SIMULATION METHODS IN CONFIGURATIONAL THERMODYNAMICS

Rafał Kozubski

Institute of Physics
Jagellonian University
Krakow, Poland

- **MONTE CARLO**
- **Molecular Dynamics**
- **Phase Field Method**

Monte Carlo methods are a widely used class of computational algorithms for simulating the behavior of various physical and mathematical systems. They are distinguished from other simulation methods (such as molecular dynamics) by being stochastic, that is nondeterministic in some manner - usually by using random numbers (or more often pseudo-random numbers) - as opposed to deterministic algorithms. Because of the repetition of algorithms and the large number of calculations involved, Monte Carlo is a method suited to calculation using a computer, utilizing many techniques of computer simulation.

Statistical Physics dealing with macroscopic systems often composed of a number of components comparable to Avogadro's number appeared an important beneficient of new computer facilities.

A macrosystem may be found in one of its *macroscopic* states determined by particular *microscopic* states $\{\sigma\}$ of all the components and classically represented by points in a 6N-dimensional phase space (N is the number of system components).

The macroscopic states characterised by macroscopic parameters (observables *A*) such as energy, volume, degree of chemical order, magnetisation etc. are usually highly degenerate with respect to the microscopic ones $\{\sigma\}$. The values of observables *A* measured in particular conditions (temperature, pressure, external field etc.) are identified with corresponding averages $\langle A \rangle$ over all microscopic states $\{\sigma\}$ in which the system may be found in this conditions.

The central problem of statistical physics (statistical thermodynamics) is a calculation of the values of <A>. The averaging is performed over an appropriate ensemble of macroscopic systems representing the related microscopic states. An ensemble is characterised by so called density $\rho(\sigma)$ defined in the way that

$$P(\sigma) = \frac{\rho(\sigma)}{\sum_{\sigma} \rho(\sigma)}$$

is a probability that a system in the ensemble is in the microscopic state σ (see e.g. Huang, 1963).

The principle achievement of the founders of statistical physics was the derivation of formulae for the densities $\rho_{eq}(\sigma)$ corresponding to ensembles of systems in equilibrium state.

Complete description of the system thermodynamics is derivable from the sum

$$Z = \sum_{\sigma} \rho_{eq}(\sigma)$$

called a partition function

Type of ensemble	Usage	Density function ρ_{eq}, H denotes Hamiltonian of the system
Microcanonical ensemble	Isolated systems with fixed energy E	$\delta_{H(\{\sigma_i\}),E}$
Canonical ensemble	Systems with fixed volume V and number of particles N studied at fixed temperature T determined by thermal bath	$\exp\left[-\frac{H(\{\sigma_i\})}{k_B T}\right]$
Isothermal-Isobaric ensemble	Systems with fixed number of particles N studied at fixed pressure P and temperature T determined by thermal bath	$\exp\left[-\frac{H(\{\sigma_i\})+PV}{k_B T}\right]$
Grand Canonical ensemble	Opened systems with fixed volume V studied at fixed temperature T determined by thermal bath	$\exp\left[-\frac{H(\{\sigma_i\})+\sum_k N_k \mu_k(\{\sigma_i\})}{k_B T}\right]$ μ_k – chemical potential

SAMPLING

If $A(\sigma)$ denotes the value of the observable A in the microscopic state σ then:

$$\langle A \rangle = \sum_{\sigma} \left[P(\sigma) \times A(\sigma) \right] = \frac{1}{Z} \sum_{\sigma} \left[\rho(\sigma) \times A(\sigma) \right] \qquad \star$$

where the sum covers all possible microscopic states σ (whose number is most often extremely large or even infinite) and its strict calculation is usually unfeasible. The basic idea is to approximate the complete sum (★) by a partial one performed over some subset $\{\sigma_i,\ i = 1, \ldots, M\}$ of the microscopic states σ

$$\langle A \rangle \approx \frac{\sum_{i=1}^{M} \left[\rho(\sigma_i) \times A(\sigma_i) \right]}{\sum_{k=1}^{M} \rho(\sigma_k)} \qquad \star\star$$

Simple sampling: the random choice of the states σ_i runs according to a uniform distribution. **Drawback**: many σ_i states may correspond to the low value of the density ρ making the approximation poor.

Importance sampling: the states σ_i are randomly chosen with a non-uniform distribution $\Pi(\sigma)$:

$$\langle A \rangle \approx \frac{\sum_{i=}^{M}\left[\rho(\sigma_i)\times A(\sigma_i)\times \Pi^{-}(\sigma_i)\right]}{\sum_{k=}^{M}\left[\rho(\sigma_k)\times \Pi^{-}(\sigma_k)\right]}$$

If $\Pi(\sigma)=P(\sigma)=\dfrac{\rho(\sigma)}{\sum_{\sigma}\rho(\sigma)}$ then $\langle A \rangle = \dfrac{1}{M}\sum_{i=1}^{M} A(\sigma_i)$

Problem: how to generate a set of microstates with the desired distribution ??

Markov chains as a tool for importance sampling

Probability that an event y_n occurs at a time t_n in condition that events y_1, y_2,....occured at times t_1, t_2,...

$$\Rightarrow \quad P_{1|n-1}\left(y_n, t_n \middle| y_1, t_1; \ldots\ldots y_{n-1}, t_{n-1}\right)$$

Markov chain of events:

$$P_{1|n-1}\left(y_n, t_n \middle| y_1, t_1; \ldots\ldots y_{n-1}, t_{n-1}\right) = P_{1|1}\left(y_n, t_n \middle| y_{n-1}, t_{n-1}\right)$$

If states of the systems in an ensemble change due to Markov processes, the time evolution of the probability distribution $P(\sigma)$ is given by a **Master equation:**

$$\frac{dP(\sigma_i)}{dt} = -\sum_j W(\sigma_i \to \sigma_j) \times P(\sigma_i) + \sum_j W(\sigma_j \to \sigma_i) \times P(\sigma_j)$$

The evolution leads to a stationary distribution $P_{st}(\sigma)$: $\frac{dP_{st}(\sigma_i)}{dt} = 0$

provided that:

$$\sum_j W(\sigma_i \to \sigma_j) \times P_{st}(\sigma_i) = \sum_j W(\sigma_j \to \sigma_i) \times P_{st}(\sigma_j)$$

hence:

$$\frac{W(\sigma_i \to \sigma_j)}{W(\sigma_j \to \sigma_i)} = \frac{P_{eq}(\sigma_j)}{P_{eq}(\sigma_i)} = \frac{\rho_{eq}(\sigma_j)}{\rho_{eq}(\sigma_i)}$$

← Detailed balace condition for transition frequencies W

The detailed balance guarantees a convergence of a Markov chain to $P_{eq}(\sigma)$.

Simulation of Markov chains is a typical task realised by means of Monte Carlo algorithms:

Stochastics is digitally simulated by random number generators – i.e. computer codes generating with a uniform probability numbers from a fixed interval (most often $\langle 0,1 \rangle$).

Basic idea:

- Let a certain event occur in reality with a probability P
- Random number $R \in \langle 0,1 \rangle$ is generated
- The event occurs in Monte Carlo simulation if $R \in \langle 0,P \rangle$

The Monte Carlo method may be basically applied to diverse kinds of problems in statistical physics:

- *Simulation and characterisation of system properties in thermodynamic equilibrium:*

The procedure starts from a system in some (arbitrary) initial state. Subsequently, an evolution of the system is simulated as a Markov chain of microscopic states σ_i with the transition frequencies $W(\sigma_i \rightarrow \sigma_j)$ obeying detailed balance corresponding to the particular conditions of the equilibrium state in question. The applied algorithm must enable to follow the evolution of some macroscopic parameter of the system (for example ist energy), so that it is possible to observe the approach of equilibrium (microscopic states are in dynamical equilibrium with the distribution $P_{eq}(\sigma)$). Once this stage is attained, the microscopic states σ_i of the system appearing at particular time moments may be randomly sampled and used in the averaging procedure (effectively, time averaging is done).

