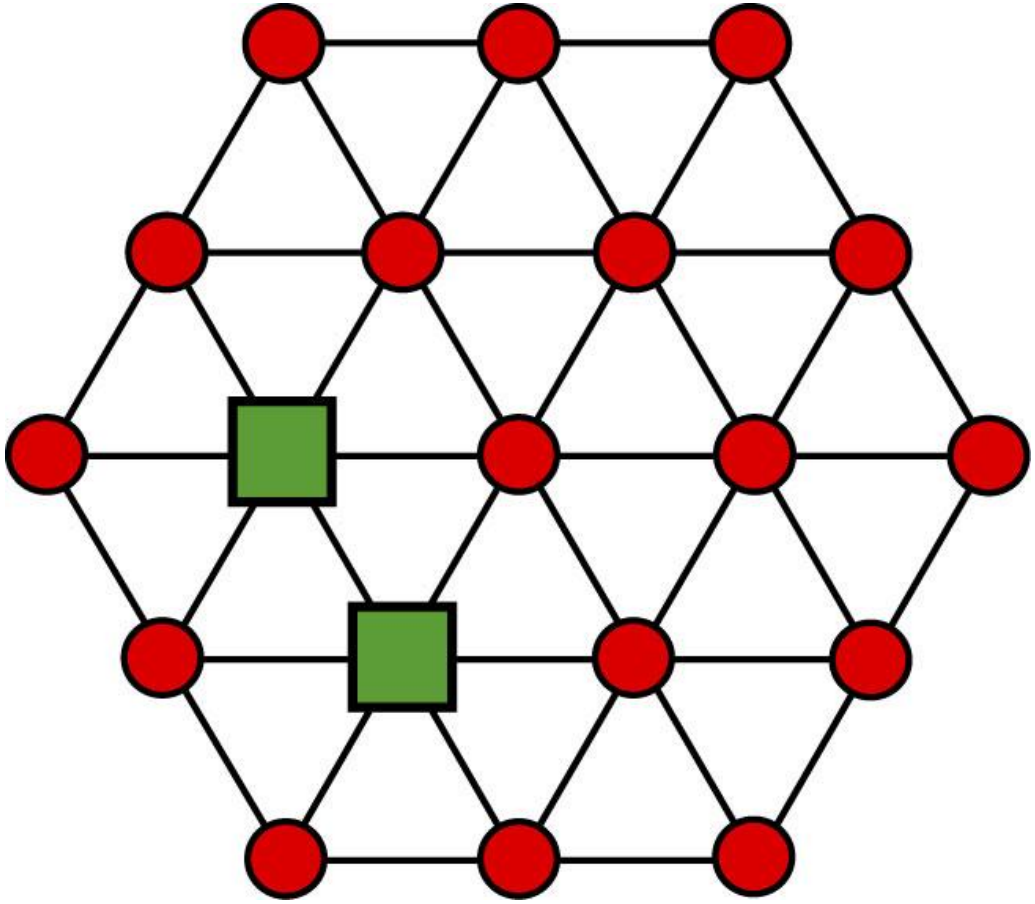


Thermodynamic factor Θ

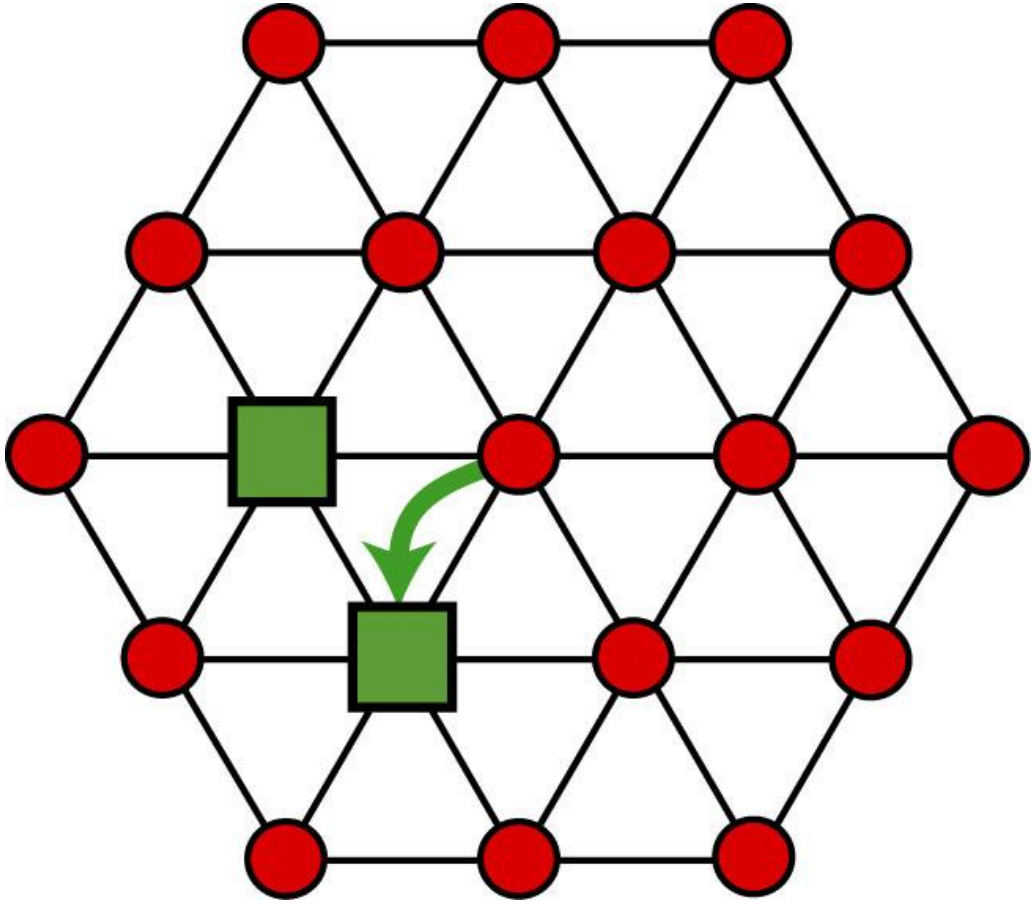


A. Van der Ven, G. Ceder, M. Asta, P.D. Tepesch, Phys Rev. B 64 (2001) 064112

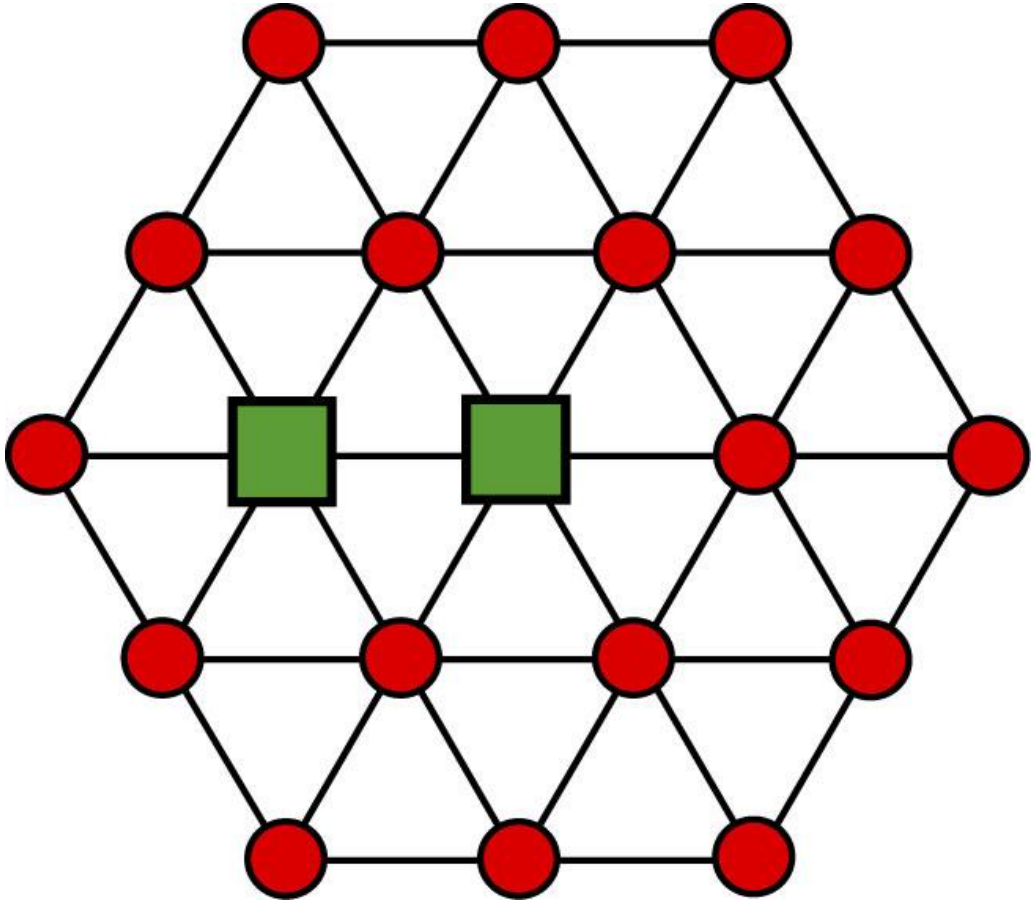
Divacancy diffusion mechanism



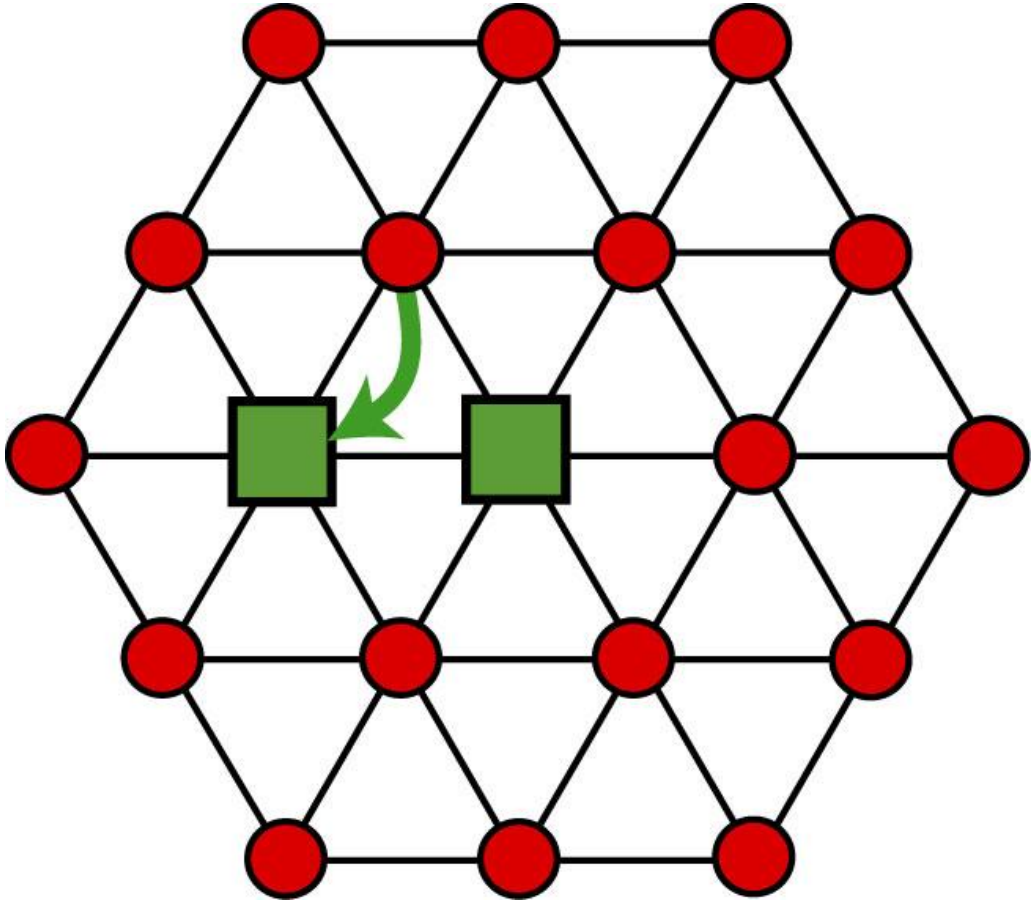
Divacancy diffusion mechanism



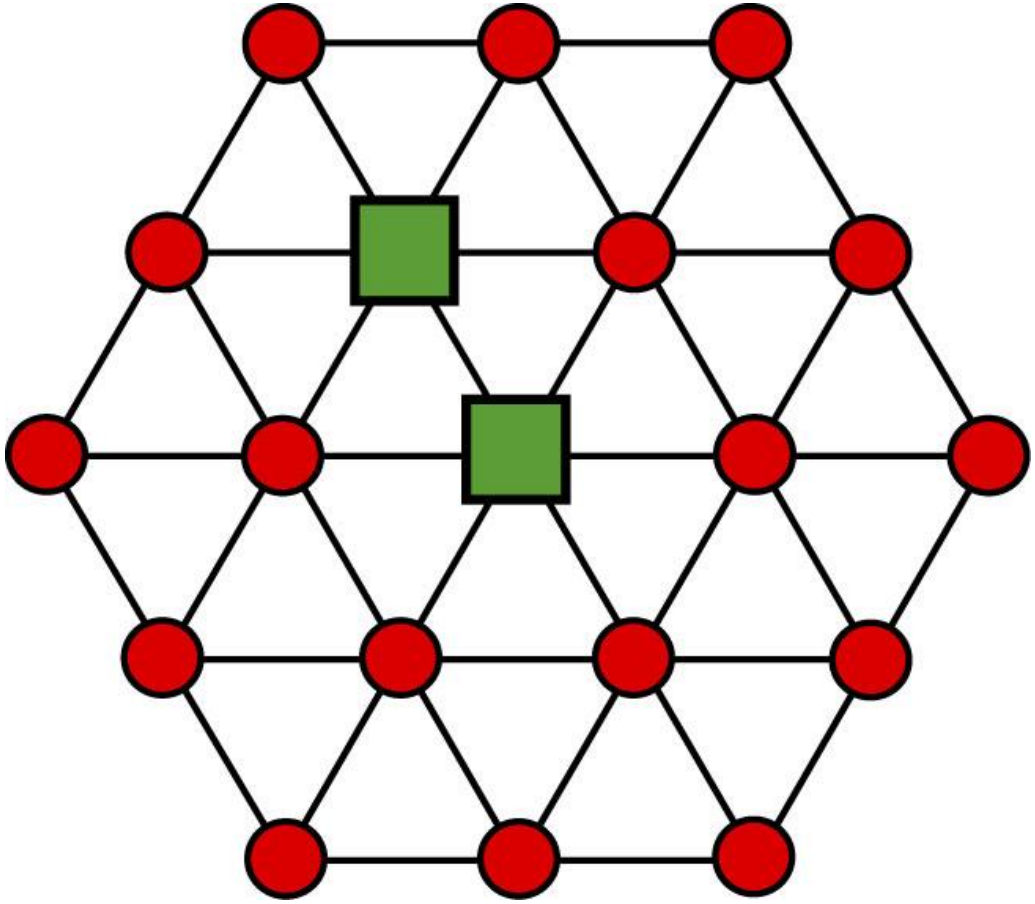
Divacancy diffusion mechanism



