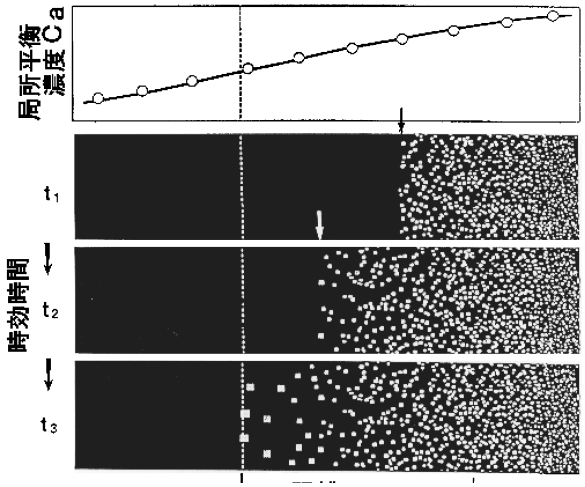
- Fe-Cu系の核生成
  - 核生成，熱力学，空孔

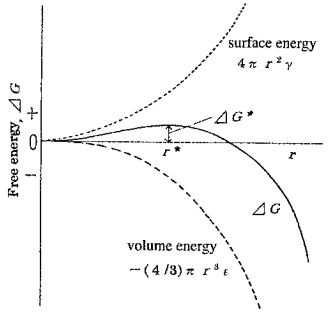
Ni-Al組成傾斜合金からのNi_3Alの析出

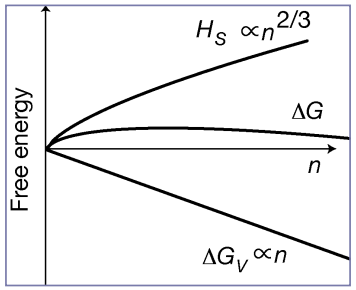


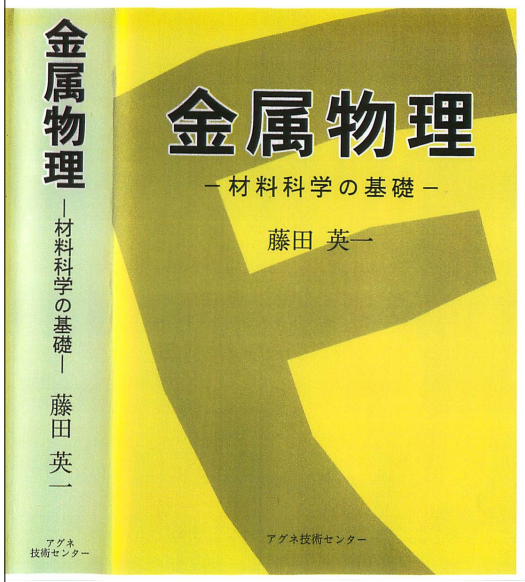
宮崎亨，まてりあ, vol.48 (2009),397-403, 図12.

Outline

- あたらしい計算法の概略
  - Fe-Cuの計算例
- 核生成の自由エネルギー変化
  - クラスター理論とか，Becker-Doringとか…
- 藤田dilemma
- 応用
  - 三元系，精緻化







