Computational Materials Design Worksh

March 2, 2018

Osaka University

PCoMS within educational activities in HPCI and Cluster Variation Method as a Theoretical Tool for Multiscale Phase Transformation studies

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Entropy and Cluster Variation Method (CVM)

Bragg-Williams approx.

$$S = k_B \cdot \ln \frac{N!}{\prod_i \{N x_i!\}} = -k_B \left(x \ln x + (1-x) \ln(1-x) \right)$$

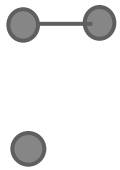
$$F = F(x)$$

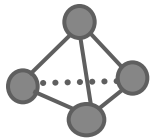
concentration = point probability

Local Atomic Conf.?

CVM

$$S = k_B \cdot \ln \frac{\prod_{i,j} \{N y_{ij}!\}^6 \cdot \{N!\}}{\prod_i \{N x_i!\}^5 \cdot \prod_{i,j,k,l} \{N w_{ijkl}!\}^2}$$





$$F = F(x_i, y_{ij})$$

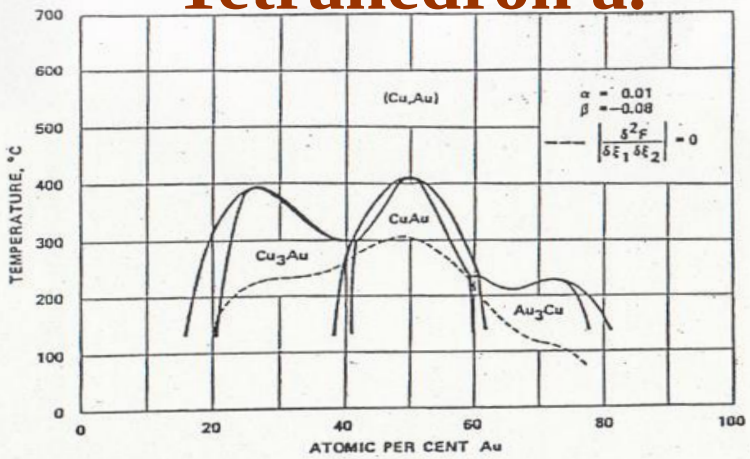
$$F = F(x_i, y_{ij}, z_{ijk} \cdots)$$

cluster probability

configurational freedom

CVM vs BW approximations

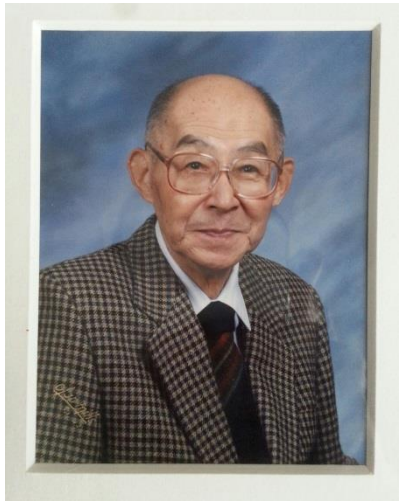
Tetrahedron a.



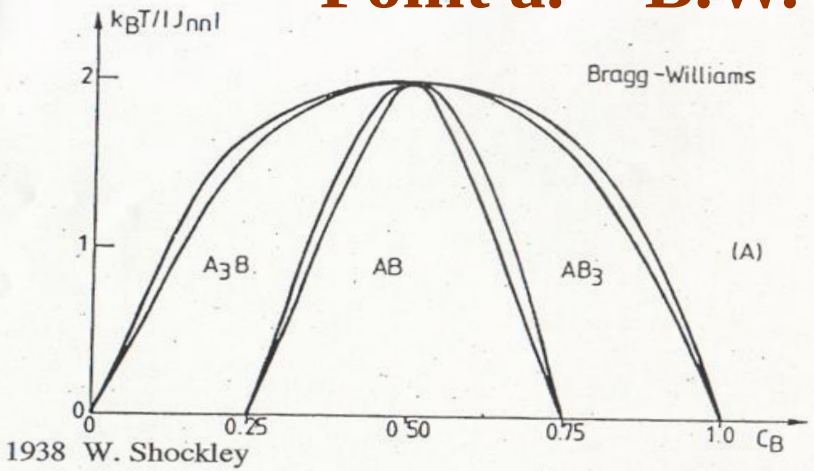
1979 R. Kikuchi & D. de Fontaine

E( )

S( )



Point a. = B.W.



1938 W. Shockley

E( ) *S*( )

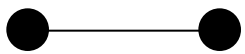
Basic cluster and Cluster Variation Method

Bragg-Williams approx.=point approx.

fcc

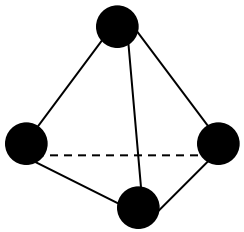
$$S_{pt} = \frac{1}{L} \cdot k_B \cdot \ln\left(\frac{N!}{\{Point\}_N}\right)^L = k_B \cdot \ln \frac{N!}{\prod_i (Nx_i!)} = k_B \cdot \ln \frac{N!}{\prod_i (N_i!)} \qquad (1)$$

Bethe approx.= pair approx.



$$S_{pair} = \frac{1}{L} \cdot k_B \cdot \ln\left[\frac{(\{Point\}_N)^{2\omega-1}}{(N!)^{\omega-1} \cdot (\{Pair\}_N)^{\omega}}\right]^L = k_B \cdot \ln \frac{\left(\prod_i (N \cdot x_i)!\right)^{2\omega-1}}{(N!)^{\omega-1} \cdot \left(\prod_{i,j} (N \cdot y_{ij})!\right)^{\omega}} \qquad (2)$$

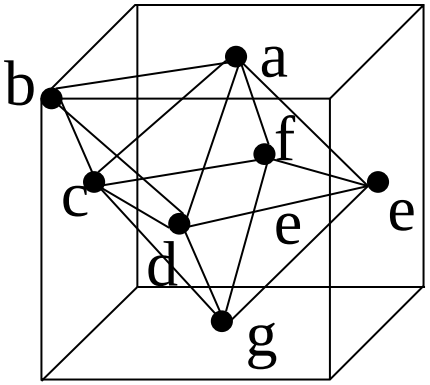
Tetrahedron approx.



$$S_{tetra} = k_B \cdot \ln \frac{\left(\prod_{i,j} (N \cdot y_{ij})!\right)^6 \cdot N!}{\left(\prod_i (N \cdot x_i)!\right)^5 \cdot \left(\prod_{i,j,k,l} (N \cdot w_{ijkl})!\right)^2} \qquad (3)$$

Tetrahedron-Octahedron approx.

$$S_{TO} = k_B \cdot \ln \frac{\left(\prod_{i,j,k} (N \cdot z_{ijk})!\right)^8 \cdot \left(\prod_i (N \cdot x_i)!\right)}{\left(\prod_{i,j,k,l,m,n} (N \cdot v_{ijklmn})!\right) \cdot \left(\prod_{i,j,k,l} (N \cdot w_{ijkl;})!\right)^2 \cdot \left(\prod_{i,j} (N \cdot y_{ij})!\right)^6} \qquad (4)$$



Extensions of CVM [1]

Cluster Expansion Method

First-principles phase equilibria calculations

Electronic structure calculations

Phase equilibria

CVM

$$F_{CVM}(\{\xi\})$$

Phase Equilibria

Showing: Atomic weight

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA		IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
1 H 1.0079																2 He 4.0026
3 Li 6.94	4 Be 9.0121										5 B 10.81	6 C 12.011	7 N 14.006	8 O 15.999	9 F 18.998	10 Ne 20.17
11 Na 22.989	12 Mg 24.305										13 Al 26.981	14 Si 28.086	15 P 30.973	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.955	22 Ti 47.90	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.546	30 Zn 65.38	31 Ga 69.735	32 Ge 72.59	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.467	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906	44 Ru 101.07	45 Rh 102.90	46 Pd 106.4	47 Ag 107.86	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
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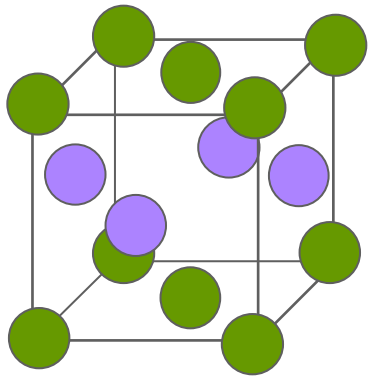
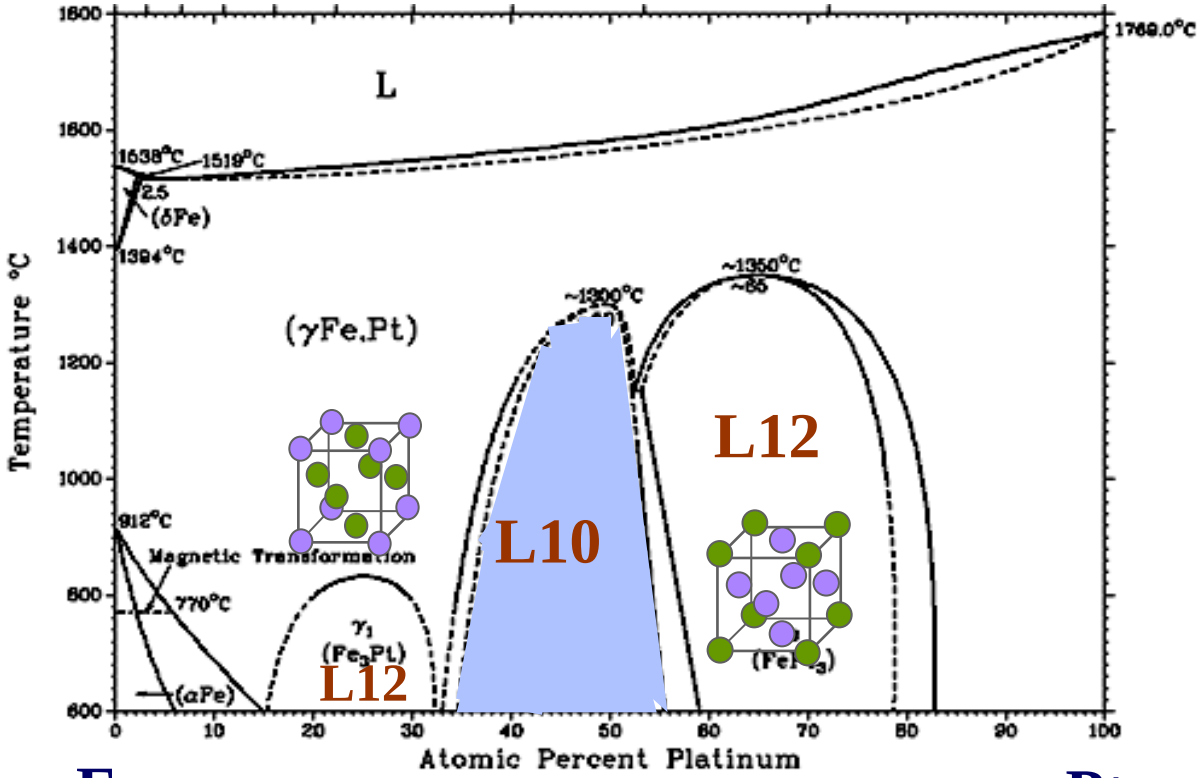
First-principles calculation for Fe-Pt

Fe-Pt



L10

high density magnetic recording media



Theoretical Procedure

- **Total energy calculation at the ground state**
- **Cluster Expansion Method (CEM)**

$$\Delta E\left(V(r), \{\xi_i\}\right) = \sum_j v_j\left(V(r)\right) \cdot \xi_j^m$$

($\cdots$; $\xi_i^m = \langle \sigma_1 \cdot \sigma_2 \cdots \sigma_i \rangle$

$$v_i = \sum_m \left\{\xi_j^m\right\}^{-1} \cdot \Delta E^{(m)}$$

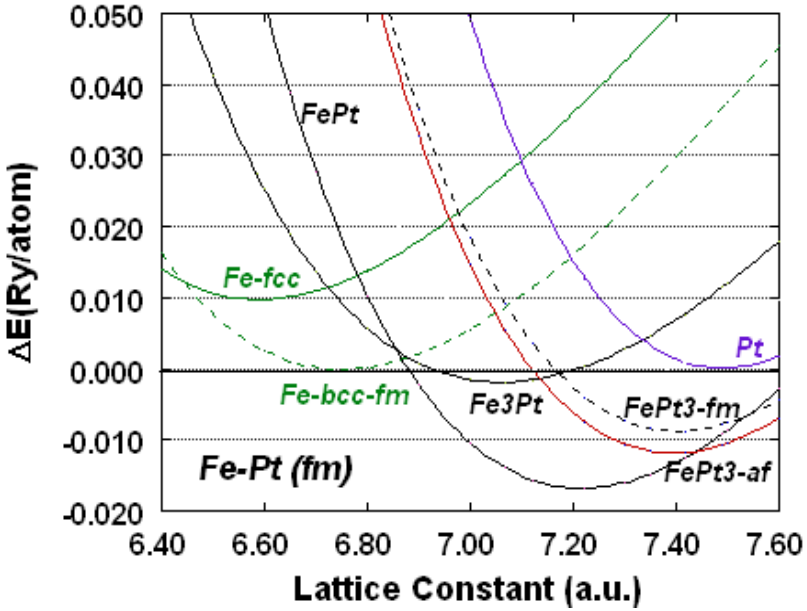
- **Cluster Variation Method (CVM)**

$$S = k_B \cdot \ln \frac{\prod_{i,j} \left\{N y_{ij}!\right\}^6 \cdot \left\{N!\right\}}{\prod_i \left\{N x_i!\right\}^5 \cdot \prod_{i,j,k,l} \left\{N w_{ijkl}!\right\}^2}$$

