SYMULACYJNE MODELOWANIE PROCESÓW DYFUZYJNYCH

P. Sowa, J. Betlej, A. Biborski, M. Kozłowski, R. Kozubski

**M. Smoluchowski Institute of Physics,
Jagellonian University in Krakow, Poland**

E.V. Levchenko, A.V. Evteev, I.V. Belova, G.E. Murch

**School of Engineering, The University of Newcastle,
Callaghan, Australia**

B. Sepiol

Faculty of Physics, Vienna University, Austria

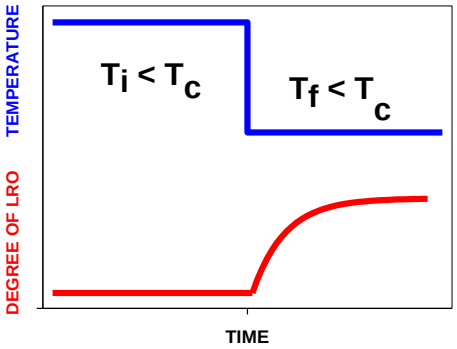
Support is acknowledged from the COST Action MP0903 NANOALLOY, the European Community's Seventh Framework Programme (FP7-PEOPLE-2013-IRSES) under EC-GA no. 612552 and from the funds of the Polish Ministry of Science and High Education (Grant no. 3135/7. PR/2014/2).
Access to the computation facilities at the ACK Cyfronet AGH, Krakow (supercomputer "Zeus") is greatly appreciated. The authors are also grateful to Dr. Lukasz Zosiak for the valuable assistance at the numerical calculations.

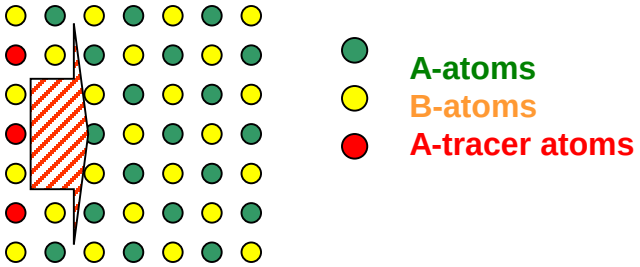
OUTLINE:

- ATOMIC-MIGRATION-CONTROLLED PHENOMENA IN SOLIDS
- EXPERIMENTAL RESULTS on self-diffusion and „order-order" kinetics in intermetallics: thermodynamic activation energies $E_A^{(D)}$ and $E_A^{(O-O)}$
  - fcc intermetallics (Ni_3Al)
  - bcc intermetallics (NiAl)
- MONTE CARLO ATOMISTIC SIMULATION of self-diffusion and „order-order" kinetics:
  - Methodology: (i) model, (ii) SGCMC: vacancy thermodynamics, (iii) KMC: vacancy-mediated atomic migration.
  - Results: thermodynamic activation energies
- ORIGIN OF $E_A^{(D)} > E_A^{(O-O)}$: elucidation in terms of thermal activation of elementary atomic jumps

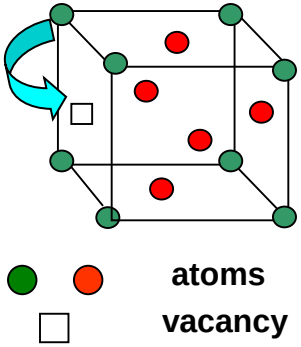
„ORDER-ORDER” AND DIFFUSION

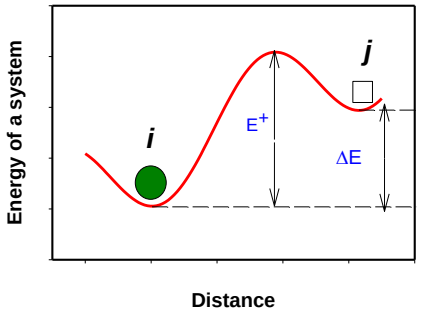
in intermetallics





COMMON ELEMENTARY MECHANISM:
atomic jumps to vacancies





SPECIFIC FEATURES: correlation of atomic jumps

Minimisation of the energetic cost of local LRO perturbation by jumping atoms:

„six-jump-cycle”, ASB, triple defect mechanism, antisite diffusion etc.