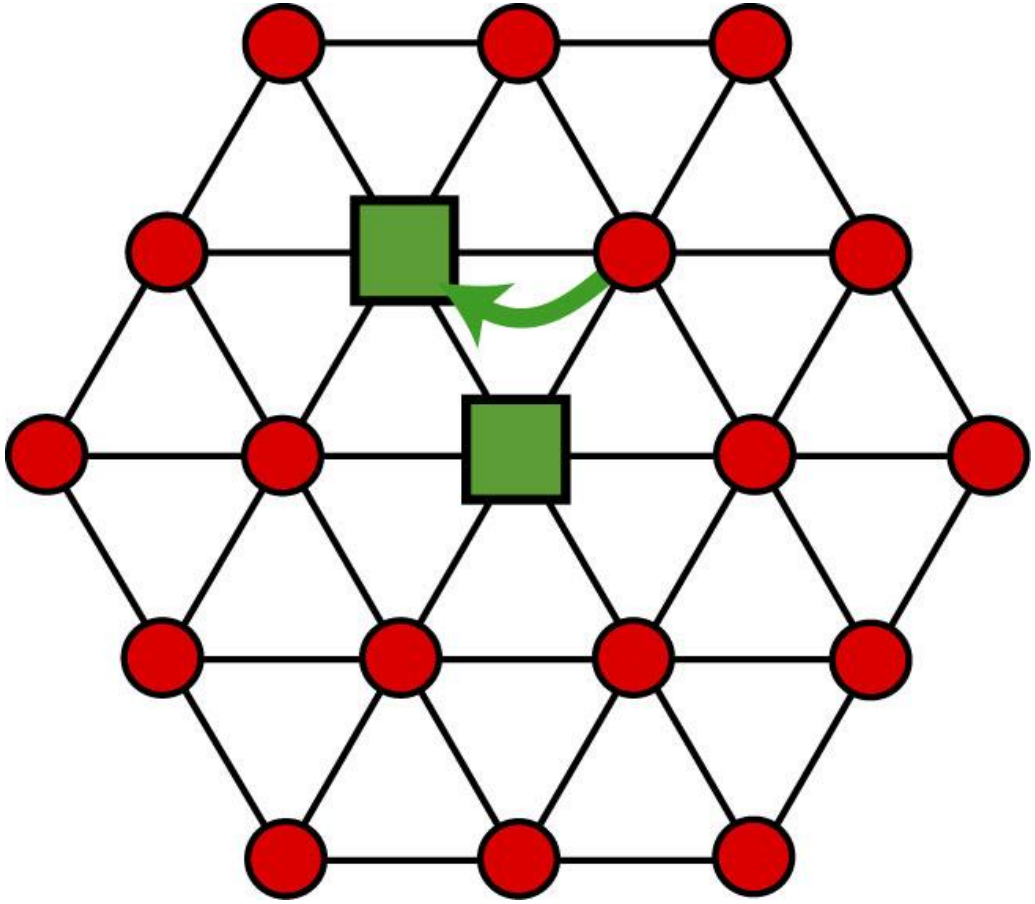
Divacancy diffusion mechanism



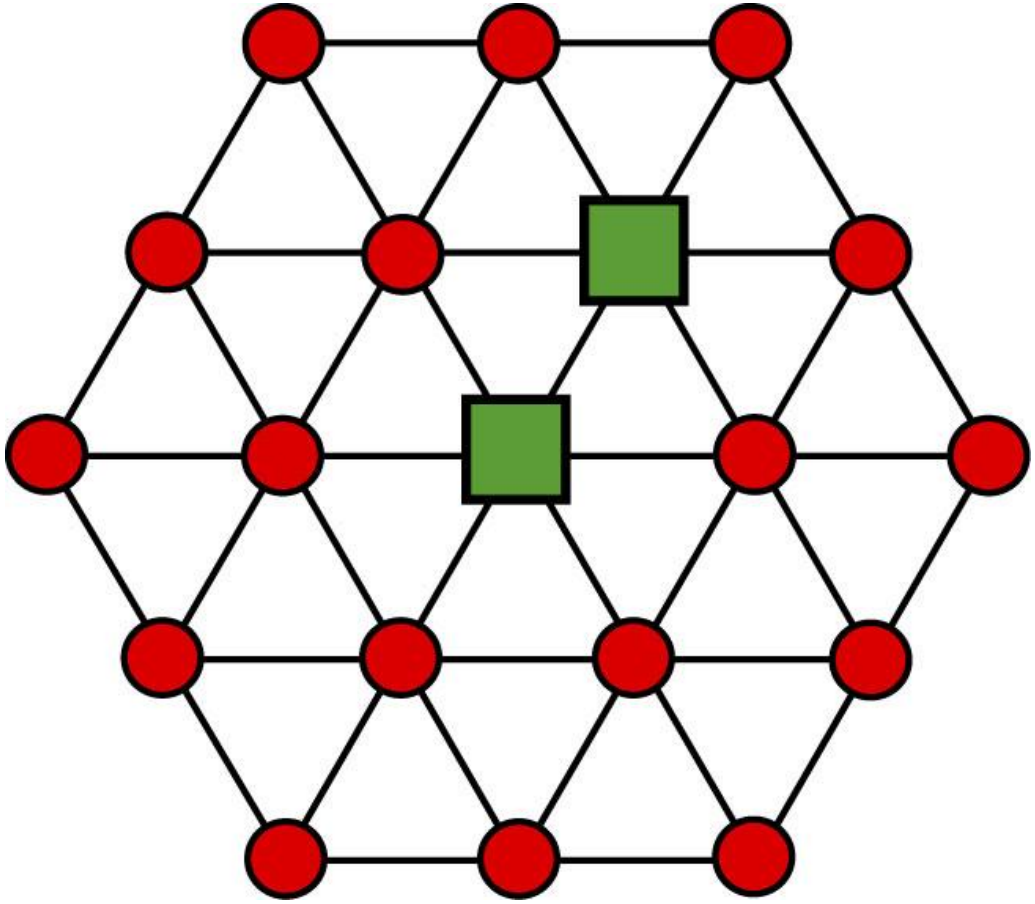
Divacancy diffusion mechanism



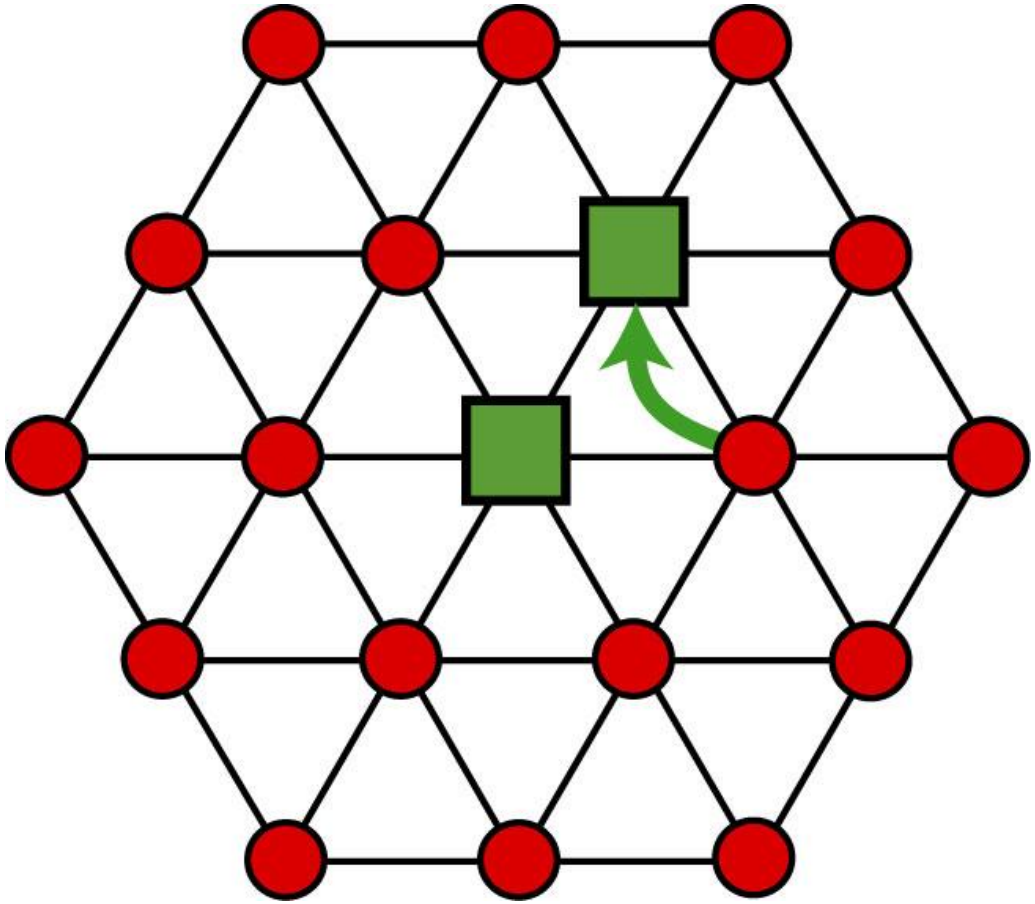
Divacancy diffusion mechanism



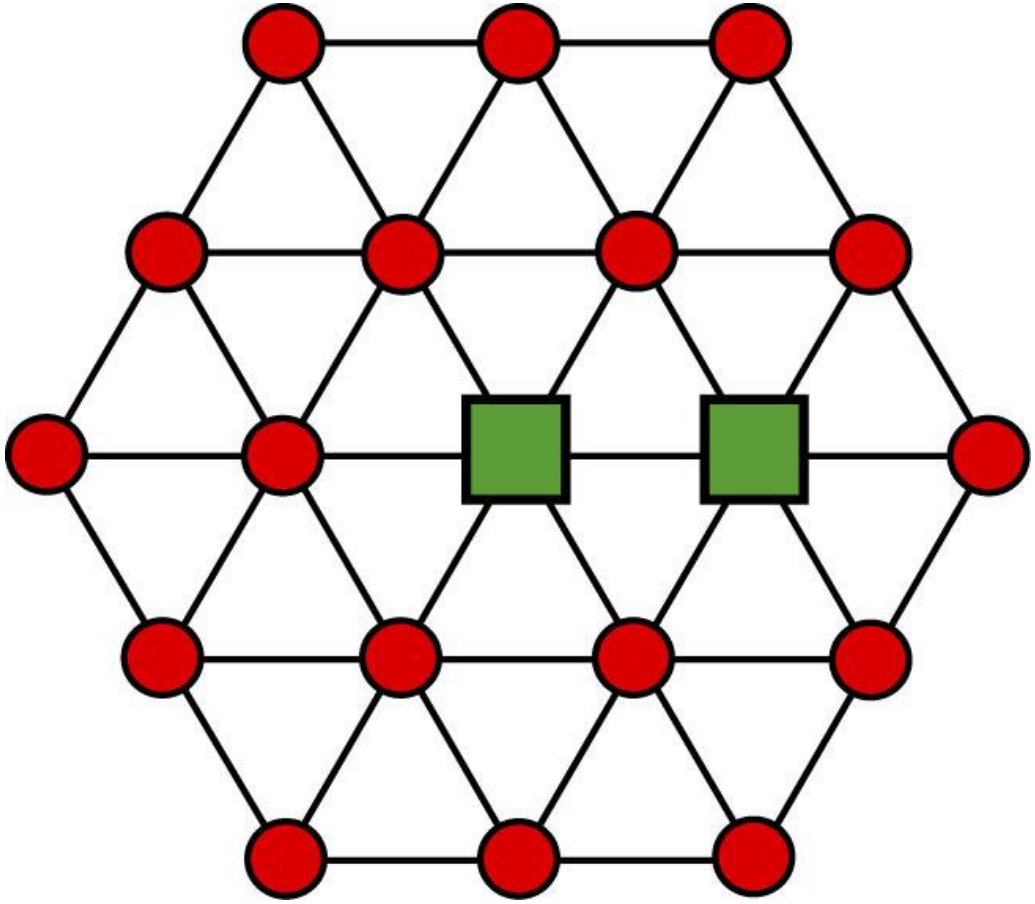
Divacancy diffusion mechanism



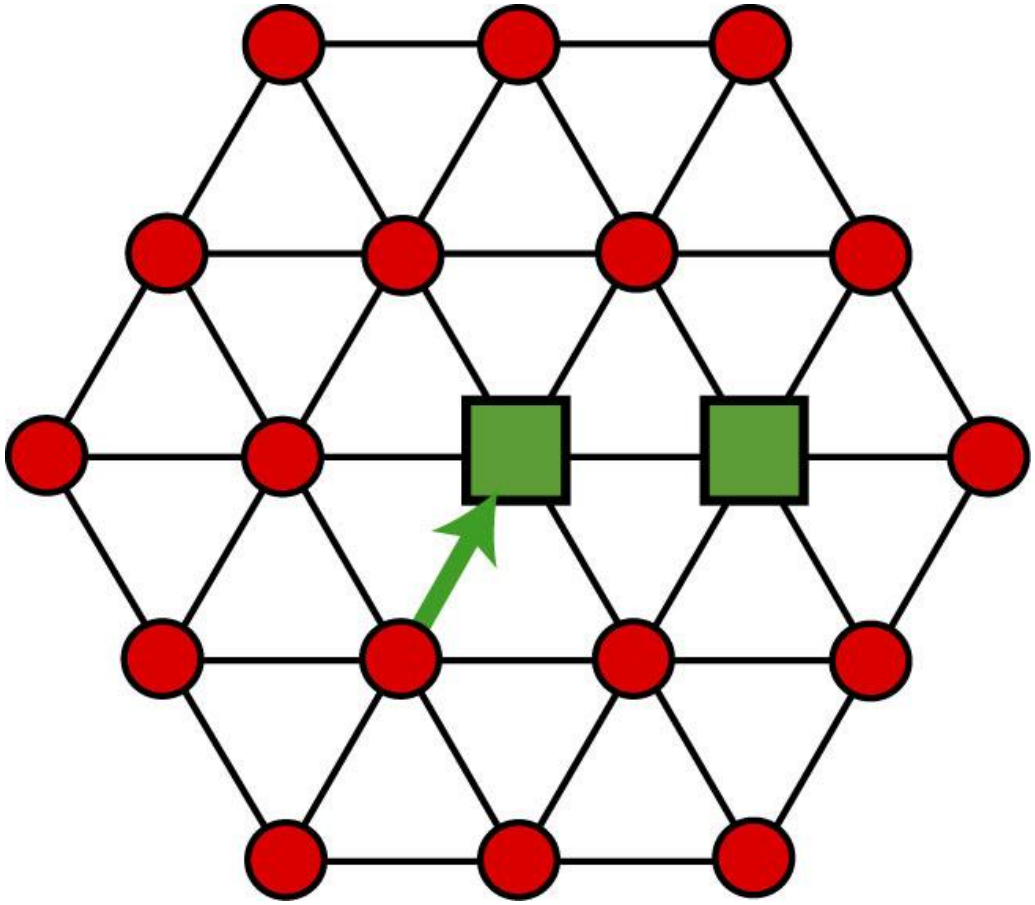
Divacancy diffusion mechanism



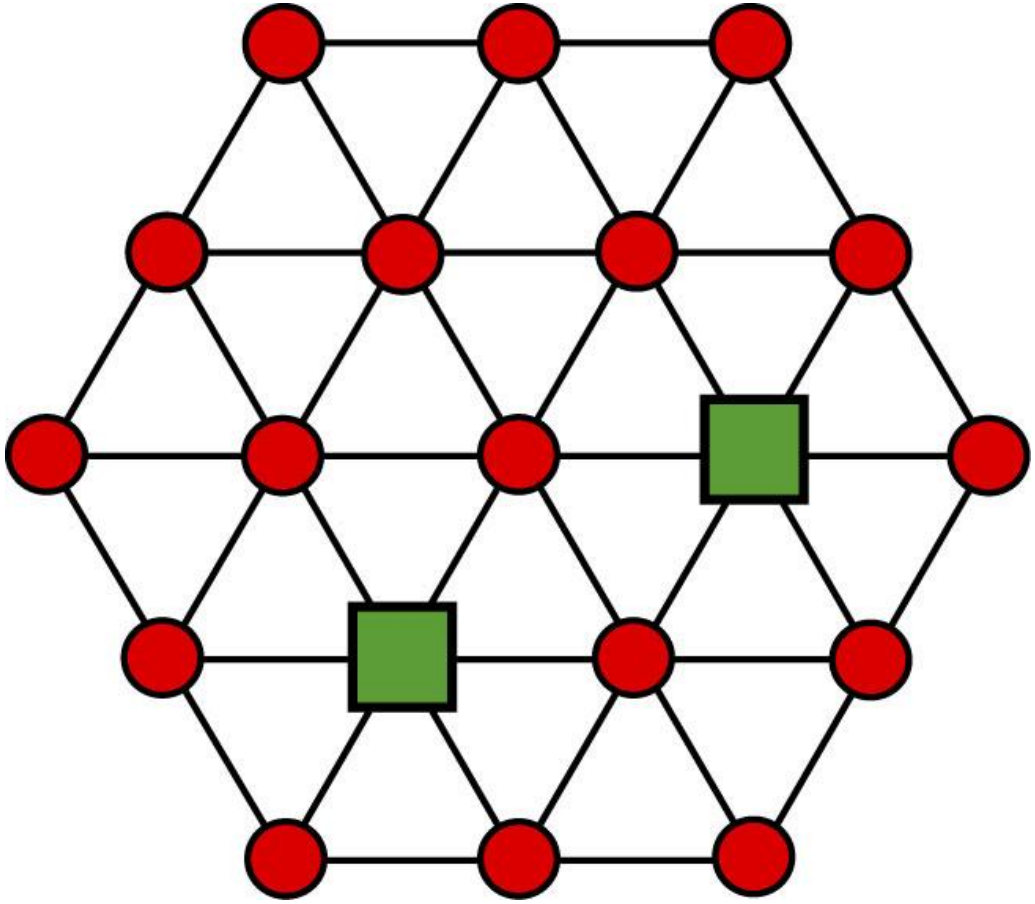