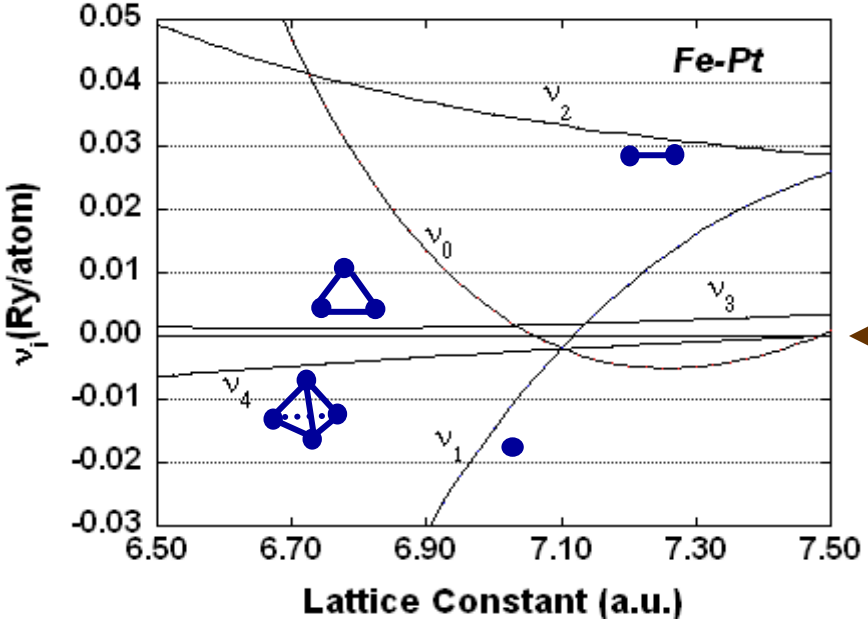
Ground State

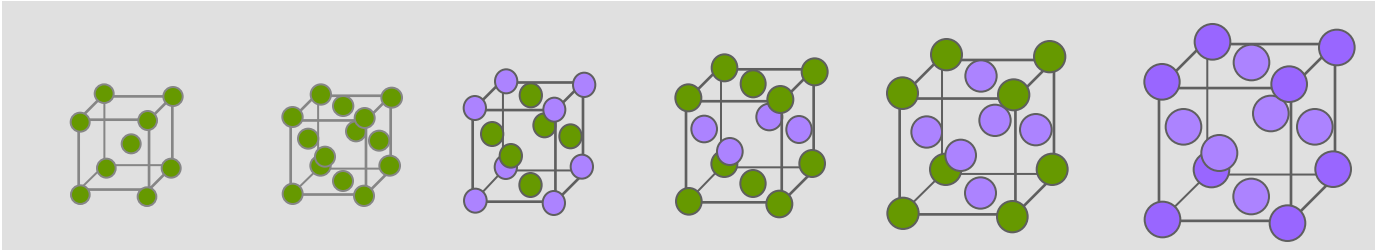
Fe-Pt (fm/am)

Spin polarized calc. FLAPW



Cluster Expansion Method





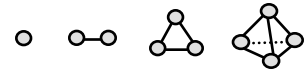
Fe-bcc Fe-fcc Fe_3Pt-$L1_2$ FePt-$L1_0$ FePt3-$L1_2$ Pt-fcc

Prof. Y. Chen
(Tohoku Univ.)

Theoretical Procedure

- **Total energy calculation at the ground state: FLAPW**
- **Cluster Expansion Method (CEM)**

$$\Delta E\left(V(r),\{\xi_i\}\right) = \sum_j v_j\left(V(r)\right)\cdot \xi_j^m$$

( ... ; $\xi_i^m = \langle \sigma_1 \cdot \sigma_2 \cdots \sigma_i \rangle$

$$v_i = \sum_m \left\{\xi_j^m\right\}^{-1} \cdot \Delta E^{(m)}$$

- **Cluster Variation Method (CVM)**

$$S = k_B \cdot \ln \frac{\prod_{i,j}\left\{N y_{ij}!\right\}^6 \cdot \left\{N!\right\}}{\prod_i \left\{N x_i!\right\}^5 \cdot \prod_{i,j,k,l}\left\{N w_{ijkl}!\right\}^2}$$

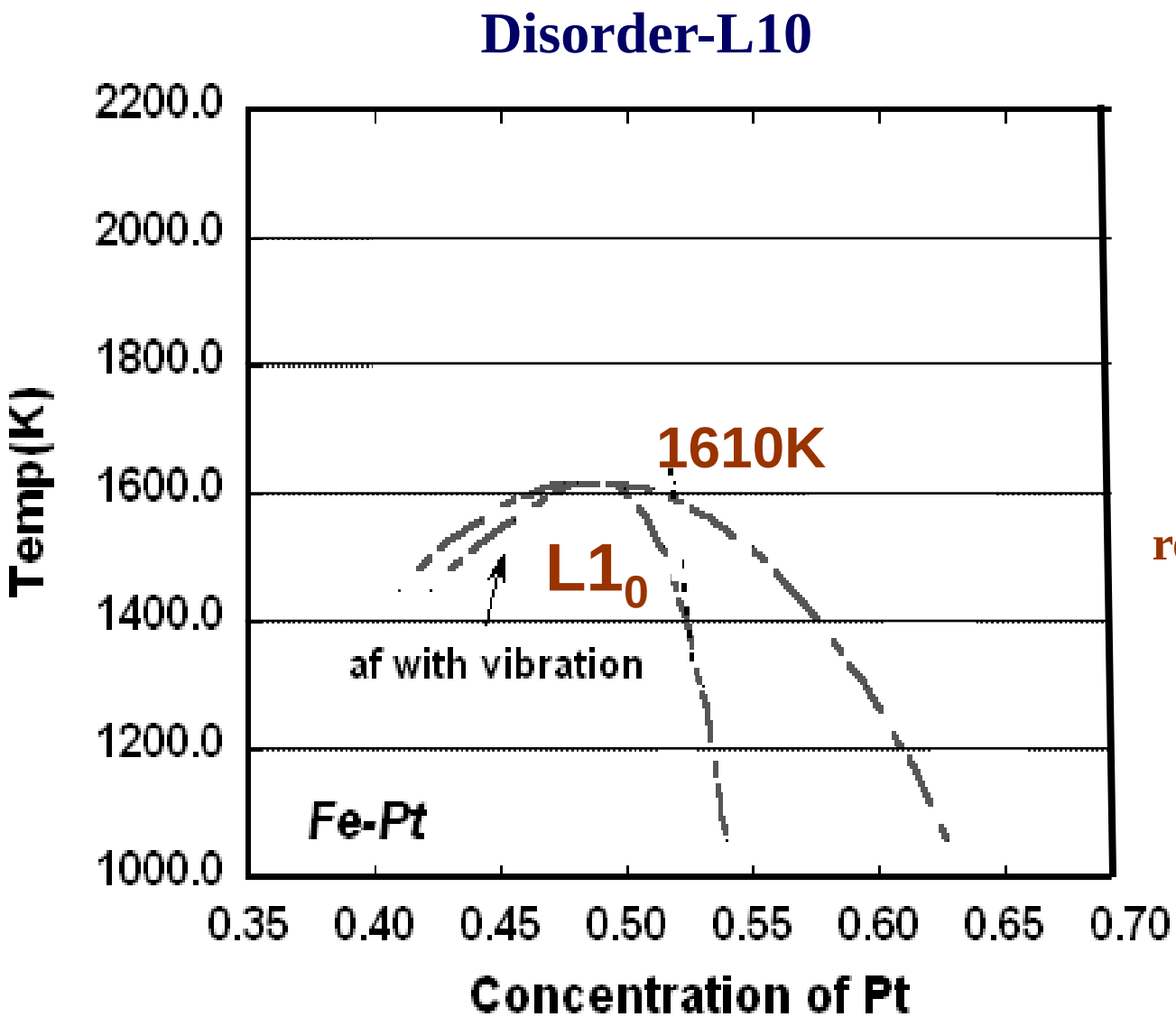
Lattice thermal vibration effects : Debye-Gruneisen model

$$g\left(T, V(r),\{\xi_i\}\right) = E\left(V(r),\{\xi_i\}\right) - T\cdot S\left(\{\xi_i\}\right)$$

$$\frac{\partial g}{\partial\{\xi_i\}} = 0 \qquad \frac{\partial g}{\partial V} = 0$$

Phase Diagram (1)

Fe-Pt



reproducibility

Exp. 1600

Phase Equilibria

Showing: Atomic weight

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Peculiarity origin of Invar property

The Nobel Prize in Physics 1920

"in recognition of the service he has rendered to precision measurements in Physics by his discovery of anomalies in nickel steel alloys"

Charles Edouard Guillaume

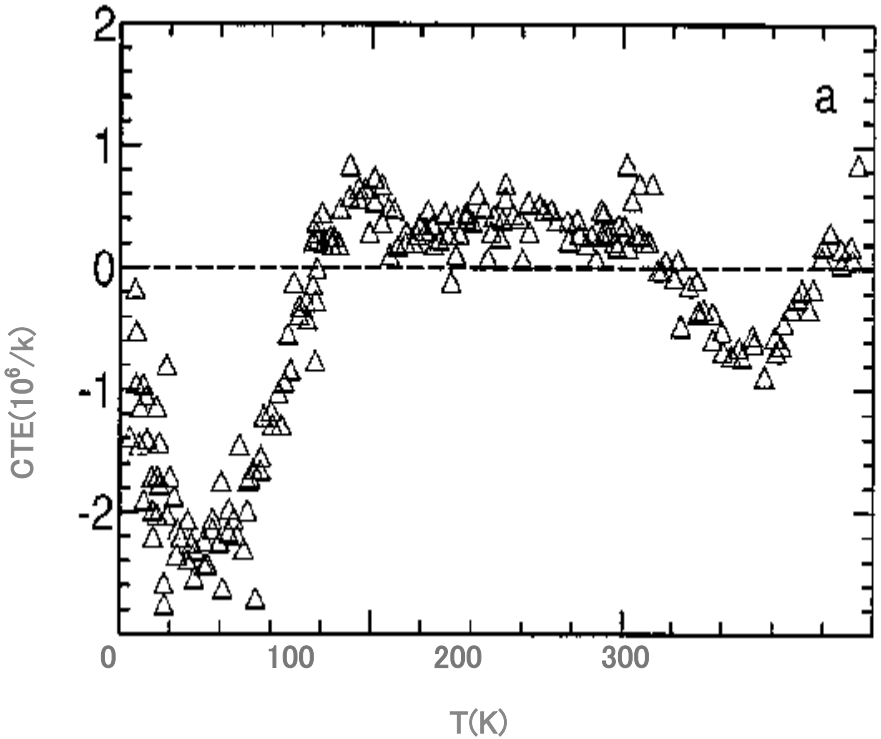
Switzerland

Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
Sèvres, France

b. 1861
d. 1938

Fe-Ni alloy

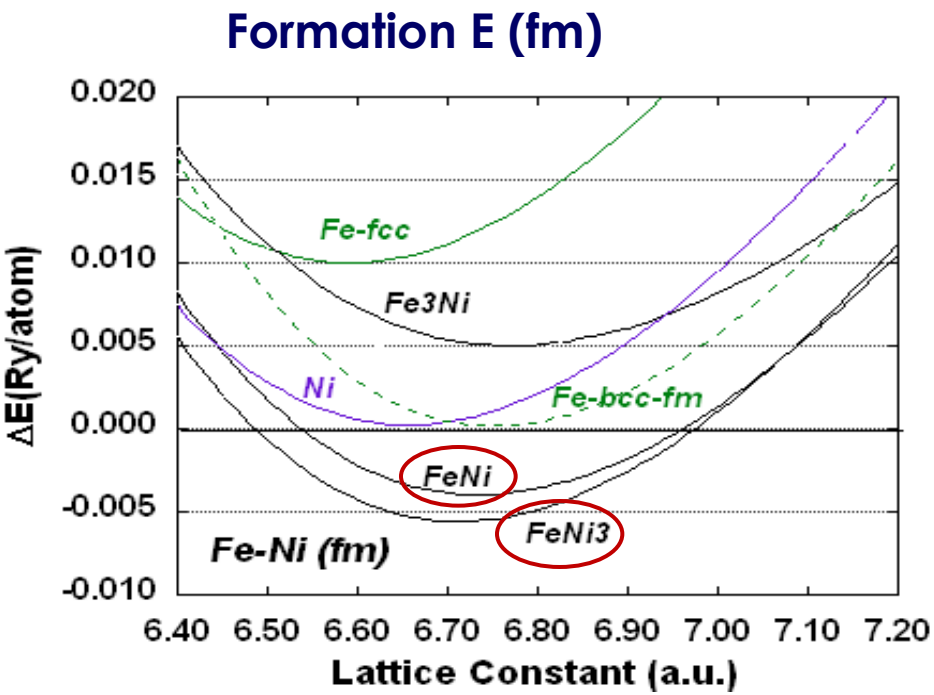
Fe-35%Ni: Invar Effect ? (1897)

