Thermodynamics of nucleation

Physical Techniques

- Condensation from vapor phase
- Free expansion (molecular beams)
- Sputtering (Physical Vapor Deposition)
- Ion implantation
- Ball-milling
- Lithography, Nanofabrication
- Laser ablation

Chemical Techniques

- Colloidal Chemistry
- Sol-gel
- Chemical Vapor Deposition

Mixed approaches combining physical and chemical techniques

Nucleation Theory

- Nucleation
  - Homogeneous
    - Pure System
  - Heterogeneous
    - Defects / Surface Impurities

Simple hypothesis:

*Nucleating Embryos are modeled as **spherical droplets***

(macroscopic thermodynamic properties)

Gibbs Free Energy (reversible work): ΔG

$$\Delta G(N) \equiv W(N) = -N\Delta g_N + \gamma A(N)$$
$$\Delta G(R) \equiv W(R) = -\frac{4\pi}{3} R^3 \Delta g_V + 4\pi R^2 \gamma$$

Volume (Gibbs-Thomson equation)

$$-N\Delta g_N \equiv -N(\mu_V - \mu_L) = -N k_B T \ln P^*$$

$$\Delta g_V \equiv \rho \, \Delta g_N$$

$$P^* = P/P_e > 1$$ **Super-saturation**

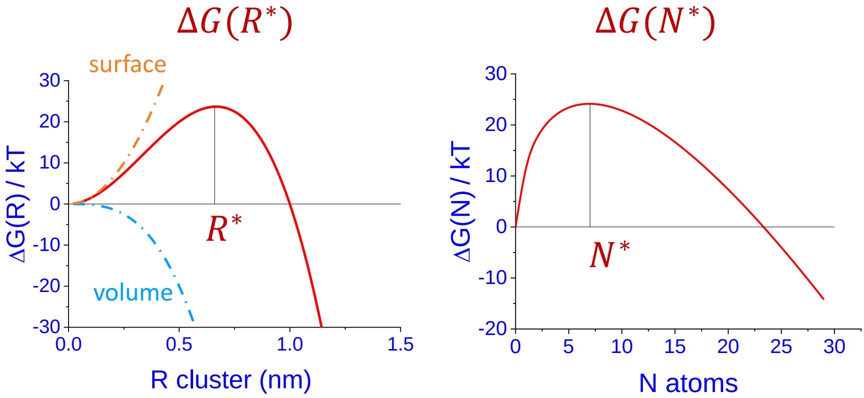
Surface

$$\gamma A(N) = \gamma 4\pi R^2$$

$$R = R_0 N^{1/3}$$

$$\Delta G(N) = -N k_B T \ln P^* + \gamma 4\pi R_0^2 N^{2/3}$$

Nucleation Theory



$$\frac{\partial \Delta G(R)}{\partial R} = 0$$

Find the maximum

$$\frac{\partial \Delta G(N)}{\partial N} = 0$$

R^* critical radius

N^* critical nucleus

Nucleation Theory

$$N^* = \frac{32\pi\gamma^3}{3\rho^2 \Delta g_N{}^3} = \frac{32\pi\gamma^3}{3\rho^2 (k_B T \ln P^*)^3}$$

$N*$ critical nucleus

$$R^* = \frac{2\gamma}{\Delta g_V} = \frac{2\gamma}{\rho k_B T \ln P^*}$$

$R*$ critical radius

$$\Delta G(N^*) = \frac{16\pi\gamma^3}{3\Delta g_V{}^2} = \frac{16\pi\gamma^3}{3\rho^2 \Delta g_N{}^2} = \frac{16\pi\gamma^3}{3(\rho k_B T \ln P^*)^2}$$

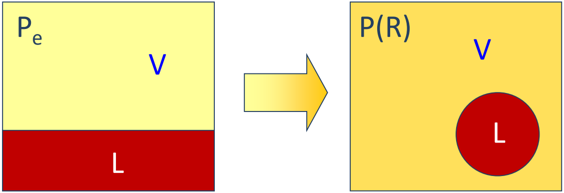
$$J = K \exp(-\Delta G(N^*)/k_B T)$$

Nucleation Speed

Gibbs-Thomson equation

Gibbs-Thomson equation

T fixed



P(R) = ?

1. Isothermal compression for an ideal gas

$$G \equiv U + PV - TS \qquad dG = VdP - SdT$$

$$\Delta G = \int_{P_e}^{P(R)} V dP = N k_B T \int_{P_e}^{P(R)} \frac{dP}{P} = N k_B T \ln \frac{P(R)}{P_e}$$

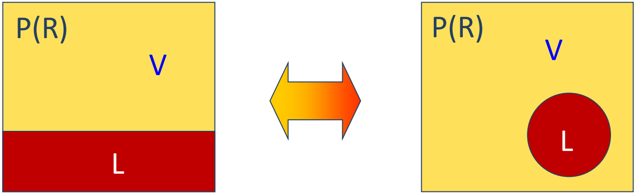
$$\mu_V[P(R)] - \mu_V[P_e] = \frac{\Delta G}{N} = k_B T \ln \frac{P(R)}{P_e}$$

2. Isothermal Compression of the liquid

Assume that for the liquid the compression occurs with no volume variation

$$\mu_L(\infty)[P(R)] \cong \mu_L(\infty)[P_e]$$

Compare the thermodynamics of the following two configurations:



