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 σ 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 *<A>* 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

$$P(\sigma) = \frac{\rho(\sigma)}{\sum\limits_{\sigma} \rho(\sigma)}$$

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

$$Z = \sum\limits_{\sigma} \rho_{eq}(\sigma)$$

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 and fixed chemical potentials μ_k	$$\exp\left[-\frac{H(\sigma_i)-\sum_k N_k(\sigma_i)\mu_k}{k_B T}\right]$$ μ_k – chemical potential

SAMPLING

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

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

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 ($\bigstar$) by a partial one performed over some subset $\{\sigma_i, \, i = 1, \, ..., \, M\}$ of the microscopic states σ

$$\langle A \rangle \approx \frac{\sum\limits_{i=1}^{M} \left[\rho(\sigma_i) \times A(\sigma_i) \right]}{\sum\limits_{k=1}^{M} \rho(\sigma_k)} \quad \bigstar\bigstar$$

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 $\Pi(\sigma)$:

$$\langle A \rangle \approx \frac{\sum\limits_{i=1}^{M}\left[\rho(\sigma_i) \times A(\sigma_i) \times \Pi^{-1}(\sigma_i)\right]}{\sum\limits_{k=1}^{M}\left[\rho(\sigma_k) \times \Pi^{-1}(\sigma_k)\right]}$$

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

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,...

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

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:**

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

$$W(\sigma_i \rightarrow \sigma_j) = \frac{\Pi(\sigma_i \rightarrow \sigma_j)}{\Delta t} \qquad \textbf{Transition probability per time}$$

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

provided that:

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

hence: $\qquad \dfrac{W(\sigma_i \rightarrow \sigma_j)}{W(\sigma_j \rightarrow \sigma_i)} = \dfrac{P_{eq}(\sigma_j)}{P_{eq}(\sigma_i)} = \dfrac{\rho_{eq}(\sigma_j)}{\rho_{eq}(\sigma_i)}$ $\longleftarrow$ **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 its **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:

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

$$\Longrightarrow$$

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

$$S = -k_B \sum_i P(\sigma_i) \times \ln\left[P(\sigma_i)\right]$$

$P(\sigma_i)$ 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$_3$Al)
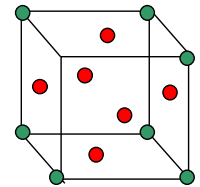
Example
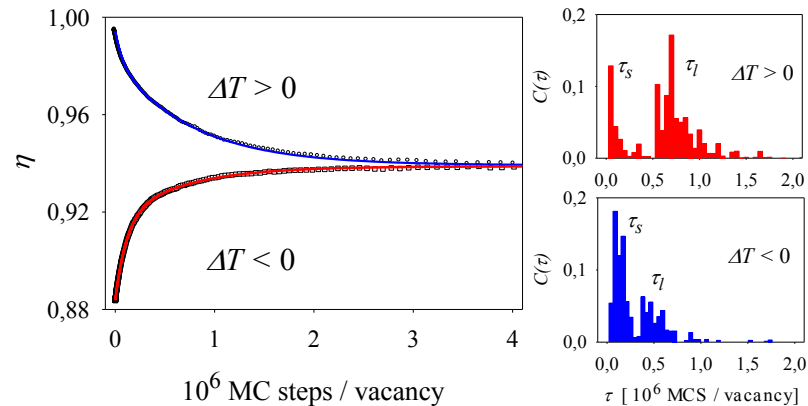
● *Simulation of non-equilibrium processes and transport phenomena*

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 $D_{V(A)}$:

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

Correlation factor for atoms A

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

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.

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Numerical implementation of MC
(choice of transition frequencies $W(\sigma_i \rightarrow \sigma_j)$)

Classical approach

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

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

$\Delta E = E_{fin} - E_{ini}$, 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)

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

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

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

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 $W(\sigma_i \to \sigma_j)$ 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 $\{\sigma\}$

- Transition $\sigma_i \to \sigma_j$ is executed <u>*or suppressed*</u> according to the probability $\tau \times W(\sigma_i \to \sigma_j)$

- Time is incremented by τ

Drawback:

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

PHASE EQUILIBRIA BY MONTE CARLO SIMULATION

A-B, μ_A, μ_B

A

OPEN SYSTEM

B
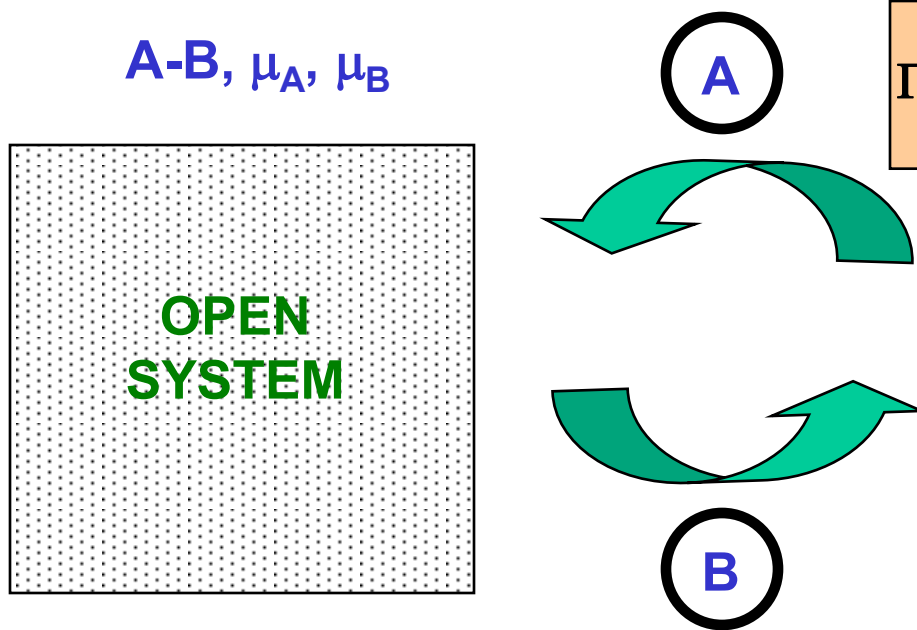
$$\Pi_{A\leftrightarrow B} = \min\left\{1, \exp\left[-\frac{\Delta E_{A\leftrightarrow B} - (\mu_A - \mu_B)}{k_B T}\right]\right\}$$

Such a Markov chain leads to a configuration with equilibrium N_A and N_B corresponding to the assumed values of μ_A and μ_B – to a state corresponding to the minimum of Ω

$$P(\sigma) \propto \exp\left[-\frac{E(\sigma) - N_A\mu_A - N_B\mu_B}{k_B T}\right]$$

DECOMPOSITION PROCESSES
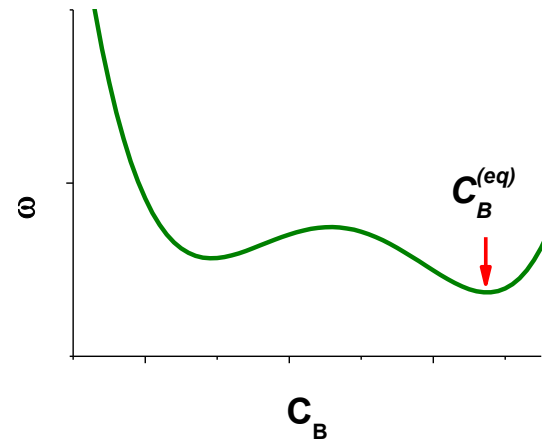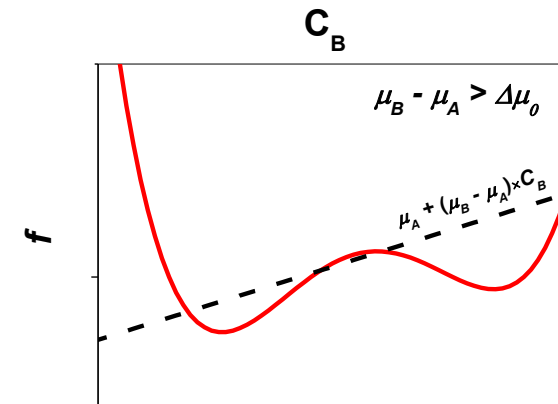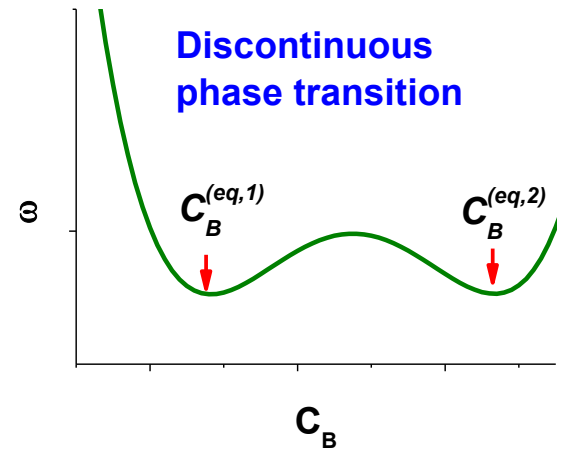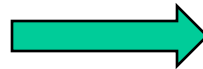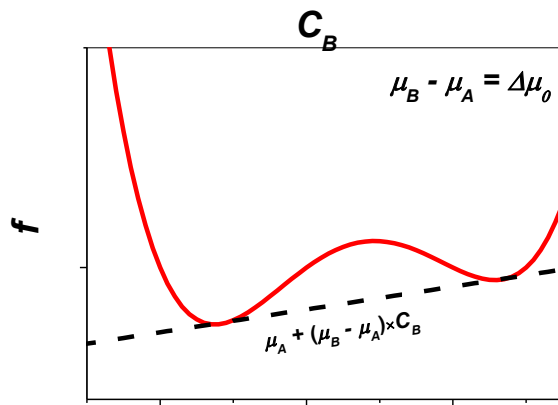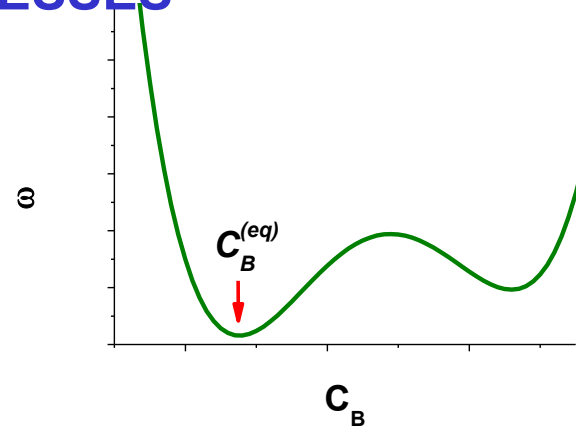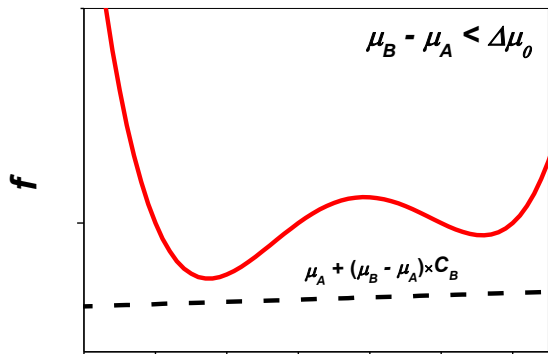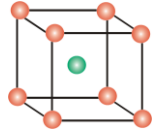
Two phase coexistence region