Example:

$$F = U - T \times S$$

$$U = \frac{1}{M}\sum_{i=1}^{M} E(\sigma_i)$$

$$S = -k_B \sum_{i} P(\sigma_i) \times \ln\left[P(\sigma_i)\right]$$

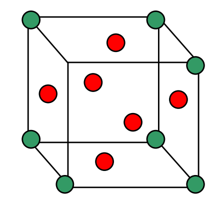
$P(\sigma_i)$ is the probability for the occurrence of the microstate σ_i.

● *Simulation of relaxation processes towards equilibrium:*

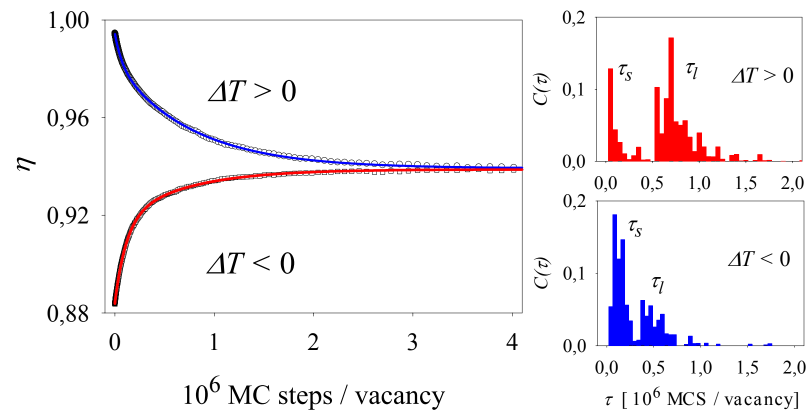
The Master equation basically can be regarded as describing relaxation and migration processes. The Monte Carlo method becomes, therefore, a natural tool for simulating such processes. Instead of sampling the microscopic states σ_i after the saturation of the particular Markov chain one now simulates and observes an ensemble of independent parallel Markov chains and performs the averaging of the observable of interest over all of them at particular consecutive time moments also before the saturation. In this way the time evolution (relaxation) $\langle A\rangle(t)$ of the observable is obtained. Since for a unique choice of transition rates, the condition of detailed balance is not sufficient, the treatment of such problems is, however, sophisticated, involving a number of problems including e.g. the relationship between the computer and real time scales. In general, the relaxation path towards equilibrium can sensitively depend on the particular physical model for the transition rates.

„ORDER-ORDER" RELAXATION

A_3B (Ni_3Al)



Example



● *Simulation of non-equilibrium processes and transport phenomena*

Such processes, as consisting of effective transitions between microscopic states constitute a natural object for studies by means of MC methods. Non equilibrium character of the phenomenon means that detailed balance must no longer be obeyed by the transition frequencies which are to model particular microscopic reactions involved in the process.

Examples:

Crystal growth according to the Kossel model. In this model three atomistic-scale processes: deposition, evaporation and diffusion compete. Particular frequency (rate) is modelled and attributed to each process and its selective influence on the overall effect (e.g. crystal growth rate) may then be studied by means of MC.

Transport phenomena may be studied by means of MC both in stationary and non-stationary states of the systems simply by monitoring the process of transport during the simulated Markov chain. The standard method consists of monitoring mean-squared displacement $R^2_{A(V)}(t)$ of a tracer atom (A)/vacancy (V) as a function of MC time.

Vacancy/tracer diffusion constant $D_{V(A)}$:

$$D_{V(A)} = \lim_{t\to\infty}\left[\frac{1}{6N_{V(A)}}\frac{\partial}{\partial t}\left(\sum_{V(A)} R^2_{V(A)}(t)\right)\right]$$

Correlation factor for atoms *A*

$$f_A = \frac{\left\langle R_A^2(n_A)\right\rangle}{a^2 \times n_A}$$

Limitations:

Thermodynamic laws correspond in statistical physics to the thermodynamic limit $N \to \infty$, where N denotes the number of particles in the system. It is obvious that when numerically simulating a system, one always operates with a finite value of N.

The "simplest" task aiming in the elimination of the parasitic influence of the sample limits on the simulated effects is usually realised by the application of periodic boundary conditions consisting of the consideration of the opposite sample boundaries as neighbouring parts. The well-known two-dimensional analogue of this idea is a transformation of a plane into a torus.

Despite compensating the boundary (surface) effects, periodic boundary conditions cannot remove the finite-size-caused limitation in the consideration of any distance-dependencies. This applies e.g. to correlation lengths ξ (which cannot exceed the sample size) and results in characteristic blunting (rounding) of singularities marking continuous and discontinuous phase transitions.

Numerical implementation of MC

(choice of transition frequencies $W(\sigma_i \to \sigma_j)$)

Classical approach

(Metropolis, N., Rosenbluth, A.W., Rosenbluth, N.N., Teller, A.H., and Teller, E. (1953), *J.Chem.Phys.* 21, 1087)

$$W(\sigma_i \to \sigma_j) = \begin{cases} \tau^{-1} \times \exp\left[-\frac{\Delta E}{k_B T}\right], & \Delta E > 0 \\ \tau^{-1}, & \Delta E < 0 \end{cases} \equiv \min\left\{\tau^{-1}, \tau^{-1} \times \exp\left[-\frac{\Delta E}{k_B T}\right]\right\}$$

$\Delta E = E_{fin} - E_{ini}$, system energy equals E_{ini} in the microstate σ_i and E_{fin} in the microstate σ_j;
k_B and T denote the Boltzmann constant and temperature, respectively and τ is a time scale constant

Although the Metropolis transition frequencies obviously fulfil the detailed balance their use may be disadvantageous at high temperatures, where due to the transition probabilities approaching the value of 1, the system being off equilibrium keeps oscillating between different microscopic states, which makes the simulated process not perfectly ergodic.

Glauber algorithm: (Glauber, R.J., (1963), *J.Math.Phys.* 4, 294)

$$W(\sigma_i \to \sigma_j) = (\tau)^{-1} \times \frac{\exp\left[-\frac{E_{fin}}{k_B T}\right]}{\exp\left[-\frac{E_{ini}}{k_B T}\right] + \exp\left[-\frac{E_{fin}}{k_B T}\right]} = (\tau)^{-1} \times \frac{\exp\left[-\frac{\Delta E}{k_B T}\right]}{1 + \exp\left[-\frac{\Delta E}{k_B T}\right]}$$

$$W(\sigma_i \to \sigma_j) \to \frac{1}{2\tau} \qquad (T \to \infty)$$

$$\forall \Delta E, \;\; W(\sigma_i \to \sigma_j) \le 1$$

Probabilistic rationale:

The probability of an event: "the system either transforms from σ_i to σ_j or remains in σ_i" is in this particular case equal to 1. On the other hand, it must be equal to a sum of the two corresponding probabilities.

The simulation algorithms involving the above formulae for $W(\sigma_i \rightarrow \sigma_j)$ work usually in the following cycles:

- The system is in some microscopic state σ_I
- Another microscopic state $\sigma_j \neq \sigma_i$ is chosen at random from the set $\{\sigma_j\}$
- Transition $\sigma_i \rightarrow \sigma_j$ is executed ***or suppressed*** according to the probability $\tau \times W(\sigma_i \rightarrow \sigma_j)$
- Time is incremented by τ

Drawback:

A number of MC steps are „lost" – no transition is executed

„Residence Time" algorithm:

The basic idea is instead of making a number of unsuccessfull attempts to perform a transition; one computes the (average) time for the system to stay in its microstate *i*, then performs one of the possible transitions with a choice, which respects the proper weights.

The algorithm works in the following steps:

- All possible transitions $\sigma_i \rightarrow \sigma_j$ between the microstates of the system are listed and numbered and their corresponding Metropolis frequencies

$$W_k = W(\sigma_i \rightarrow \sigma_j) = \tau^{-1} \times \exp\{-[E(\sigma_j) - E(\sigma_i)]/k_B T\}$$

are determined.

