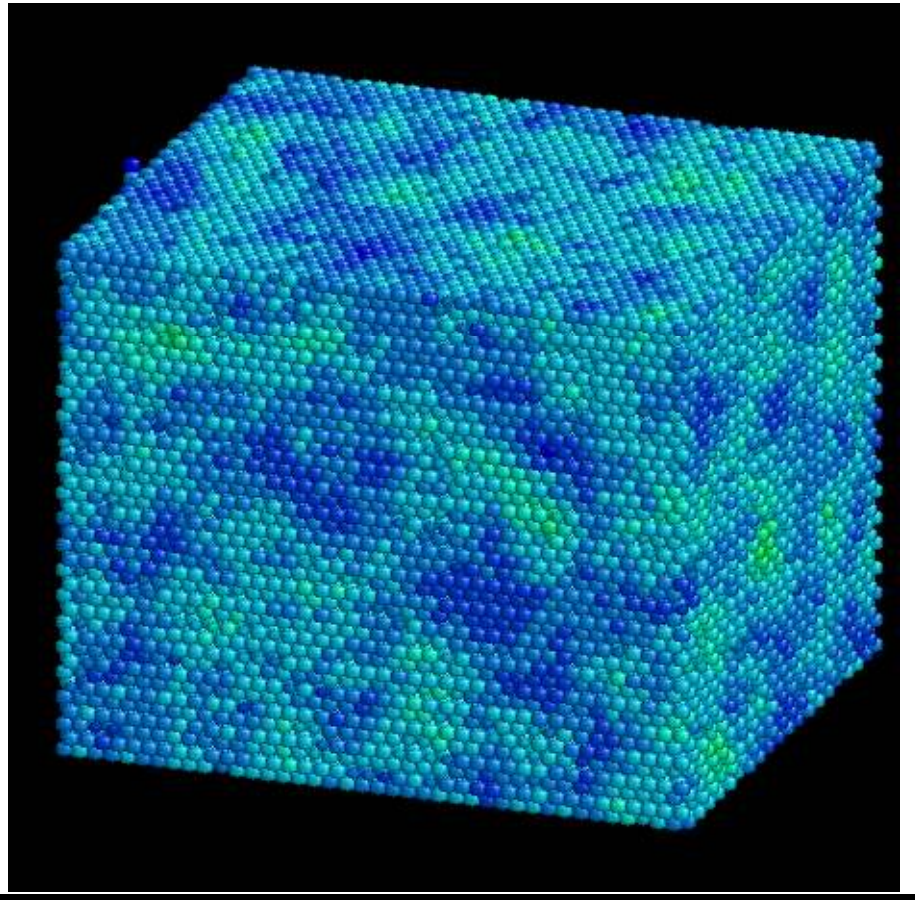
Monte Carlo Simulation



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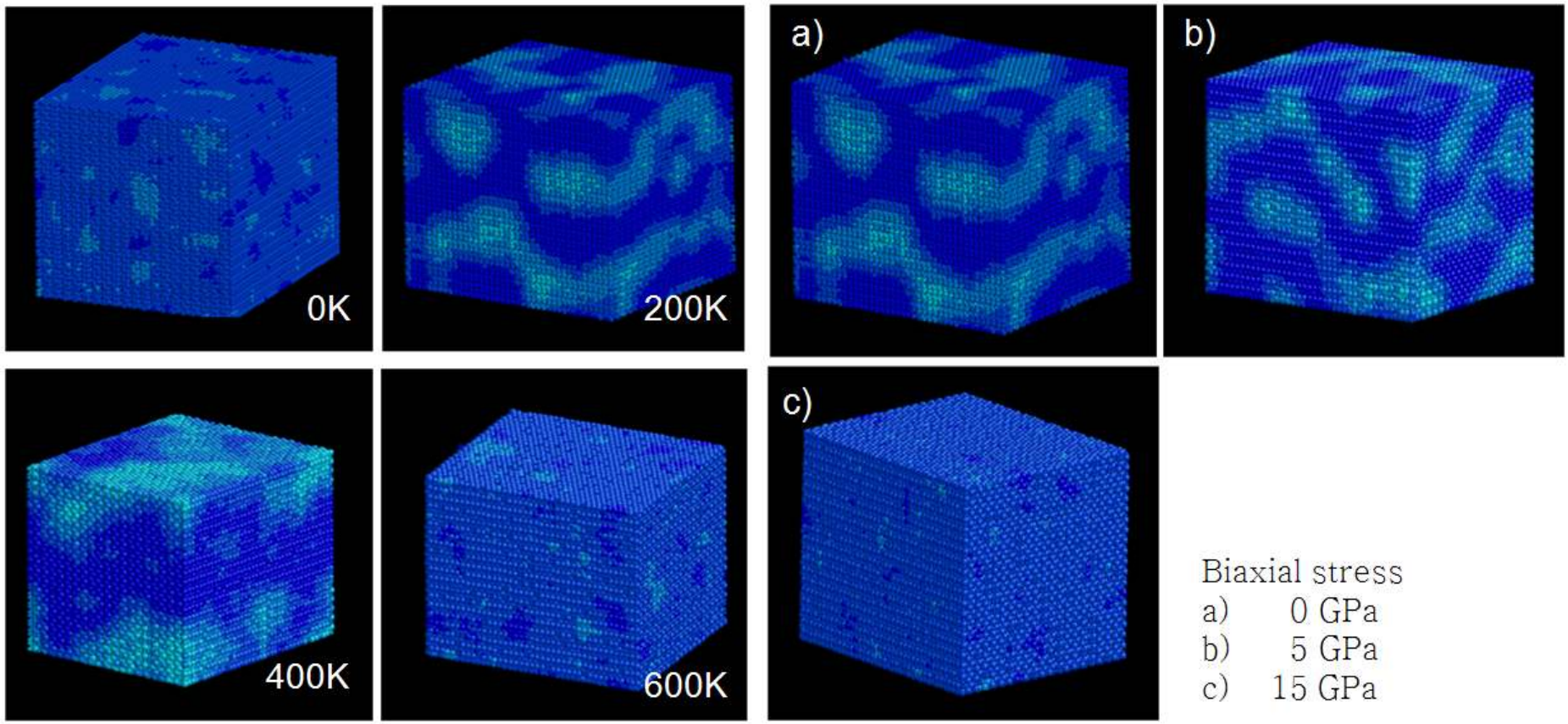