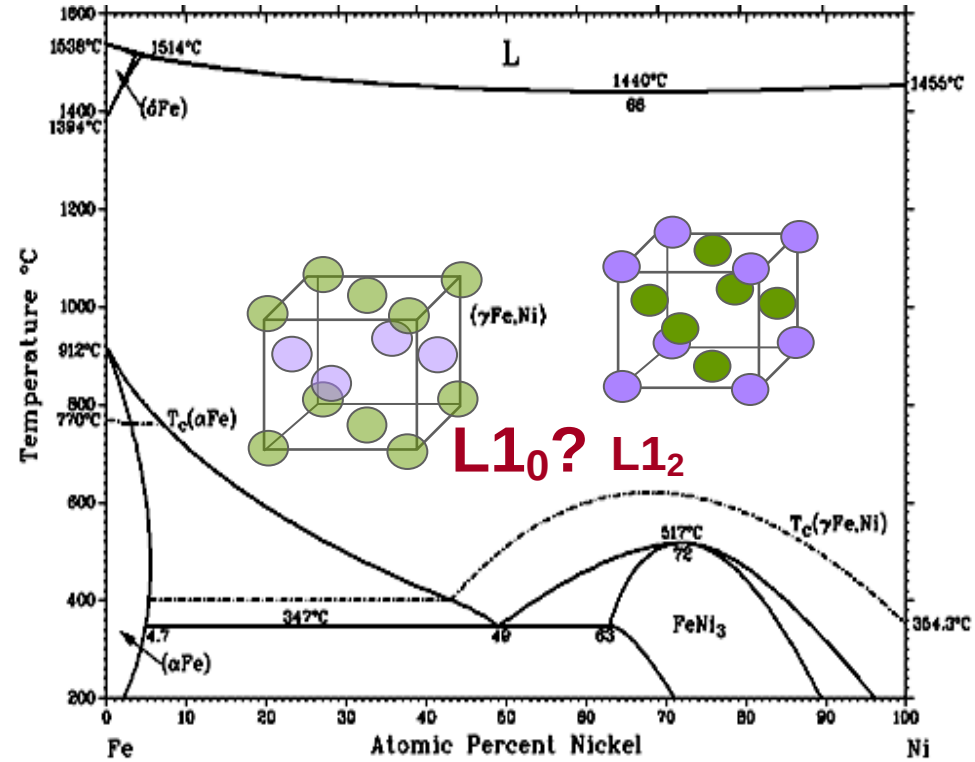


Q. Li etc., J. Mat. Res. 12(1997), 83

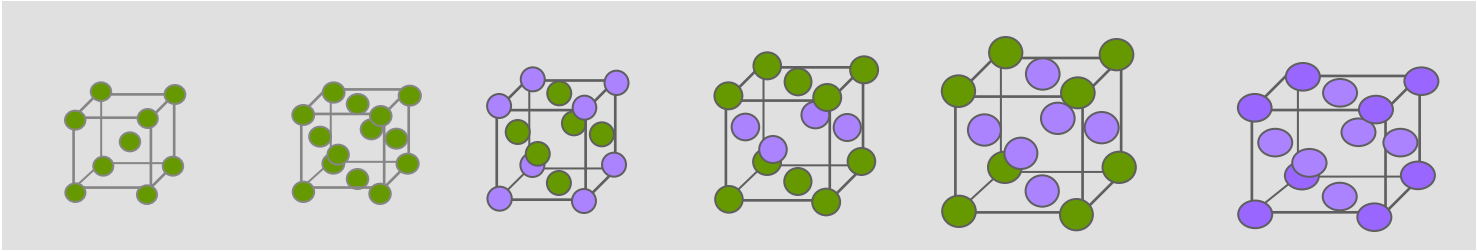
Fe-Ni stability of L10 ordered phase [1]

Formation Energy





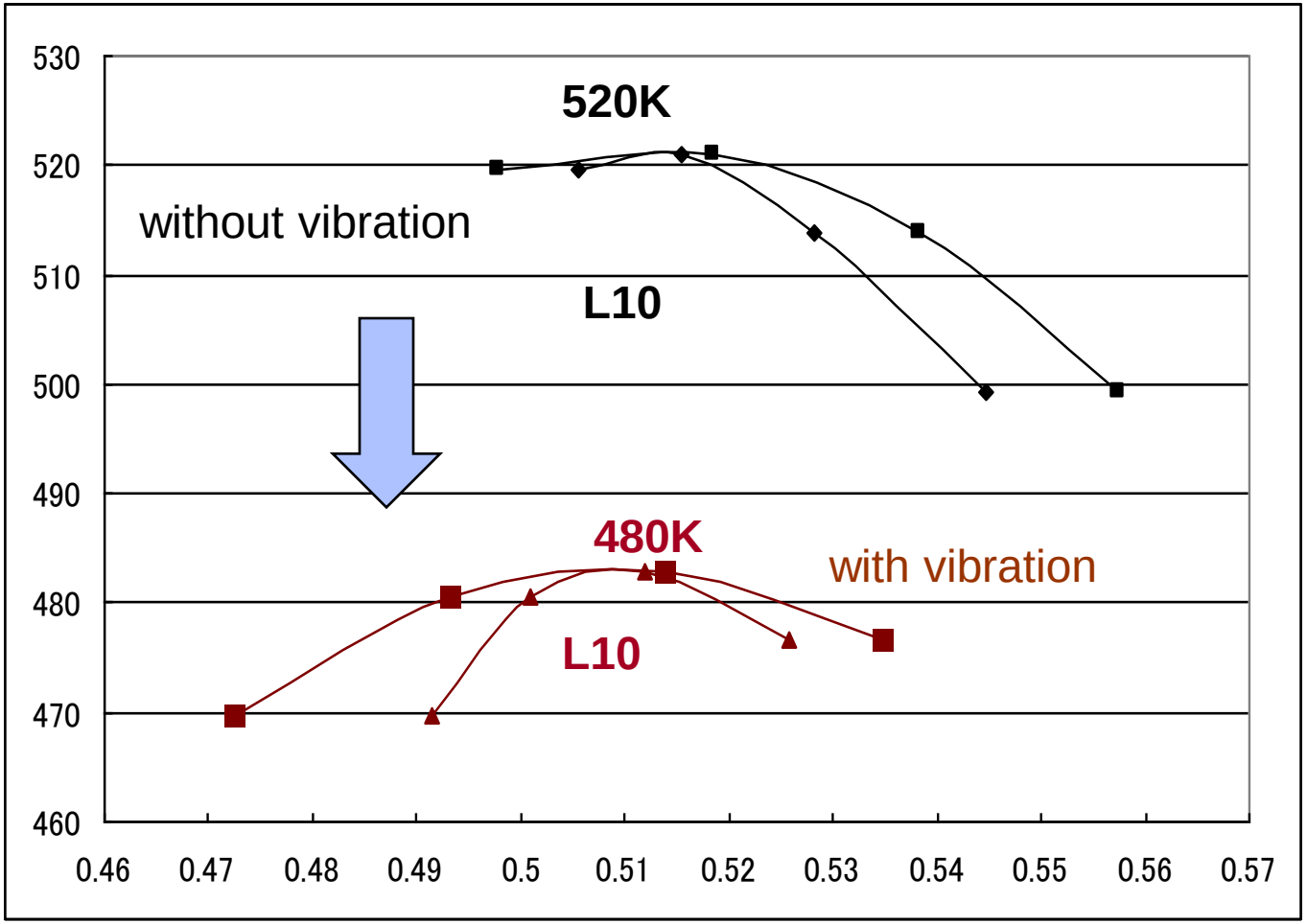
Y. Chen



Fe-bcc Fe-fcc Fe_3Ni-$L1_2$ FeNi-$L1_0$ $FeNi_3$-$L1_2$ Ni-fcc

Fe-Ni stability of L10 ordered phase [2]