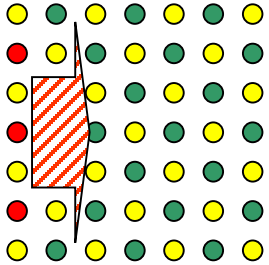
Formation of equilibrium atomic configuration:

generation/elimination of antisite defects

CONSEQUENCE: COMPLEMENTARY INSIGHT INTO ATOMIC JUMP DYNAMICS

TYPES OF DIFFUSION

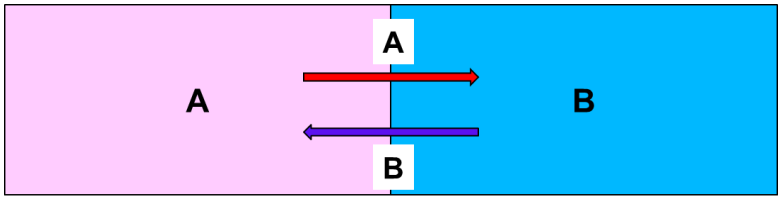
Self- (tracer) diffusion



A-atoms
B-atoms
A-tracer atoms

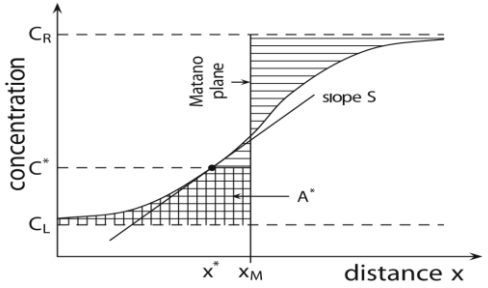
$$J_A = -D_A \times \frac{\delta C_A}{\delta x} \qquad D_A = \lim_{t\to\infty}\left[\frac{1}{6}\frac{\partial}{\partial t}\left(\langle R_A^2(t)\rangle\right)\right]$$

Interdiffusion



$$J_{A(B)} = -\widetilde{D} \times \frac{\delta C_{A(B)}}{\delta x}$$

$\widetilde{D}$ may be evaluated by analysing the concentration profile in the diffusion couple (Boltzmann-Matano analysis)



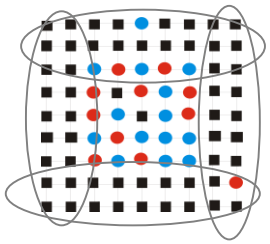
Any process controlled by (vacancy-mediated) atomic migration may be modelled by means of atomistic simulations:

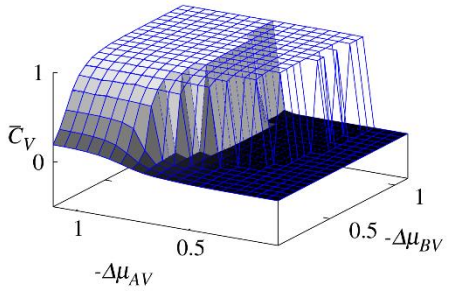
- Monte Carlo – long time-scales covered
- Molecular Dynamics – only short time-scales covered

Semi Grand Canonical Monte Carlo (SGCMC):

Fast determination of equilibrium parameters (atomic configuration, defect (vacancy) concentration

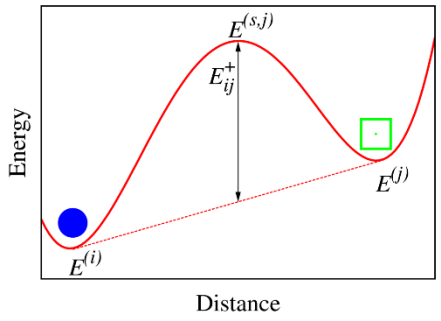
$$\Pi_{p\to q} = \min\left\{1, \exp\left[-\frac{\Delta E_{p\to q} - \left(\Delta\mu_{qV} - \Delta\mu_{pV}\right)}{k_B T}\right]\right\}$$





Kinetic Monte Carlo (KMC):

Combined with SGCMC enables simulation of steady-state atomic migration (at equlibrium configuration and vacancy concentration) with particular (e.g. vacancy) mechanism



$$P_{i\to j} = \frac{\tau \times \exp\left[-\frac{E_{ij}^{(s)}}{k_B T}\right]}{\sum_{ij} \exp\left[-\frac{E_{ij}^{(s)}}{k_B T}\right]}$$

$$\Delta t = \tau \times \left(\sum_{ij} \exp\left[-\frac{E_{ij}^{(s)}}{k_B T}\right]\right)^{-1}$$

DIRECT KMC SIMULATION RESULT:

$w_{\mu\to\nu}^{(X)}$ ⟵ **frequency of X-atom jumps from μ -sublattice to vacancies on ν-sublattice**