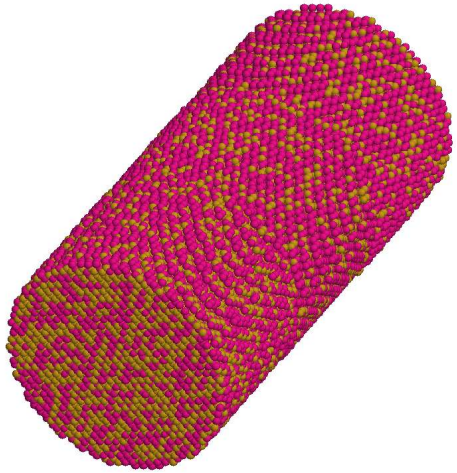
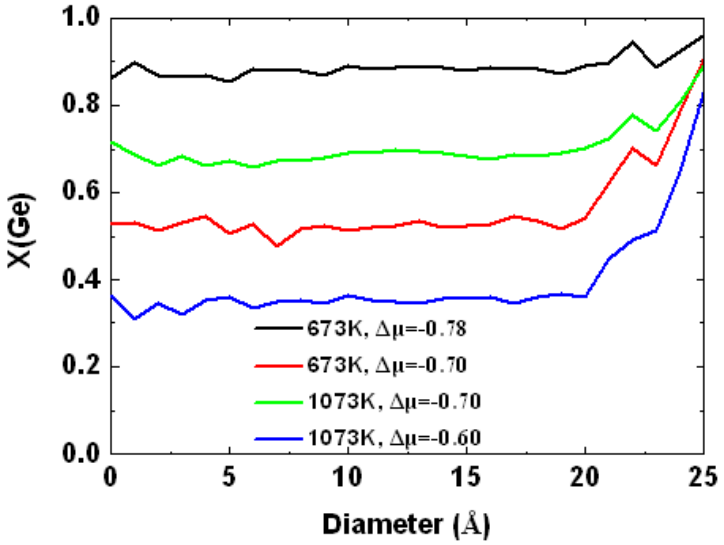
Background - Phase Separation in GaInN