- Two random numbers R_1 and R_2 between 0 and 1 are generated

- The transition *k is chosen and executed (!)*, for which:

$$\sum_{i=1}^{k-1} \frac{W_i}{\sum_j W_j} < R_1 \leq \sum_{i=1}^{k} \frac{W_i}{\sum_j W_j}$$

- Time is incremented by: $\Delta t = -\frac{\ln R_2}{\sum_j W_j}$ ⟸ to be justified in the following

Problem of time scale

Interpretation of MC simulation results in terms of natural physical phenomena requires that the MC-time – i.e. the sequence of simulation steps, is related to real time.

A solution of the problem depends on the particular algorithm applied

Metropolis-type algorithms:

- In each MC step a number N of *possible* transitions $\sigma_i \rightarrow \sigma_j$ has to be determined.
- Each MC step is associated with time increment $\Delta t = \tau / N$

„Residence-time" algorithm

Let the system be in the microstate σ_i at $t = 0$ and let $P(t)$ be a probability that it **still remains** in this microstate at $t > 0$ (t is thus the residence time). If $\{W_i\}$ denote the frequencies of all possible transitions starting from σ_i the following differential equation holds:

$$\frac{d}{dt}P(t) = -\left(\sum_i W_i\right) \times P(t)$$

hence:

$$P(t) = C \times \exp\left[-\left(\sum_i W_i\right) \times t\right]$$

probability distribution for residence times with the normalisation factor $C = \sum_i W_i$.

and

$$\langle t \rangle = \frac{1}{\sum_i W_i}$$

The above is realised numerically by putting:

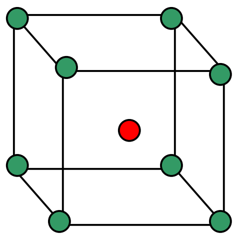
$$t = -\frac{\ln R_2}{\sum_j W_j}$$

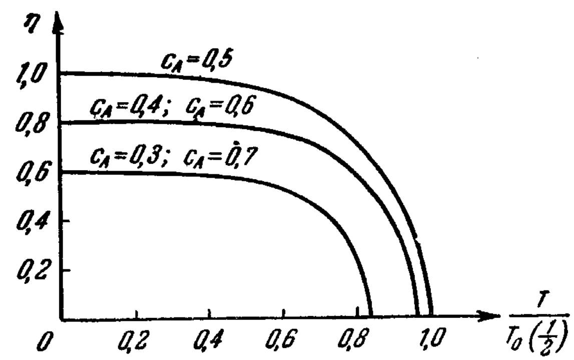
APPLICATION:

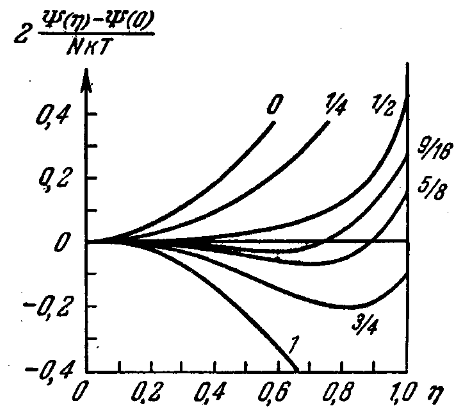
LONG-RANGE ORDERING IN INTERMETALLICS

„Order-disorder” phase transformations

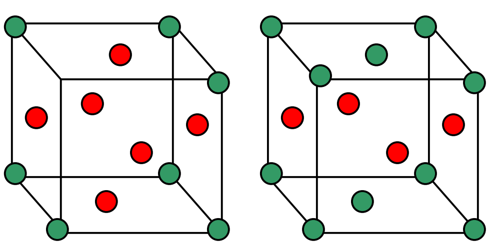
Continuous (2nd-order) transformation

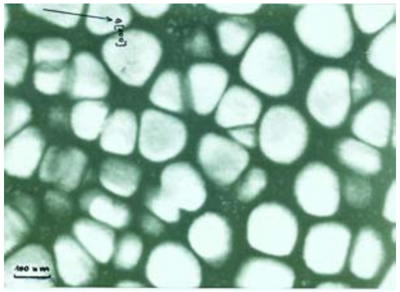


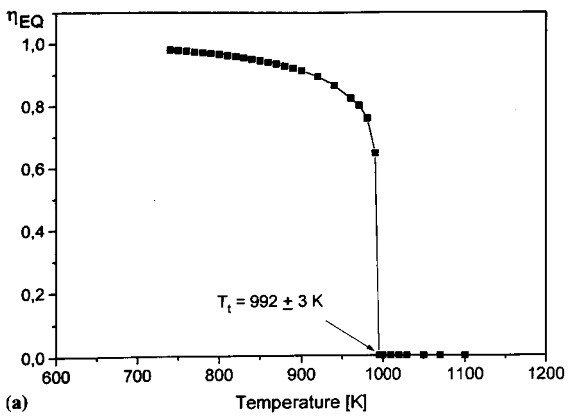


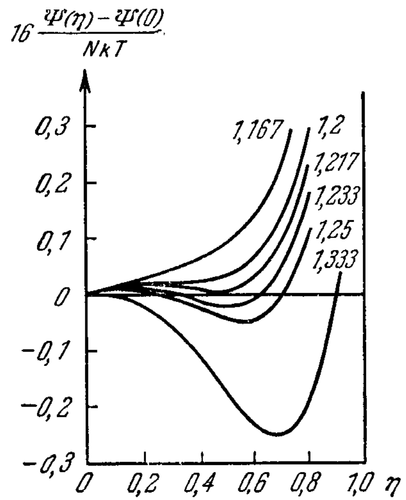


Discontinuous (1st-order) transformation



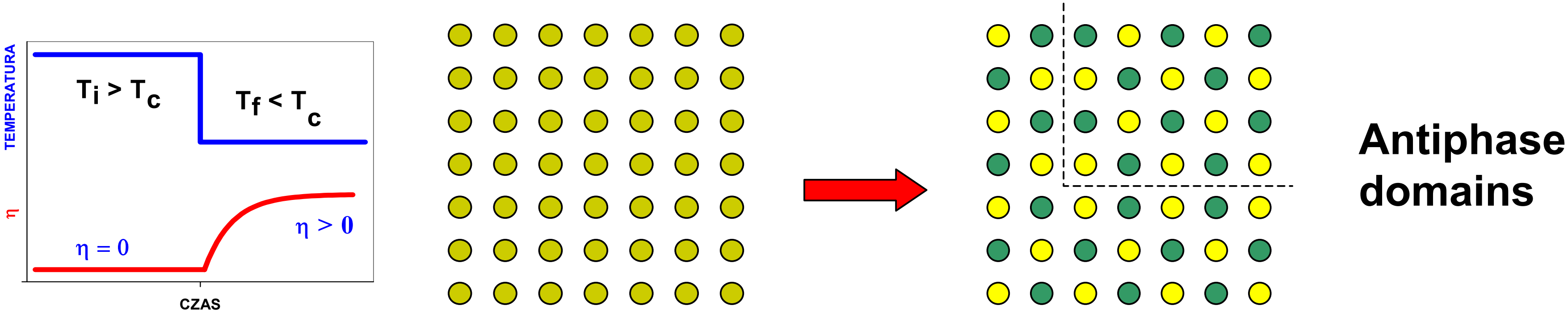




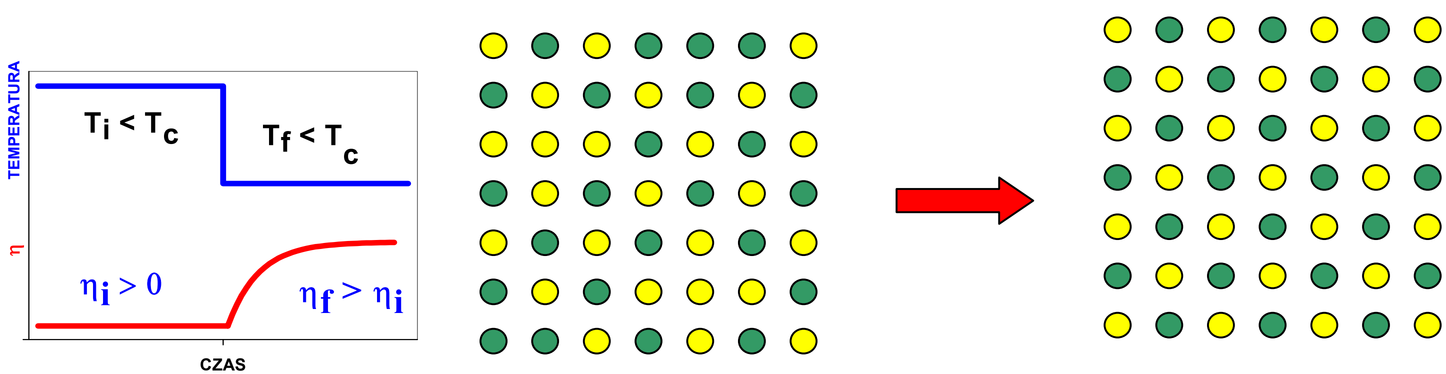


ORDERING KINETICS

- **„Order-disorder"** ***transformation***

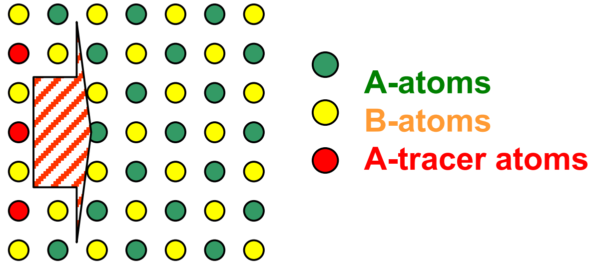


- **„Order-order"** ***process***

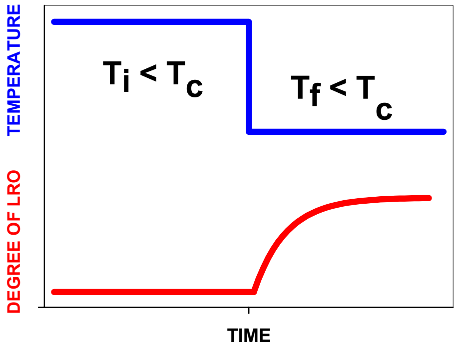


DIFFUSION AND „ORDER-ORDER”

in intermetallics

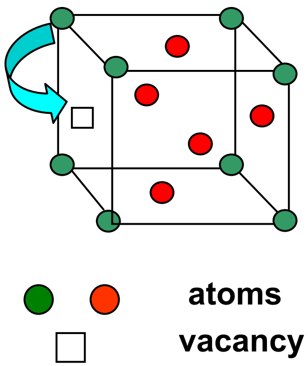


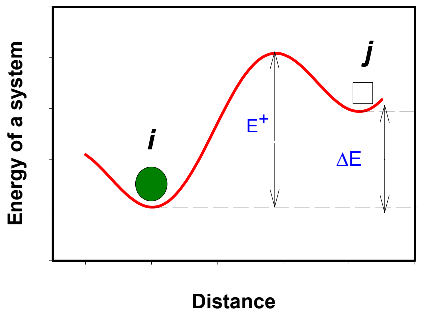
T = const, degree of LRO = const



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:

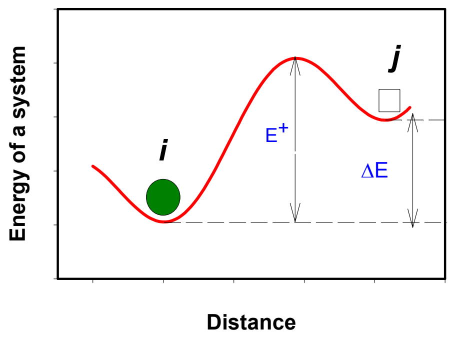
generation/elimination of antisite defects

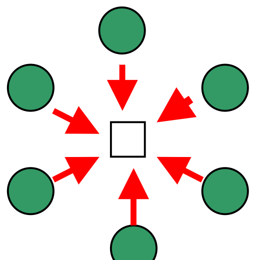
CONSEQUENCE: COMPLEMENTARY INSIGHT INTO ATOMIC JUMP DYNAMICS

MONTE CARLO SIMULATIONS:

- A_3B or AB binary system with $L1_2$, $L1_0$ or B2 superstructure,
- $40 \times 40 \times 40$ cubic cells,
- 1 vacancy (*10 vacancies in a piloting study*)

<u>general assumption</u>: vacancy mechanism of atomic migration





Glauber dynamics algorithm:

$$w_{i \to j} = \tau^{-1} \times \frac{\exp\left[-\frac{\Delta E}{kT}\right]}{1 + \exp\left[-\frac{\Delta E}{kT}\right]}$$

„Residence-time“ algorithm:

$$w_i = \Pi_0 \times \exp\left[-\frac{E_i^+ - E_i}{kT}\right]$$

$$\Pi_0 = \left[\sum_l \exp\left(-\frac{E_l^+ - E_l}{kT}\right)\right]^{-1}, \quad \langle \Delta t \rangle = \frac{\tau}{\Pi_0}$$

Kinetic Monte Carlo
KMC

Glauber algorithm:

- Random choice of an atom in the 1st co-ordination shell of the vacancy.
- Execution or rejection of its exchange with the vacancy - according to Glauber probabilities
- Repetition of the above steps for each vacancy in the system
- Increment of time by τ/Z, where Z is the 1st shell co-ordination number

Residence time algorithm:

- Metropolis transition frequencies w_i ($i = 1,\ldots,Z$) are calculated for all potential exchanges of a vacancy with atoms in 1st co-ordination shell,
- The exchange chosen at random according to the frequencies w_i is executed,
- Time is incremented either by $\Delta t = -\frac{\ln R}{\sum_j w_j}$ (by generating each time a random fraction R), or by an average $\langle \Delta t \rangle = \frac{1}{\sum_i w_i}$

Ising-type Hamiltonian:

pair interactions between nn and nnn atoms:

$$E_{Conf} = \sum_{i,k,r} N_{ik}^{(r)} V_{ik}(r)$$

Criteria for pair interaction energy evaluation:

- superstructure stability
- $V_{AA} = \alpha \times V_{BB}$
- no interaction with vacancies

Sources:

Ni_3Al:

DNS (experiment), P.Cenedese et al. J.Phys (France) 50 2193 (1989).

FePt:

CE („ab initio”), T. Mohri et al. Mater.Trans. 43 2104 (2002).

„Embedded Atom Method" (EAM) Hamiltonian

M.S.Daw, M.I.Baskes, *Phys.Rev.B* **29**, 6443, (1984).

The EAM system energy is given by:

$$E = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i \neq j} \varphi_{ij}(r_{ij})$$

where $F_i(\rho_i)$ denotes so-called embedding energy depending on the electron density ρ_i in the system *without* an atom *"i"* at a position *"i"* and $\varphi_{ij}(r_{ij})$ is a short-range pair-potential describing the repulsion between cores of *"i"* and *"j"* atoms occupying the positions *"i"* and *"j"* and separated by a distance r_{ij}.

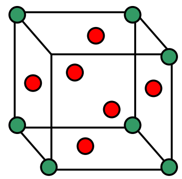
Parameters evaluated by fitting to experimental data – elaborated e.g. for Ni-Al.