金属物理 —材料科学の基礎—

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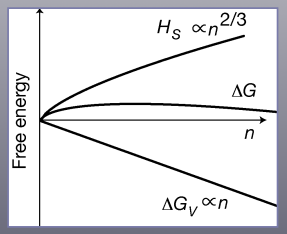
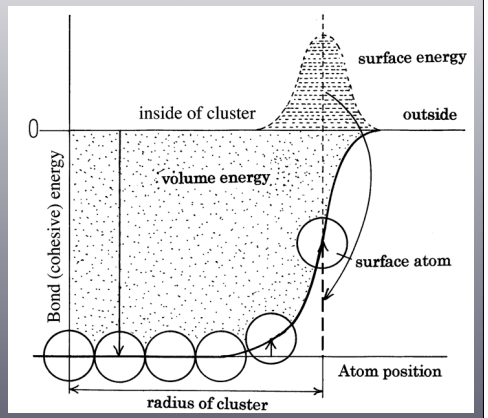
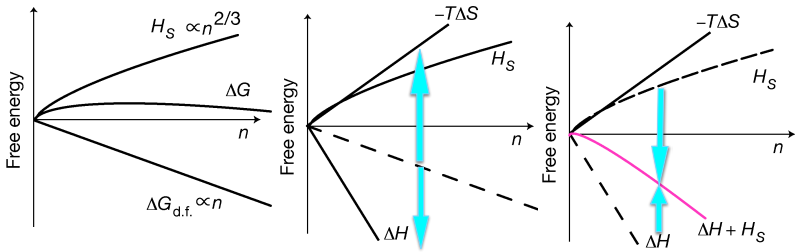
Fujita's dilemma

r が小さいところでは，欠損分が全体分を凌駕するという矛盾をはらんでいる．





New grouping of energies

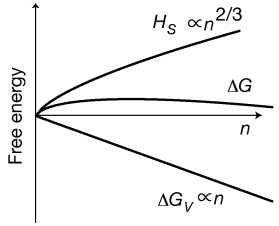


$\Delta G_{d.f.} = -\Delta G$
$\Delta G \propto n$

Divide $\Delta G_{d.f.}$ with ΔH and $T\Delta S$.

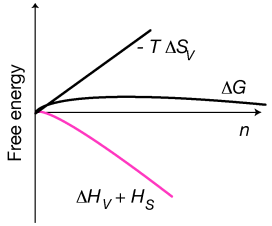
Add ΔH and H_S.

Classical treatment



$\Delta G(n) = \Delta G_V + H_S$
$= \Delta H_V - T\,\Delta S_V + H_S$
$= \boxed{\Delta H_V + H_S} - T\,\Delta S_V$

