“ Fundamentals of Thermodynamic Modelling of Materials ”

November 15-19, 2010
INSTN – CEA Saclay, France

PROFESSOR & TOPIC

Frédéric SOISSON

Service de Recherches de Métallurgie Physique, CEA Saclay

*Monte Carlo
Simulation*

[02003]

Organized by

Bo SUNDMAN bo.sundman@cea.fr
Constantin MEIS constantin.meis@cea.fr

Monte Carlo simulations

Applications to the kinetics of phase transformations

F. Soisson
Service de Recherches de Métallurgie Physique
CEA Saclay

Outline

Atomistic Kinetic Monte Carlo simulations (AKMC) : from an atomistic description of diffusion mechanisms to the kinetics of phases transformations and microstructure evolutions

- Monte Carlo simulations : principles and algorithms
- Lattice models and diffusion models
- Selected applications :
 - precipitation kinetics, phase ordering in model systems of industrial interest (FeCu, FeNbC, Al-Zr-Sc, etc.)
 - thermal ageing and phase transformation under irradiation

Monte Carlo : thermodynamics and kinetics

- Equilibrium properties of a system in the canonical ensemble (NVT)
configurations i , energies E_i

$$P_i^{eq} = \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right) \quad \text{partition function : } Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right)$$

(Boltzmann distribution)

$$\text{Average value of } A : \langle A \rangle = \frac{1}{Z} \sum_i A_i \exp\left(-\frac{E_i}{k_B T}\right)$$

- Monte Carlo simulation : statistical sampling on a finite number of configurations

“direct sampling” : random choice of (i)

very inefficient because only a very few configurations have a significant probability

“importance sampling” : the configurations are generated with the probabilities of the Boltzmann distribution

- Master equation : dynamical interpretation

Master equation and detailed balance principle

- The system explores its phase space, transitions $i \rightarrow j$ with transition rates W_{ij}
Master equation :

$$\frac{dP_i}{dt} = \sum_j \left[-W_{ij} P_i(t) + W_{ji} P_j(t) \right]$$

Markov processes : the transitions rates are time independent (no memories)

- If the transition mechanism is ergodic and fulfills the detailed balance principle :

$$\frac{W_{ij}}{W_{ji}} = \frac{P_j^{eq}}{P_i^{eq}} = \exp\left(\frac{E_i - E_j}{k_B T}\right)$$

the system evolves towards its equilibrium state, i.e. towards the equilibrium distribution

$$P_i^{eq} = \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right)$$

Master equation : some comments

- For equilibrium properties, one can choose any mechanism that fulfills the detailed balance condition.

One can choose a mechanism that minimizes the total CPU time
(e.g. permutation between two atoms in the simulation box)

- For the simulation of kinetics pathways, the transition mechanisms and the transition rates W_{ij} must be realistic
- For “driven systems” (e.g. alloys under irradiation) the detailed balance is not fulfilled and the system does not evolve towards an equilibrium state. The kinetic pathway and the stationary state depend on the transition mechanism and the transition rates.
- Various Monte Carlo algorithms can be used to implement this procedure

The Metropolis algorithm (1953)

(1) Initial configuration

(2) Choice of a transition $i \rightarrow j$ and calculation of the transition rate

$$W_{ij} = \tau^{-1} \exp\left(-\frac{\Delta E}{k_B T}\right)$$

(3) Calculation of a random number RND

(4) if $\Delta E \leq 0$: the transition is accepted

if $\Delta E > 0$: the transition is accepted if $\exp\left(-\frac{\Delta E}{k_B T}\right) > \text{RND}$

- Several possible choices for ΔE
Equilibrium properties : $\Delta E = E_j - E_i$ (final – initial)
Kinetics : $\Delta E = E_{\text{Saddle-Point}} - E_i$ (= migration barrier of the diffusion mechanisms)
 $\tau \rightarrow$ time scale
- Main drawback :
 $\Delta E = 0.5 - 1.0$ eV almost all the transitions are rejected for $T < 1000$ K

The Residence Time Algorithm

Young et Elcock 1966, Bortz-Kalos-Lebowitz 1975

- (1) Initial configuration i
- (2) Calculation of ΔE and W_{ij} for the N_t possible transitions
- (3) Calculation of a random number RND
- (4) Choice of the transition $i \rightarrow k$

$$\sum_{j=1}^{k-1} W_{ij} \leq \text{RND} \times \sum_{j=1}^{N_t} W_{ij} < \sum_{j=1}^k W_{ij}$$