$L1_0$-disorder boundary

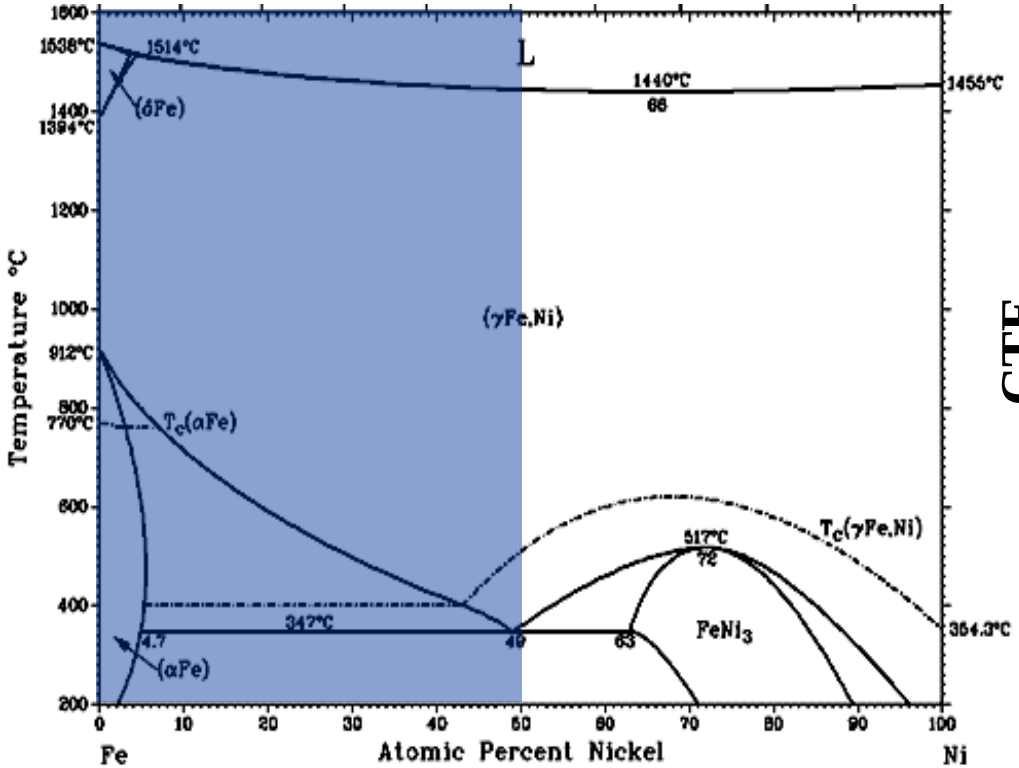


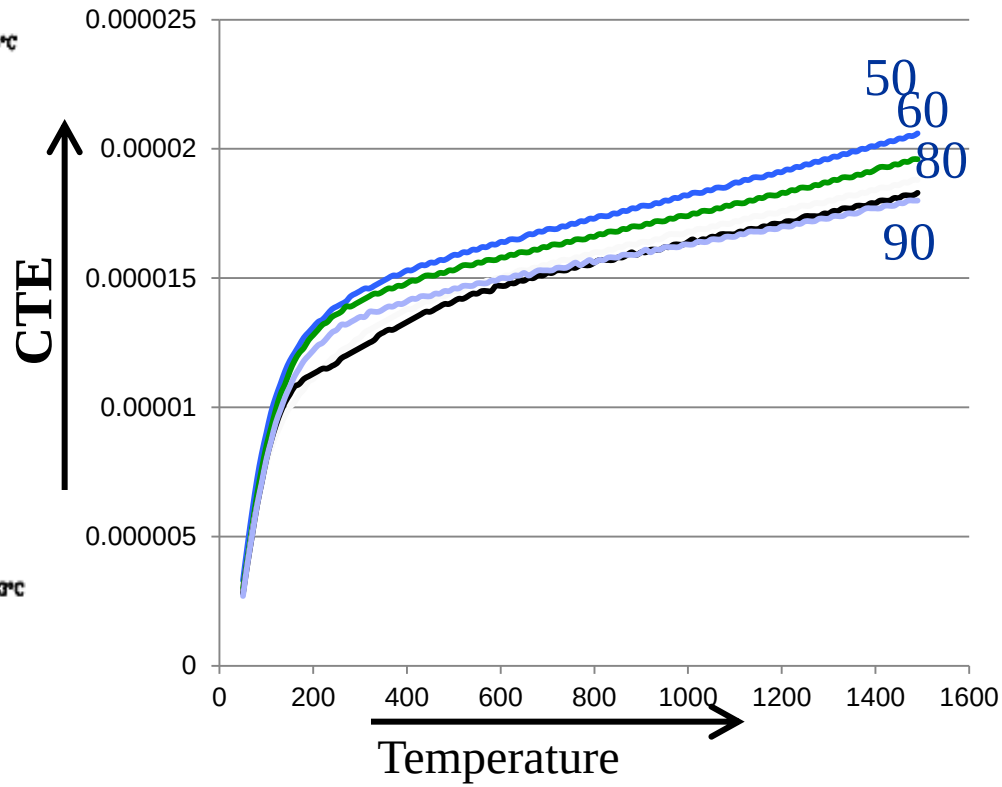
predictability

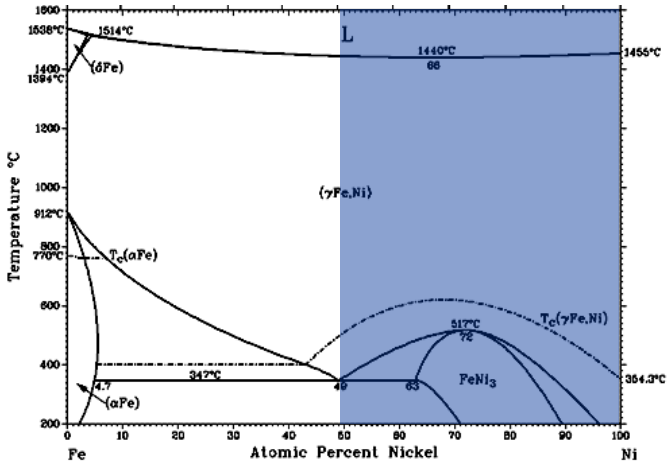
Exp.(1962), MC(1996): 590K～775K

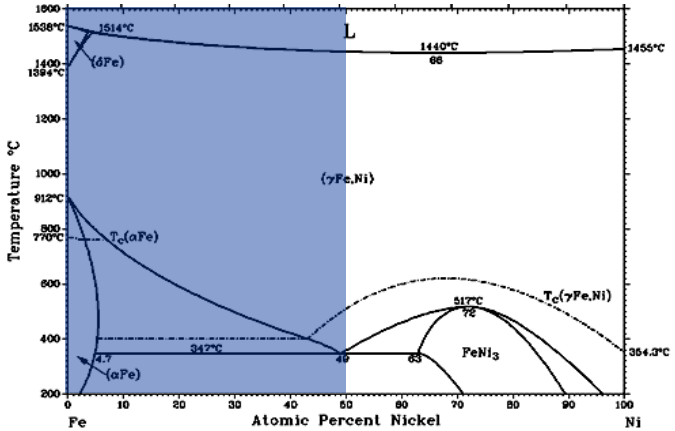
meteolite

CTE (disordered) in Fe-Ni









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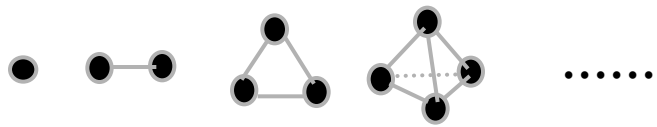
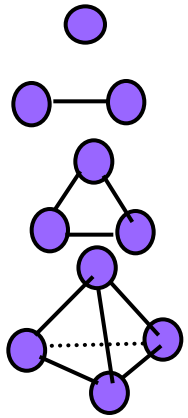
Effect of distant pair and multi-body interaction[2]

$$\Delta E_j^{(m)} = \sum_m \left(\{\xi_i\}_j^{(m)}\right)^{-1} \cdot v_i \cdot \Delta E_i^{(m)}$$



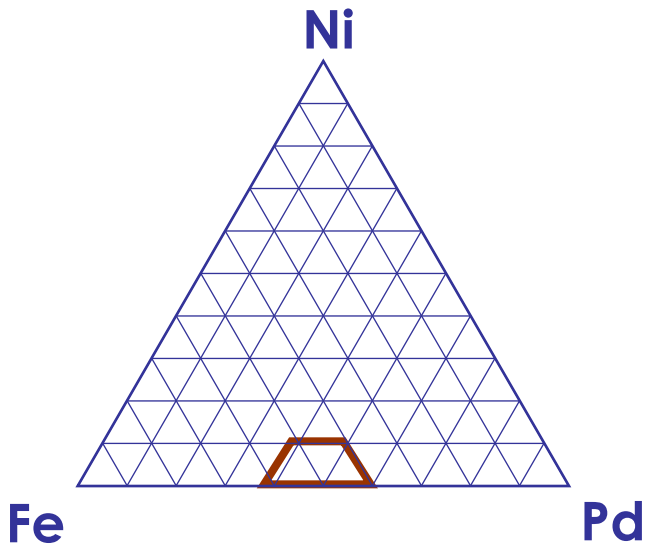
v_i; **Effective cluster interaction energy**

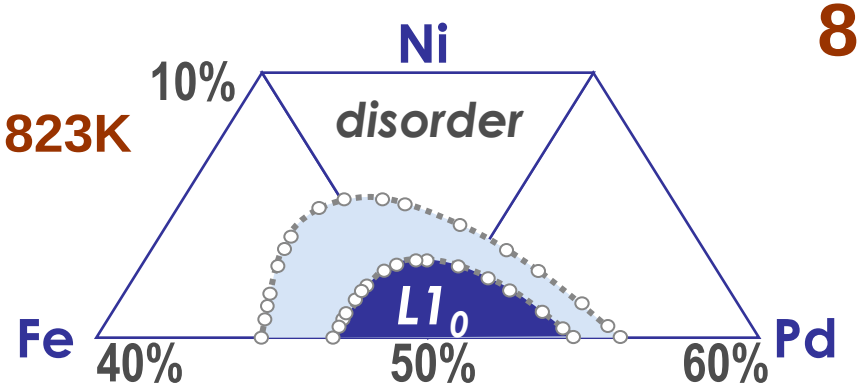
ξ_i^m; **Correlation function,** $\xi_i^m = \langle \sigma_1 \cdot \sigma_2 \cdots \sigma_i \rangle$



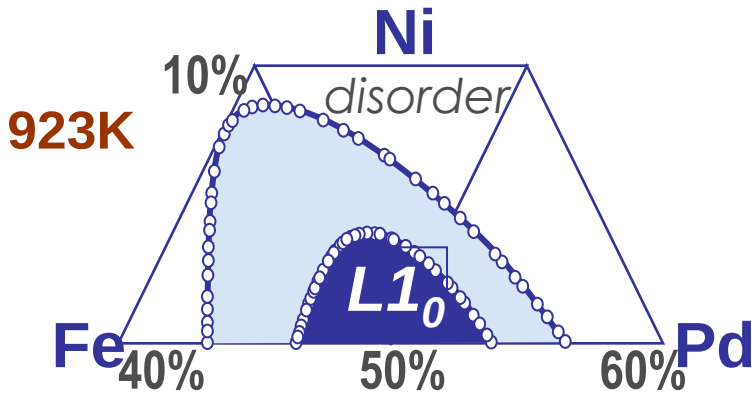
$$\begin{pmatrix} v_0(r) \\ v_1(r) \\ v_2(r) \\ v_3(r) \\ v_4(r) \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1/2 & 0 & -1/2 & -1 \\ 1 & 0 & -1/3 & 0 & 1 \\ 1 & -1/2 & 0 & 1/2 & -1 \\ 1 & 0 & 1 & -1 & 1 \end{pmatrix}^{-1} \cdot \begin{pmatrix} \Delta E_{Fe}(r) \\ \Delta E_{Fe_3Pt}(r) \\ \Delta E_{FePt}(r) \\ \Delta E_{FePt_3}(r) \\ \Delta E_{Pt}(r) \end{pmatrix}$$

Phase Diagram (3) Fe-Pd-Ni

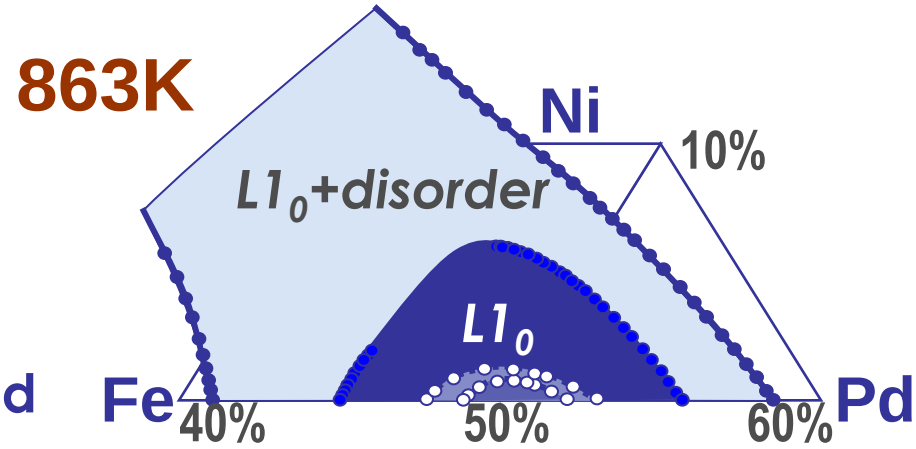




without tetragonality

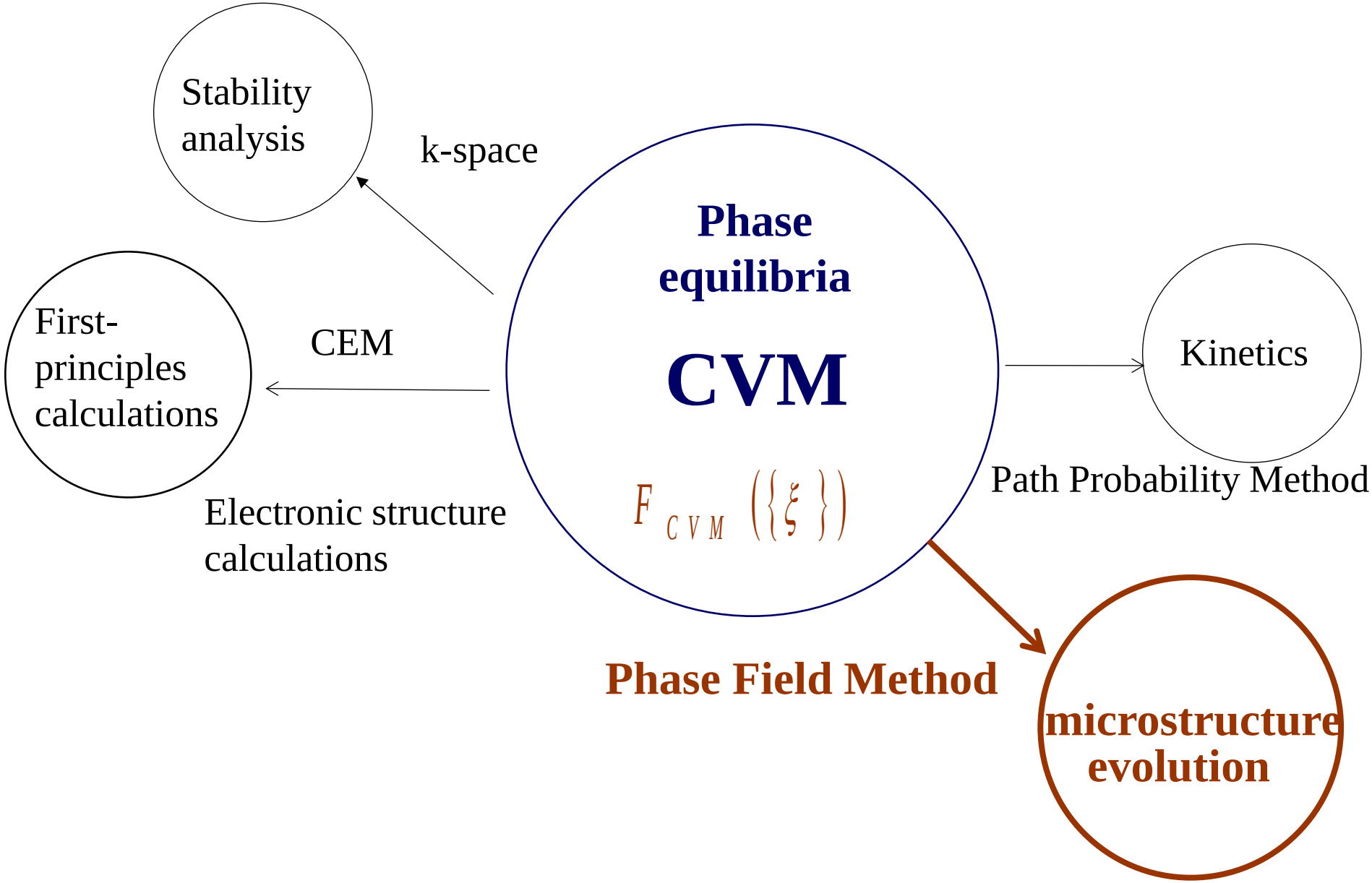


with tetragonality



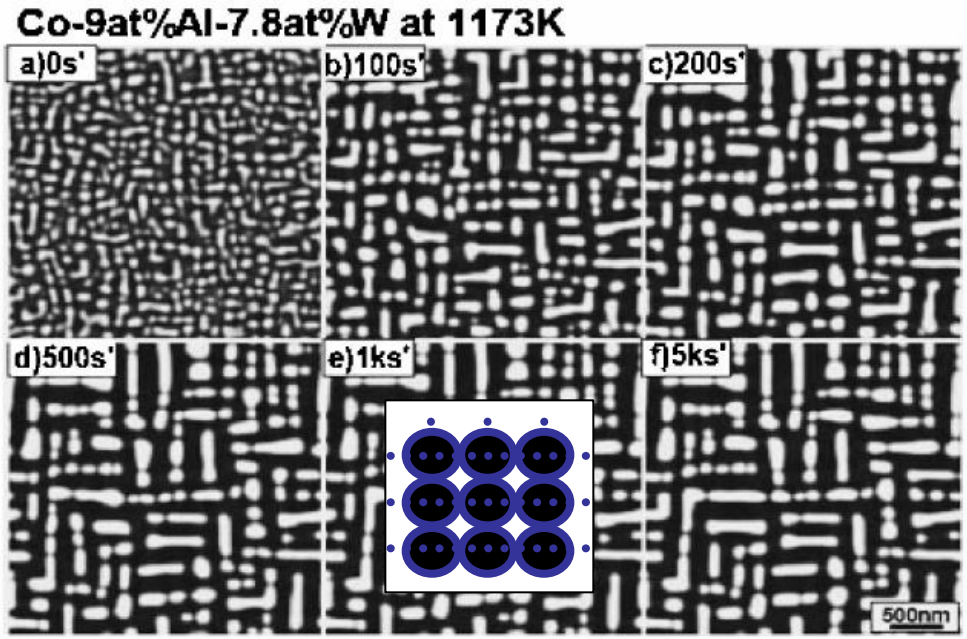
< 6at.%Ni is contained in Fe-Pd based $L1_0$ at 863K