New treatment

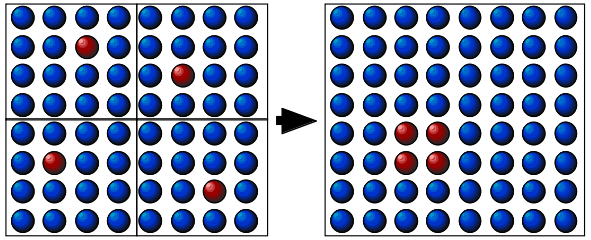


$\Delta S_V \sim k_B(n\text{-}1)\ln(x)$

T. Kamijo and H. Fukutomi, Phil. Mag. A, **48**(1983), 685.

Illustration of precipitation

Initial state *Final state*



n x $H = H$(dilution limit)
$S = k_B \ln(x)$

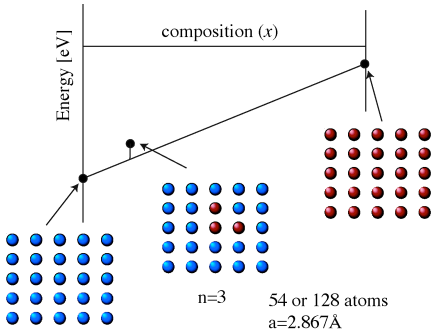
$H = H(n$ - cluster$)$
$S = k_B \ln(x)$

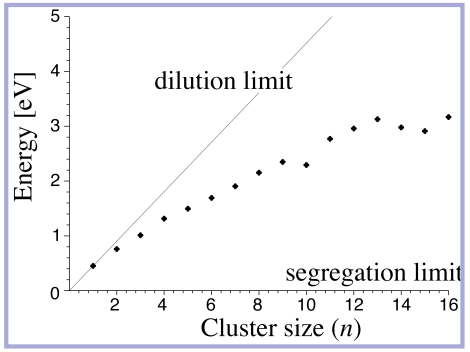
Fe-Cu系での配置の効果

bcc-Cu precipitates in Fe

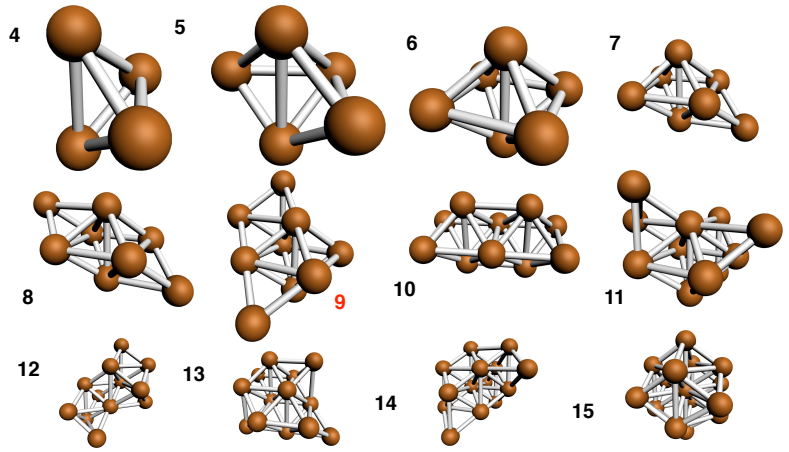
- Industrial necessity
  - Nuclear reactor pressure vessel
  - Ultra high strengthened steels
    - Ferrous nano metal project(NEDO)
- Coherent, homogeneous, spherical
- Small differences on size, weight, and bulk modulus.
  - Neglect the strain energy and vibrational entropy effect
- Small critical size
  - Neglect the internal configurational entropy of the clusters

Calculation details



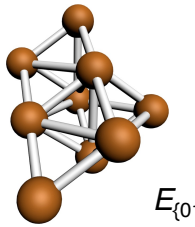


Cluster configurations

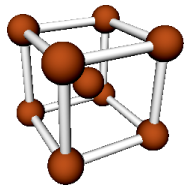


Cluster energy (n =9)

$E_{cluster}$ = 2.35 eV



$E_{cluster}$ = 2.97 eV



$E_{\{011\}}$=0.24 J/m^2
$E_{\{111\}}$=0.38 J/m^2
$E_{\{001\}}$=0.60 J/m^2

Cluster configurations

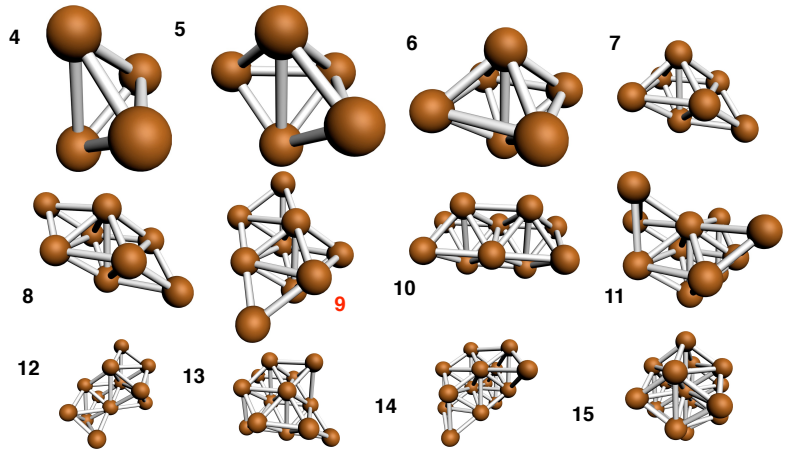
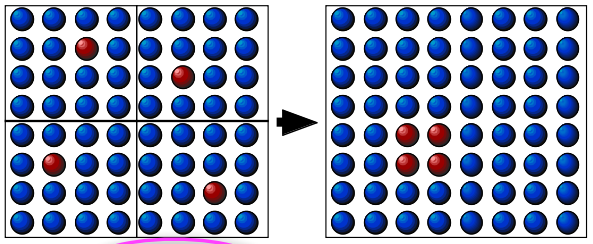