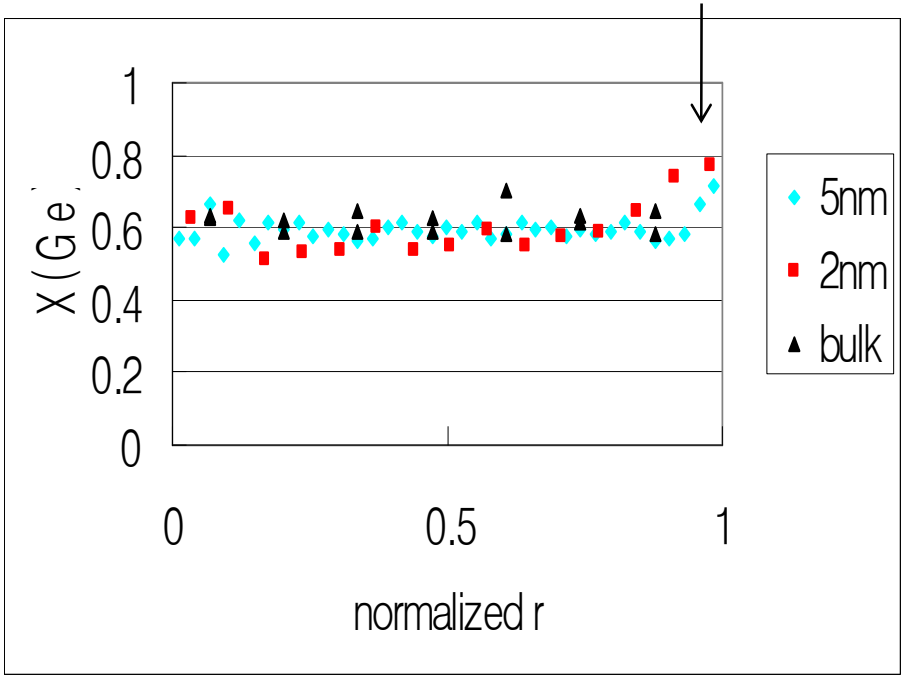


Background – Atomic distribution in SiGe nanowires

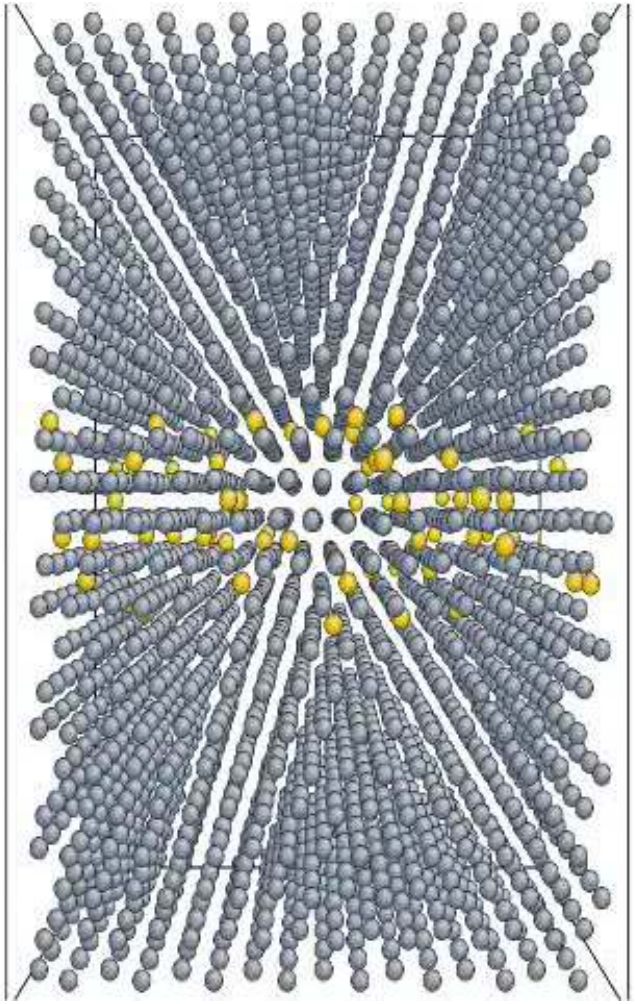


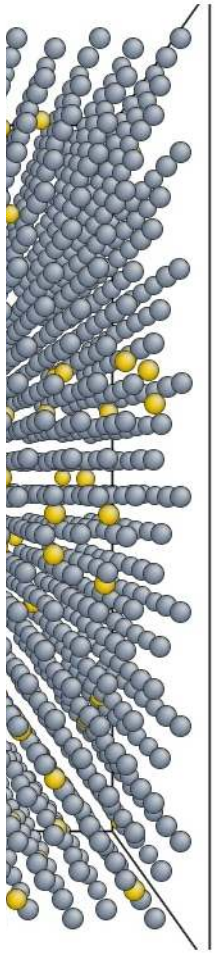


Surface Segregations

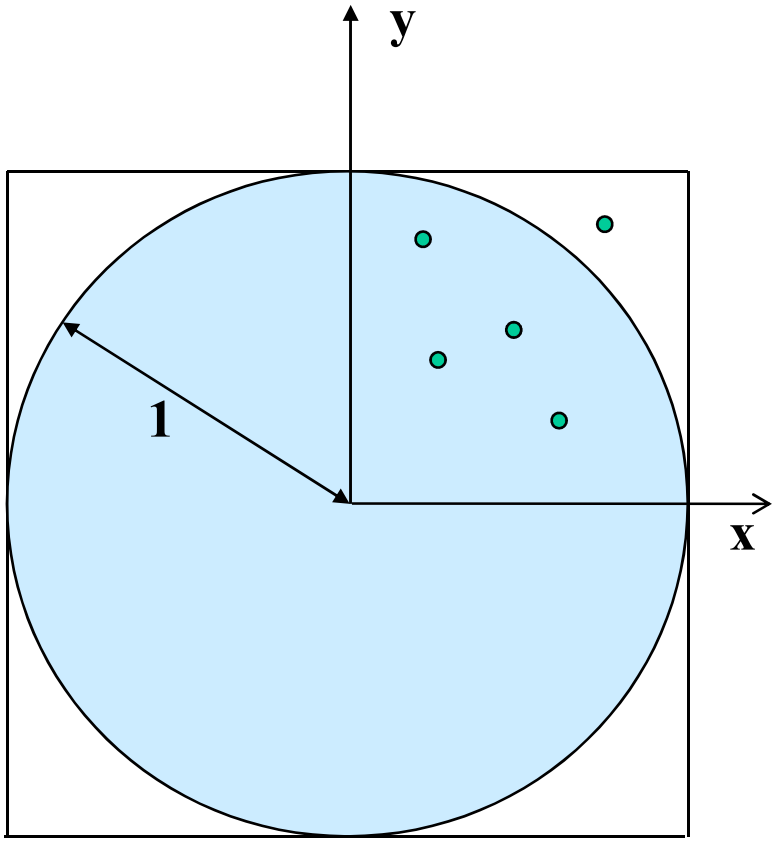


Why Monte Carlo ?





What is Monte Carlo ?




```
      implicit integer (i-n)
      implicit double precision (a-h,o-z)
      call random_seed
      i_circle = 0
      do i = 1, 100000000
         call random_number(x)
         call random_number(y)
         r2 = x*x + y*y
         if(r2 .lt. 1.d0) i_circle = i_circle + 1
         if(mod(i,1000000) .eq. 0) then
            pi = 4.0d0 * dble(i_circle) / dble(i)
            write(*,*) i, pi
         endif
      enddo
c
      stop
      end
```