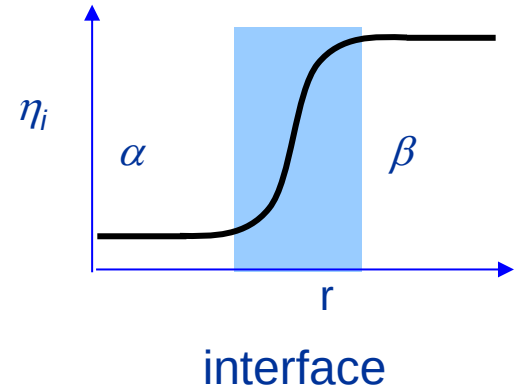
Extensions of CVM [4]



Phase Field Method

Free energy of microstructure





T. Koyama, J.Japan. Metals (2009)

η_i(**r**) : *field variable*

Time evolution of η_i(r)

Conserved
C

$$\frac{\partial \eta_i}{\partial t} = -\nabla\left(-M\nabla \frac{\delta F_{chem}}{\delta \eta_i}\right)$$

Non-Conserved
LRO

$$\frac{\partial \eta_i}{\partial t} = -\sum_j L_{ij} \frac{\delta F_{chem}}{\delta \eta_j}$$

κ_i : gradient energy coefficient,
M : mobility
L_{ij} : relaxation constant.

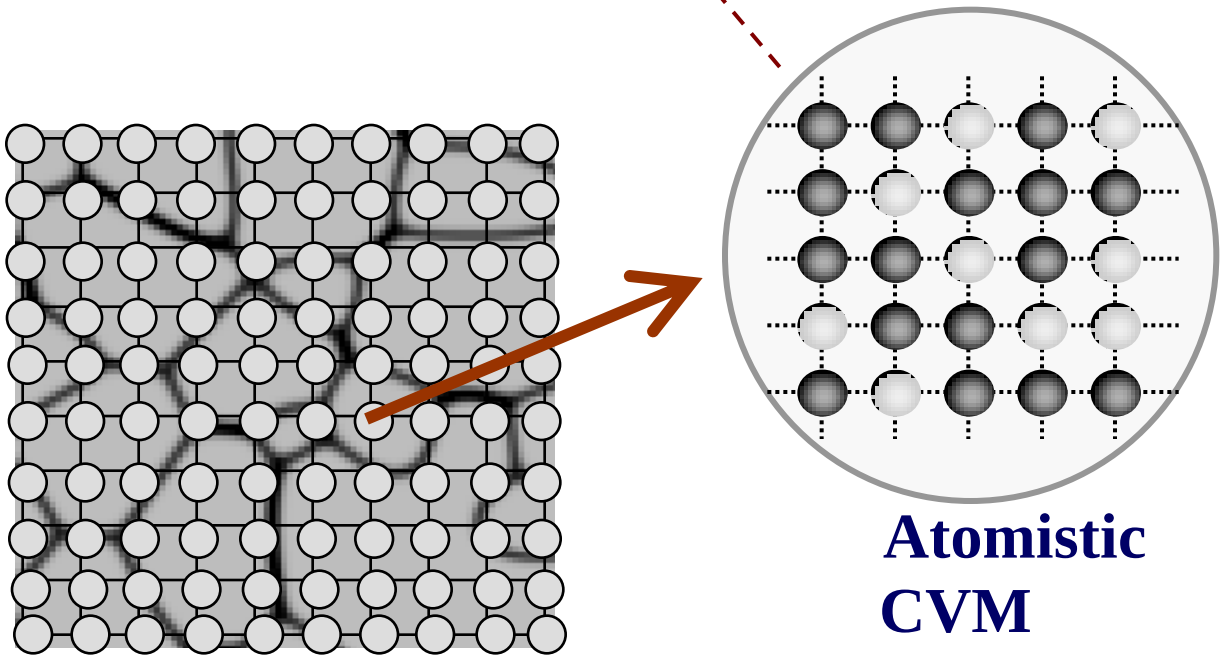
$$F_{chem} = \int \left(f_0\left[\{\eta_i\}\right] + \sum_{i=1} \kappa_i \left(\nabla \eta_i\right)^2 \right) \cdot dV$$

f_0 free energy of homogeneous system

Hybrid Model

1:1

$$\frac{\partial \xi_i}{\partial t} = -L_i \left\{ \frac{\partial f_{\mathrm{CVM}}}{\partial \xi_i} - \kappa_i \nabla^2 \xi_i \right\}$$



Microstructure
PFM

Atomistic
CVM

Multi-scale

Simultaneous calculations for Multi-scales (APB)

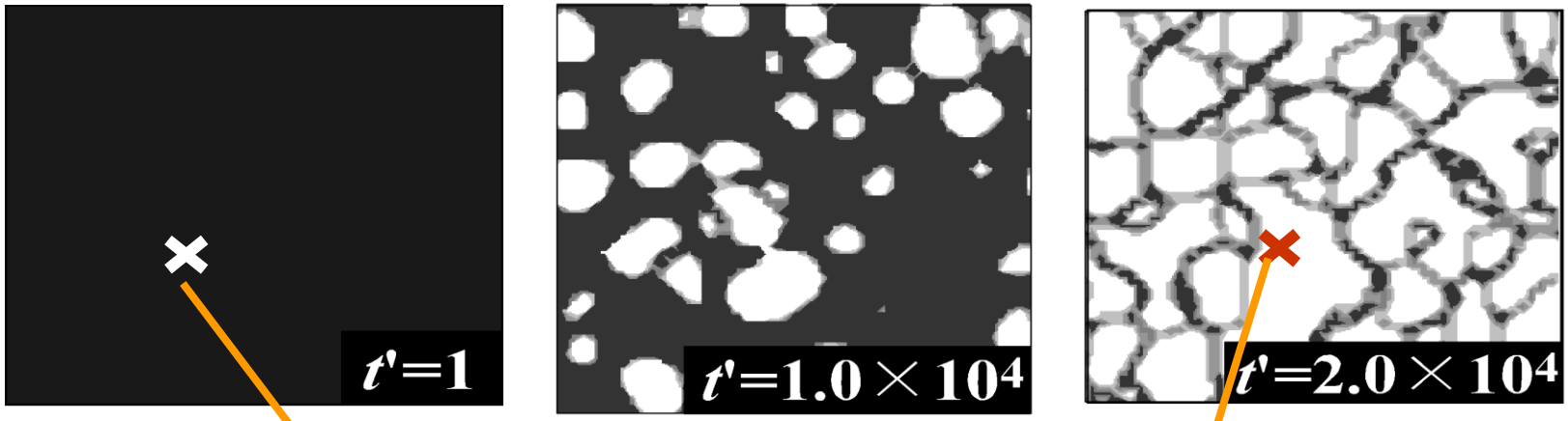
x'=1000

Microstructure

50at% T=1.6

L10

$|\mu|^2$

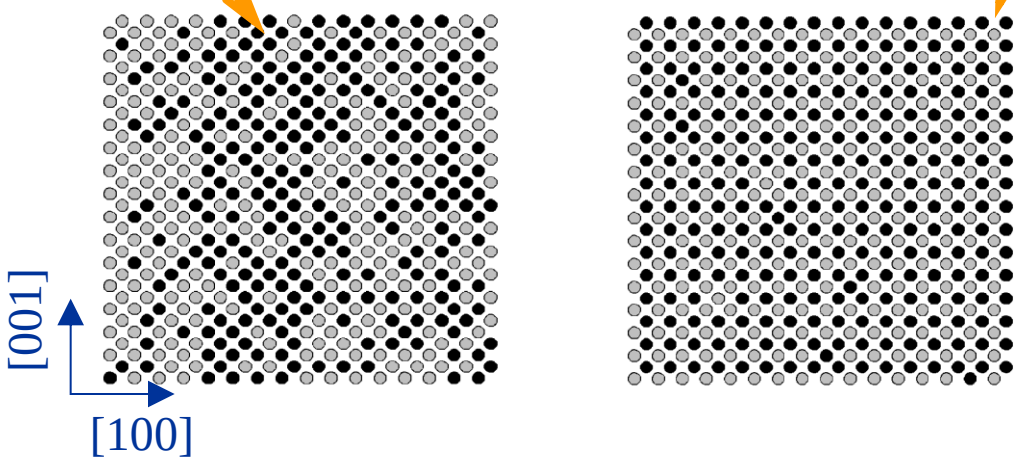


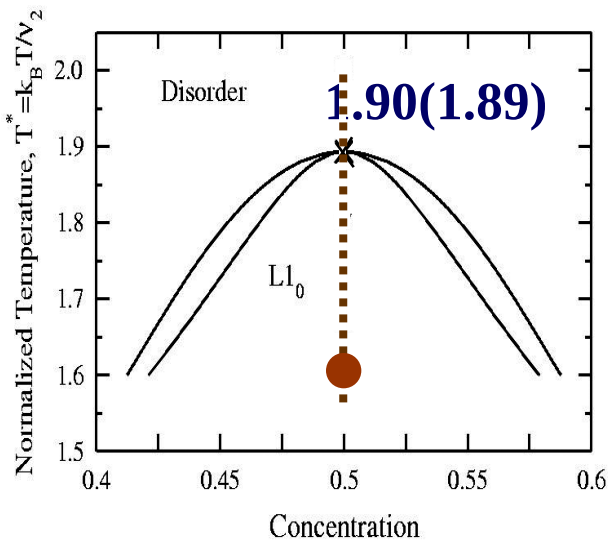
120x120x120 fcc algorithm; Williams

f_{CVM}

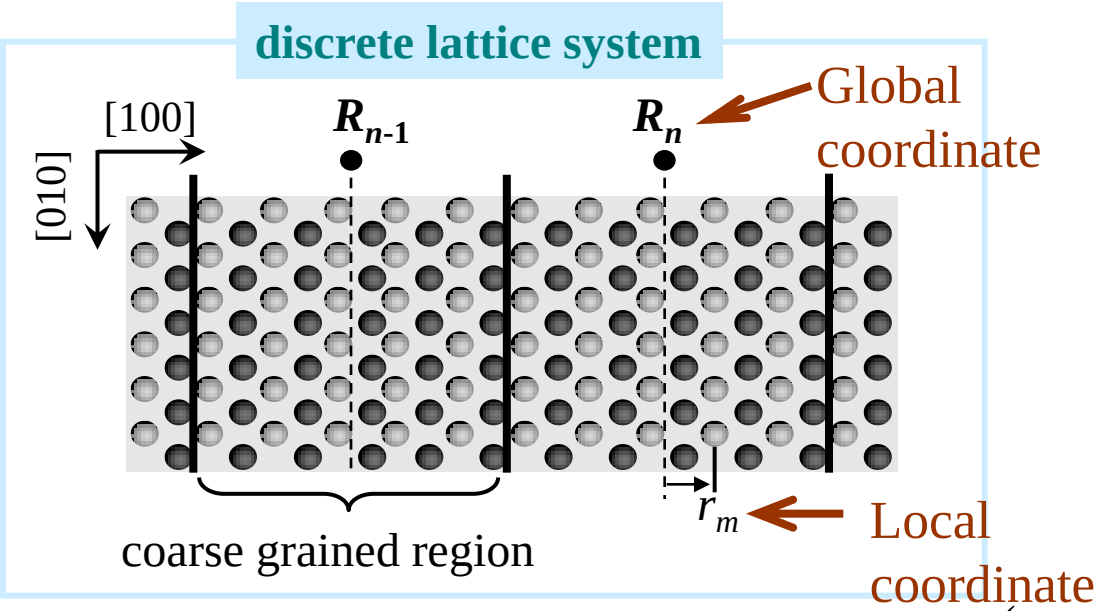
$$\sum_i |\{\xi\}_{in} - \{\xi\}_{out}| < 0.01$$

Atomistic

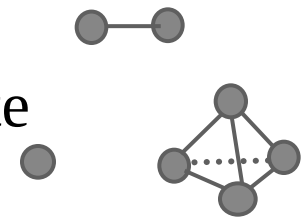




Coarse Graining PFM formulation of APB evolution



cells



R_n; Global coordinate

r_m; Local coordinate

$p_l = R_n + r_m$;atomic plane

$\phi_s(R_n + r_m + h(a))$;cluster probability

$$F = \sum_l f_{CVM}(p_l) = \sum_{n,m} f_{CVM}\left[\{\phi_s(R_n + r_m + h(a))\}\right]$$

$$\phi_s(R_n + r_m + h(a)) \cong \phi_s(R_n) + (r_m + h(a)) \cdot \nabla\phi_s(R_n) + \frac{1}{2}(r_m + h(a))^2 \cdot \nabla^2\phi_s(R_n)$$

$$F \cong \sum_{n,m} f_{CVM}\left(r_m + h(a), \{\phi_s(R_n)\}, \{\nabla\phi_s(R_n)\}, \{\nabla^2\phi_s(R_n)\}\right)$$