Monitored parameters

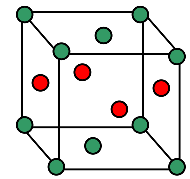
Atomic Configuration:

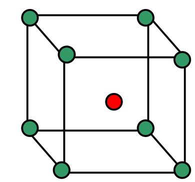
Bragg-Williams-type LRO parameter η:

$$\eta = 1 - \frac{N_A^{(B)}}{0.75 \times N^{(B)}}$$



$$\eta = 1 - \frac{N_A^{(B)}}{0.5 \times N^{(B)}}$$





where $N^{(B)}$ and $N_A^{(B)}$ denote the number of B-type sublattice sites and the number of A-antisites (A-atoms on the B-sublattice), respectively,

specific short-range order (SRO) –type parameters APC and NNCOR:

$$APC = \frac{N_{AB}^{(B)(A)}}{N_A^{(B)}}$$

$N_{AB}^{(B)(A)}$ denotes the number of nn pairs of A- and B-antisite atoms.

$$NNCOR_A = \frac{2 \times N_{AA}}{N_A}$$

N_{AA} denotes the number of nn pairs of A-atoms, N_A is the number of A-atoms

Atomic Migration:

“Jump-frequency” parameters:

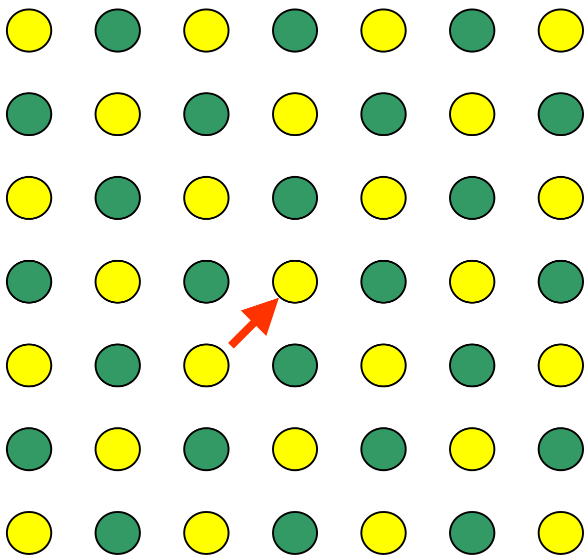
$$P_{A(B):i\rightarrow j} = \frac{N^{exec}_{A(B):i\rightarrow j}}{N_{att}}$$

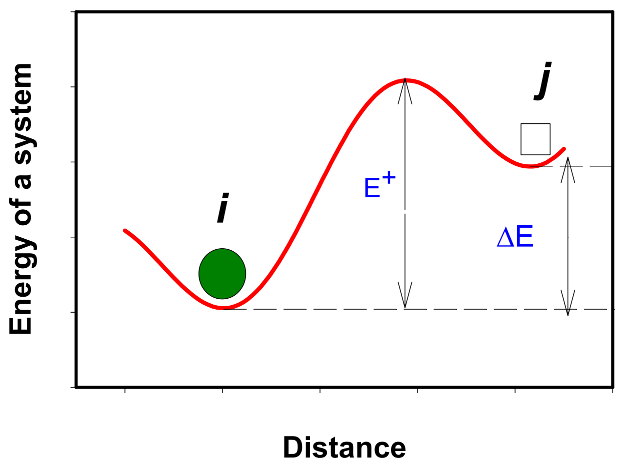
where:

$N^{exec}_{A(B):i\rightarrow j}$ denotes a number of A(B)-atom jumps from an “i”-type sublattice site to a nn vacancy residing on “j”-type sublattice *executed* within a fixed number of MC steps

N_{att} denotes the total number of *jump attempts* (executed and not executed) during the same MC-time period.

MOLECULAR STATICS – a tool for saddle-point energy evaluation



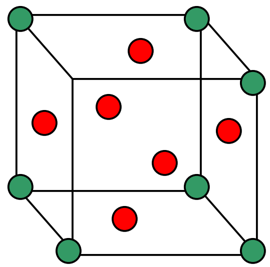


Assumption:

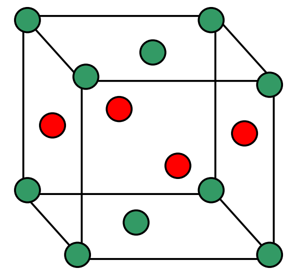
Structural relaxation occurs substantially faster than atomic migration