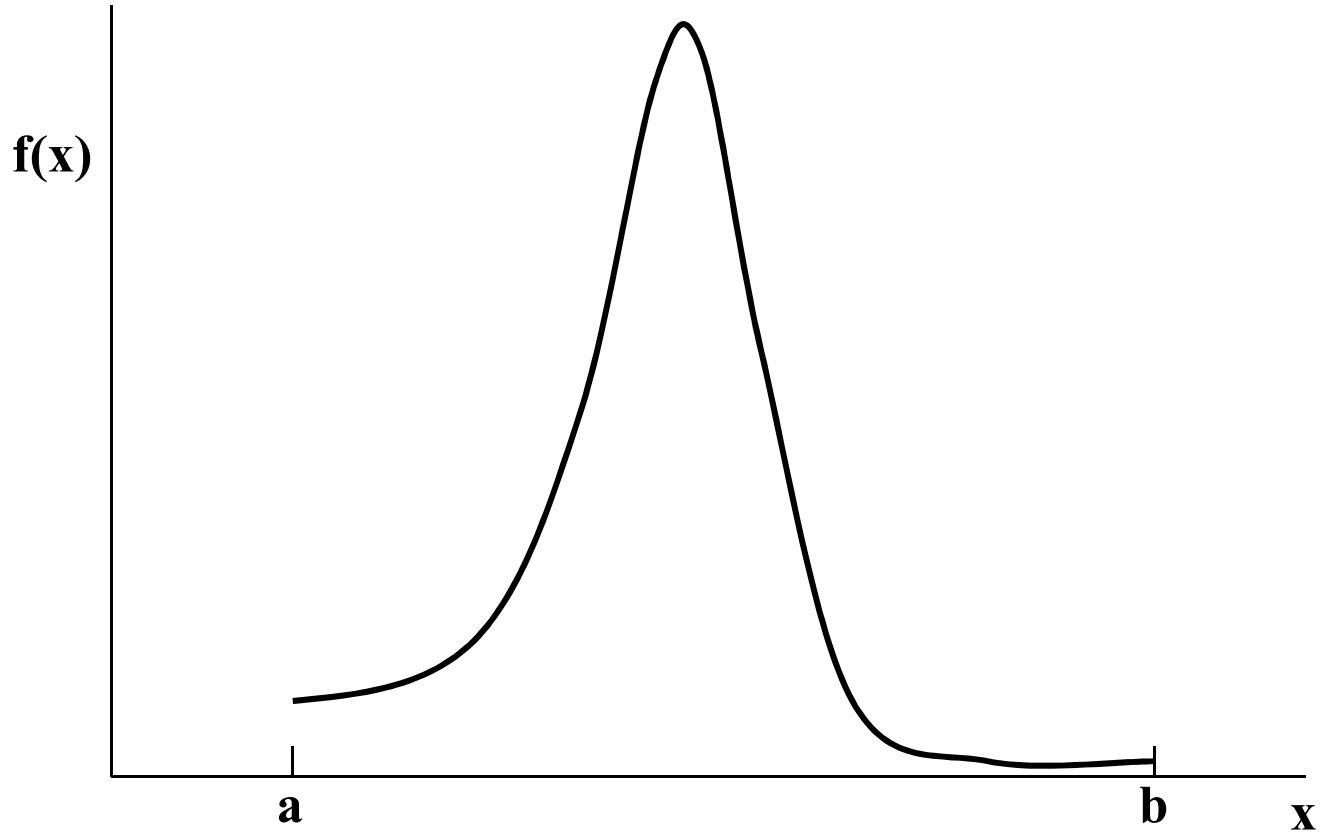
While MD solves for the time dependent development of the system studied and averaging is done over time, MC is based on the statistical mechanics notion of averaging over ensembles. In MC simulations we choose an appropriate statistical mechanics ensemble and evaluate physical quantities in this ensemble. The ergodic theorem guarantees the equivalence of the MD and MC approaches.

$$\langle A \rangle = Z^{-1} \int_{\text{Phase space}} A(\mathbf{Q}) F(\mathbf{Q}) d\mathbf{Q}$$

$$Z = \int_{\text{Phase space}} F(\mathbf{Q}) d\mathbf{Q}$$

The Monte Carlo method employs a **stochastic approach to evaluate the integrals** associated with calculation of $\langle A \rangle$ for the systems described by an equilibrium distribution function, $F(\mathbf{Q})$, and provides an **algorithm for construction of systems with this distribution**.

Monte Carlo – Distribution of states in real systems



Monte Carlo – General Monte Carlo Algorithm

(1) Specify an initial point, $\mathbf{Q}_0$, in the phase space of the system studied. *The process should be independent of this choice.*

(2) Starting from a state **Q** generate **randomly** a new state **Q'**. This is done with the help of a random number generator.

(3) Evaluate the transition probability $\rho(\mathbf{Q},\mathbf{Q}')$ defined by (MC9).

(4) Generate a random number ξ such that $0 \le \xi \le 1$.

(5) If $\rho(\mathbf{Q},\mathbf{Q}') < \xi$ then remain in the old state **Q** and go to (2).

(6) If $\rho(\mathbf{Q},\mathbf{Q}') \ge \xi$ accept the new state, i.e. $\mathbf{Q} \rightarrow \mathbf{Q}'$, and go to (2).

Quantities conserved: *The temperature T, the total number of particles N and the total volume V* (see also MD). The distribution function is the Boltzmann distribution

$$p(\mathbf{Q}) = Z^{-1} \exp\left[-\frac{\mathbf{H}(\mathbf{Q})}{k_B T}\right] \qquad \text{(MC12)}$$

where H is the Hamiltonian of the system, i. e. its energy. The transition probability $\mathbf{Q} \rightarrow \mathbf{Q}'$ then depends on $\Delta\mathbf{H} = \mathbf{H}(\mathbf{Q}') - \mathbf{H}(\mathbf{Q})$, i. e. the change of $\mathbf{H}$ when moving from one state to another

Monte Carlo – Metropolis Method

(1) Specify an initial configuration $\mathbf{X}_0$, for example positions of all the particles in the system studied.

(2) Starting from a state $\mathbf{X}$ generate randomly a new state (configuration) $\mathbf{X}'$. This is done using a random number generator.

(3) Compute the potential energy difference $\Delta E_p = E_p(\mathbf{X}') - E_p(\mathbf{X})$.

(4) If $\Delta E_p < 0$ accept the new configuration, i. e. $\mathbf{X} \rightarrow \mathbf{X}'$ and go to (2).

(5) If $\Delta E_p > 0$ compute $\exp\left[-\frac{\Delta E_p}{k_B T}\right]$.

(6) Generate a random number ξ such that $0 \leq \xi \leq 1$.

(7) If $\exp\left[-\frac{\Delta E_p}{k_B T}\right] \geq \xi$ accept the new state, i.e. $\mathbf{X} \rightarrow \mathbf{X}'$ and go to (2).

(8) Otherwise retain the old configuration and return to (2).