Crystal with equilibrium vacancy concentration
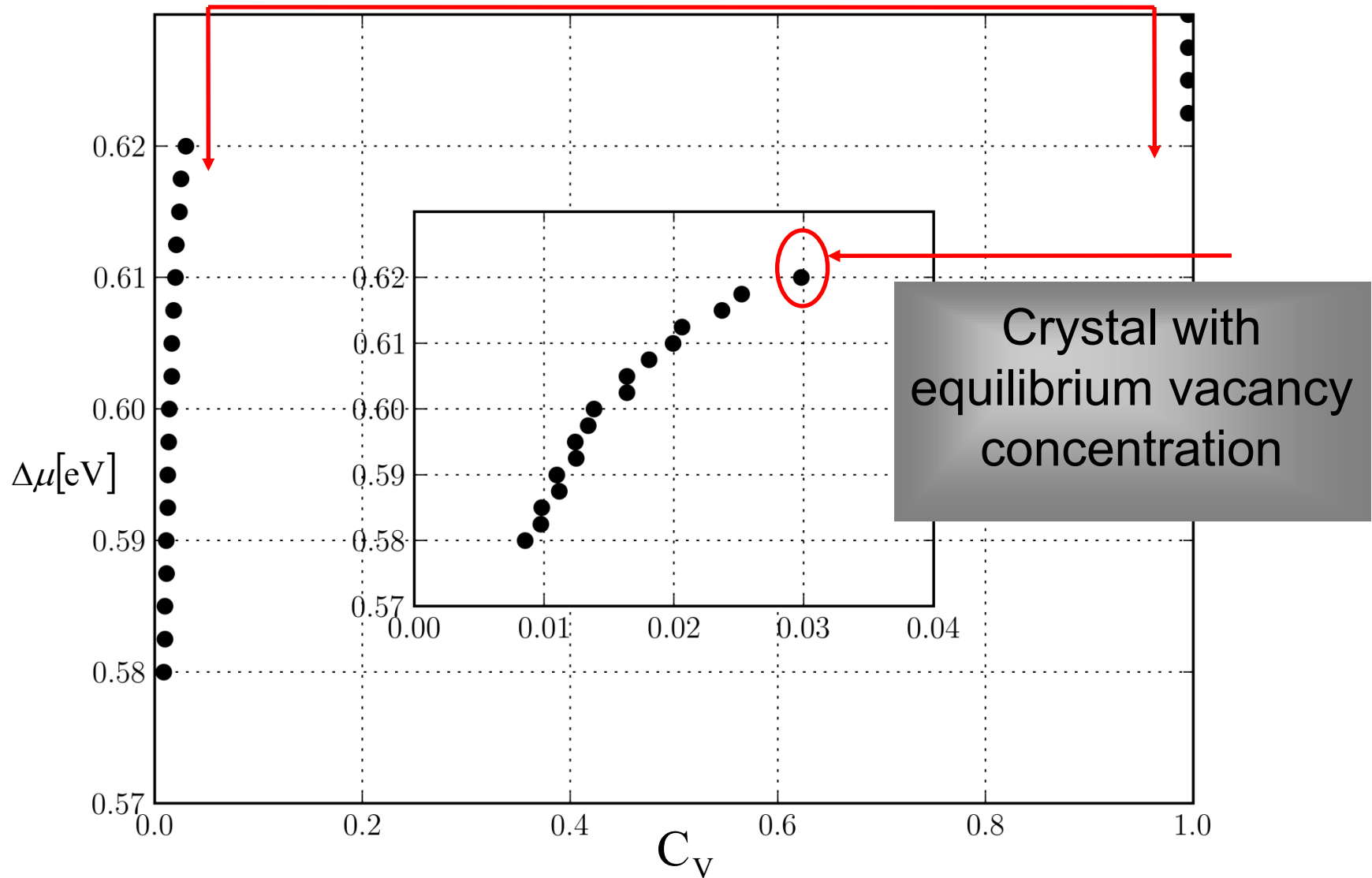
APPLICATION:
LONG-RANGE ORDERING IN INTERMETALLICS

