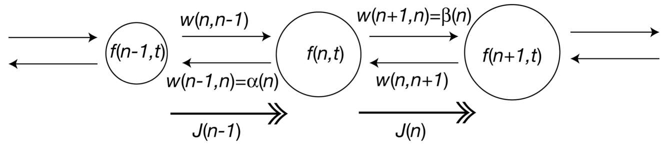
- 核生成
  - 平衡自由エネルギーが速度論にどう使われるか
    - キネティックMC
  - 振動の自由エネルギー
    - 効かない？

Binder-Stauffer:(1976)

cluster dynamics



$$\alpha(n+1) = \beta(n)\frac{\nu(n)}{\nu(n+1)}$$

$$\nu(n) \propto \exp\left(-\frac{\Delta F(n)}{kT}\right)$$

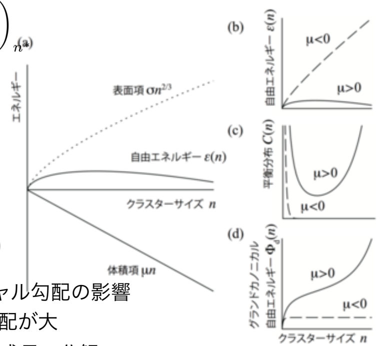
Becker-Doring:(1935)

もっとも影響する活性化の山の周りでエネルギー展開して積分

$$\Delta G(n) = \Delta G(n^*) + \frac{(n-n^*)^2}{2}\left(\frac{\partial^2 \Delta G}{\partial n^2}\right)_{n^*}$$

Federの取り扱い：Fokker-Planck方程式

$$\begin{aligned}\frac{\partial f(n,t)}{\partial t} &= J(n-1) - J(n)\\ &\vdots\\ &= \frac{\partial}{\partial n}\left[\beta(n)C(n)\frac{\partial f(n,t)/C(n)}{\partial n}\right]\\ &\vdots\\ &= \frac{\partial}{\partial n}\left(\beta(n)\frac{\partial f(n,t)}{\partial n}\right) + \frac{\partial}{\partial n}\left(\frac{\beta(n)f(n,t)}{kT}\frac{\partial \Delta G(n)}{\partial n}\right)\end{aligned}$$

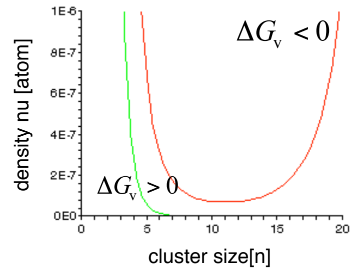


- 右辺の第１項は拡散，第２項はポテンシャル勾配の影響
- nの小さい領域ではΔG(n)のnに対する勾配が大
  - 第２項が効いて，クラスターは素早く成長，分解.
- n*付近ではポテンシャル勾配が小さく第１項が支配的
  - この領域では原子が付着と離脱を繰り返すので成長が遅く，
  - ここを通過する時間が定常拡散へいくまでの時間の大部分を占めている

Langer’s(Fisher) theory:(1969)

analytical continuation of f(H)

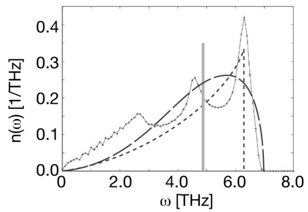
$$\Omega(\Delta G_v) = \sum_{n=1}^{\infty}\nu(n) = \sum_{n=1}^{\infty}\exp\left(-\frac{\Delta F(n)}{kT}\right)$$

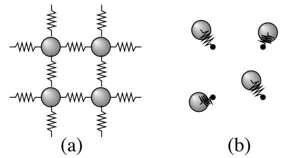


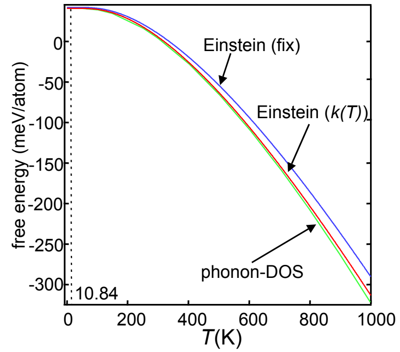
振動効果

Einstein approximation

- Comparison with quasi-harmonic approx. of Fe(bcc, FM)



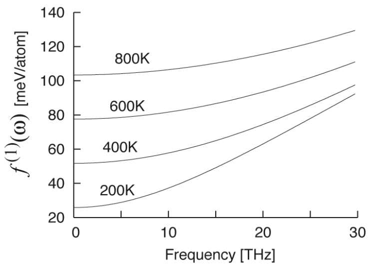




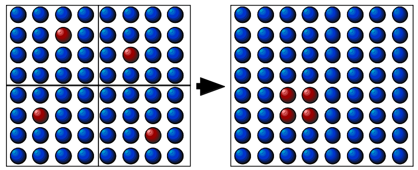
Vibrational free energy change

$$\Delta F = \sum_i \left\{ f(\omega_i + \delta\omega_i) - f(\omega_i) \right\}$$

$$\cong \sum_i f^{(1)}(\omega_i)\delta\omega_i \cong f^{(1)} \sum_i \delta\omega_i$$



Hardening sites=
Softening sites



Vanishing condition

- The vanishing condition

$$\sum_i \delta\omega_i = 0$$

will be satisfied, if the spring constant is equal to the arithmetic mean

$$k_{AB} = \frac{k_{AA} + k_{BB}}{2}$$

- This is nearly satisfied when taking AB potential with the geometric mean

$$\varphi_{AB} = \sqrt{\varphi_{AA}\varphi_{BB}}$$