Structural relaxation and atomic vibrations

One atom is picked randomly in the simulation block. The position of this atom is then changed in small increments according to the following prescription:

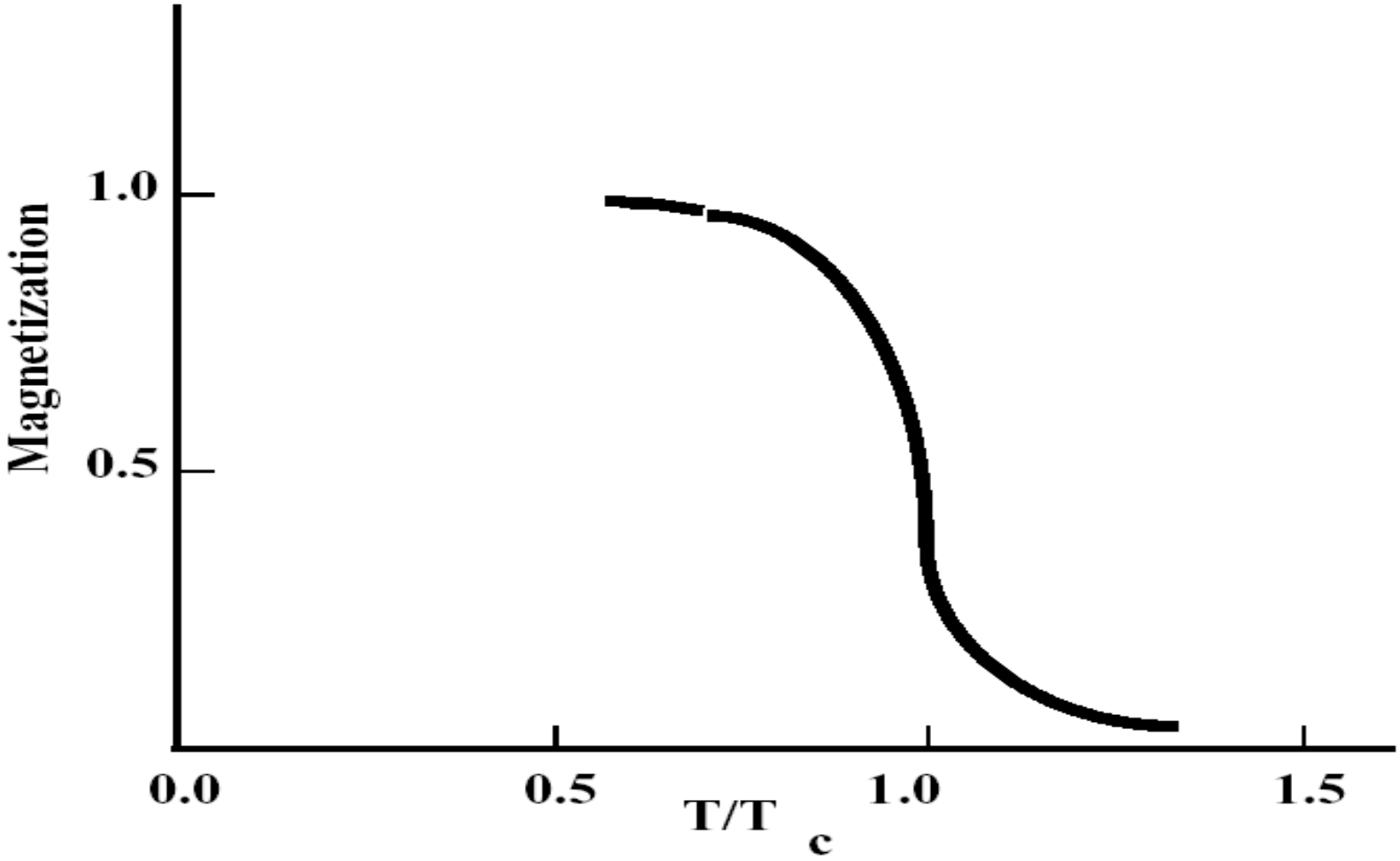
$$x \rightarrow x + \alpha\zeta_1$$
$$y \rightarrow y + \alpha\zeta_2$$
$$z \rightarrow z + \alpha\zeta_3$$

Ising model

$$H = -J\sum_{i,j} s_i s_j \qquad \Delta H(s_k \rightarrow -s_k) = 2Js_k \sum_{\substack{i=\text{neighbors} \\ \text{of } k}} s_i$$

$$m(s_1) = \frac{(\text{number of spins up} - \text{number of spins down})}{\text{total number of spins}}$$

Monte Carlo – Magnetization vs. Temperature by Ising model of spins



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Open System with a heat reservoir – Grand Canonical ensemble

Number of μVT systems with E_i & N_r: $\tilde{N} = \sum_{i,r} n_{i,r}$

Average Energy of a system: $U \equiv < E_i > = \sum_{i,r} p_{i,r} E_i$ $\quad \tilde{N}U = \sum_{i,r} n_{i,r} E_i$

Average # of ptl. of a system: $< N > = \sum_{i,r} p_{i,r} N_r$ $\quad \tilde{N} < N > = \sum_{i,r} n_{i,r} N_r$

$$\ln W = \tilde{N} \ln \tilde{N} - \sum n_i \ln n_i$$

$$d \ln W_{\max} = -\sum dn_i \ln n_i = 0$$

$$\sum dn_{i,r} = 0 \qquad \sum \alpha \delta n_{i,r} = 0$$

$$\sum E_i dn_{i,r} = 0 \qquad \sum \beta E_i dn_{i,r} = 0$$

$$\sum N_r dn_{i,r} = 0 \qquad \sum \gamma \ N_r dn_{i,r} = 0$$

$$\ln n_{i,r} + \alpha + \beta E_i - \gamma N_r = 0 \qquad n_{i,r} = e^{-\alpha} e^{-\beta E_i + \gamma N_r} \qquad e^{-\alpha} = \frac{\tilde{N}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}}$$

$$p_{i,r} = \frac{n_{i,r}}{\tilde{N}} = \frac{e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}} \qquad U = \frac{\sum_{i,r} E_i e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}} \qquad < N > = \frac{\sum_{i,r} N_r e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}}$$