„Order-disorder" phase transformations

Continuous (2nd-order) transformation
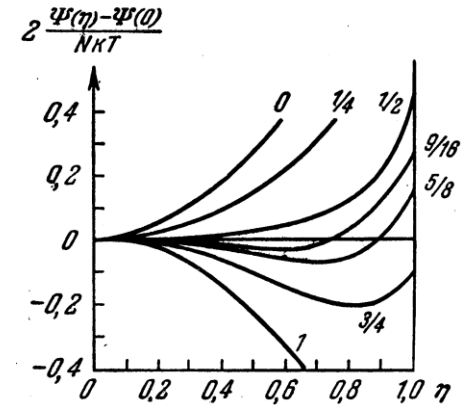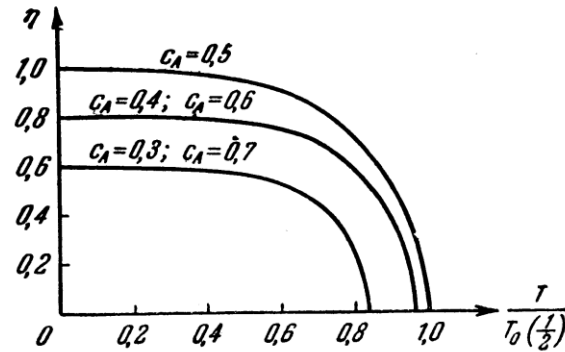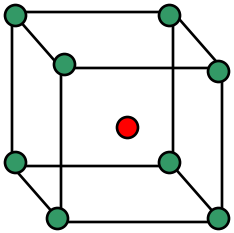
Discontinuous (1st-order) transformation
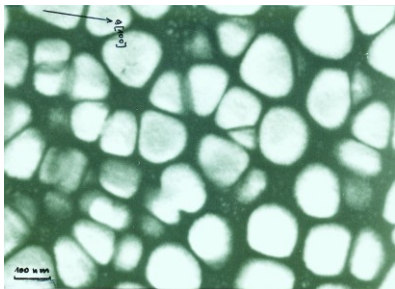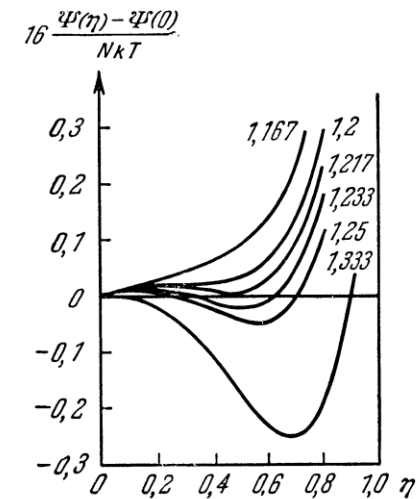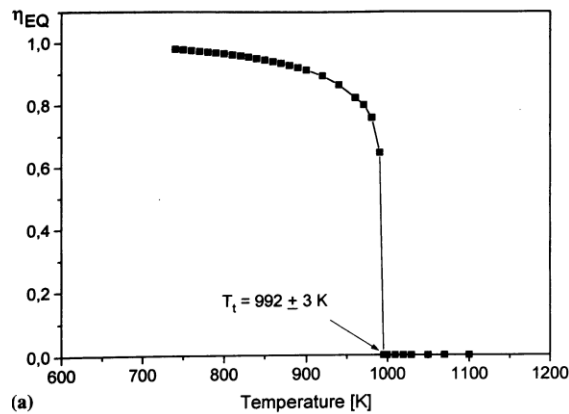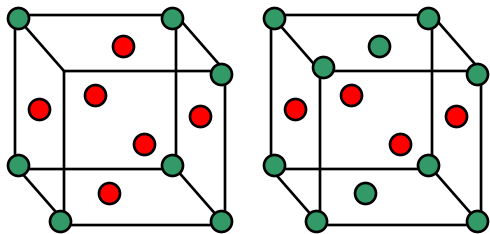
MONTE CARLO SIMULATIONS:

- **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*)**

general assumption: **vacancy mechanism of atomic migration**

Energy of a system

j

i

E^+

ΔE

Distance

Glauber dynamics algorithm:

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

„Residence-time" algorithm:

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

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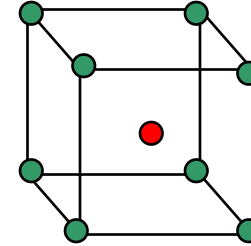
Kinetic Monte Carlo
KMC
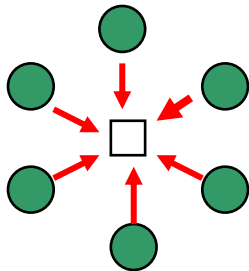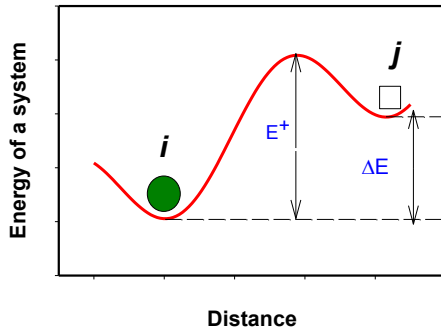
SUPERSTRUCTURE STABILITY
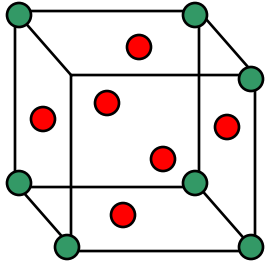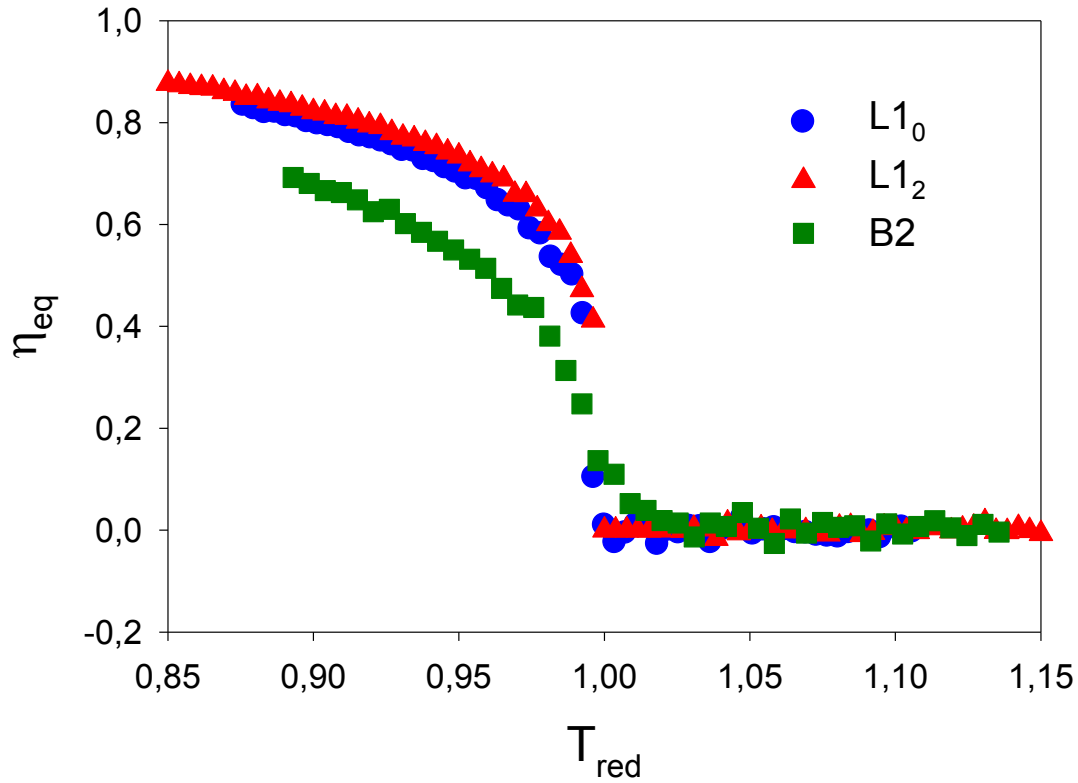

$L1_2$
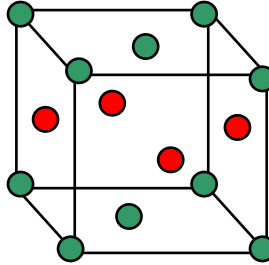
$L1_0$

$B2$

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

APPLICATION:
PHASE EQUILIBRIA
Vacancy concentration in intermetallics

MODEL: EQUILIBRIUM CONCENTRATION OF THERMAL VACANCIES IN LONG-RANGE ORDERED SYSTEMS

W. Schapink, Scr. Metall. 3, 113, (1969).
S. H. Lim, G. E. Murch, W. A. Oates, J. Phys. Chem. Solids 53, 181, (1992)
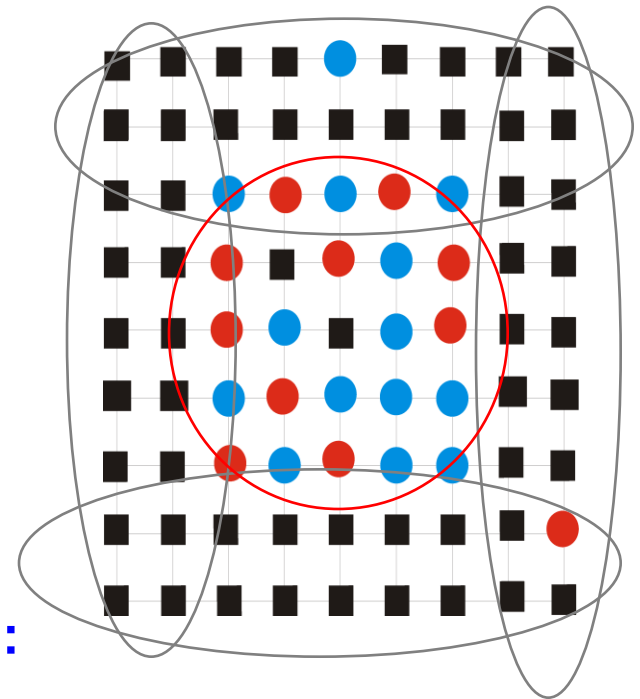R. Kozubski, Acta Metall. Mater. 41, 2565, (1993).