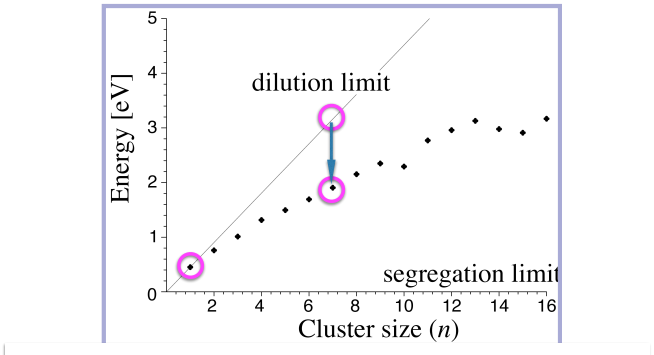
Illustration of precipitation

Initial state *Final state*

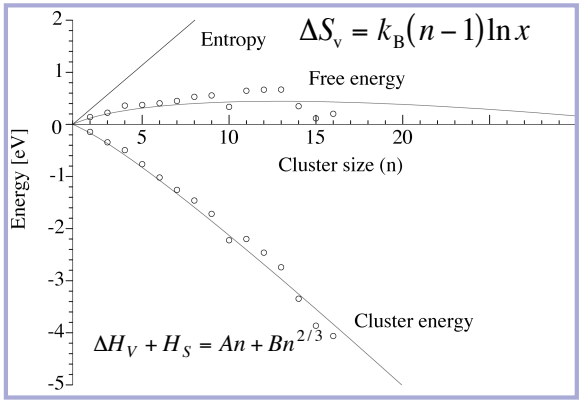


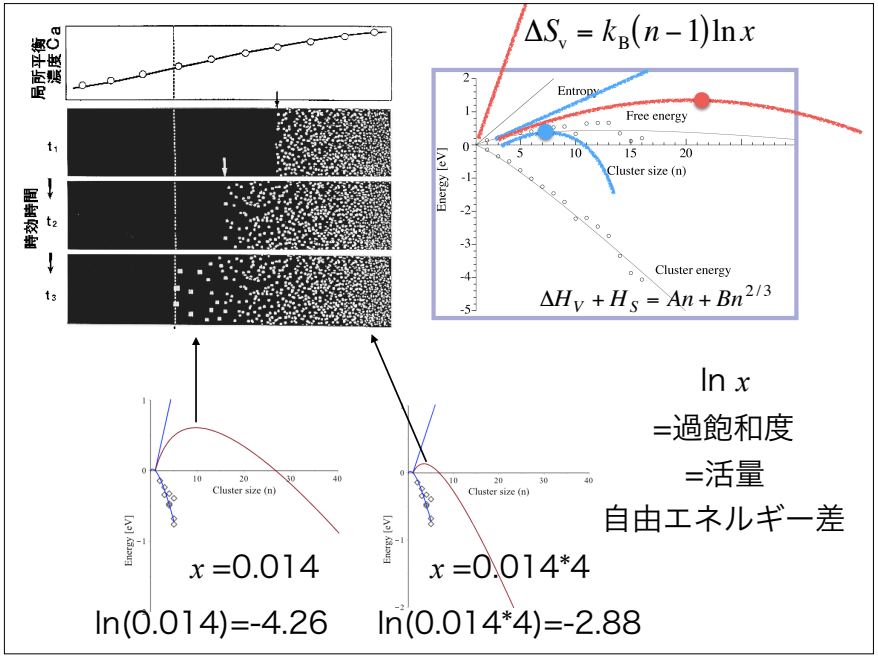
n x $H = H$(dilution limit) $S = k_B \ln(x)$