The number of particles is variable

- fluctuations of the concentration are allowed

Generally, select randomly one of the procedures

1) Change of the configuration

$$\exp(-\Delta E_p/kT)$$

2) Creation of a particle

$$\exp[-(\Delta E_p-\mu)/kT]$$

3) Destruction of particles

$$\exp[-(\Delta E_p+\mu)/kT]$$

Monte Carlo – Modified Grand Canonical Ensemble (μ,V,T)

System contains more than one species and for each species the number of atoms is allowed to change while the total number of atoms is fixed.

$$p(\mathbf{X}) = Z^{-1} \exp\left[-\frac{E_p(\mathbf{X}) - \mu_A N_A - \mu_B N_B}{k_B T}\right] \qquad \Delta\mu = \mu_A - \mu_B$$

Procedure:

(1) Select randomly either a particle A and replace it by a particle B or a particle B and replace it by a particle A. At the same time displace all the particles randomly to a different configuration. The change of the energy associated with this step is $\Delta E_p(\mathbf{X})$

(2a) If A was replaced by B accept the configuration if $\Delta E_p(\mathbf{X}) + \Delta\mu < 0$ and go to (1). Otherwise evaluate $\Delta p(\mathbf{X}) = \exp\left[-\frac{\Delta E_p(\mathbf{X}) + \Delta\mu}{k_B T}\right]$ and go to (3).

(2b) If B was replaced by A accept the configuration if $\Delta E_p(\mathbf{X}) - \Delta\mu < 0$ and go to (1). Otherwise evaluate $\Delta p(\mathbf{X}) = \exp\left[-\frac{\Delta E_p(\mathbf{X}) - \Delta\mu}{k_B T}\right]$ and go to (3).

(3) Generate a random number ξ such that $0 \le \xi \le 1$.

Segregation to an interface

$$\mu_i^{bulk}(c_i^{bulk}) = \mu_i^{int}(c_i^{int})$$

$$\Delta\mu^{bulk}(c_i^{bulk}) = \Delta\mu^{int}(c_i^{int})$$

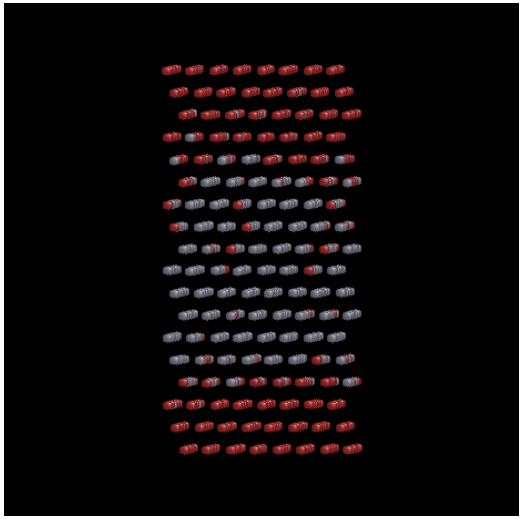
Order-disorder transition in binary alloy

Two species with the number of each species fixed

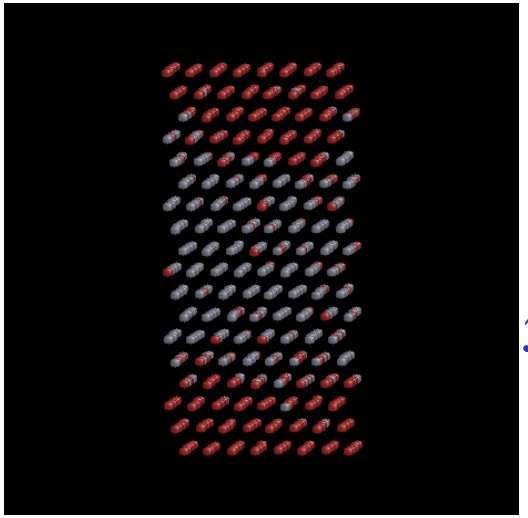
Morphology Evolution of an Alloy Particle

MD+MC+MS Hybrid Simulation

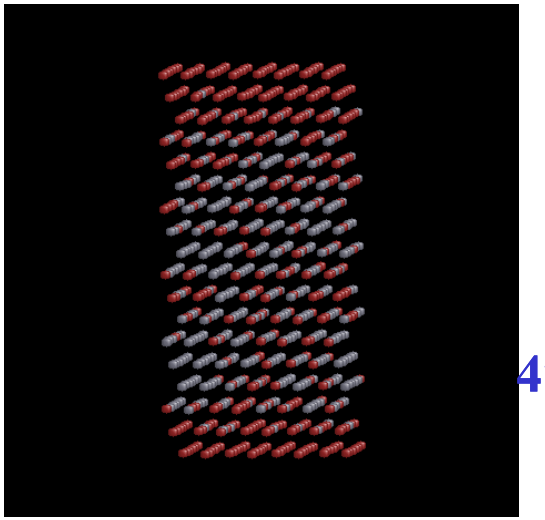
Phase Separation and Surface Segregation in Cu-Ni Thin Films