Ising lattice gas:

N_A A-atoms, N_B B-atoms, N_V vacancies
$N_A + N_B + N_V = N = $ const
$W = 2V_{AB} - V_{AA} - V_{BB} < 0$
(tendency for ordering)
$V_{VV} = 0$

The model is solved by means of two methods:

- **Bragg-Williams approximation (mean field)**

A.Biborski, L.Zosiak, R. Kozubski, V. Pierron-Bohnes, *Intermetallics,* 17, 46-55, (2009).

- **Semi-Grand Canonical Monte Carlo (SGCMC) simulations**

A.Biborski, L.Zosiak, R. Sot, R. Kozubski, V. Pierron-Bohnes, submitted to *J.Chem.Phys.*

Semi-Grand Canonical MC of a ternary A-B-V lattice gas:

- Generation of a sample 15x15x15 unit cells,
  periodic boundary conditons
- Determination of relative chemical potentials $\Delta\mu_{AV}$ and $\Delta\mu_{BV}$
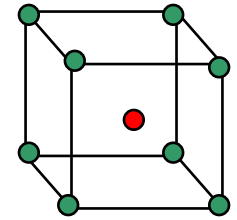- Random choice of a lattice site
- Random choice of the exchange type:

Species	Exchange type		
A	A – A	A - B	A - V
B	B - A	B - B	B - V
V	V - A	V - B	V - V

- Execution of the exchange according to Metropolis probability:

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

TYPICAL RESULT IN B2 SUPERSTRUCTURE

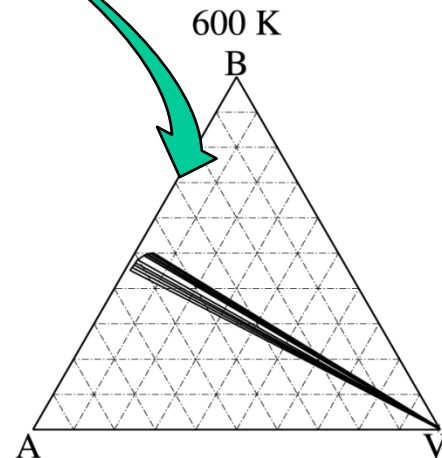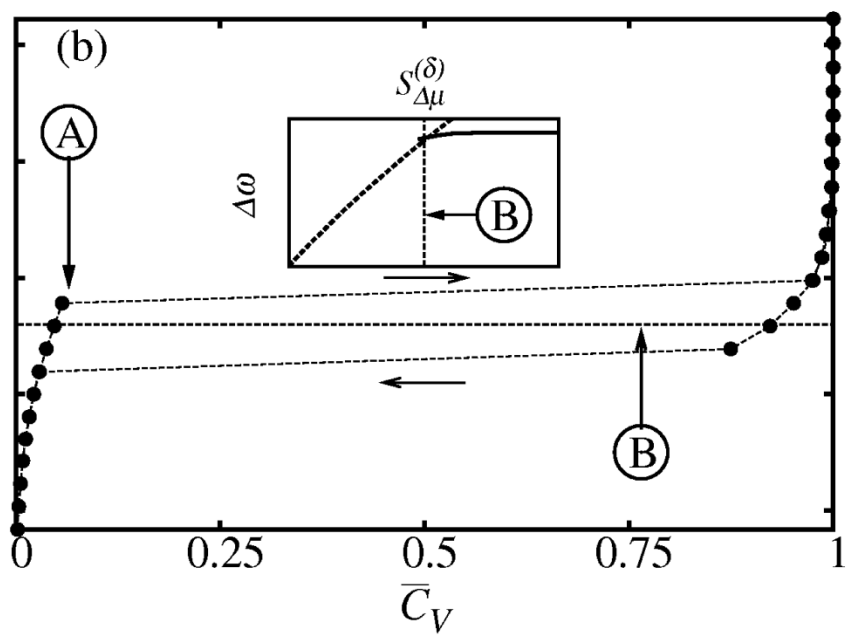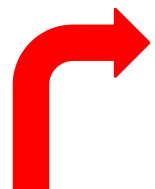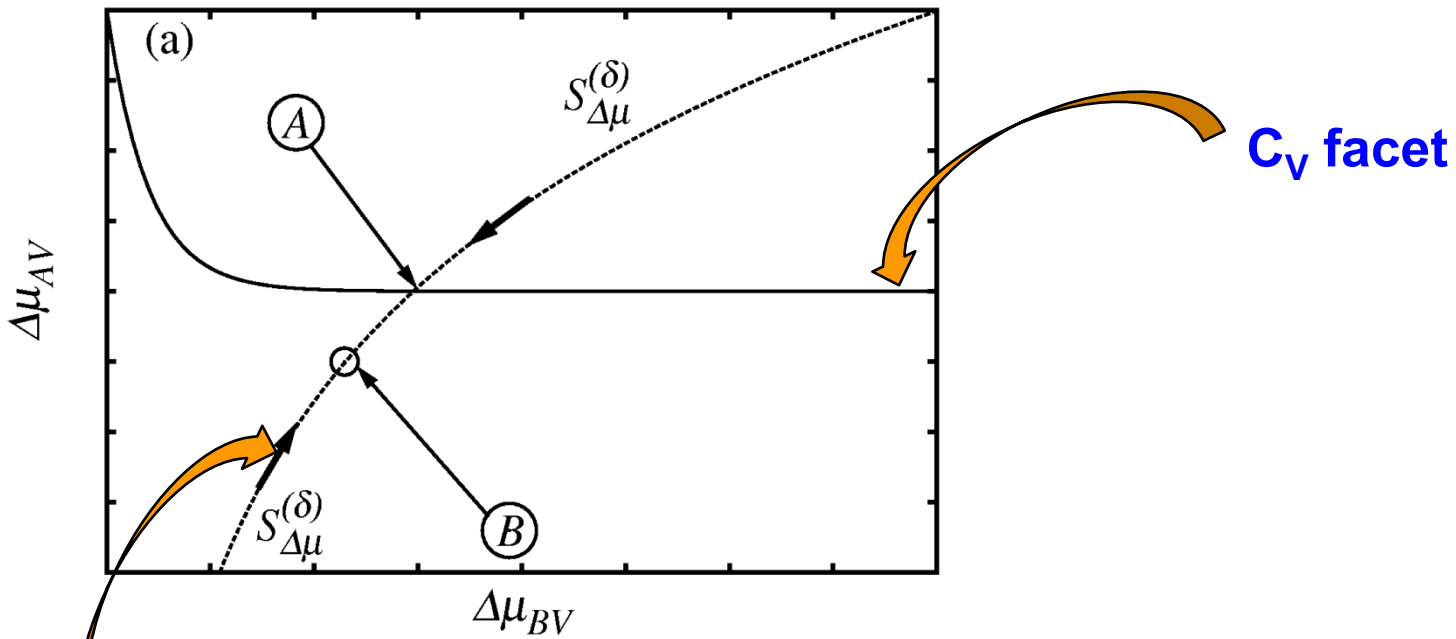**Limits of equilibrium vacancy concentration IN CRYSTALS with diverse composition (hysteresis)**