RESULTS

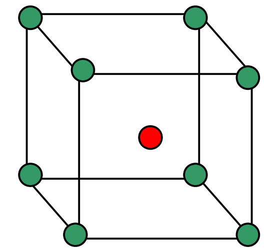
SUPERSTRUCTURE STABILITY



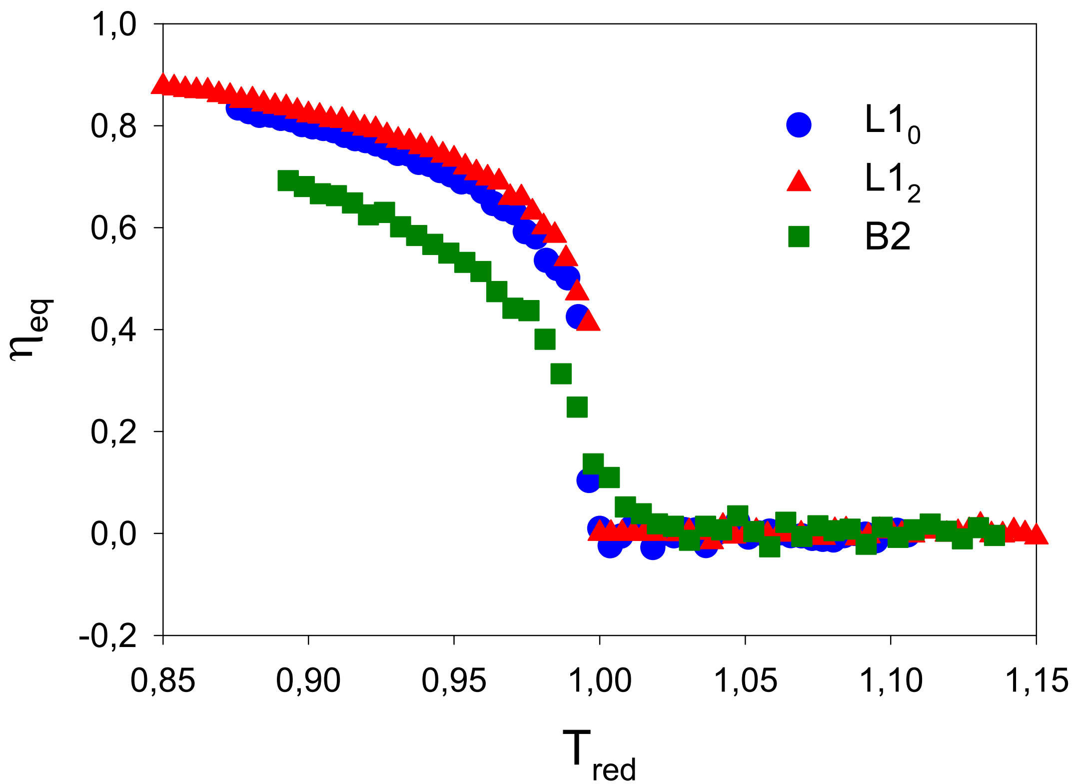
$L1_2$



$L1_0$



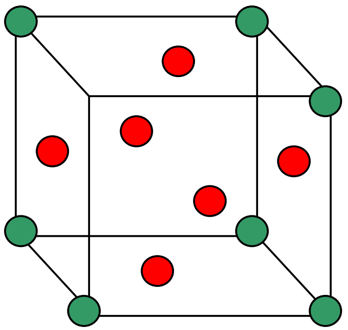
B2

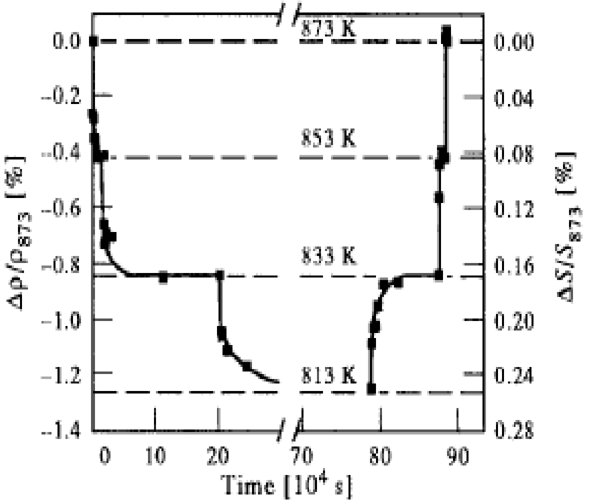


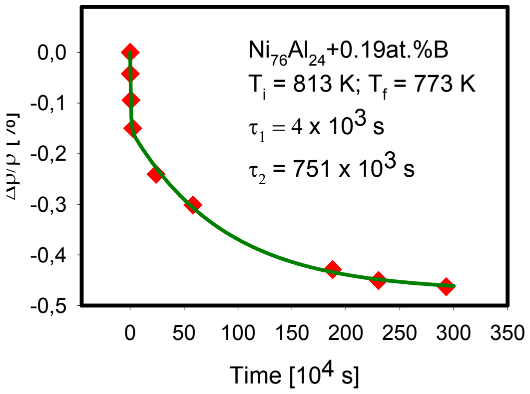
$$T_{red} = \frac{T}{T_{O-D}}$$

STRUCTURE OF „ORDER-ORDER" RELAXATIONS

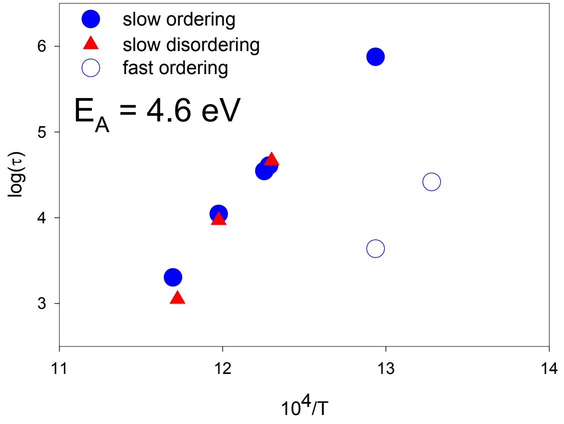
Ni_3Al (experiment):







Ni diffusion: E_A = 3 eV



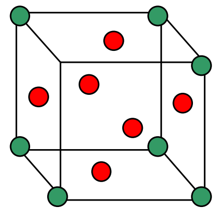
Two time scales showing up at 77 K only

R.Kozubski, *Prog.Mater.Sci.* **41**, 1, (1997).

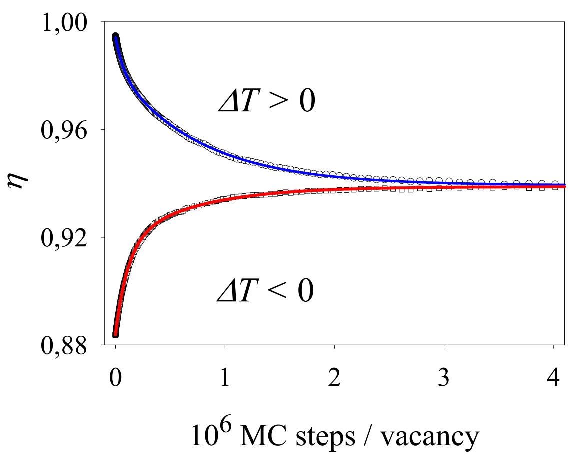
MC simulations:

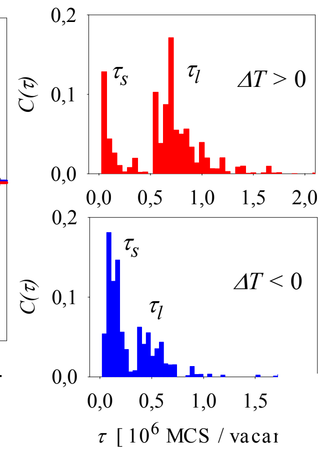
P. Oramus, R. Kozubski, V.Pierron-Bohnes, M.C.Cadeville, W.Pfeiler, *Phys.Rev.B* **63,** 174109, (2001).

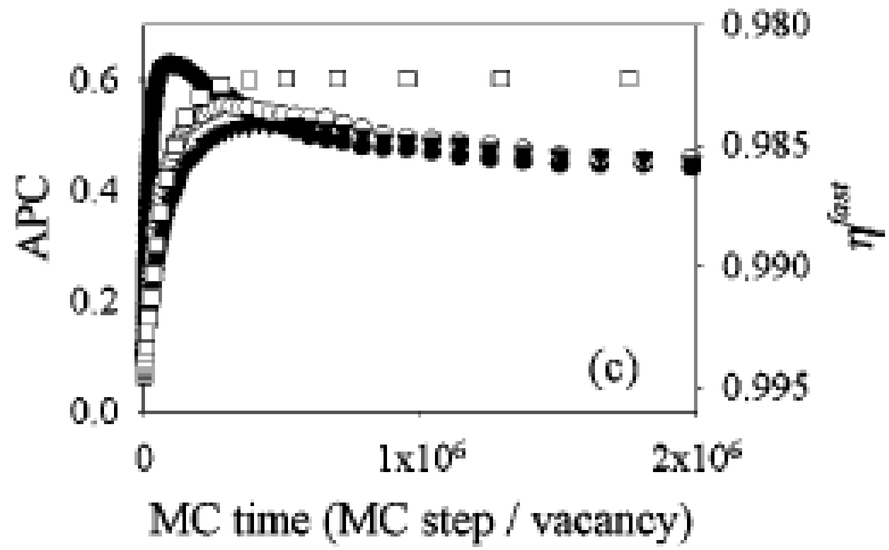
A_3B (Ni_3Al)