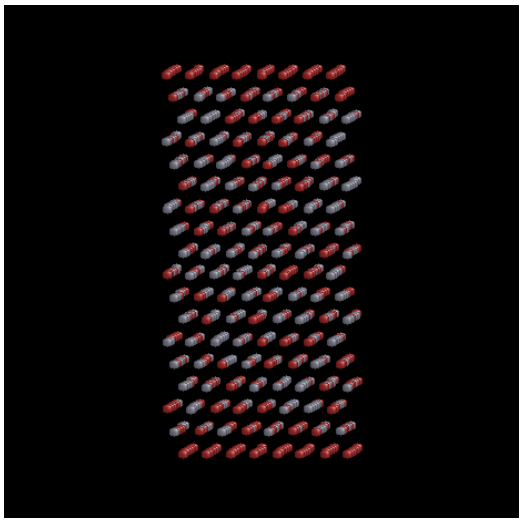
298 K



373 K

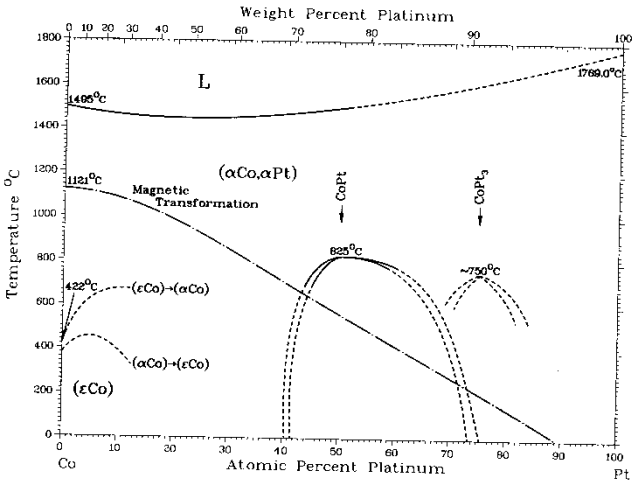


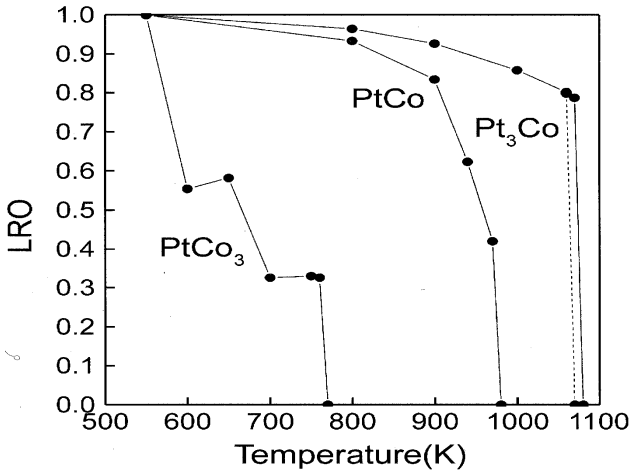
473 K



800 K

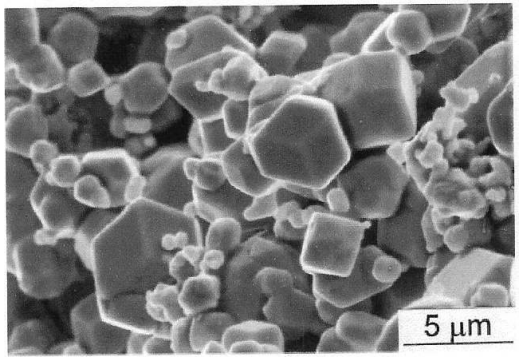
Order/Disorder in Co-Pt System - S.I. Park et al., Scripta Mater., 2001.



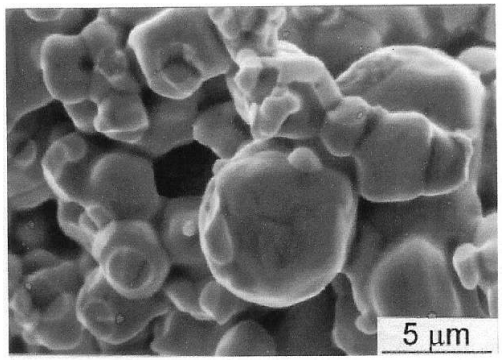


Property	Pt_3Co	PtCo	$PtCo_3$
Cohesive Energy (eV/atom)	5.500 *5.555 ±0.017*	5.215 *5.228 ±0.005*	4.873
Lattice Constant (Å)	a=3.833 *a=3.831*	3.754, c/a=.98 *3.745, c/a=.98*	3.625 *3.668*
Transition Temperature (K)	1070-1080 *1000*	970-980 *1100*	760-770 *840*

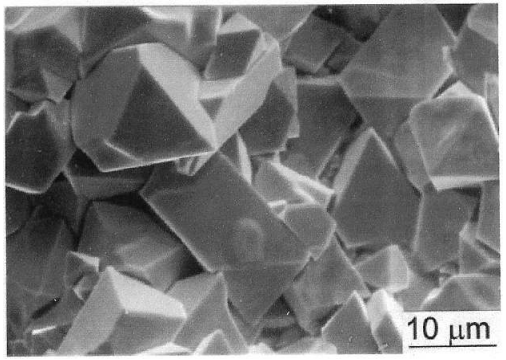
Effect of Interface Energy Anisotropy on Morphological Evolution