Equilibrium vacancy concentration IN THE LATTICE GAS
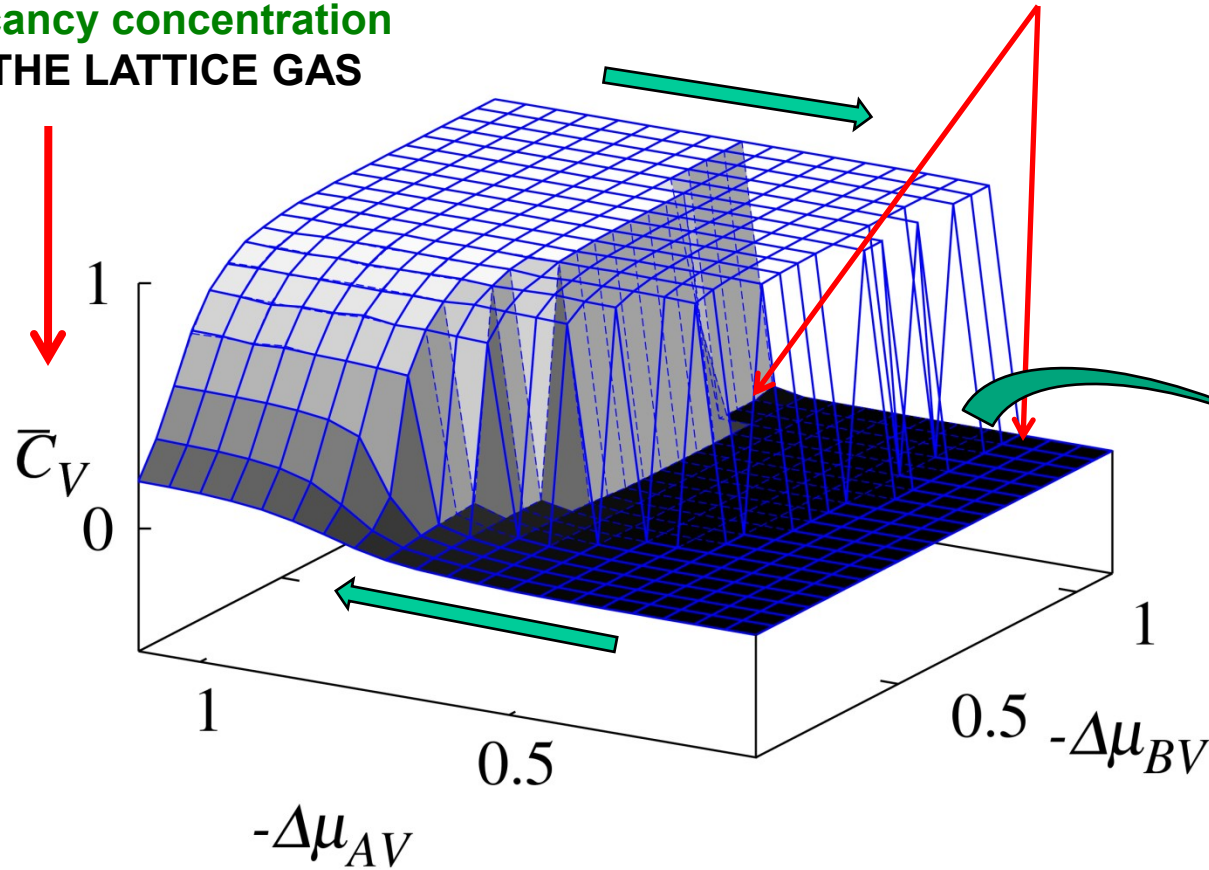
Equilibrium of vacancy-poor (crystal) and vacancy-rich phases