Coarse Graining [2]

$$F \cong \sum_{n,m} f_{CVM}\left(r_m + h(a), \{\phi_s(R_n)\}, \underbrace{\{\nabla\phi_s(R_n)\}}_{\downarrow}, \underbrace{\{\nabla^2\phi_s(R_n)\}}_{\downarrow}\right)$$

$$f_{CVM}\left(r_m + h(a), \{\phi_s(R_n)\}, \quad 0, \quad 0 \quad \right)$$

$$F \cong \sum_n \left\{ \sum_m \underbrace{f_{CVM}(\{\phi_s(R_n)\})}_{\text{homogeneous state}} + \sum_{m,s} \frac{\partial f_{CVM}}{\partial(\nabla\phi_s)}\bigg|_0 (\nabla\phi_s) + \sum_{m,s} \frac{\partial f_{CVM}}{\partial(\nabla^2\phi_s)}\bigg|_0 (\nabla^2\phi_s) + \frac{1}{2}\sum_{m,s,s'} \frac{\partial^2 f_{CVM}}{\partial(\nabla\phi_s)\partial(\nabla\phi_{s'})}\bigg|_0 (\nabla\phi_s)(\nabla\phi_{s'}) \right\}$$

Ginzburg-Landau type

$$F = \frac{1}{L}\int \left[N' \cdot f_{CVM}[\{\phi_s\}] + \sum_{s,s'} \kappa_{s,s'} (\nabla\phi_s)(\nabla\phi_{s'}) \right] \cdot dx$$

$$\kappa_{s,s'} = N \cdot k_B \cdot T \cdot \sum_J V_{s,s'}(r_m, a, \{J\})$$

Computational Materials Design Worksh

March 2, 2018

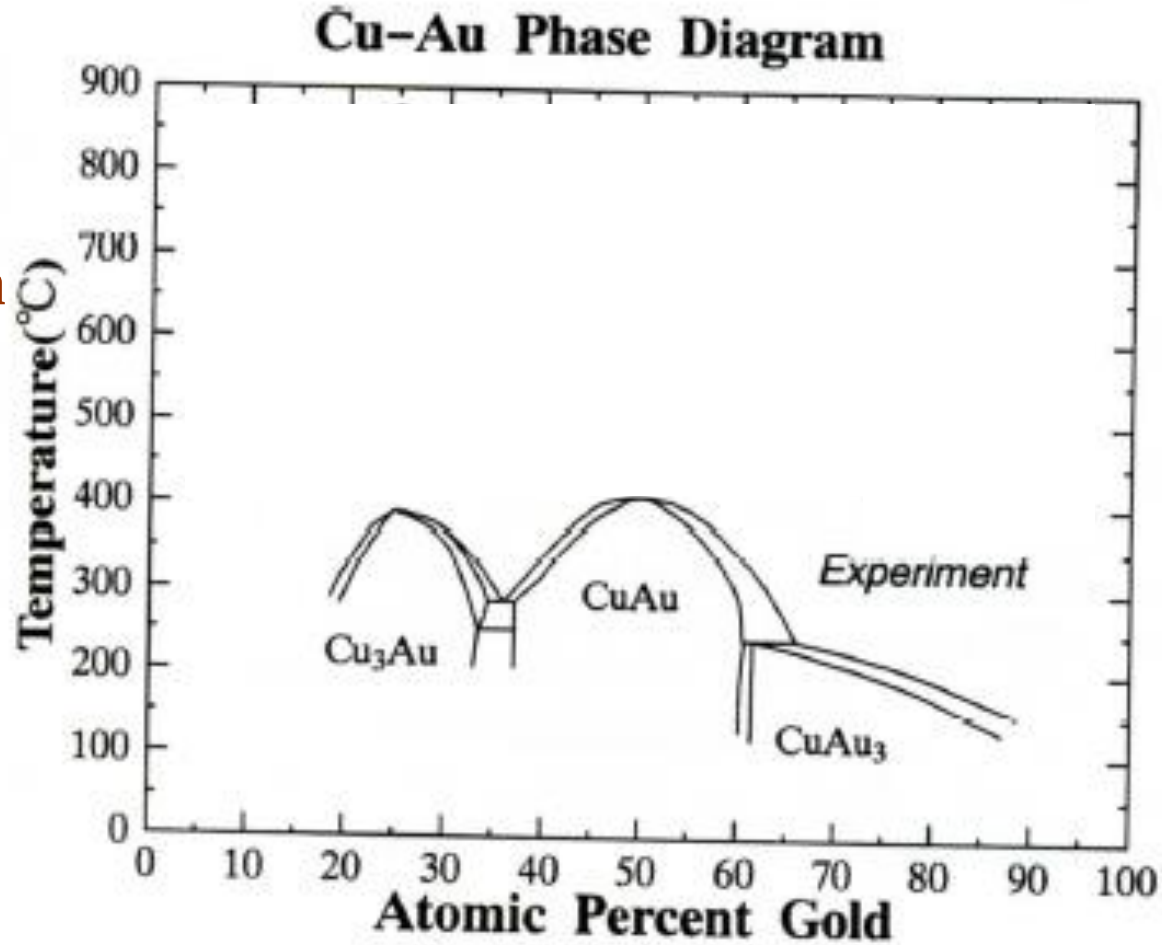
Osaka University

PCoMS within educational activities in HPCI and Cluster Variation Method as a Theoretical Tool for Multiscale Phase Transformation studies

Where we go with CVM?

Troubles; conventional CVM

Overestimation of order-disorder transition temperature

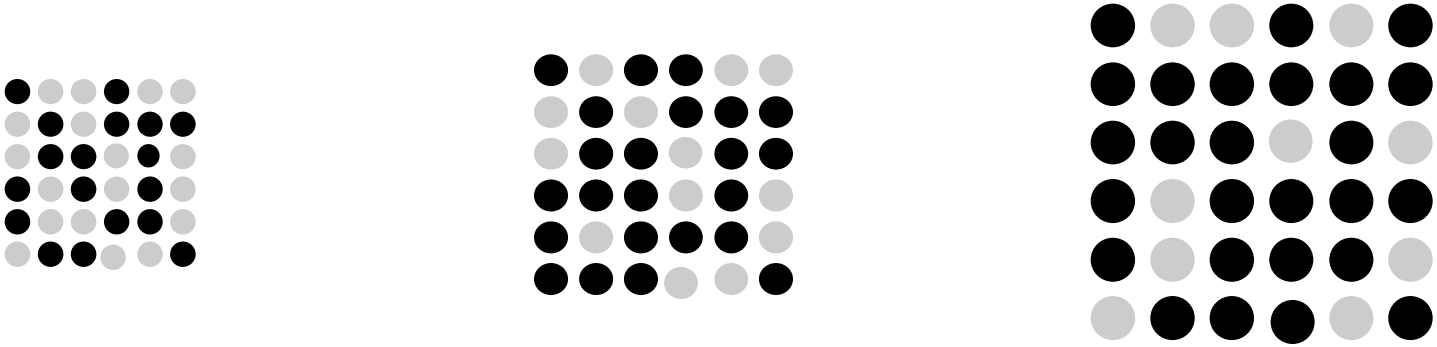


Underestimation of a single phase field

Neglect of local lattice relaxation effects

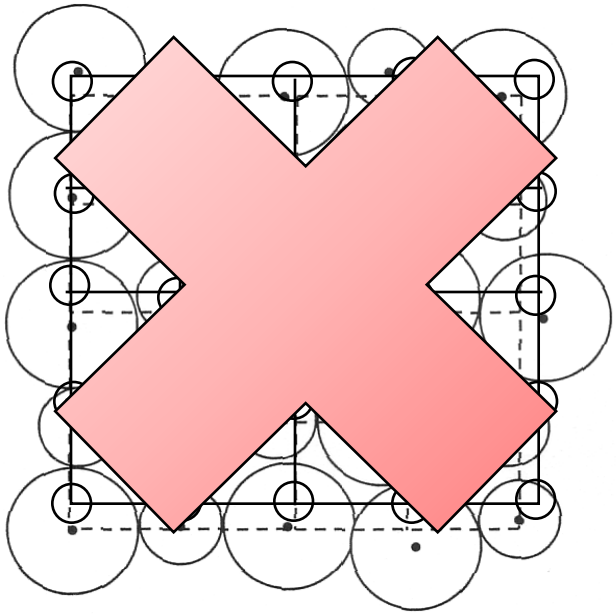
Conventional CVM

Conventional CVM (Global, local symmetry)



Continuous Displacement CVM
R.Kikuchi

Gaussian CVM
A. Finel

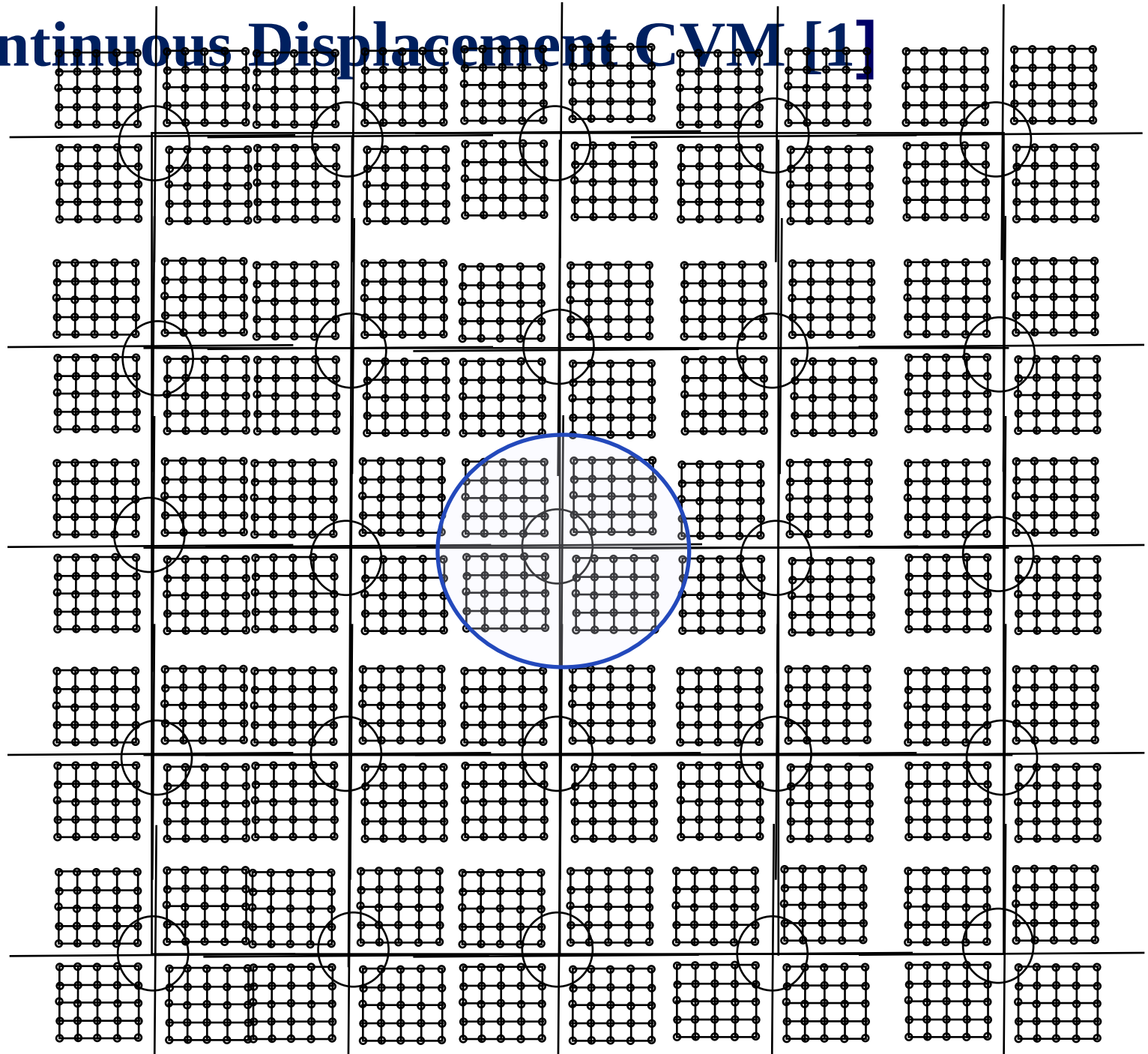


Continuous Displacement CVM [1]