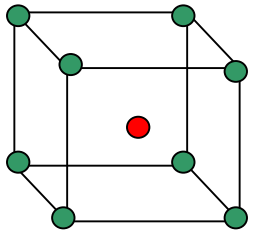
Interpretation:

$$w_{\alpha\to\beta}^{(A)}(t,T) = 8\times\Pi_0\times N_A\times C_A^{(\alpha)}(t,T)\times p_{AV}^{(\alpha\beta)}(t,T)\times exp\left[-\frac{\langle\left(E_{A,i(\alpha)\to j(\beta)}^{(m)}\right)(t,T)\rangle}{k_BT}\right]$$

$$T < T_C$$

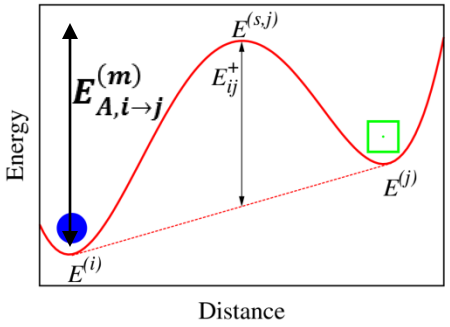
$$C_A^{(\beta)}(T,t) = \left[C_A^{(\beta)}\right]_0\times exp\left[-\frac{E_{F,A}^{(ant)}(t)}{k_BT}\right]$$

$$p_{AV}^{(\beta\alpha)}(t,T)\times exp\left[-\frac{\left(E_{A,i(\beta)\to j(\alpha)}^{(m)}\right)(t)}{k_BT}\right]\sim exp\left[-\frac{E_A^{(m,eff)}}{k_BT}\right]$$



● α sublattice

● β sublattice

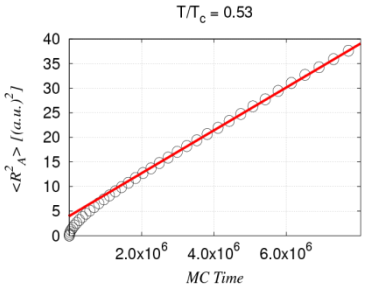


H. Bakker in: Diffusion in Crystalline Solids,
G.E. Murch, A.S. Nowick (ed.), Academic, 1984

Self-diffusion

Measured at $C_{A(B)}^{(\beta(\alpha))}$ = const

$$w_{\alpha\to\beta}^{(A)}(T) = w_{\beta\to\alpha}^{(A)}(T) = w_{eq}^{(A)}(T)$$



$$D_X = \lim_{t\to\infty}\left[\frac{1}{6}\frac{\partial}{\partial t}\left(\left\langle R_X^2(t)\right\rangle\right)\right]$$

$$D_A(T) = \frac{a^2}{3N_A} \times w_{eq}^{(A)}(T) \times f_A^{(corr)}(T)$$

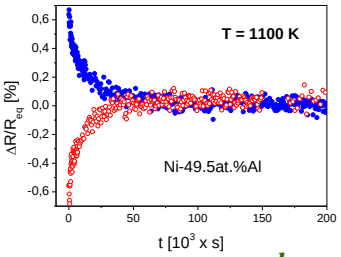
$$D_{A(B)}(T) = D_0 \times exp\left[-\frac{E_A^{(D,A(B))}(T)}{k_B T}\right]$$

$$w_{\alpha\to\beta}^{(A)}(t,T) = \left[w_{\alpha\to\beta}^{(A)}\right]_0 \times exp\left[-\frac{\left\langle\left(E_{A,i(\alpha)\to j(\beta)}^{(m)}\right)(t,T)\right\rangle}{k_B T}\right]$$

$$f_{A(B)}^{(corr)}(T) = \left[f_{A(B)}^{(corr)}\right]_0 \times exp\left[-\frac{E_{A(B)}^{(corr)}}{k_B T}\right]$$

$$E_A^{(D,A(B))} = \left\langle\left(E_{A,i(\alpha)\to j(\beta)}^{(m)}\right)(t,T)\right\rangle + E_{A(B)}^{(corr)}$$

„Order-order" relaxation



Definition of the relaxation time τ

$$\frac{\eta(t,T)-\eta(t\to\infty,T)}{\Delta\eta_{tot}} = exp\left[-\frac{t}{\tau(T)}\right]$$

$$\frac{d\eta}{dt}(t,T) = -\frac{1}{\tau(T)} \times [\eta(t,T) - \eta(t\to\infty,T)]$$