Divacancy diffusion mechanism



Divacancy separation

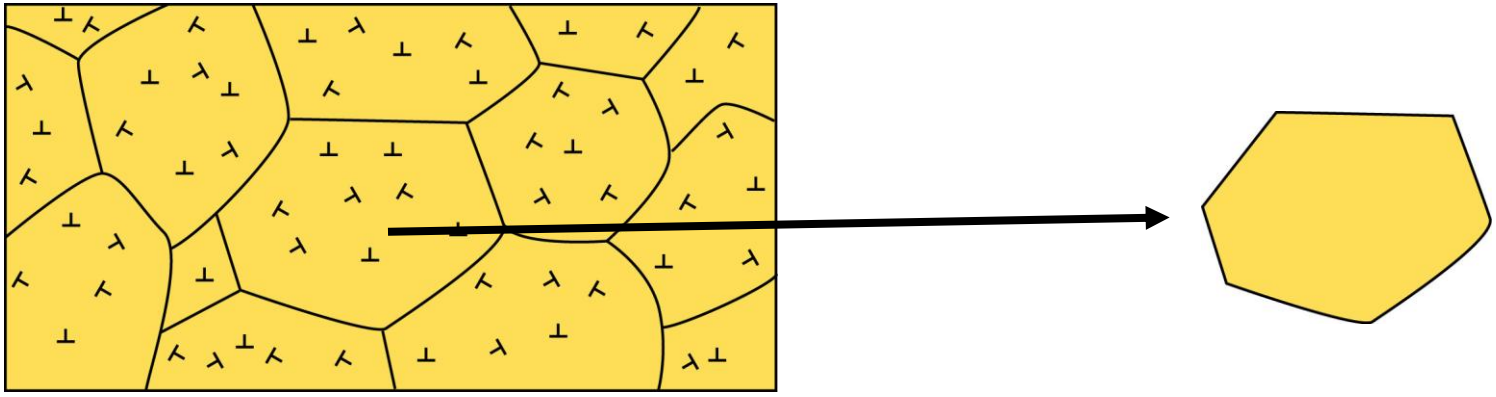


Divacancy separation



Diffusion in substitutional solids

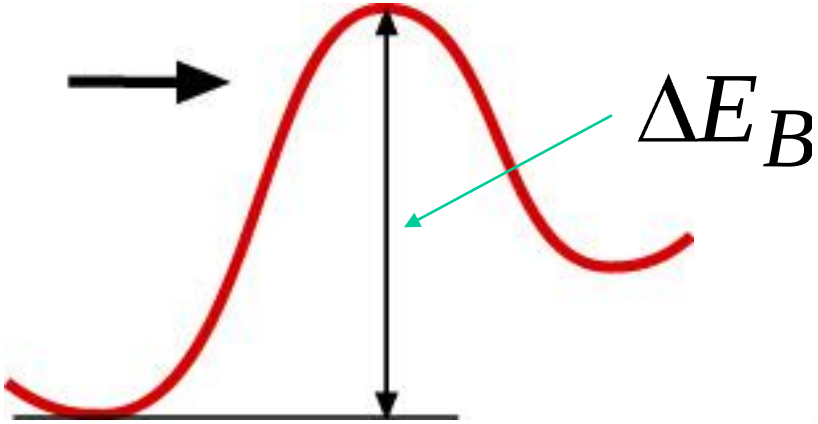
Connecting atomistic hop mechanisms with macroscopic diffusion coefficients



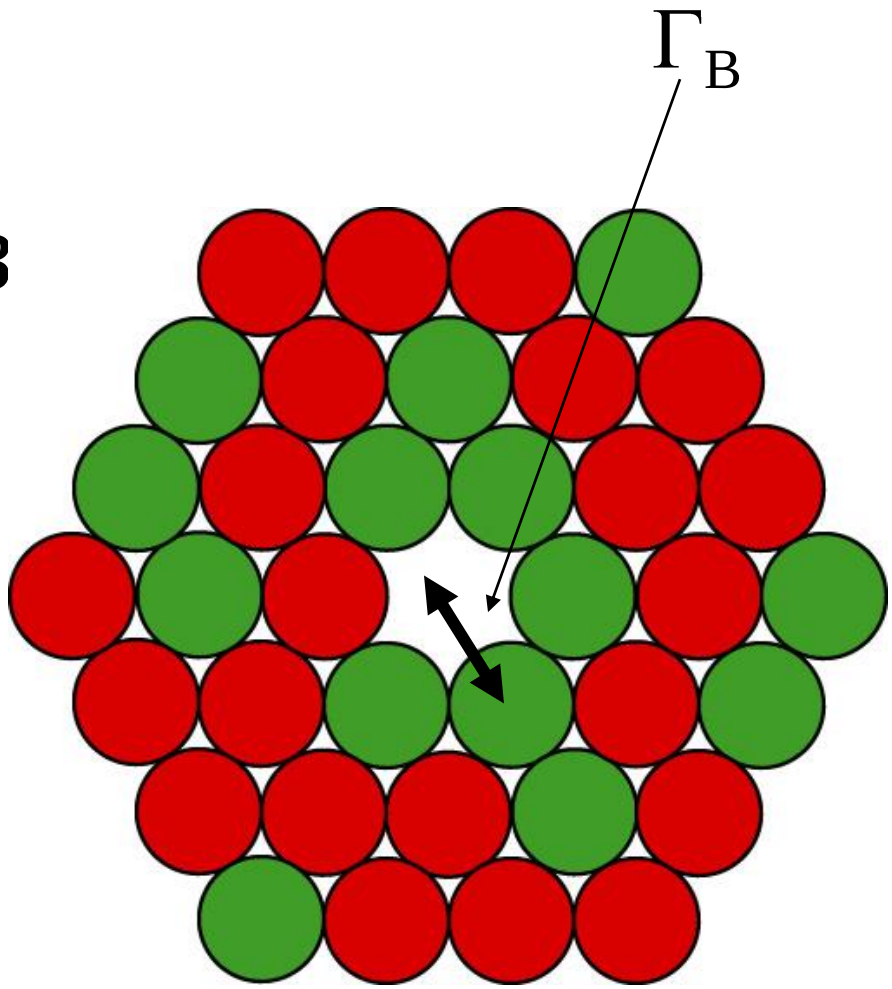
Real solids contain grain boundaries and dislocations which serve as vacancy sources and sinks