$H = H(n$ - cluster$)$ $S = k_B \ln(x)$



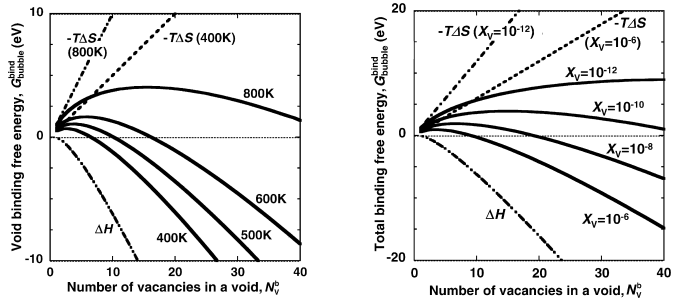
Cluster free energy





ln x
=過飽和度
=活量
自由エネルギー差

Size dependency of the total binding free energy of empty voids in bcc Fe



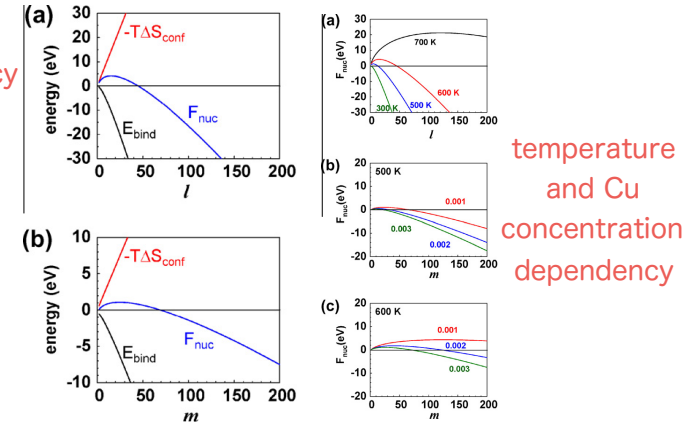
temperature

matrix vacancy concentration.

"Mechanism map for nucleation and growth of helium bubbles in metals", Kazunori Morishita, Ryuichiro Sugano, Journal of Nuclear Materials, 353(2006):52-65.

Nucleation free energy

pure vacancy clusters



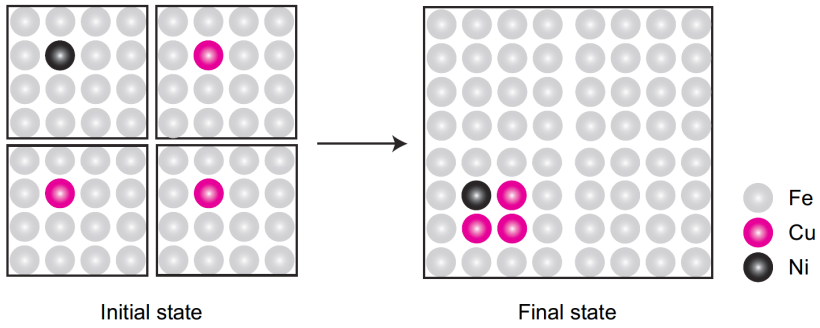
temperature and Cu concentration dependency

pure Cu clusters

"Structure, energetics and thermodynamics of copper–vacancy clusters in bcc-Fe: An atomistic study", Journal of Nuclear Materials, 414(2011):161-168, Ahmed Tamer, U. Birkenheuer et al.