- (5) Residence time in the configuration i
(time step)

$$\tau_i = \frac{1}{\sum_{j=1}^{N_t} W_{ij}}$$

- requires the calculation of all the possible transition rate, but one transition is performed at each Monte Carlo step
- especially interesting at low T and when N_t is small (e.g. diffusion by point defects)

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Application to phase transformations

- Magnetic transformations : Ising models $H = -J \sum_{ij} \sigma_i \sigma_j - h \sum_i \sigma_i$
spins $\sigma_i \pm 1$, transitions = spin-flip

- Phase transformation in alloys
Calculation of phase diagram and other equilibrium properties

- First simulations of the kinetics of phase transformations

1970-1980 : general studies of model "A-B" alloys
simplified transition mechanisms : A-B exchange
simplified transition rates : $\Delta E = E_f - E_i$

$$\Delta E = \frac{E_f + E_i}{2} + Q \quad (\text{Kinetic Ising model})$$

- ok when the systems follows the line of highest slope to minimise its free energy ?
not always the case, especially in more than binary systems...

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Application to phase transformations

- Nucleation-growth, spinodal decomposition, long term kinetic behavior :

$$R \sim t^{1/3} \text{ (Conserved Order Parameter)}$$

$$R \sim t^{1/2} \text{ (Non-Conserved Order parameters)}$$

- Self-similarity, Dynamical Scaling

Monte Carlo simulation
Fratzl et al (1991)

Neutron Scattering
Gaulin et al, 1987

Time dependence of the scaling function $F(k/k_m) = k_m^{-3} S(k, t)$ for Mn-33 at.% Cu at 450°C.

FIG. 2. Scaled structure functions of the two-dimensional Ising model for all temperatures, times, and volume fractions ϕ listed in Table I. The scaling functions for $\phi=0.3$ are shown in (a), for $\phi=0.25$ in (b) and for $\phi=0.125$ in (c). The solid lines are fits to the data with Eqs. (12), (14), (16), and (17) and the values for the constants in these equations are given in Table II.

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Spinodal decomposition

- Test of the linearized Cahn-Hilliard theory

$$F(c) = \int \left[f(c) + \frac{\kappa}{2} (\nabla c)^2 \right] dr$$

- Exponential growth of the structure factor
- Amplification factor :

$$\omega(k) = -2Mk^2 \left[\kappa k^2 + \left(\frac{\partial f^2}{\partial c^2} \right) \right]$$

M : mobility

- Good approximation with medium or long range interactions

D. W. Heermann (1984)

FIG. 3. Amplification factor $\omega(k)$ of the structure factor divided by the square of the wave vector plotted vs the square of the wave vector. The straight lines are the mean-field predictions.

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Diffusion model for metallic alloys

- Compromise between realism and CPU time → rigid lattice model (coherent phase transformations)

- Energy of the system : sum of effective pair interactions

- between atoms $\epsilon_{AA}^{(n)}, \epsilon_{AB}^{(n)}, \dots$

- between atoms and point defects $\epsilon_{AV}^{(n)}, \dots$

- Jump frequencies : $\Gamma_{AV} = \nu_A \exp \left(-\frac{\Delta E_{AV}}{k_B T} \right)$

ν_A : attempt frequency

ΔE_{AV} : migration barrier

depends on the local environment calculated in a broken-bond model

- Multiplet interactions can be implemented (*ab initio* + cluster-expansion)
- Other possibility : empirical potential on a rigid lattice or with atomic relaxations

The kinetic pathways are controlled by :

- The jump frequencies

$$\Delta E_{AV} = E(\text{SP}) - E(\text{initial}) = \underbrace{\sum_i \tilde{\epsilon}_{Ai}^{(n)}}_{\text{SP position}} - \underbrace{\sum_j \epsilon_{Aj}^{(n)}}_{\text{broken bonds (initial position)}} - \underbrace{\sum_k \epsilon_{kV}^{(n)}}_{\text{broken bonds (initial position)}}$$

Kinetic properties
(e.g. diffusion coefficients)

Equilibrium properties
(e.g. phase diagrams)

Can be fitted on experimental and/or *ab initio* calculations

- The point defect concentration

- Monte Carlo simulation with a constant number of point defects (e.g. $N_V=1$)

requires a time rescaling : $t = t_{MC} \frac{C_V^{MC}}{C_V^{eq}}$

C_V^{eq} usually evolves during the phase transformations !