Diffusion within a perfect crystal

Individual hops: Transition state theory



$$\Gamma = \nu * \exp\left(\frac{-\Delta E_B}{kT}\right)$$

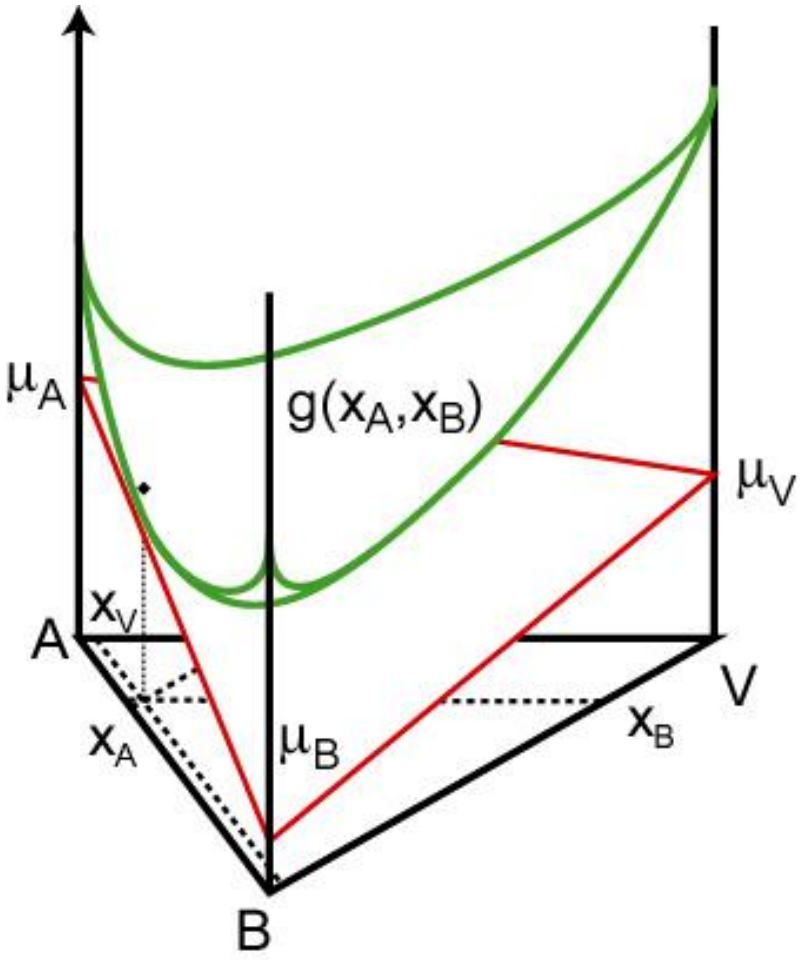


Thermodynamic driving forces for substitutional diffusion

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

$$\tilde{\mu}_A = \mu_A - \mu_V$$
$$\tilde{\mu}_B = \mu_B - \mu_V$$



Kubo Green formalism

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

$$L_{AA} = \frac{\left\langle \left(\sum_{\varsigma} \Delta\vec{R}_{\varsigma}^{A}(t) \right)^2 \right\rangle}{(2d)tVkT}$$

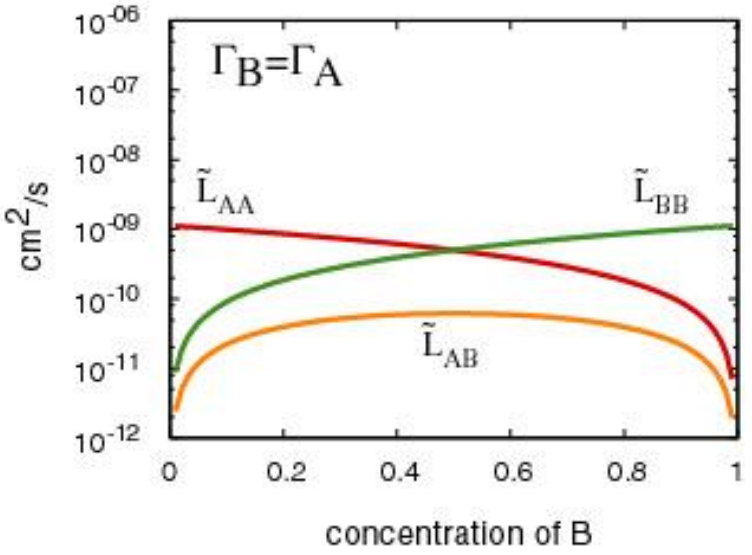
$$L_{BB} = \frac{\left\langle \left(\sum_{\varsigma} \Delta\vec{R}_{\varsigma}^{B}(t) \right)^2 \right\rangle}{(2d)tVkT}$$

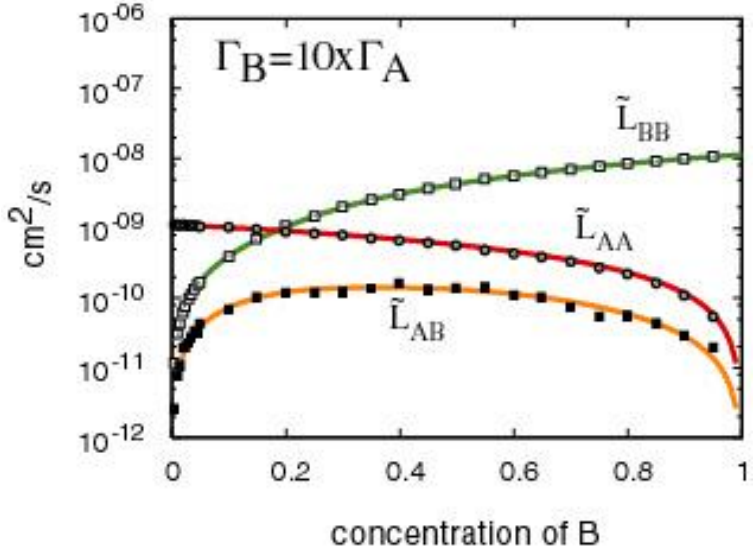
$$L_{AB} = \frac{\left\langle \left(\sum_{\xi} \Delta\vec{R}_{\xi}^{A}(t) \right) \cdot \left(\sum_{\varsigma} \Delta\vec{R}_{\varsigma}^{B}(t) \right) \right\rangle}{(2d)tVkT} = L_{BA}$$

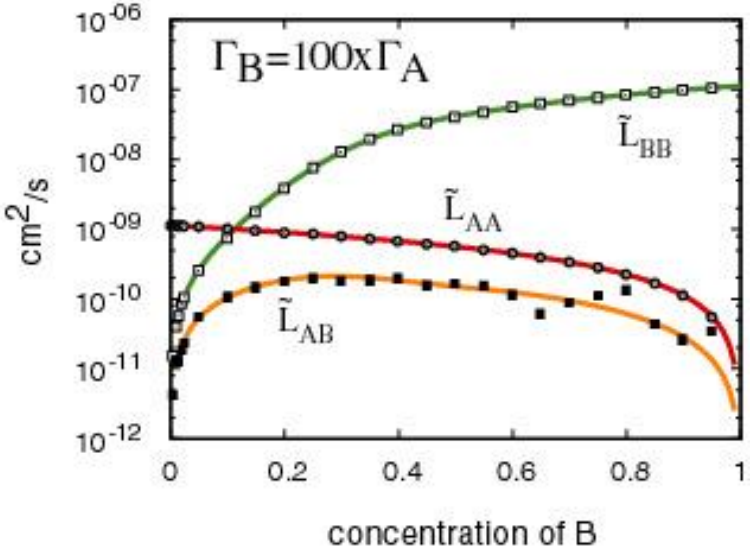
Kinetic coefficients
(fcc lattice in dilute vacancy limit, ideal solution)

Kubo-Green

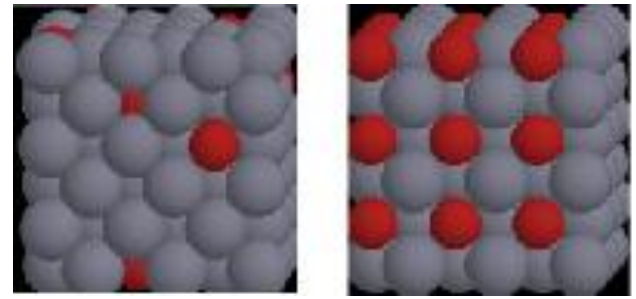
$$\tilde{L}_{ij} = \frac{\left\langle \left(\sum_{\varsigma} \Delta \vec{R}_{\varsigma}^{\,i} \right) \cdot \left(\sum_{\xi} \Delta \vec{R}_{\xi}^{\,j} \right) \right\rangle}{2d\,t\tilde{M}}$$