$\overline{C}_V$

1

0

1

0.5

$-\Delta\mu_{AV}$

1

0.5 $-\Delta\mu_{BV}$

600 K

B

A

V

T = const

(a) $S^{(\delta)}_{\Delta\mu}$

$\Delta\mu_{AV}$

$\Delta\mu_{BV}$

$S^{(\delta)}_{\Delta\mu}$

C_V facet

C_A/C_B = const path

**Hysteresis
and thermodynamic integration result**

(b) $S^{(\delta)}_{\Delta\mu}$

$\Delta\omega$

$S^{(\delta)}_{\Delta\mu}$
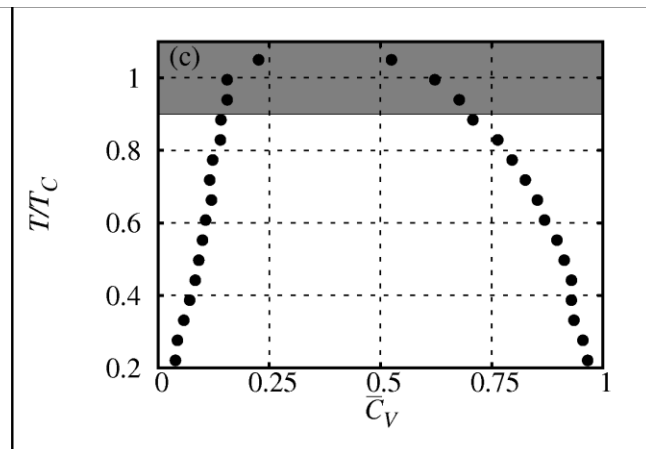
$\overline{C}_V$

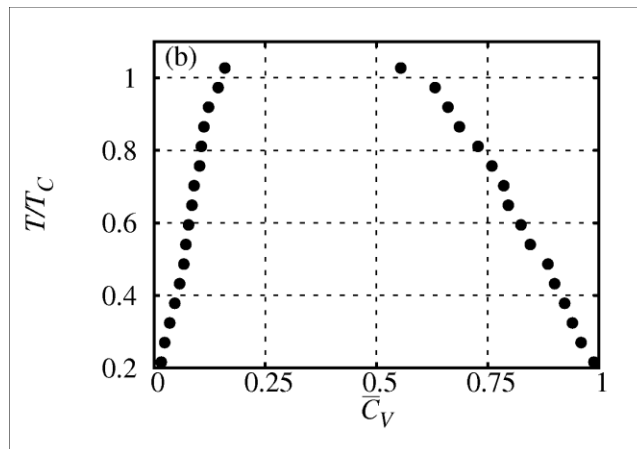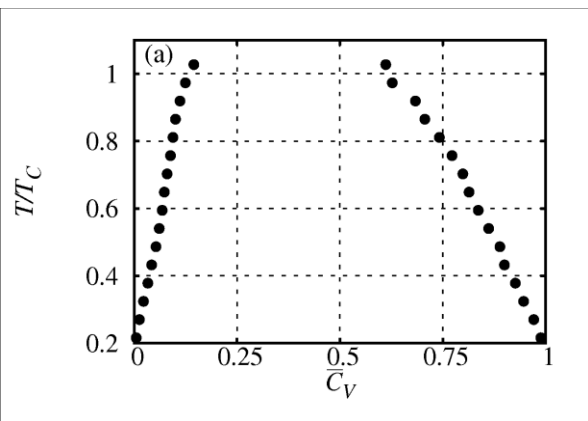0   0.25   0.5   0.75   1

Fig.5. Sections of the miscibility gap of the A-B-V lattice gas. Vacancy-poor borders of the sections correspond to: (a) $A_{0.52}B_{0.48}$-V (d=0.48); (b) $A_{0.5}B_{0.5}$-V (d=0.5); (c) $A_{0.48}B_{0.52}$-V