2-dim. Square lattice

quasi lattice point

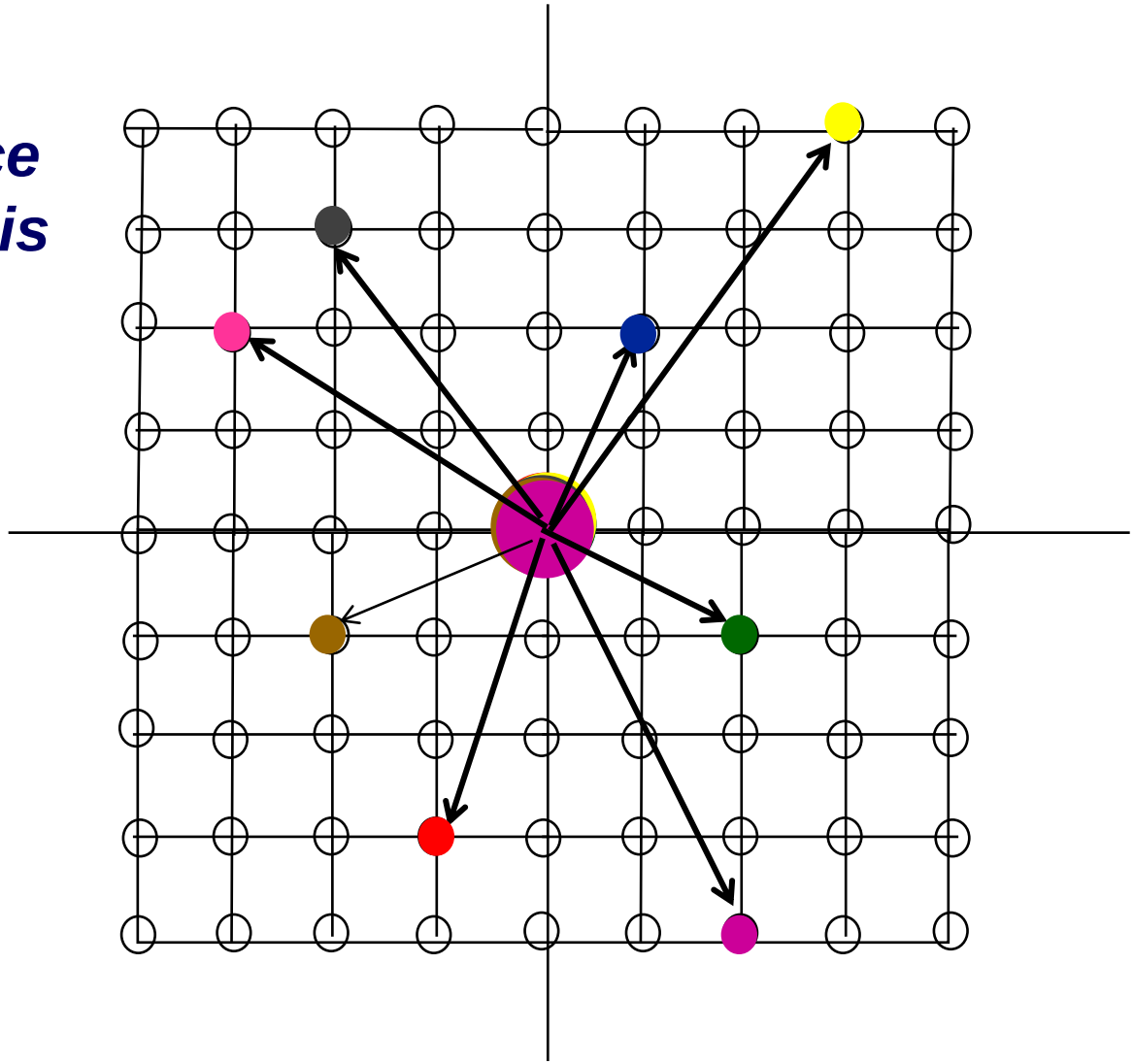
normal lattice point (Bravais lattice)



Continuous Displacement CVM [2]

normal lattice point (Bravais lattice)

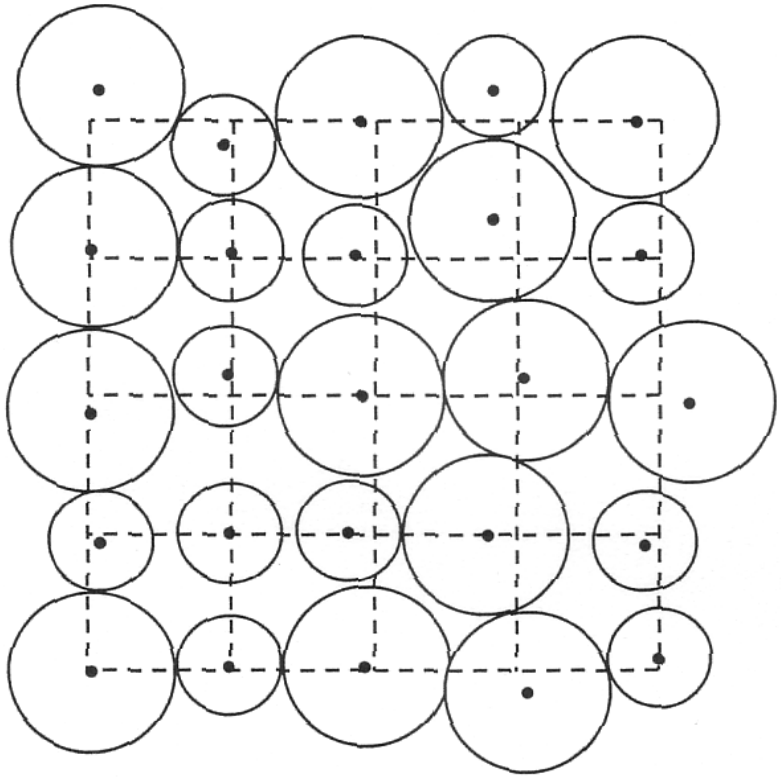
quasi lattice point

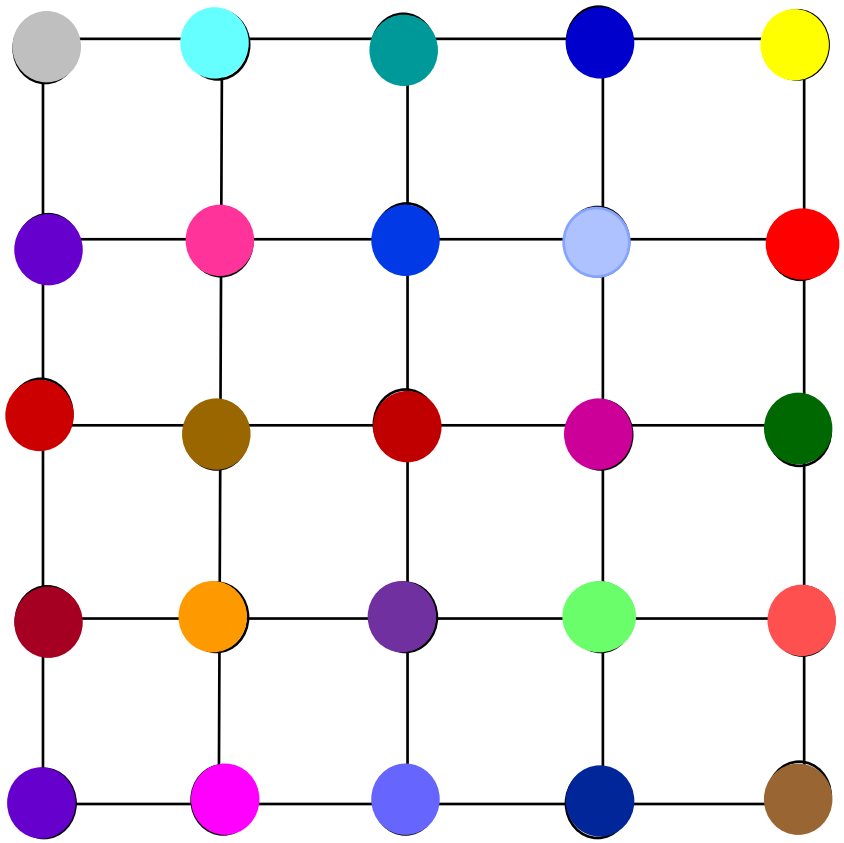


9x9 quasi lattice points

81 component systems = pure

Continuous Displacement CVM [3]