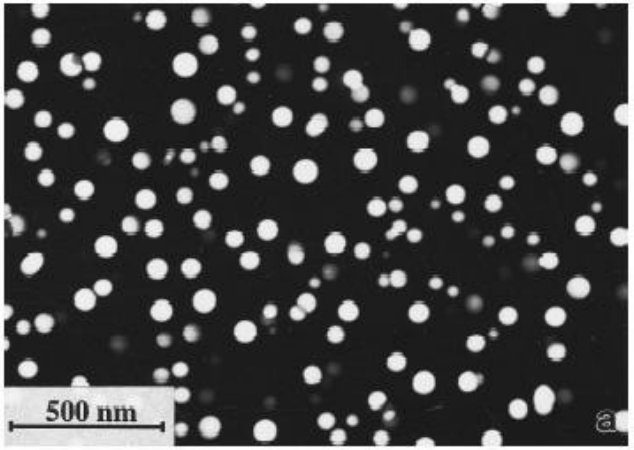






Diffusion in Al-Li alloys

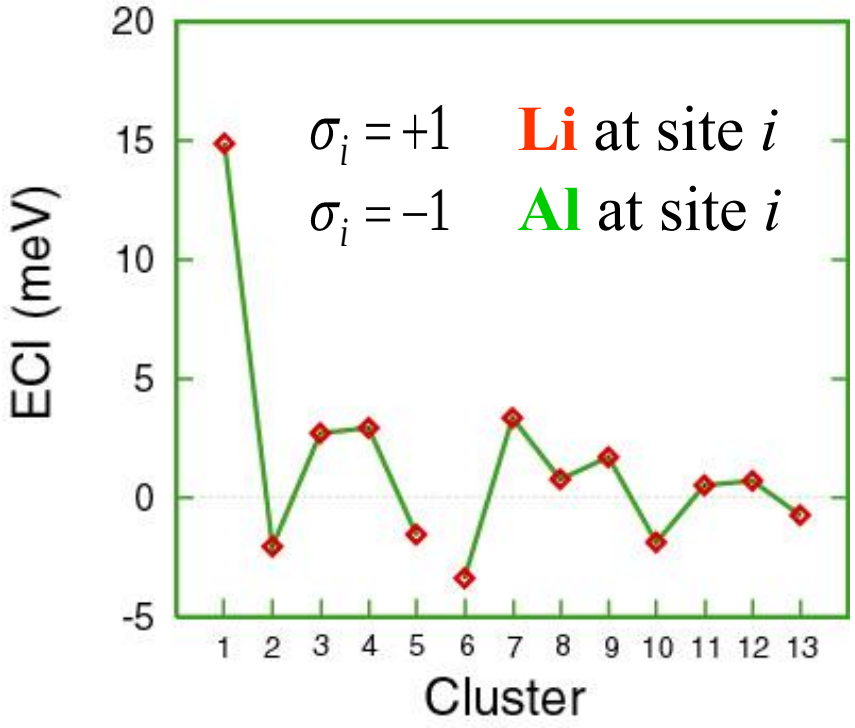


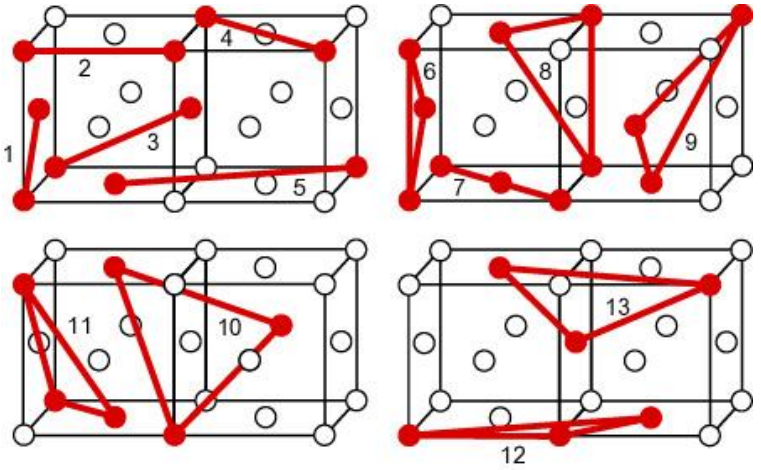


Dark field TEM
A. Kalogeridis, J. Pesieka, E. Nembach, Acta Mater 47 (1999) 1953

fcc Al-Li alloy

Binary cluster expansion



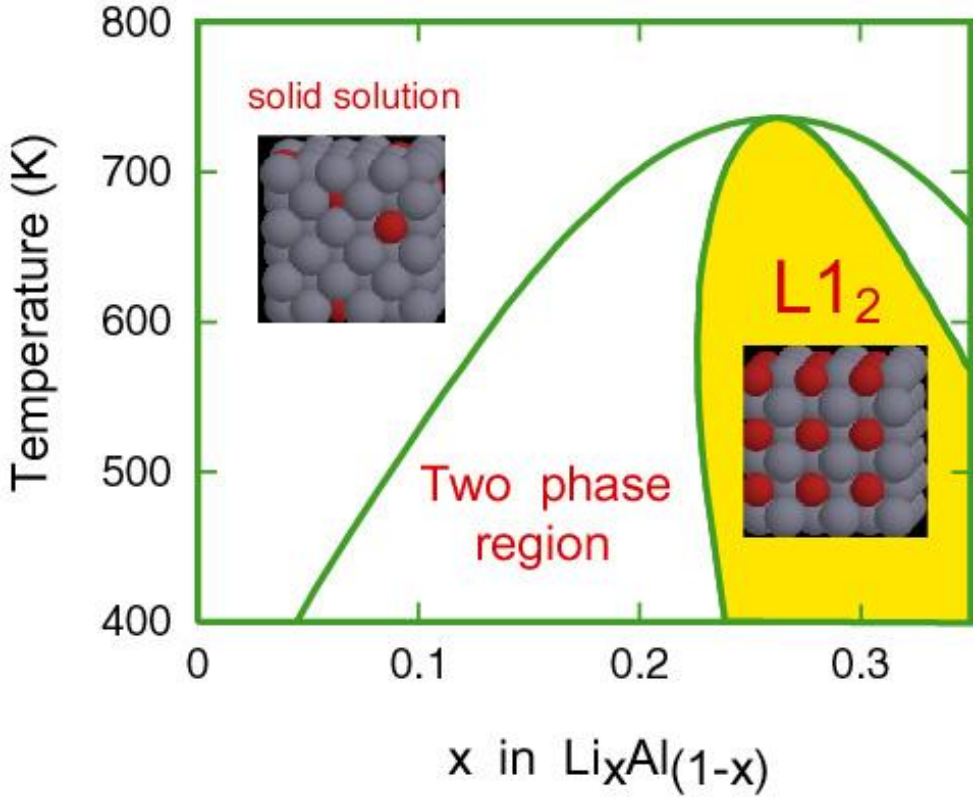


Fit to LDA energies of 70 different Al-Li arrangements on fcc

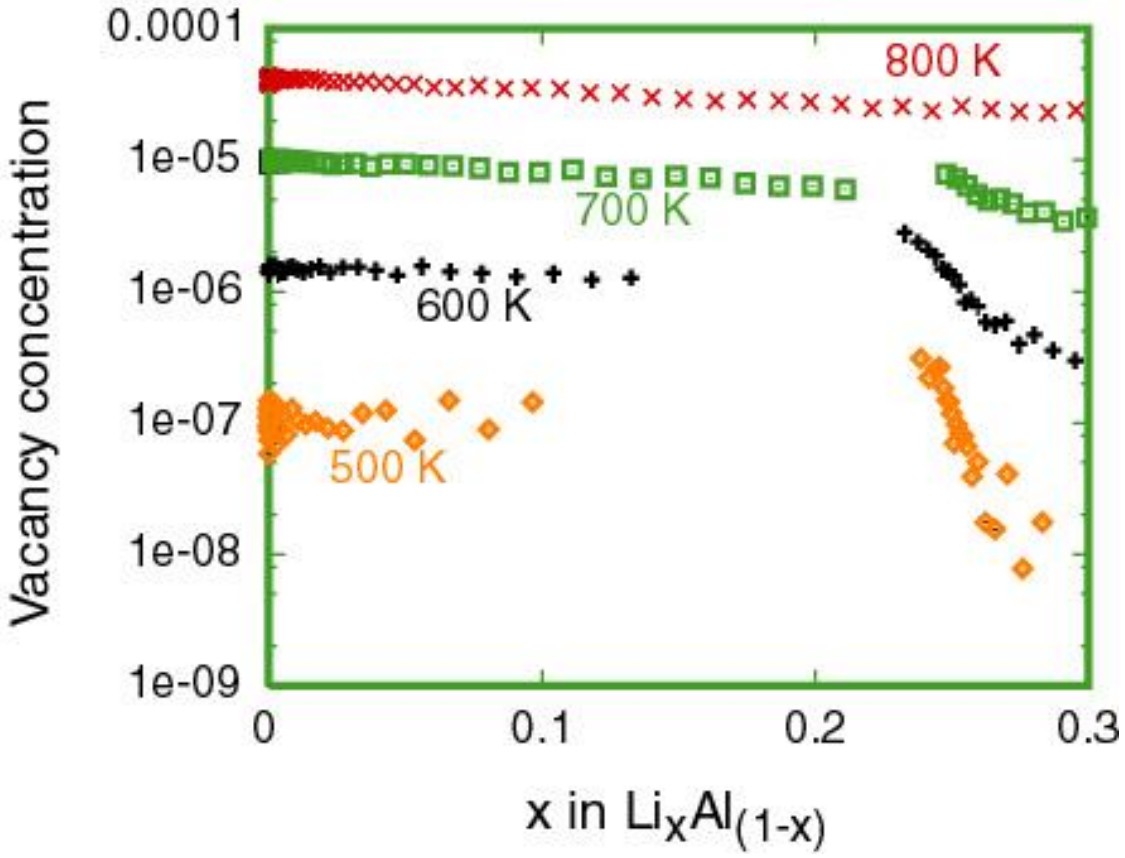
$$E\ \sigma = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

Calculated thermodynamic and kinetic properties of Al-Li alloy

First principles cluster expansion + Monte Carlo



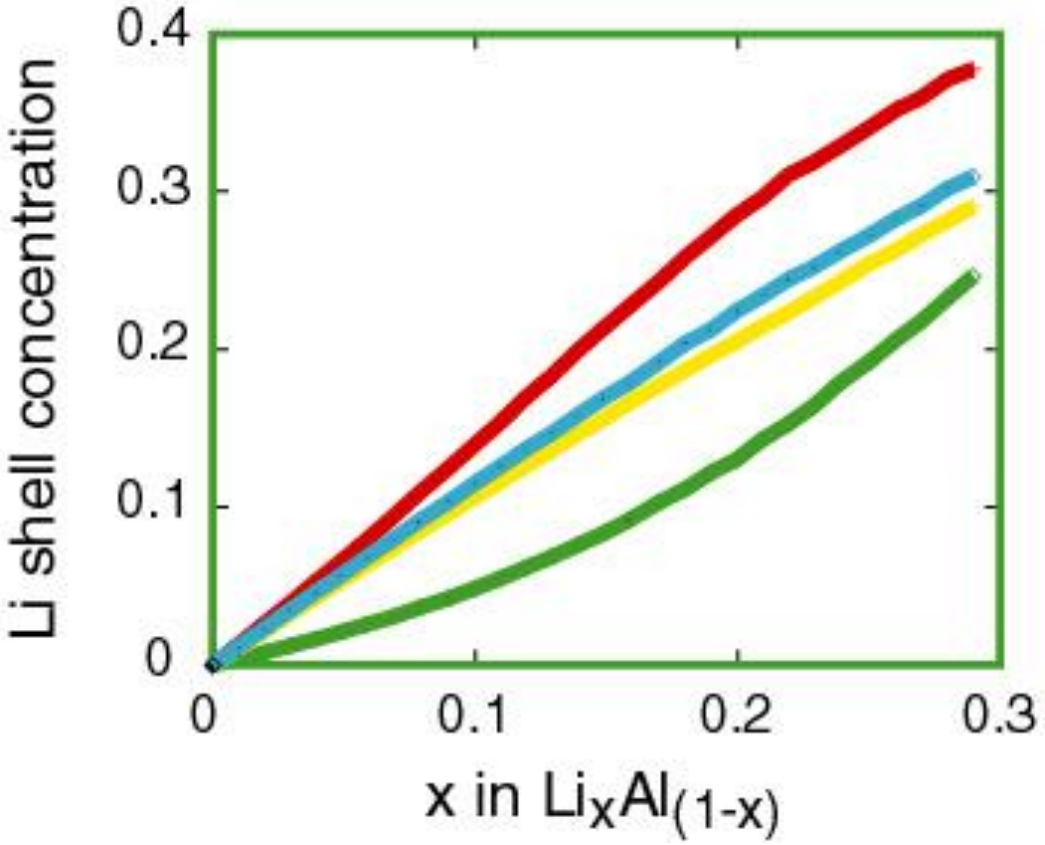
Equilibrium vacancy concentration
(Monte Carlo applied to cluster expansion)

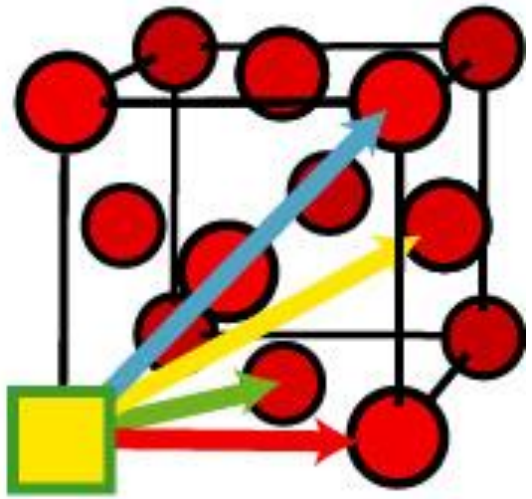


A. Van der Ven, G. Ceder, Phys. Rev. B**71**, 054102(2005)

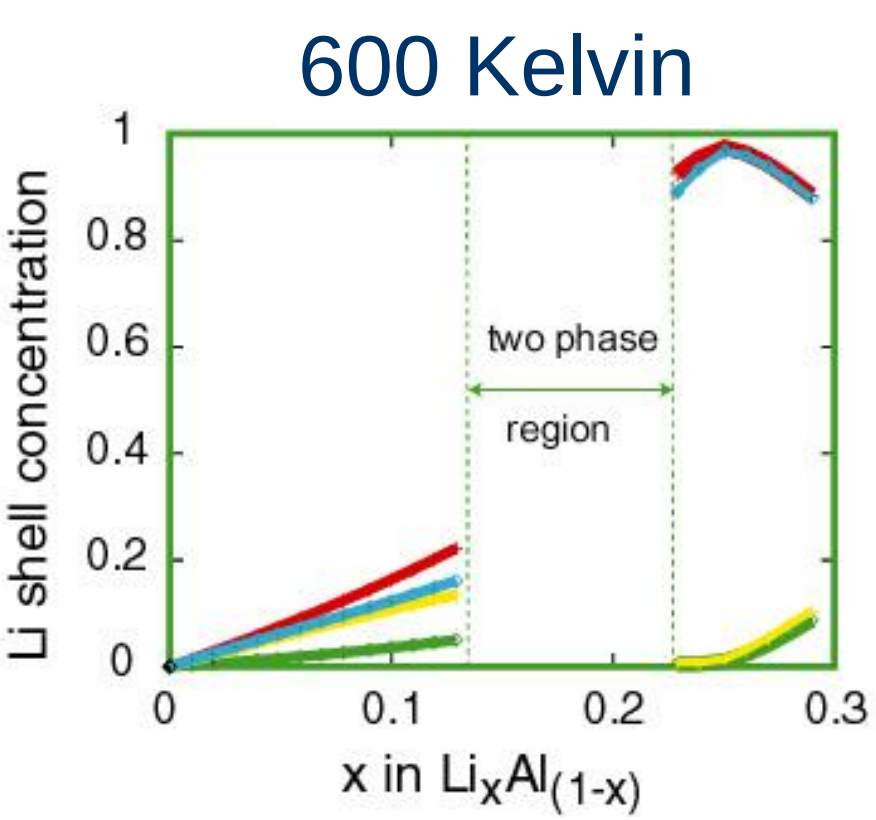
Vacancy surrounds itself by Al
Short range order around a vacancy

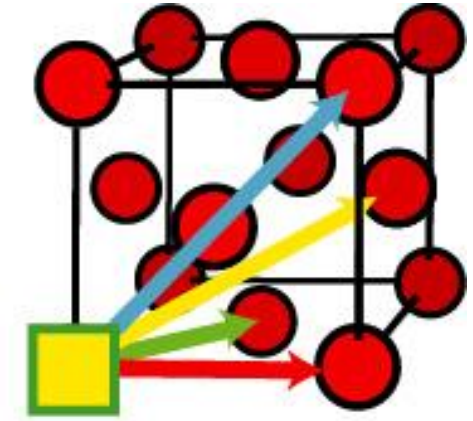
750 Kelvin

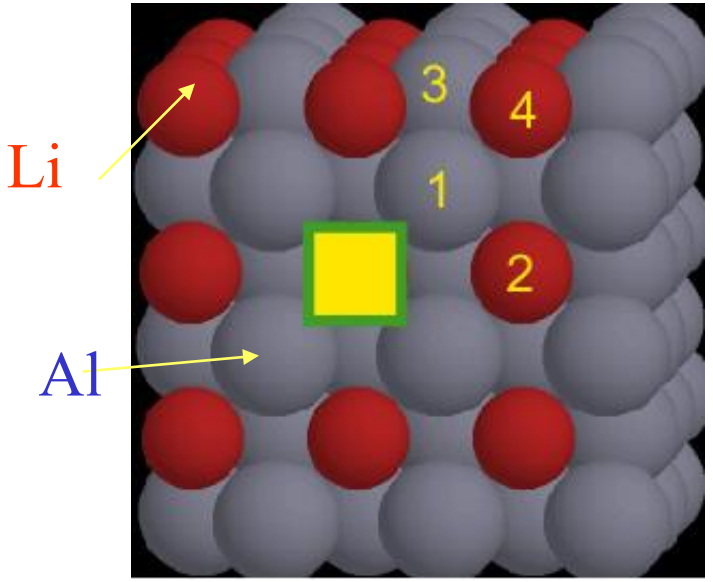




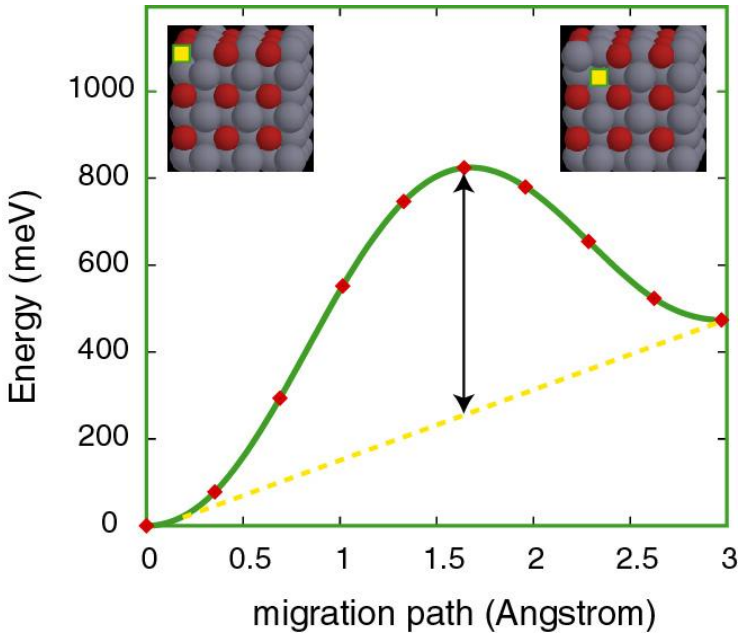
Vacancies reside on lithium sublattice in L12