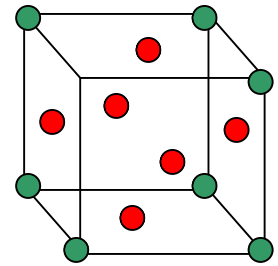
Laplace transforms

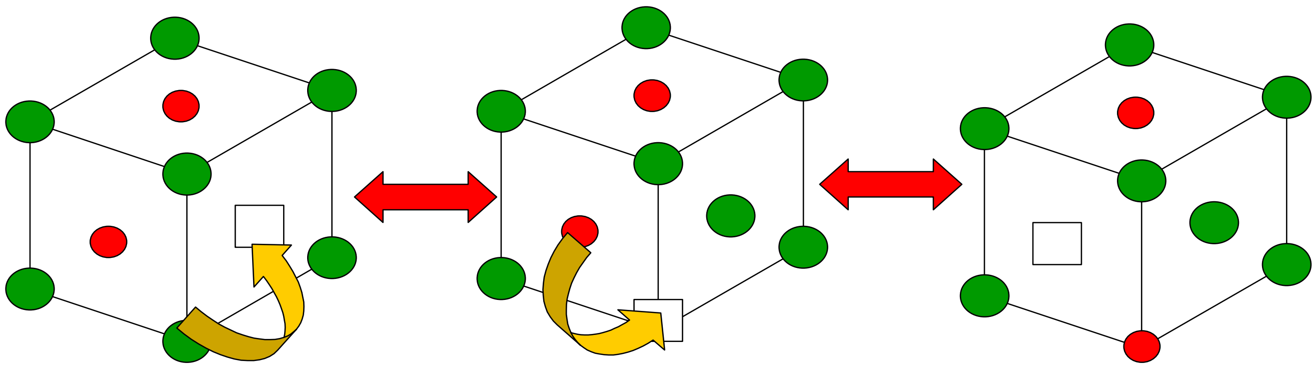




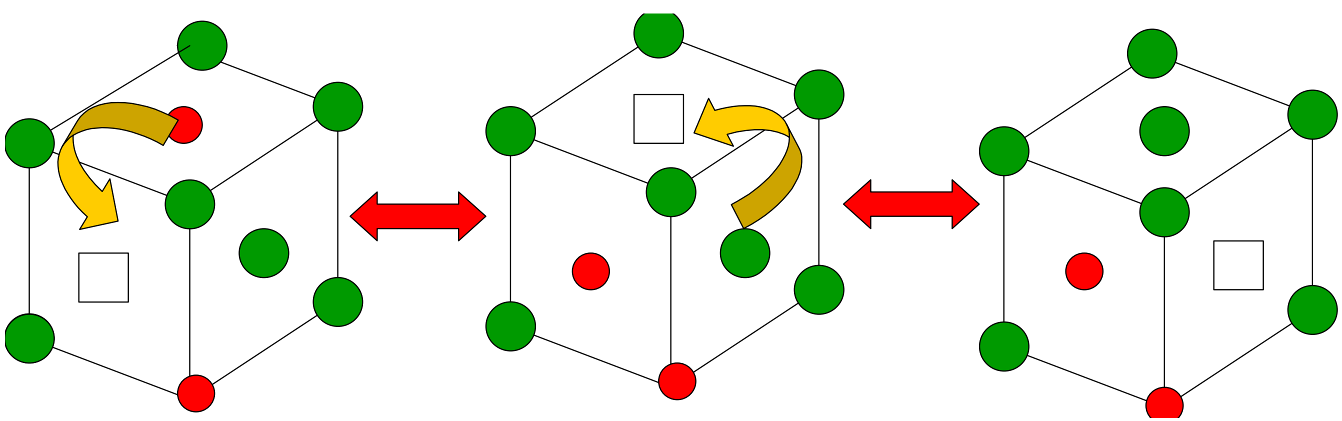


ORIGIN OF TWO TIME SCALES IN „ORDER-ORDER” KINETICS IN $L1_2$-ORDERED A_3B





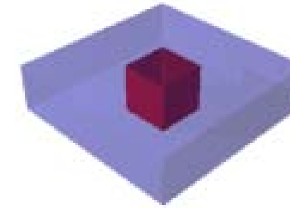
Fast process:
APC saturates earlier than η



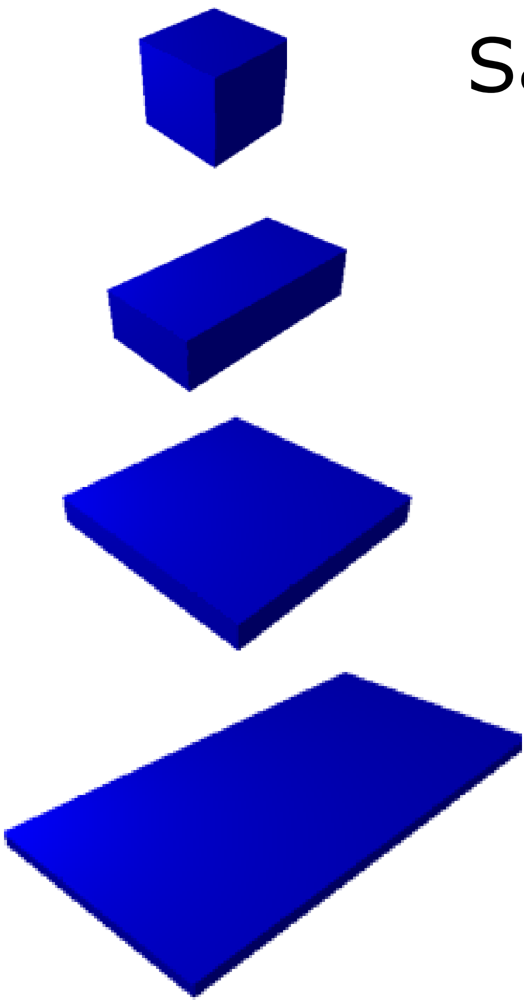
Slow process:
Further change of η after decreasing APC by B-antisite diffusion

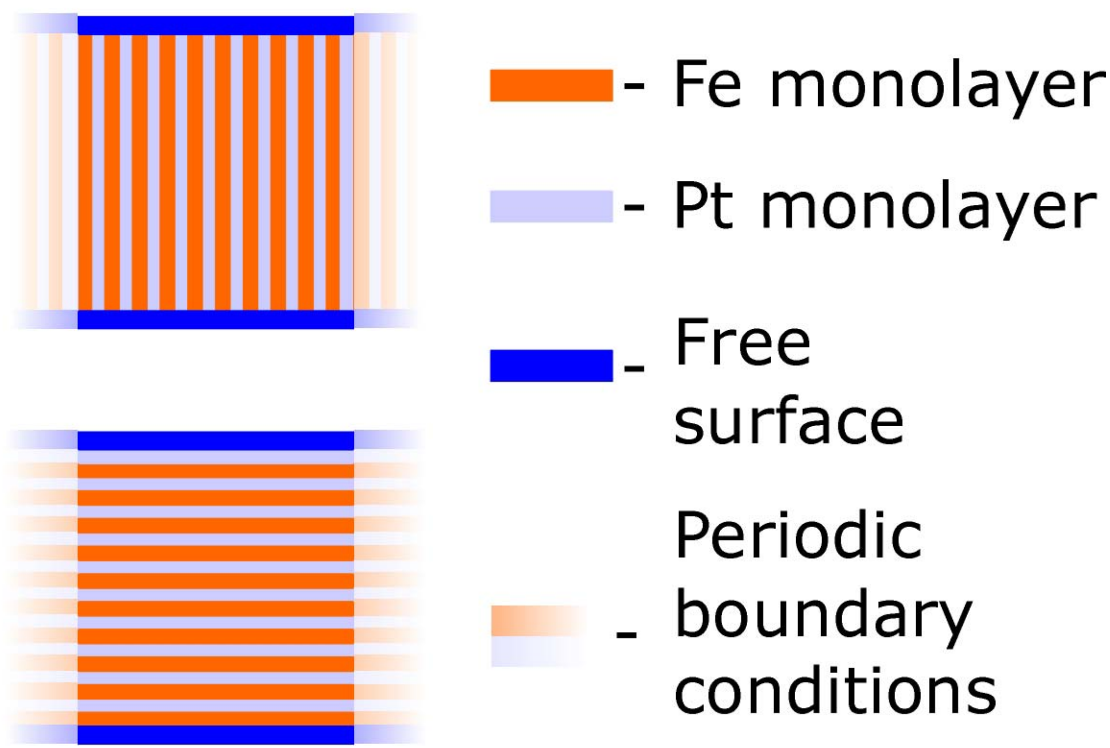
P. Oramus, R. Kozubski, V.Pierron-Bohnes, M.C.Cadeville, W.Pfeiler, *Phys.Rev.B* **63,** 174109, (2001).