Atomistically:

$$\frac{dC_A^{(\beta)}}{dt}(t,T) = -\frac{d\eta_A}{2dt}(t,T) = \frac{1}{N_A}\left[w_{\alpha\to\beta}^{(A)}(t,T) - w_{\beta\to\alpha}^{(A)}(t,T)\right]$$

$$\frac{1}{\tau_A(T)} = \frac{1}{2N_A} \times \frac{w_{\alpha\to\beta}^{(A)}(t,T) - w_{\beta\to\alpha}^{(A)}(t,T)}{C_A^{(\beta)}(t\to\infty,T) - C_A^{(\beta)}(t,T)}$$

$$\tau(T)^{-1} = \tau_0^{-1} \times exp\left[-\frac{E_A^{(O-O)}(T)}{k_B T}\right]$$

$$\left[w_{\alpha\to\beta}^{(A)}(t,T) - w_{\beta\to\alpha}^{(A)}(t,T)\right] \approx \left[\Delta w_{\alpha\to\beta}^{(A)}\right]_0 \times exp\left[-\frac{E_{A(B)}^{(eff,dis)}}{k_B T}\right]$$

$$\left[C_{A(B)}^{(\beta(\alpha))}(t\to\infty,T) - C_{A(B)}^{(\beta(\alpha))}(t_0,T)\right] \approx \left[\Delta C_{A(B)}^{(\beta(\alpha))}\right]_0 \times exp\left[-\frac{E_{F,A(B)}^{\prime(ant)}}{k_B T}\right]$$

$$E_A^{(O-O,A(B))} = E_{A(B)}^{(eff,dis)} - E_{F,A(B)}^{\prime(ant)}$$

Elucidable topics

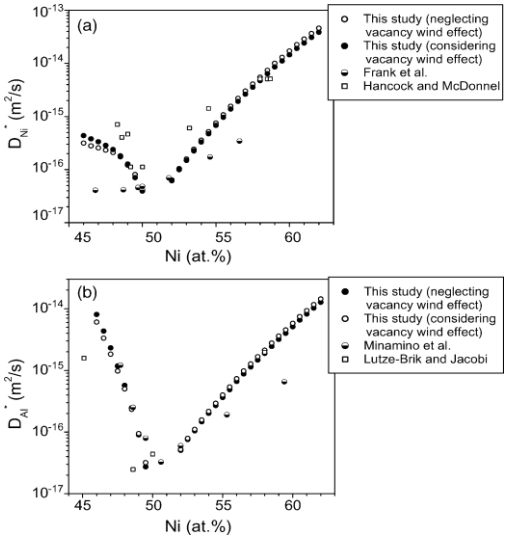
- **Interrelation diffusion – relaxations**

Example: $E_A^{(D)} > E_A^{(O-O)}$ **in Ni-Al**

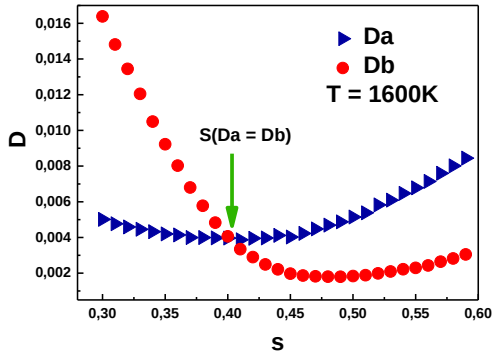
P.Sowa et al. Philos.Mag. 2017

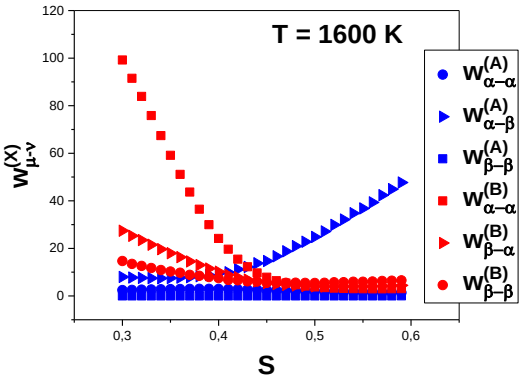
- **Features of self-diffusion**

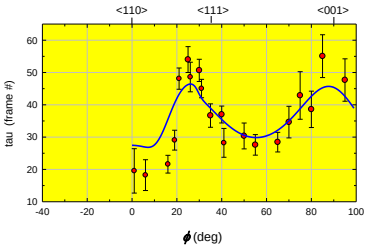
Example:



Ni-Al







Single atom jump determined with XPCS - (100) NNN jumps

THANK YOU FOR YOUR ATTENTION