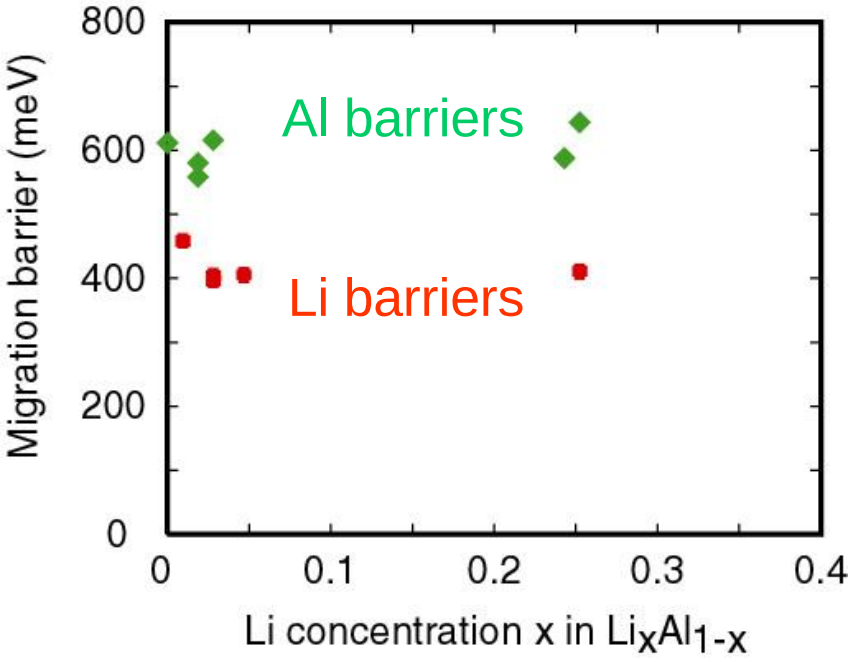






Migration barriers for lithium and aluminum differ by ~150 meV





Calculated (LDA) in 107 atom supercells

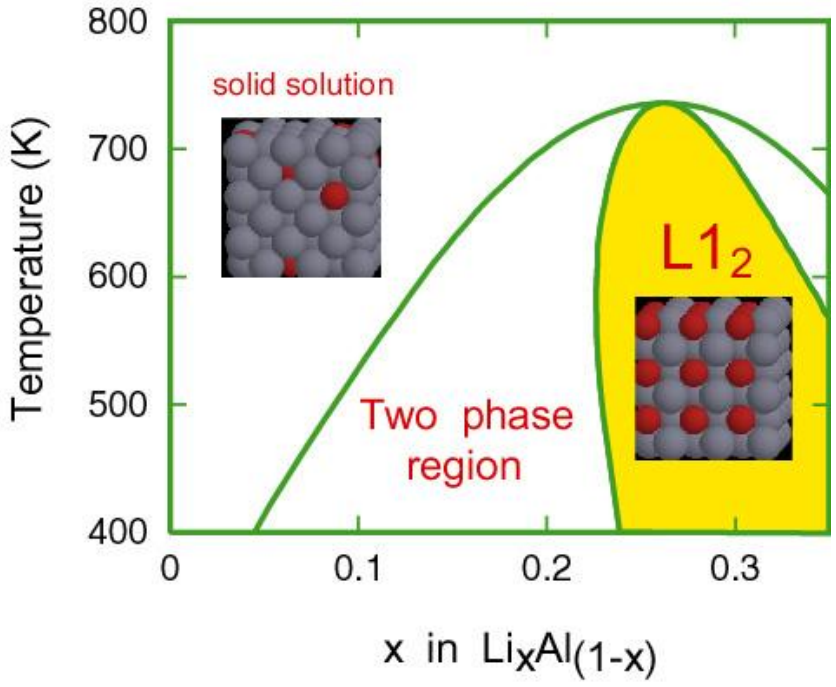
$$\nu_{Al}^{*} \approx 4.5 \times 10^{13}\, Hz$$

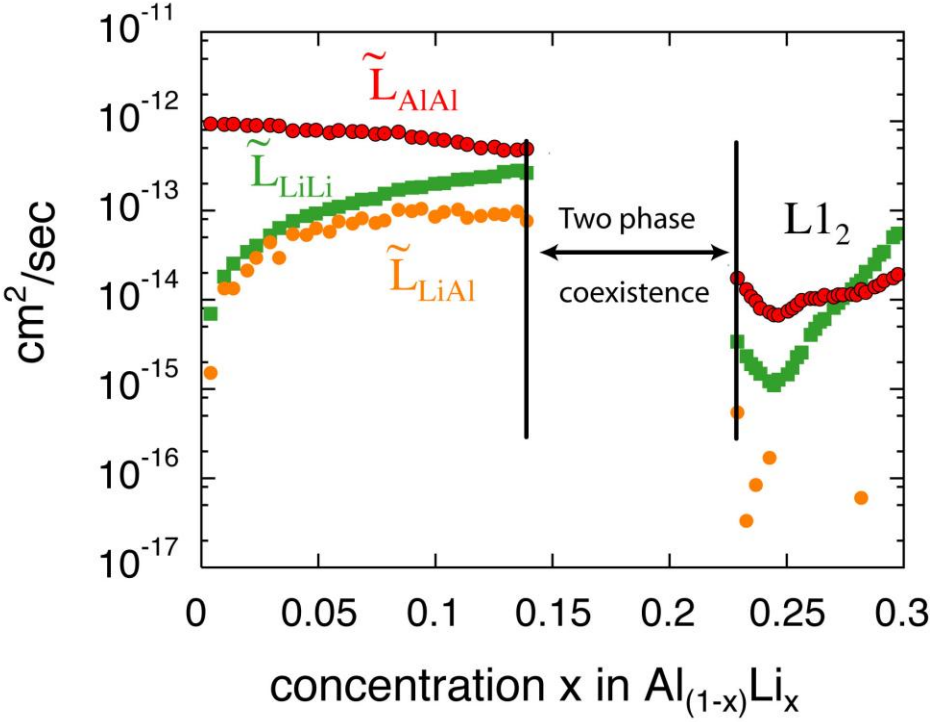
$$\nu_{Li}^{*} \approx 7 \times 10^{13}\, Hz$$

L-coefficients for Li-Al contains an ordered phase

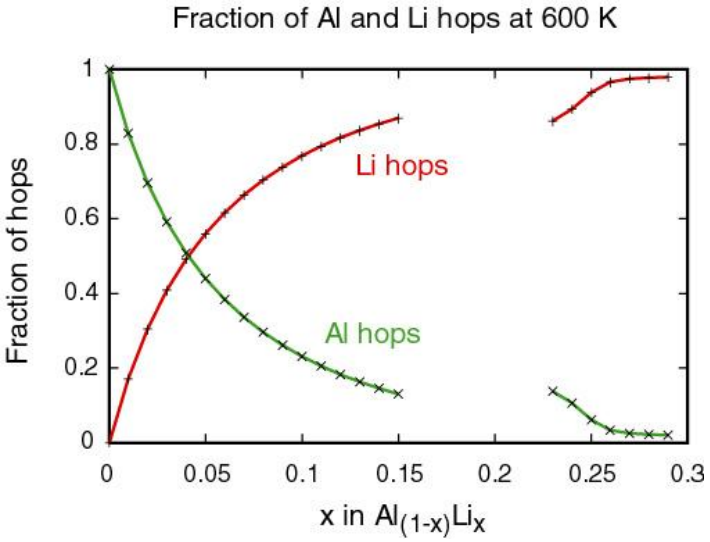
$$J_{Li} = -L_{LiLi}\nabla\tilde{\mu}_{Li} - L_{LiAl}\nabla\tilde{\mu}_{Al}$$

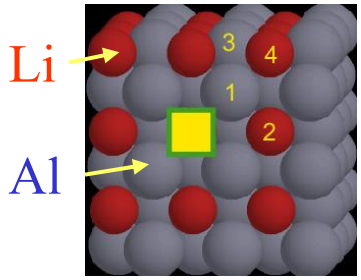
$$J_{Al} = -L_{AlLi}\nabla\tilde{\mu}_{Li} - L_{AlAl}\nabla\tilde{\mu}_{Al}$$

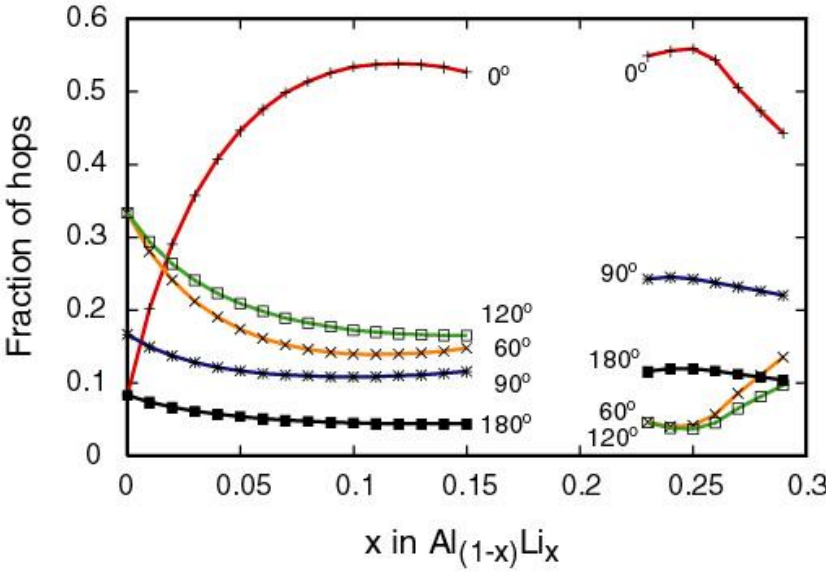


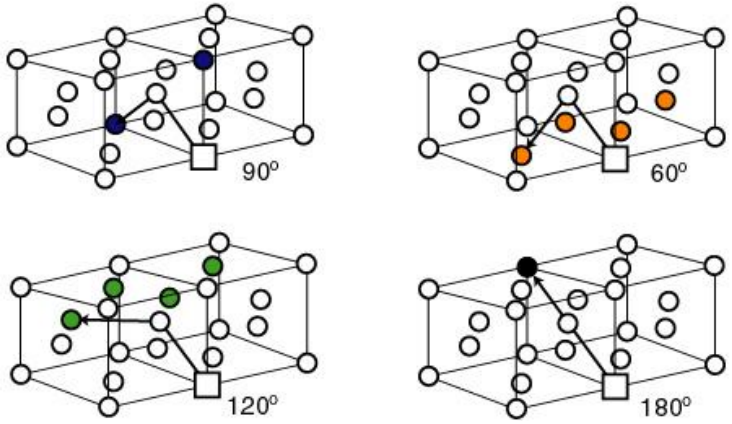


Frequency of hop angles between successive hops









A. Van der Ven, G. Ceder, Phys. Rev. Lett. **94**, 045901 (2005).

Perfect crystal
Fickian flux expressions

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = \begin{pmatrix} \tilde{L}_{AA} & \tilde{L}_{AB} \\ \tilde{L}_{BA} & \tilde{L}_{BB} \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial\left(\frac{\tilde{\mu}_A}{kT}\right)}{\partial x_A} & \frac{\partial\left(\frac{\tilde{\mu}_A}{kT}\right)}{\partial x_B} \\ \frac{\partial\left(\frac{\tilde{\mu}_B}{kT}\right)}{\partial x_A} & \frac{\partial\left(\frac{\tilde{\mu}_B}{kT}\right)}{\partial x_B} \end{pmatrix}$$

$$J_A = -D_{AA}\nabla C_A - D_{AB}\nabla C_B$$

$$J_B = -D_{BA}\nabla C_A - D_{BB}\nabla C_B$$

Diagonalize the D-matrix

Yields a mode corresponding to
(a) density relaxation (vacancy mobility)
(b) interdiffusion

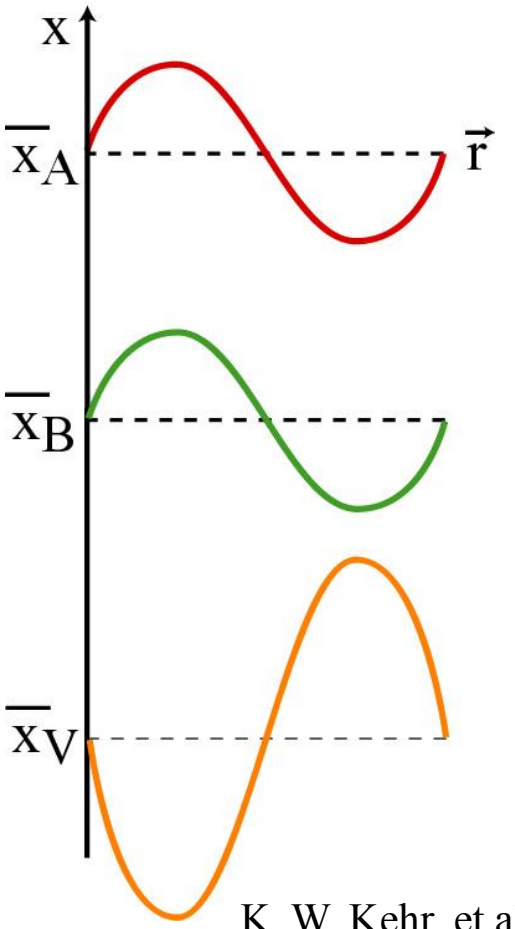
$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = E \cdot \begin{pmatrix} \lambda^{+} & 0 \\ 0 & \lambda^{-} \end{pmatrix} \cdot E^{-1}$$