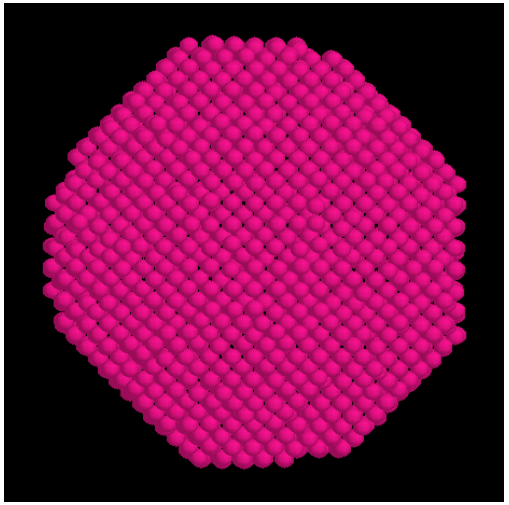
Pure W



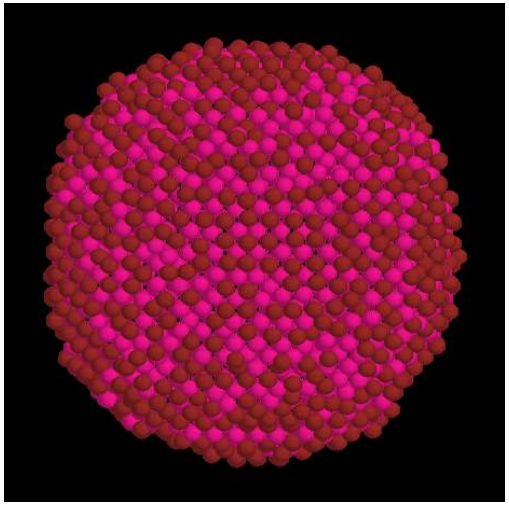
W + 0.4wt% Ni



Vacuum Annealing

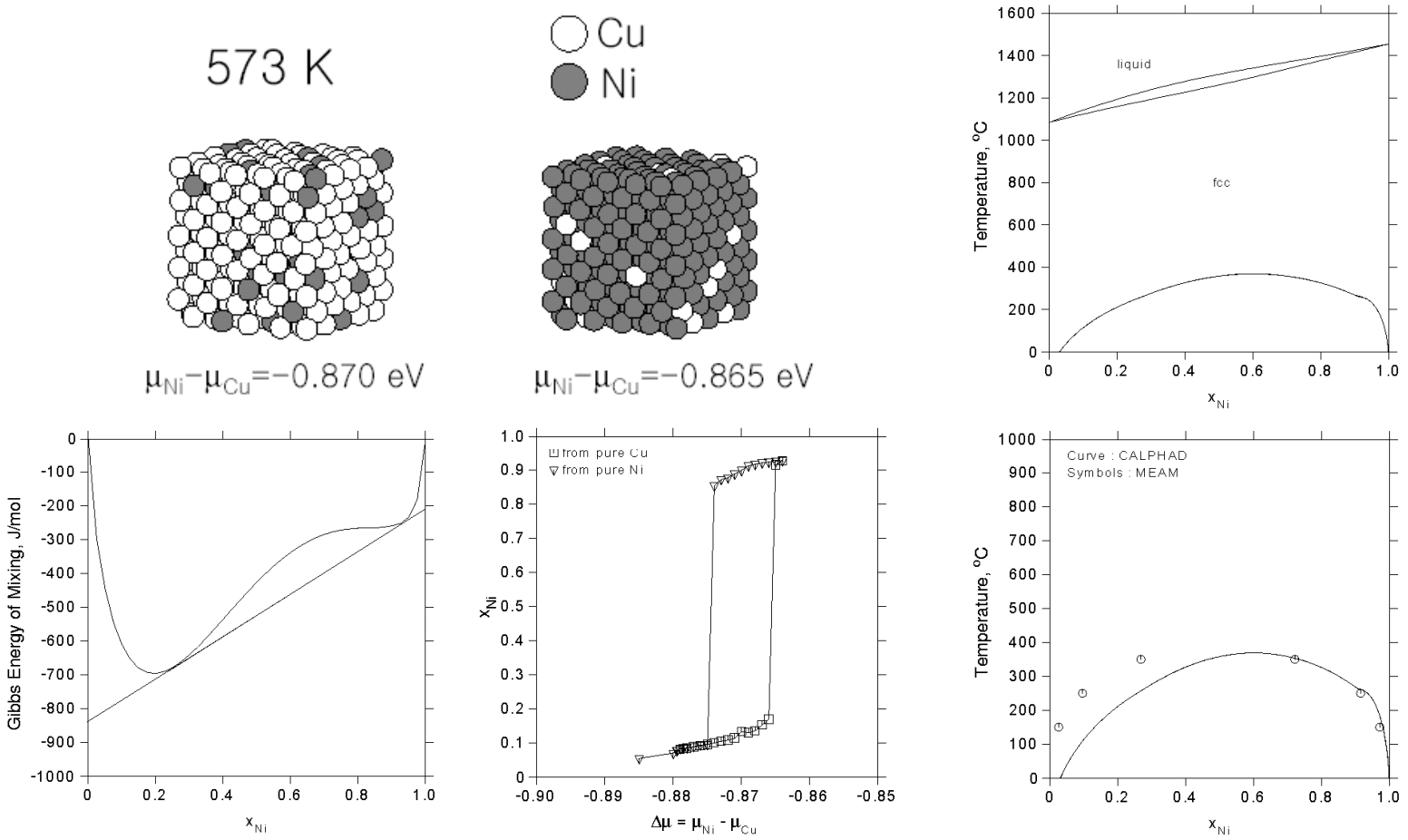


Pure W



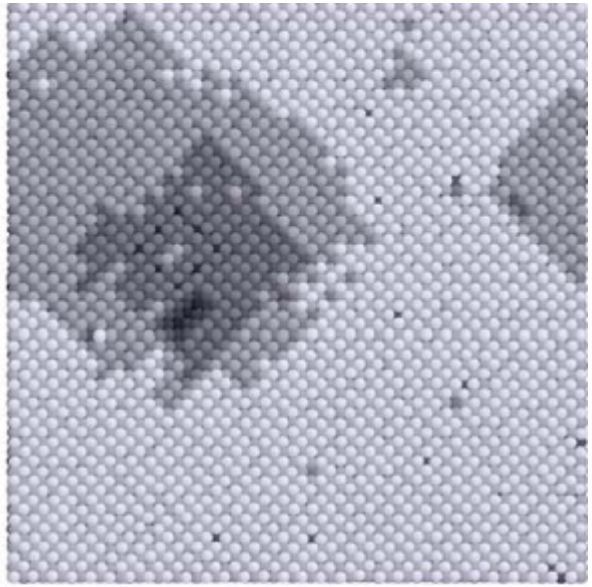
W-14at%Ni

Monte Carlo – Determination of Phase Diagram



A Modified Embedded Atom Method Interatomic Potential for the Cu-Ni System
Byeong-Joo Lee and Jae-Hyeok Shim, CALPHAD 28, 125-132 (2004).

Monte Carlo – Deposition or Etching



$\Delta\mu$ = −3.525, (100)

$\Delta\mu$ = −3.56, (100)