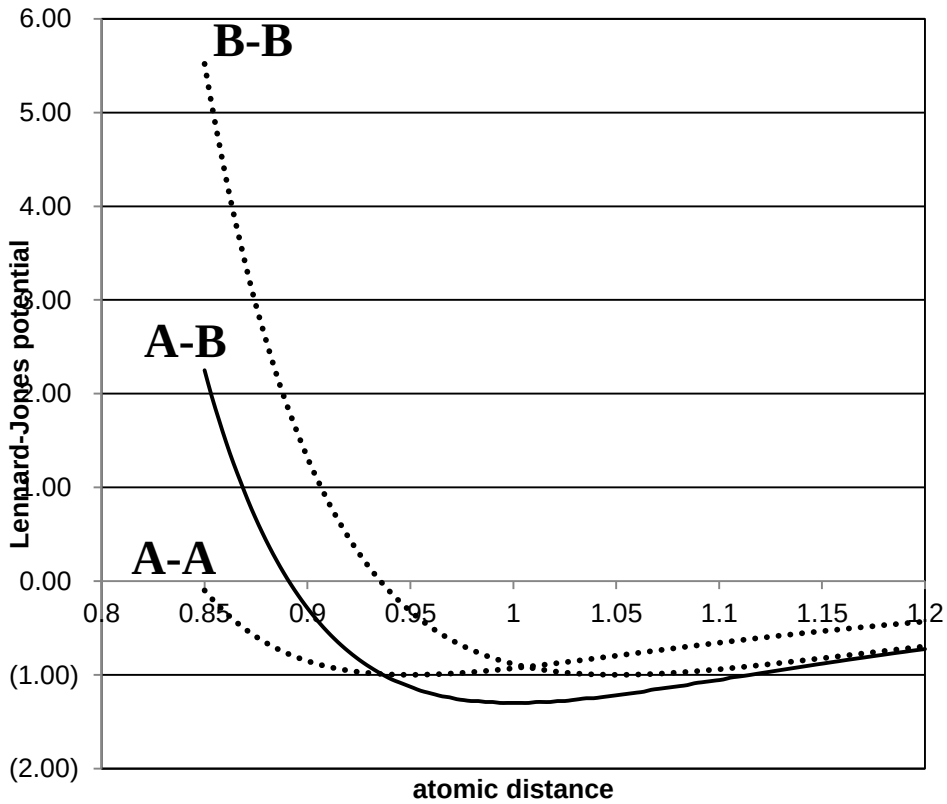




Configurational free energy of a multi-component system

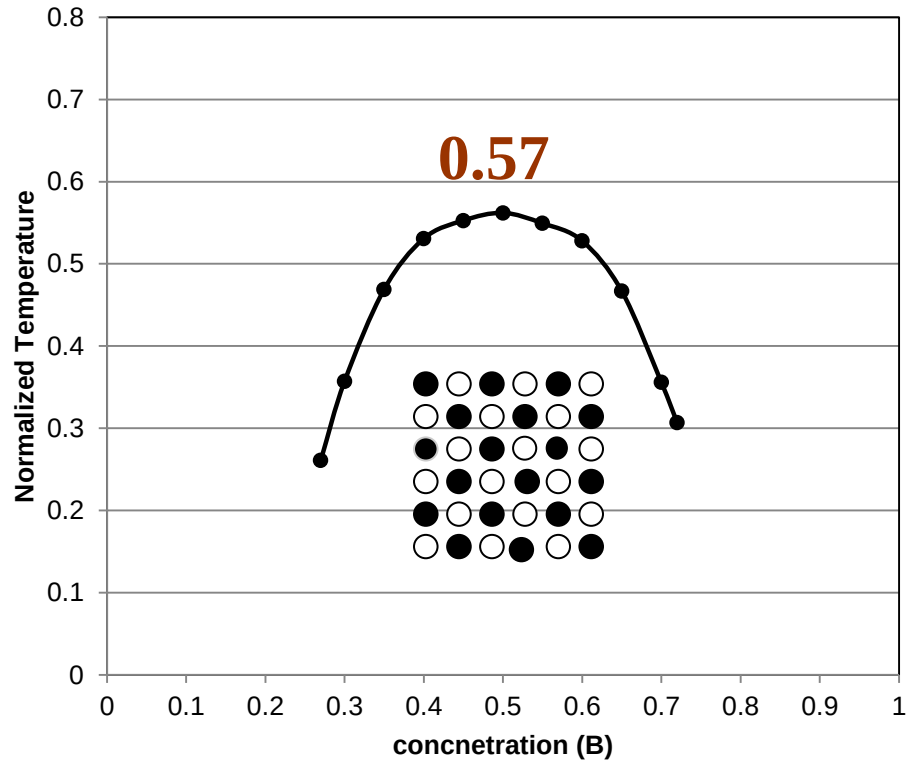
Conventional CVM

two-dimensional square lattice

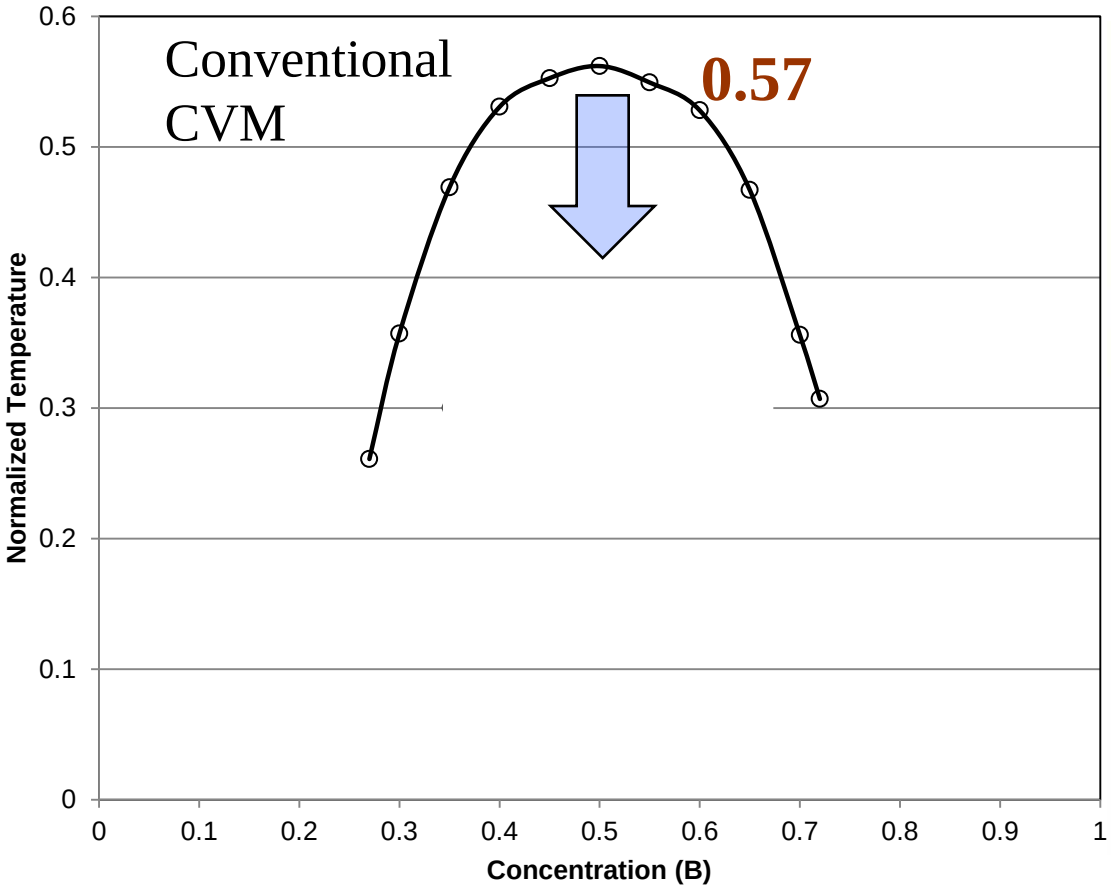


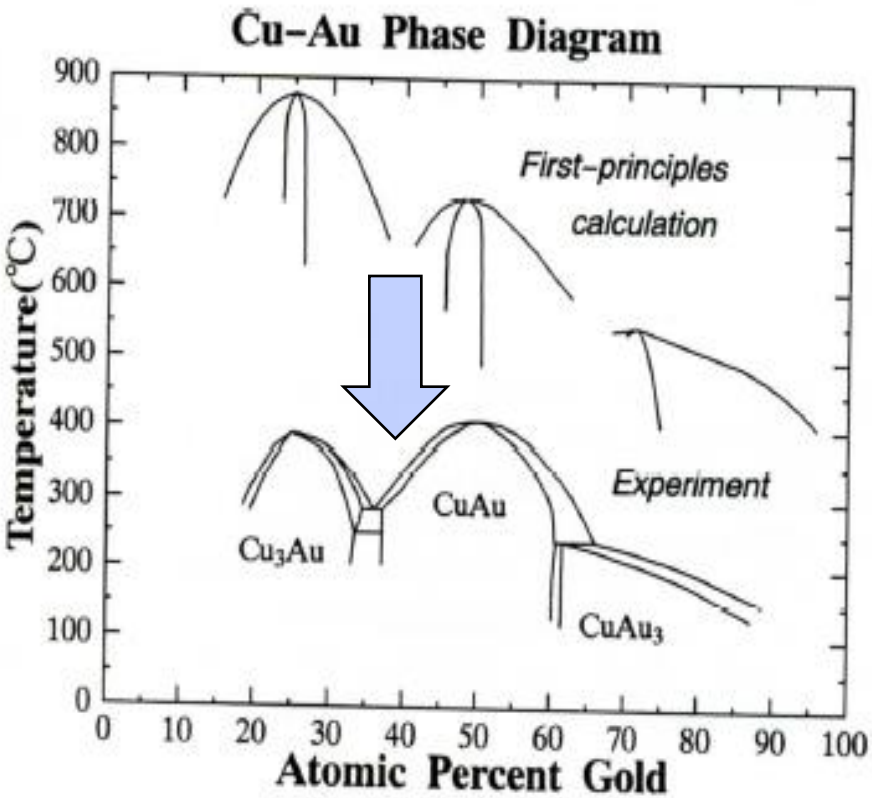
$$e_{ij}(\mathbf{r}) = e_{ij}^{0}\left\{\left(\frac{r_0}{|\mathbf{r}|}\right)^{12} - \left(\frac{12}{6}\right)\left(\frac{r_0}{|\mathbf{r}|}\right)^{6}\right\}$$

Conventional CVM



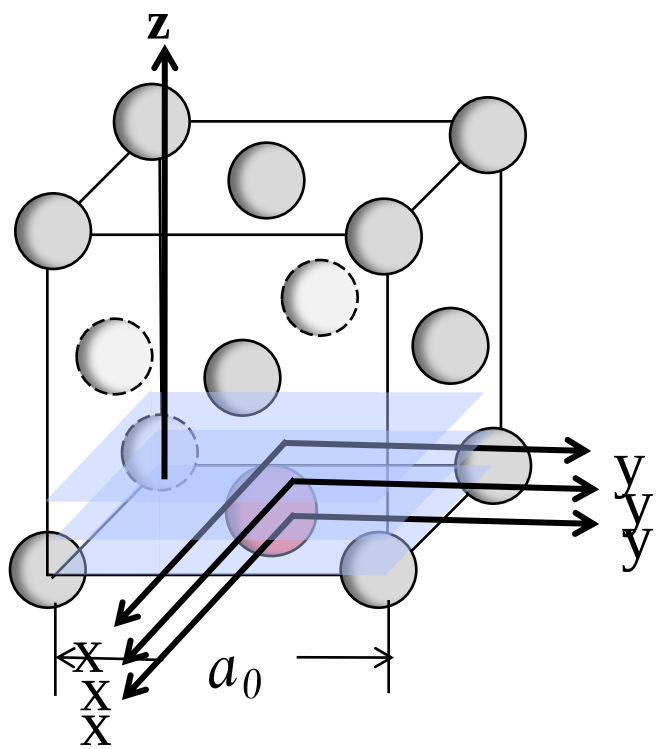
Continuous Displacement CVM [4]

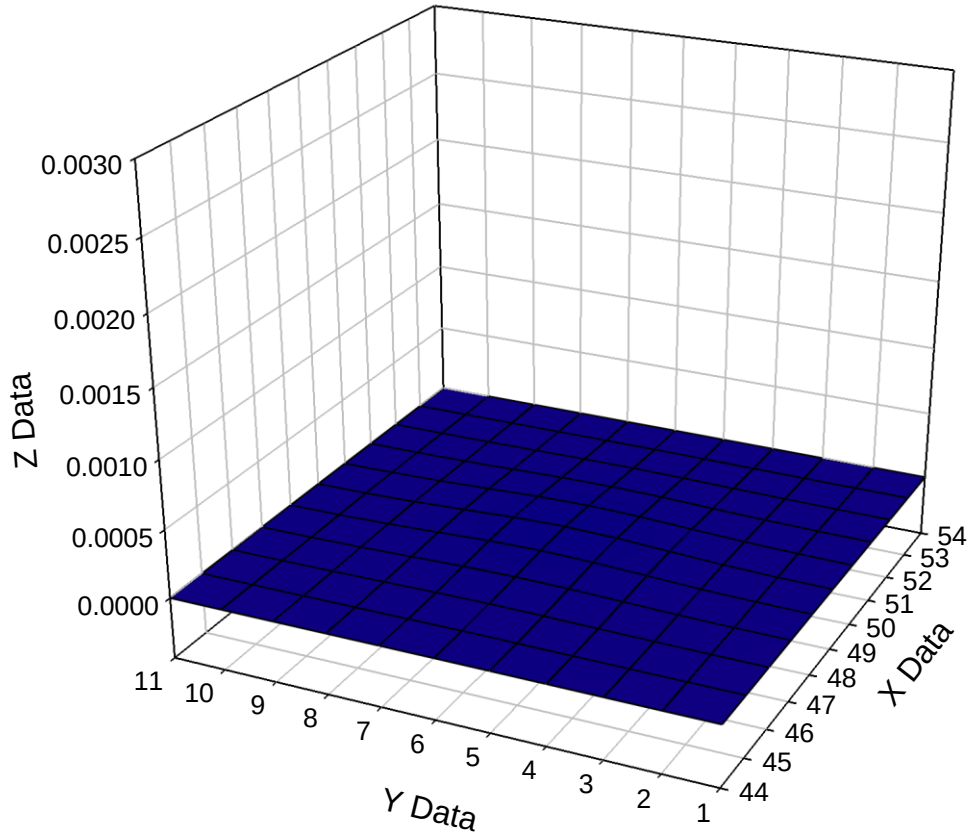




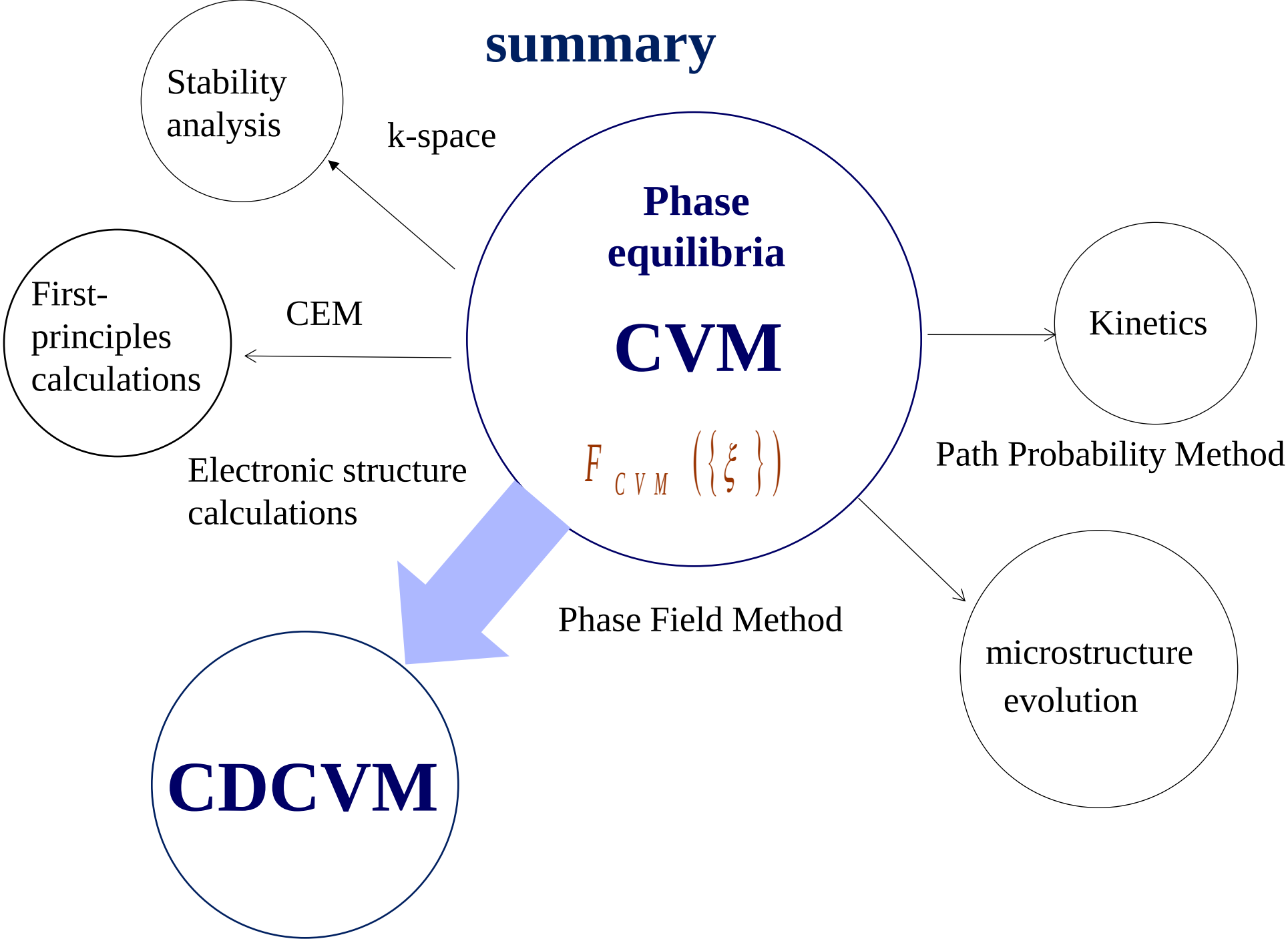
Atomic distribution FCC

c=0.5, $k_B T/e_{AA}=0.35$





summary


Stability analysis
k-space
Phase equilibria
CVM
$F_{CVM}(\{\xi\})$
First-principles calculations
CEM
Kinetics
Path Probability Method
Electronic structure calculations
Phase Field Method
microstructure evolution
CDCVM

Thank you ！