K. W. Kehr, et al, Phys. Rev. B **39**, 4891 (1989)

Physical meaning of modes λ^+ and λ^-

Physical meaning of modes λ^+ and λ^-

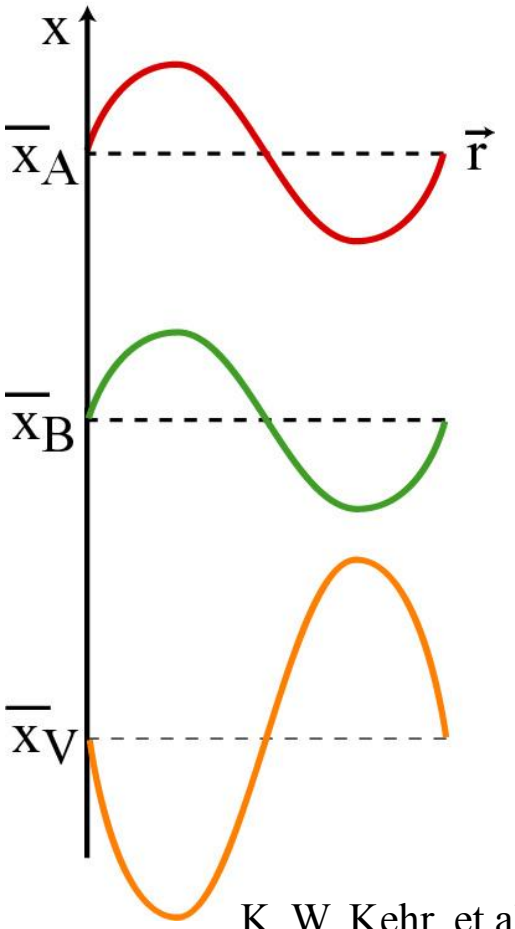
Density fluctuations relax with a time constant of λ^+



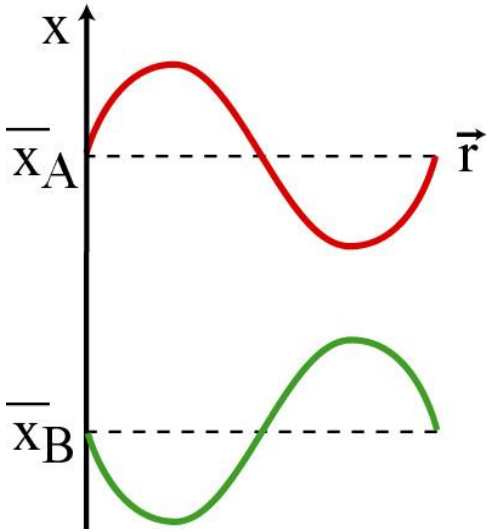
K. W. Kehr, et al, Phys. Rev. B **39**, 4891 (1989)

Physical meaning of modes λ^+ and λ^-

Density fluctuations relax with a time constant of λ^+



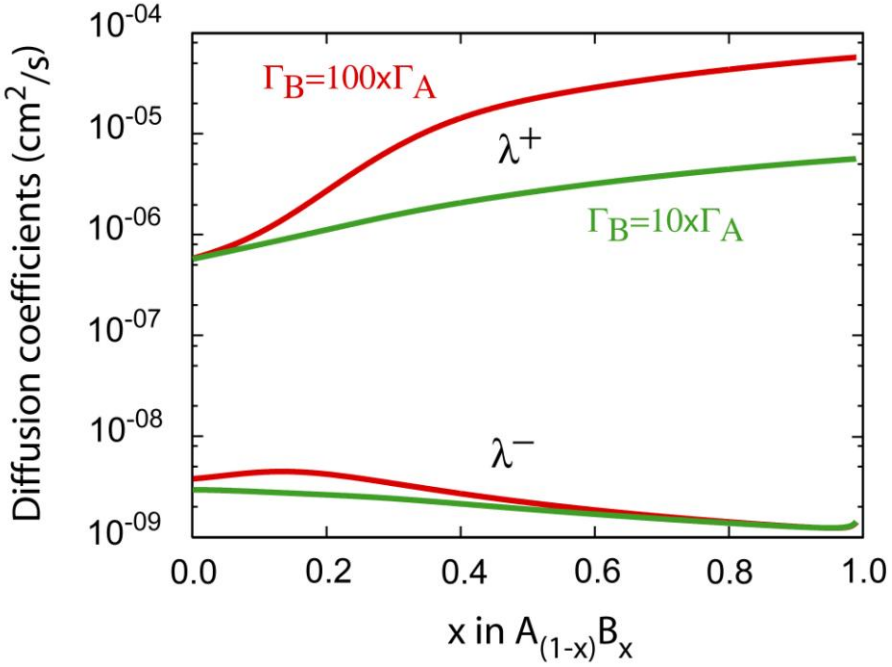
Compositional inhomogeneities decay with a time constant of λ^-



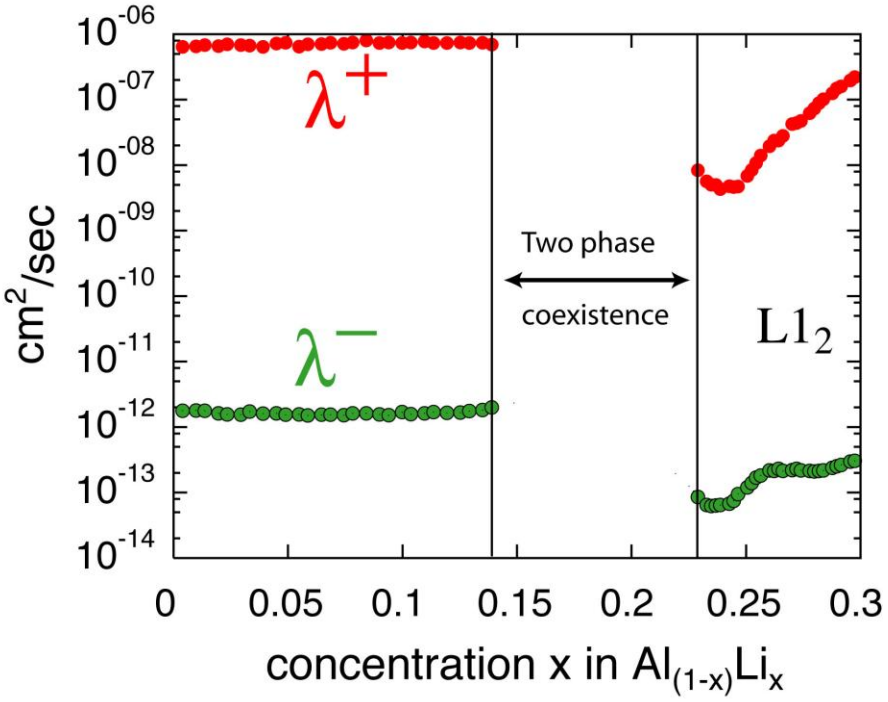
K. W. Kehr, et al, Phys. Rev. B **39**, 4891 (1989)

Vacancy mobility and interdiffusion

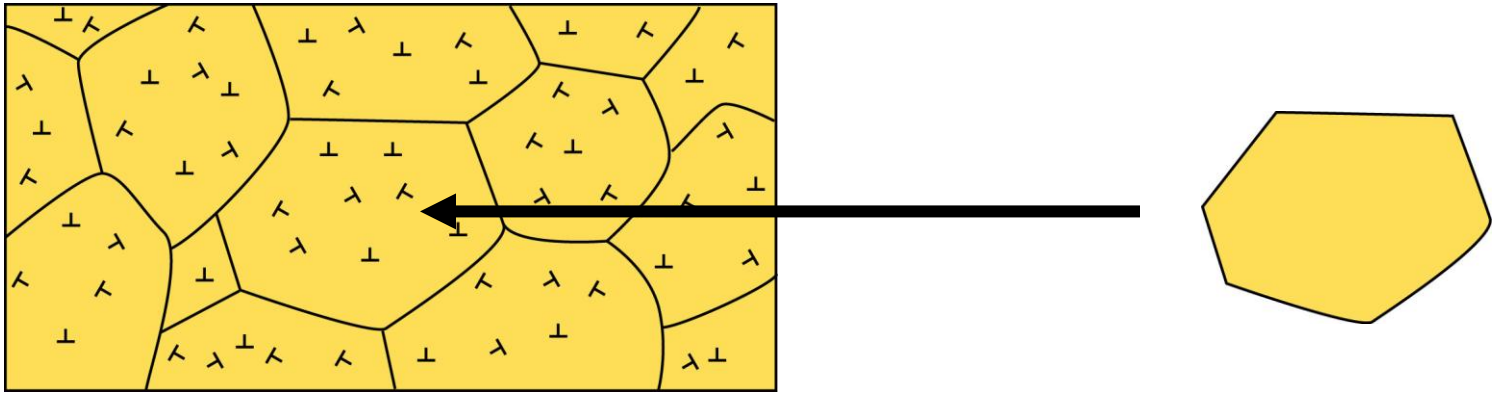
Random alloy
Thermodynamically ideal



Al_xLi_{1-x} alloy
Non-ideal thermodynamics



The role of vacancy sources and sinks



Real solids contain grain boundaries and dislocations which serve as vacancy sources and sinks

Diffusion within a perfect crystal

Uniform source sink approximation

$$J_A = -L_{AA}\nabla\tilde{\mu}_A - L_{AB}\nabla\tilde{\mu}_B$$

$$J_B = -L_{BA}\nabla\tilde{\mu}_A - L_{BB}\nabla\tilde{\mu}_B$$

Assume vacancy concentration in equilibrium everywhere

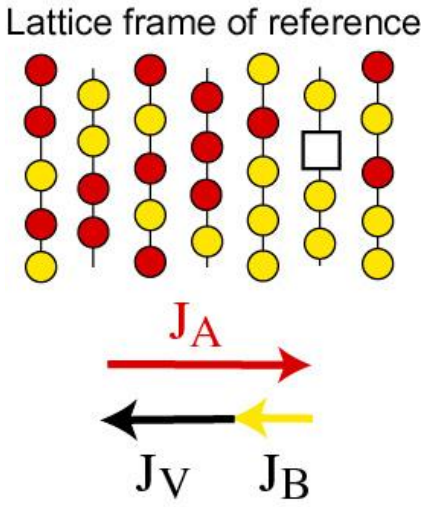
$$\mu_V = 0 \qquad d\mu_V = 0$$

Gibbs-Duhem ↓ $x_A d\mu_A + x_B d\mu_B = 0$

$$J_A = -D_A\nabla C_A$$

$$J_B = -D_B\nabla C_B$$

Lattice frame and laboratory frame of reference



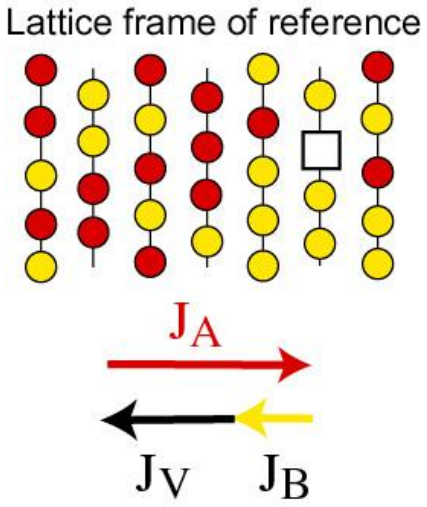
$$v_{lattice} = V_m \cdot J_V = -V_m \cdot (J_A + J_B)$$