Ternary system

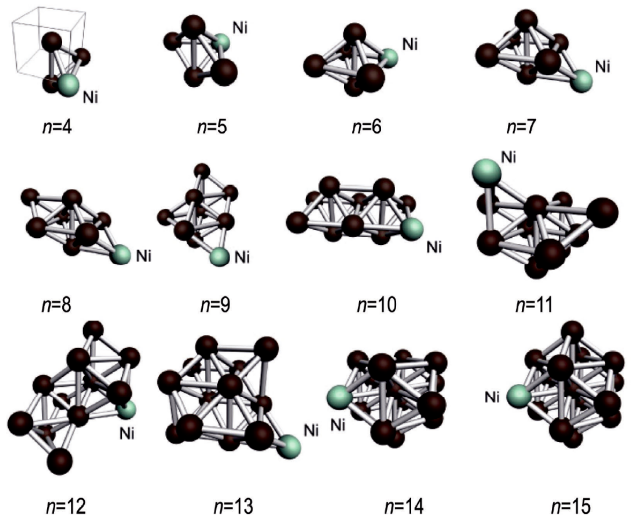
Model for ternary system



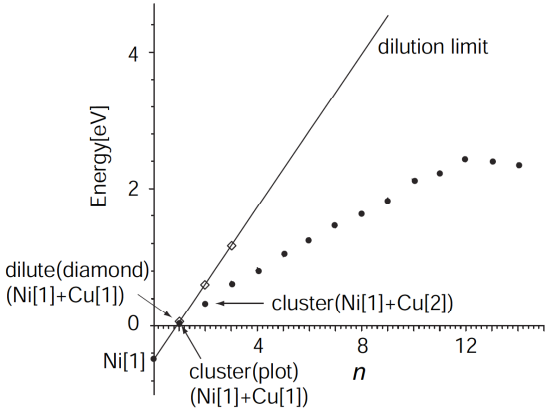
Entropy expression

$$\Delta S_V = k_B (n-1) \ln(x_{Cu})$$

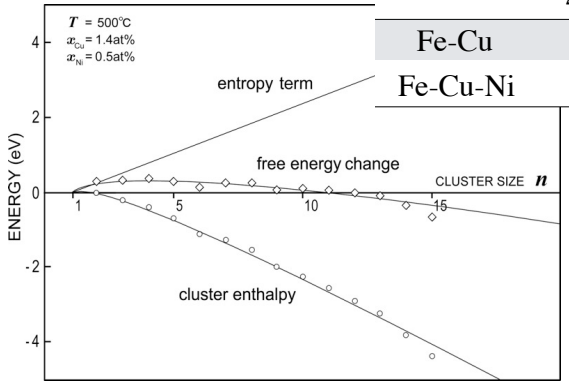
$$\Delta S_V = k_B \left\{ \begin{array}{l} (n-1)\ln(x_{Cu}) \\ +\ln \dfrac{x_{Ni}}{x_{Cu}} (n-1) \\ +\ln n \end{array} \right\}$$



Cluster enthalpy

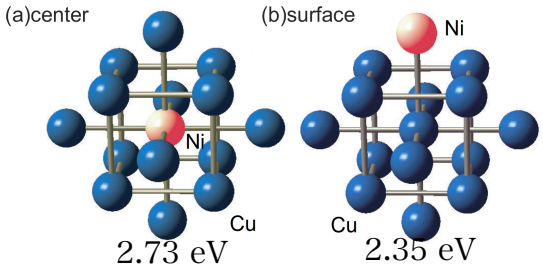


Free energy for Fe-Cu-Ni



	ΔG[eV]	n[atom]
Fe-Cu	0.67	13
Fe-Cu-Ni	0.31	4

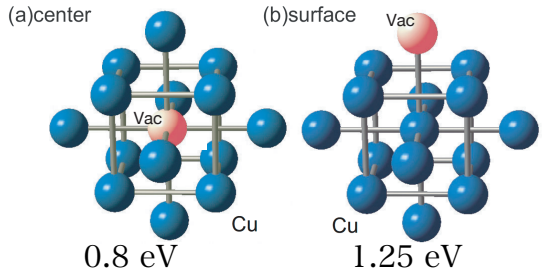
T=500℃
x(Cu)=1.4at%
x(Ni)=0.5at%



Interaction parameter

Fe-Cu	59.0meV
Cu-Ni	-0.7meV
Fe-Ni	0.5meV

Vacancy + Cu cluster



Evac(Cu) = 0.6 eV

Evac(Fe) = 2.3 eV