- Monte Carlo simulations with point defect formation/annihilation mechanisms (real defect concentrations)

Copper precipitation in α -iron

Fe - 1.34at.%Cu – thermal ageing at 500°C

- Strong vacancy trapping in copper precipitates

DFT : $E_V^{for}(Fe) = 2.2 \text{ eV} \gg E_V^{for}(BCC - Cu) = 0.9 \text{ eV}$

- Good agreement with experimental kinetics but limited to the first precipitation regimes (nucleation and growth)

- Precipitation of pure copper clusters

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Copper precipitation in α -iron

Classical theories of nucleation, growth and coarsening: emission/absorption of individual solute atoms

- A simple KMC simulation (T = 500 K) :

1 copper cluster of 27 atoms

+

1 isolated atom

- Cluster diffusion coefficients

without vacancies (Binder et al)

(large cluster size) $\frac{D_n}{D_1} \propto n^{-4/3}$

vacancy trapping $\frac{D_n}{D_1} \propto \frac{C_V^{int}}{C_V^{Cu}} \frac{\Gamma_V^{int}}{\Gamma_V^{Cu}} n^{-4/3}$

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

- Clusters dynamics without cluster mobility, evolution of clusters concentrations :

$$\frac{dC_n}{dt} = J_{n-1 \rightarrow n} - J_{n \rightarrow n+1}$$

$$J_{n \rightarrow n+1} = \beta_n C_1 C_n - \alpha_{n+1} C_{n+1}$$

$$\text{absorption rate : } \beta_n = 4\pi(r_n + r_1)D_1 / \Omega$$

$$\text{absorption rate : } \alpha_{n+1} = \beta_n \exp \left[-\frac{A}{k_B T} (\sigma_1 + \sigma_n n^{2/3} - \sigma_{n+1} (n+1)^{2/3}) \right]$$

Interface energy fitted on Monte Carlo simulations

Long term behavior

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Precipitation in Al-Zr-Sc alloys

3D atom probe
(W. Lefevbre et al)

High-angle annular dark field
(T. Epicier)

Al-0.03 at.% Zr-0.09 at.% Sc
128h at 400°C

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Precipitation in Al-Zr-Sc alloys

AKMC simulations (E. Clouet et al) : core-shell structures (Sc-rich core, Zr-rich periphery)

Diffusion coefficients : $D_{Sc}(Al) \gg D_{Zr}(Al)$

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Segregation and Precipitation in undersaturated alloys

Undersaturated solid solution with an unmixing tendency ($\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} < 0$)

$$C_B = 5\% - C_B^{eq} = 8\%$$

$$D_B^v / D_A^v \approx 0.06 \text{ and } D_B^i / D_A^i \approx 1$$

$$G = 10^{-6} \text{ dpa.s}^{-1} \quad T = 800\text{K}$$

Fundamentals of Thermodynamic Modelling of Materials

Saclay, November 15-19, 2010

Beyond rigid lattice approximations

- Monte Carlo simulations with relaxations of atomic positions
→ effect of long-range elastic interactions

A. Finel (2000)
LJ potential $\delta a/a = 0.16$
Soft A (●) – hard B (○)

Mason, 2004 MC simulation
In Al-4 at.% Cu system

- On-the-fly calculations of the jump frequencies : much more time consuming
- Much more time consuming
- Validity of the interatomic potentials ?
- Incoherent phase transformations ?

Conclusions

Atomistic KMC : an efficient tool for studying the kinetic of phase transformations especially when coupled with ab initio calculations

- Advantages :
 - takes into account the real diffusion mechanisms, including the dependence of migration barriers with the local environment and correlations effects → realistic diffusion properties
 - thermal fluctuations → nucleation processes
- Drawbacks :
 - time consuming : limited to relatively short times
can be coupled with other simulation methods
(cluster dynamics, Object KMC, PF kinetics)
 - rigid lattice approximations

References

A Guide to Monte Carlo Simulations in Statistical Physics

David P. Landau, Kurt Binder, Cambridge University Press, 2005

Monte Carlo Methods in Statistical Physics

M. E. J. Newman and G. T. Barkema, Oxford University Press, 1999

Atomic simulations of diffusional phase transformations

E. Clouet and F. Soisson, C. R. Physique 11 (2010) 226–235