Fluxes in the laboratory frame

$$\tilde{J}_A = J_A + x_A J_V$$

$$\tilde{J}_B = J_B + x_B J_V$$

Lattice frame and laboratory frame of reference



$$v_{lattice} = V_m \cdot J_V = -V_m \cdot (J_A + J_B)$$

Fluxes in the laboratory frame

$$\tilde{J}_A = J_A + x_A J_V$$
$$\tilde{J}_B = J_B + x_B J_V$$

$$J_V = -\tilde{W} \nabla C_B$$
$$J_B + x_B J_V = -\tilde{D} \nabla C_B$$

Drift

$$\tilde{W} = D_A - D_B$$

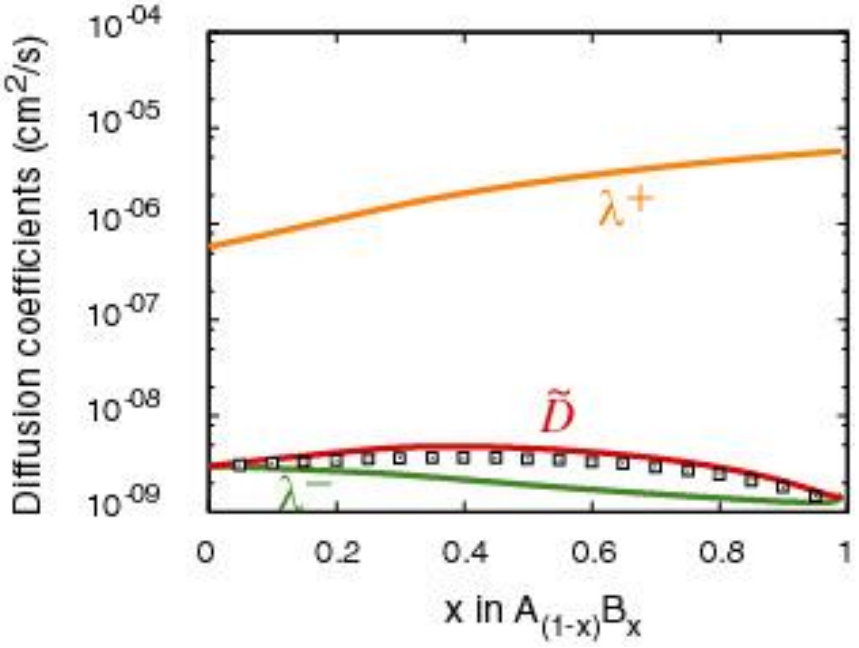
Interdiffusion

$$\tilde{D} = x_B D_A + x_A D_B$$

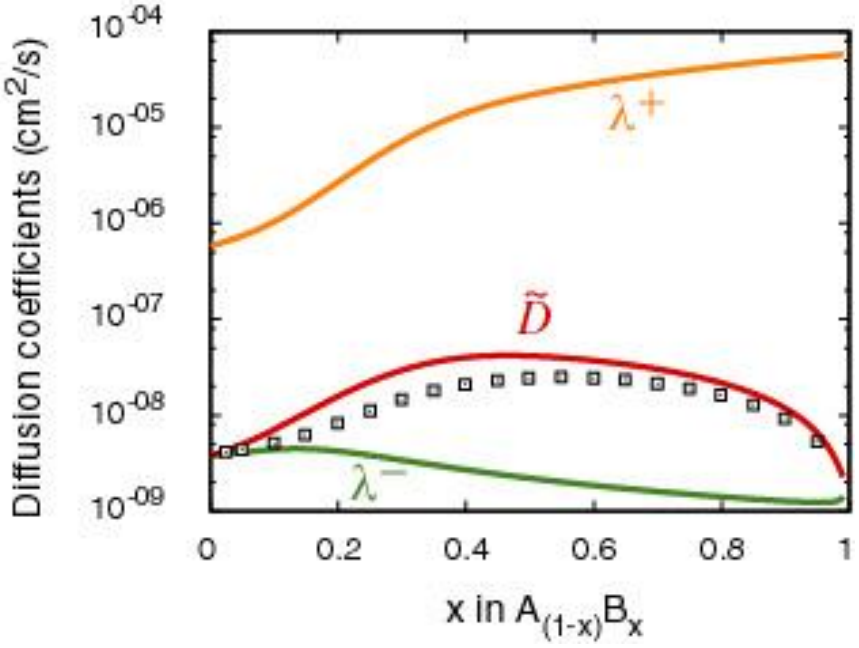
Comparisons of different treatments

Random alloy

$\Gamma_B = 10 \times \Gamma_A$



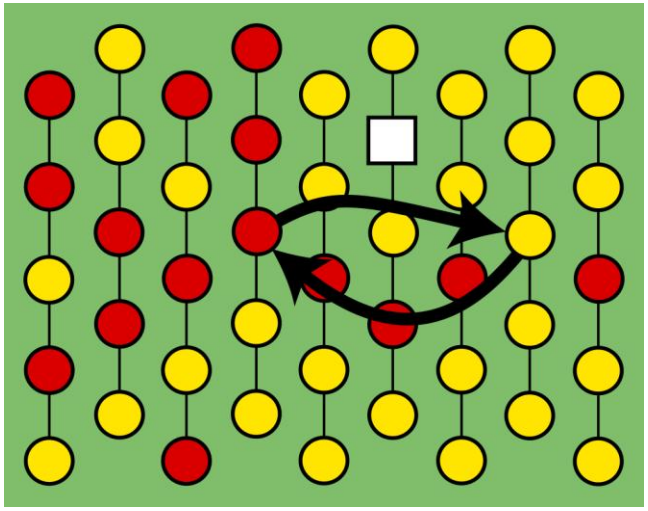
$\Gamma_B = 100 \times \Gamma_A$

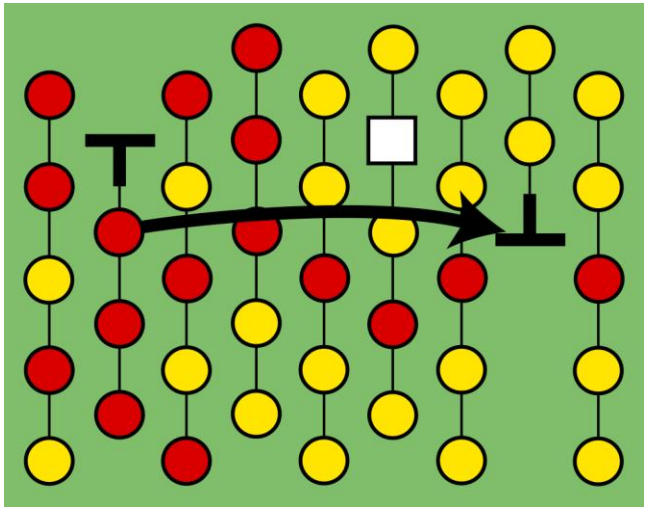


Physical difference between $\tilde{D}$ and λ^-

Perfect crystal

Plenty of vacancy sources and sinks

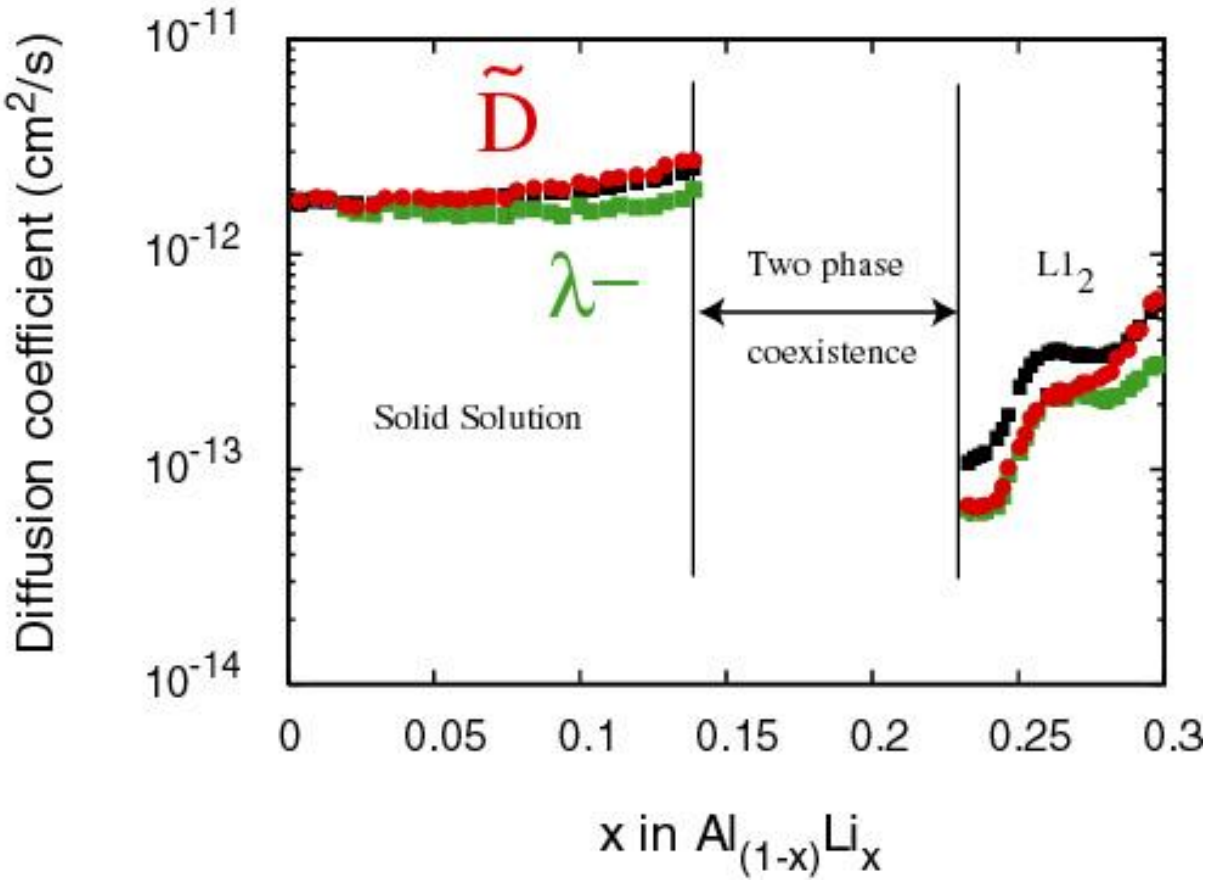


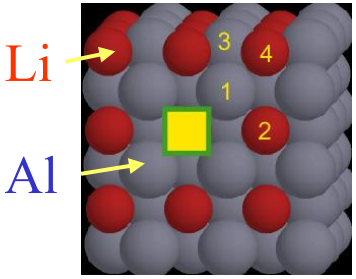


λ^-

$\tilde{D}$

Calculated interdiffusion coefficient





A. Van der Ven, G. Ceder, Phys. Rev. Lett. **94**, 045901 (2005).

Conclusion

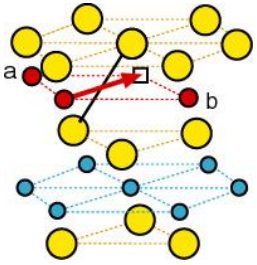
- First-principles methods can be used to comprehensively characterize diffusion in interstitial and substitutional alloys
- The role of vacancy sources and sinks needs to be further investigated (both theoretically as well as experimentally)

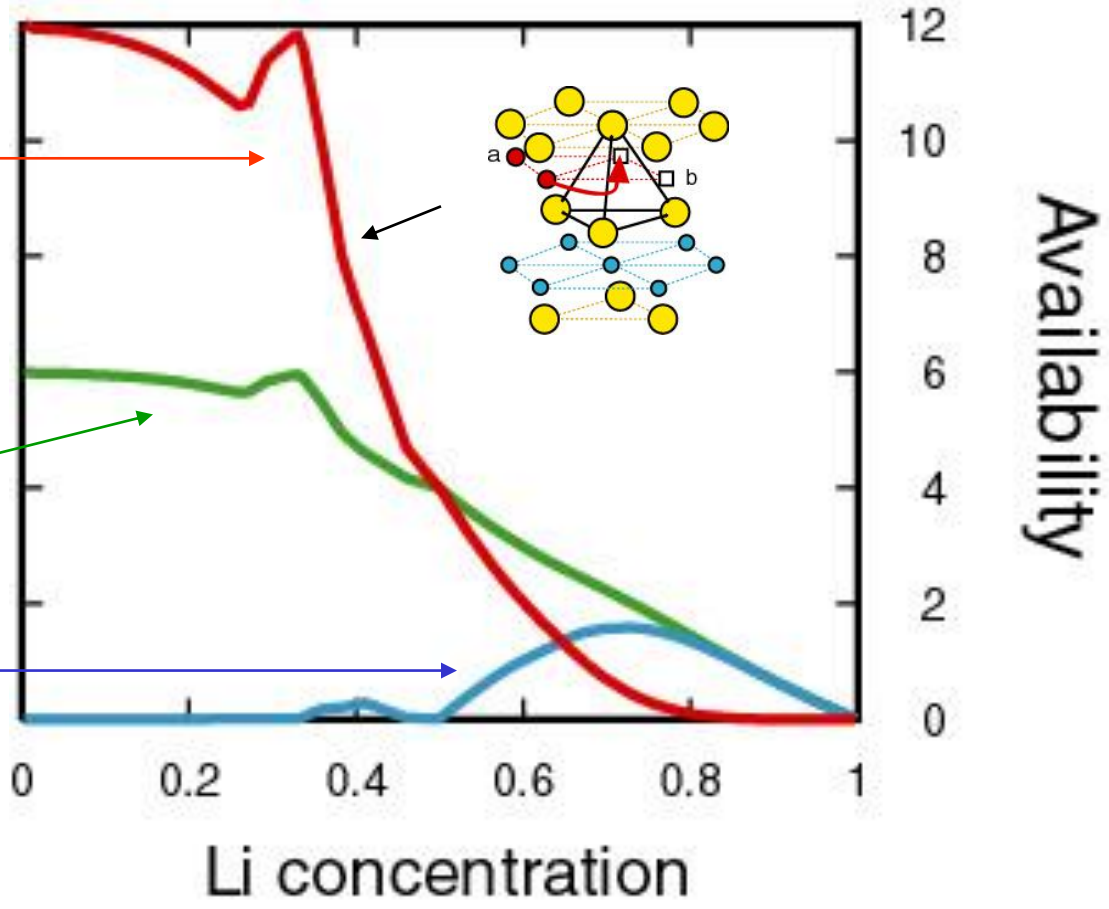
Available migration mechanisms for each lithium ion

Channels into a divacancy

Number of vacancies around lithium

Channels into isolated vacancies





Diffusion occurs with a divacancy mechanism