3. Growth of a cluster with radius R at the pression $P(R)$

Cluster of radius R in equilibrium with a super-saturated vapor at pressure $P = P(R)$ (μ_L (R) = free energy per atom)

$$\mu_L(R)[P(R)] = \mu_V[P(R)]$$

$$\Delta G(R) = -\frac{4}{3}\pi R^3 \Delta g_{vol} + 4\pi R^2 \gamma$$

Minimize $\Delta G(R)$ with respect to R

$$0 = \frac{\partial \Delta G(R)}{\partial R} = -4\pi R^2 \Delta g_{vol} + 8\pi R\gamma$$

$$\Delta g_{vol} = \frac{2\gamma}{R} = \frac{\Delta G}{V} = \frac{\Delta G}{N}\frac{N}{V} = \Delta\mu \ \rho$$

$$\Delta\mu = \frac{\Delta g_{vol}}{\rho} = \frac{2\gamma}{\rho R}$$

Gibbs-Thomson equation

Thus, for a cluster with radius R and for an infinite surface

$$\mu_L(R)[P(R)] = \mu_L(\infty)[P(R)] + \frac{2\gamma}{\rho R}$$

Substituting

$$\mu_V[P(R)] = \mu_L(\infty)[P(R)] + \frac{2\gamma}{\rho R}$$

Since we obtained that during the isothermal compression for the vapor results:

$$\mu_V[P(R)] - \mu_V[P_e] = k_B T \ln \frac{P(R)}{P_e}$$

and considering that for the liquid:

$$\mu_L(\infty)[P(R)] \cong \mu_L(\infty)[P_e]$$

Gibbs-Thomson equation

Thus

$$\mu_V[P(R)] = \mu_L(\infty)[P_e] + \frac{2\gamma}{\rho R}$$

At the liquid-vapor equilibrium pressure P_e (vapor phase tension):

$$\mu_L(\infty)[P_e] = \mu_V[P_e]$$

Therefore, on substituting finally:

$$\mu_V[P(R)] - \mu_V[P_e] = \frac{2\gamma}{\rho R} = k_B T \ln \frac{P(R)}{P_e}$$

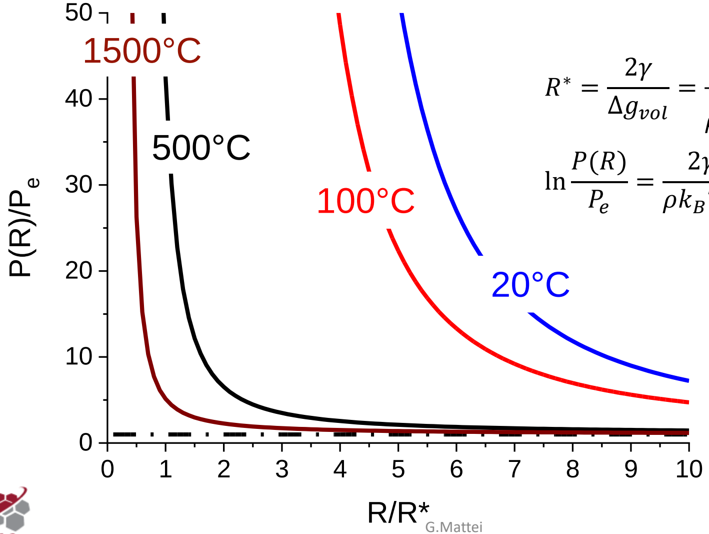
Gibbs-Thomson Equation

$$\boxed{k_B T \ln \frac{P(R)}{P_e} = \frac{2\gamma}{\rho R}}$$

$$\boxed{P(R) = P_e e^{\frac{2\gamma}{k_B T \rho R}}}$$

Gibbs-Thomson equation

$$P(R) = P_e e^{\frac{2\gamma}{k_B T \rho R}}$$

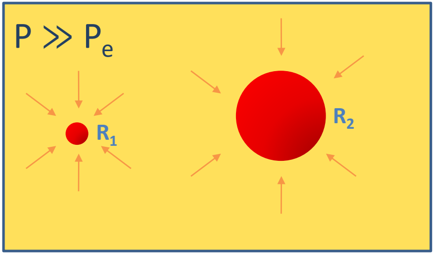


$$R^* = \frac{2\gamma}{\Delta g_{vol}} = \frac{2\gamma}{\rho k_B T \ln \frac{P(R^*)}{P_e}}$$

$$\ln \frac{P(R)}{P_e} = \frac{2\gamma}{\rho k_B T R} = \frac{R^*}{R} \ln \frac{P(R^*)}{P_e}$$

Diffusion Limited Aggregation (DLA)

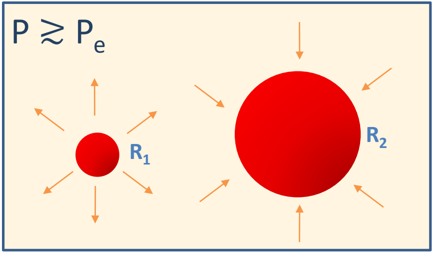
Until the supersaturation degree is high nuclei growth independently



$R_1 < R_2$ $\quad$ $P > P(R_1) > P(R_2)$

Ostwald Ripening (OR)

When supersaturation is reduced a competitive growth starts where the cluster stability is controlled by the Gibbs-Thomson equation



$R_1 < R_2$ $\quad$ $P(R_1) > P > P(R_2)$