Simulations of FePt thin films



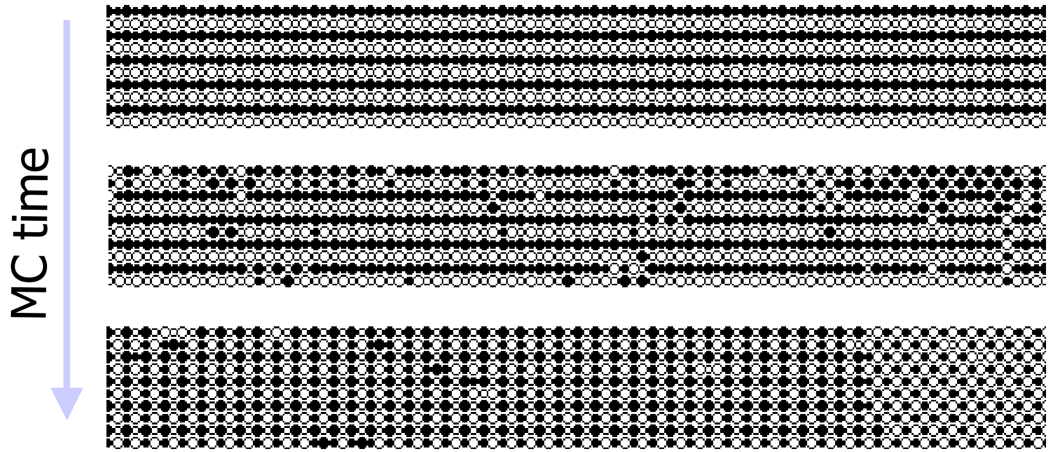
Sample Geometry

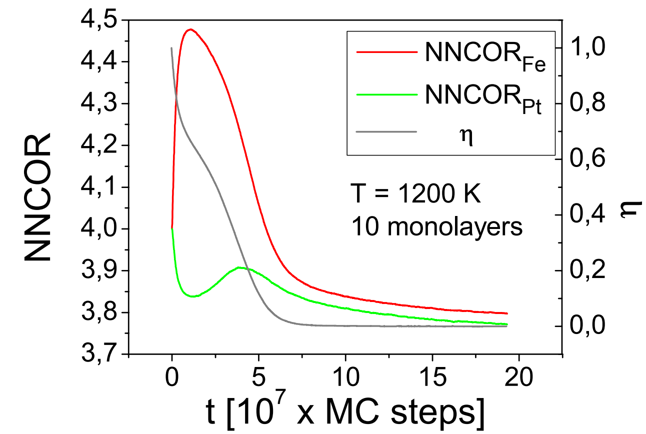


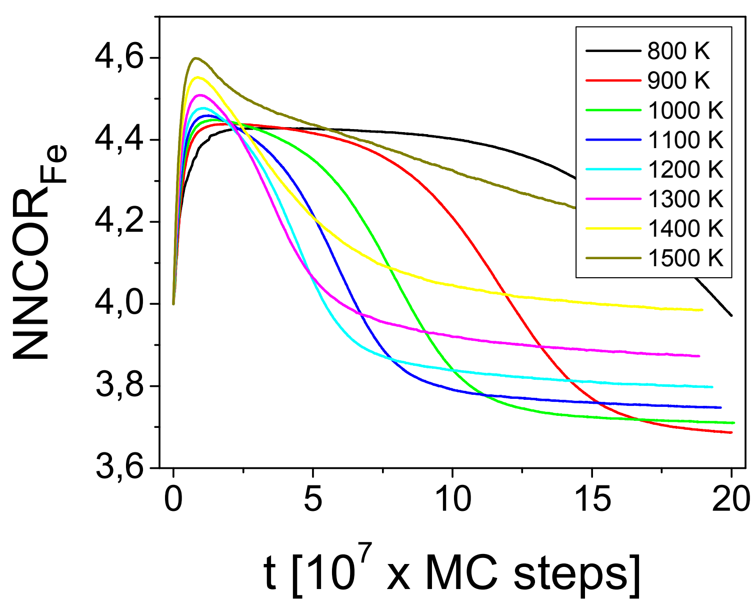


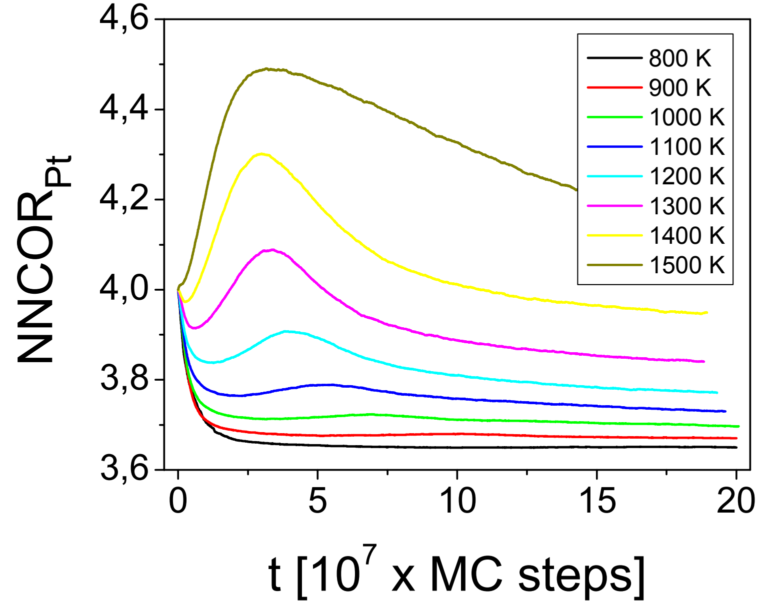
Results - free surfaces parallel to monoatomic planes

M. Kozłowski, R. Kozubski, V. Pierron-Bohnes, W. Pfeiler, *Comput.Mater.Sci.* **33**, 287, (2005).

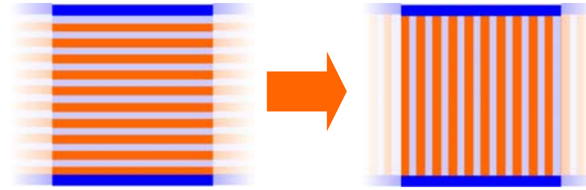








Reorganization of the superstructure



Sample:

40 x 40 x 40 unit cells

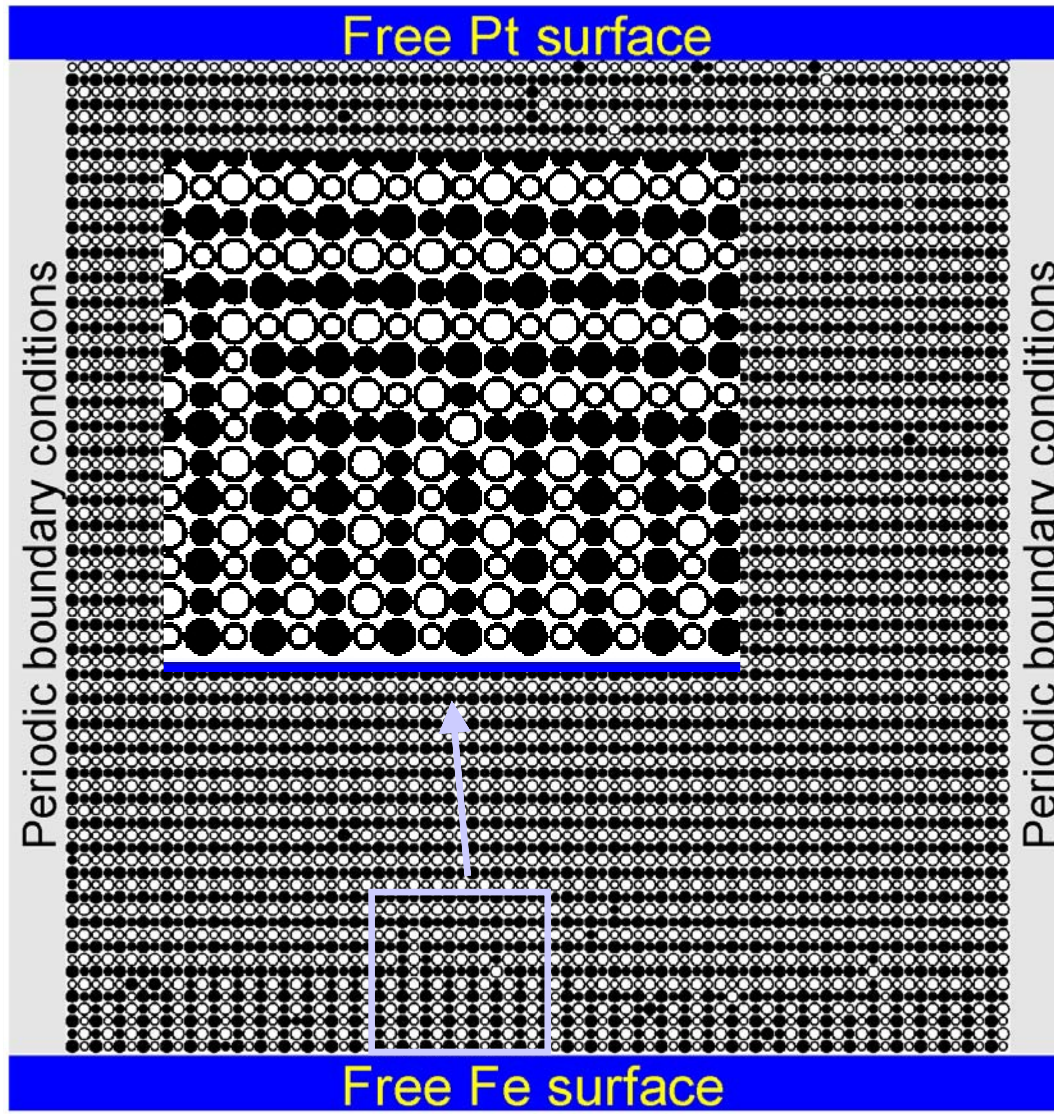
free surfaces in x direction

Picture:

t = 50 * 10^7 MC steps

(0 40 0) (bigger dots)

(0 41 0) (smaller dots)



○ - Pt atoms

● - Fe atoms