Nucleation/Growth under supersaturation

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

$$P^* = P/P_e$$

P: Gas pressure

P_e: Vapor pressure (increases if T increases)

To promote P* (supersaturation):

1. decrease P_e *(i.e., decrease T)*

Adiabatic expansion with cooling:

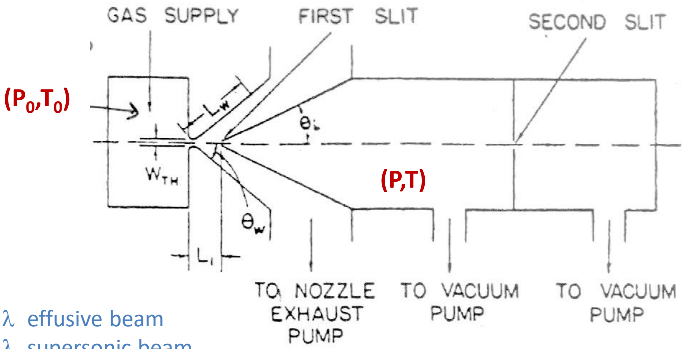
- Supersonic molecular beams

2. increase P

Production of condensable species:

- Chemical or photo-chemical decomposition in the gas phase
- sputtering
- thermal evaporation
- laser ablation
- ion implantation

Free Jet Expansion



d < λ effusive beam

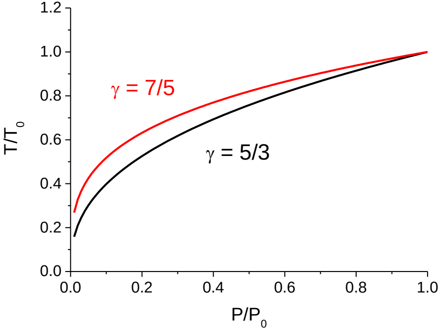
d > λ supersonic beam

The vapor – mixed with an inert gas (*gas carrier*) – expands adiabatically through a *nozzle* with diameter *d* from the initial chamber at (P_0, T_0) in a vacuum chamber with pressure $P < P_0$:

Free Jet Expansion

$$PV^{\gamma} = const \qquad \gamma \equiv \frac{C_P}{C_V} > 1$$

$$\frac{P^{\frac{\gamma-1}{\gamma}}}{T} = const \qquad T = T_0 \left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}}$$



During expansion the vapor cools down becoming supersaturated with the formation of *clusters*

The cluster density increases by:

- increasing P_0 and *d*
- decreasing T_0

Nucleation and growth

Kinetics vs. Energetics

time

1. Nuclei formation (supersaturated solution)

- $< R > =$ critical radius R^*
- E.g., ion implantation: heterogeneous nucleation

$$R^* = \frac{2\gamma}{\Delta g_V}$$

2. Diffusion limited aggregation (DLA)

- non competitive growth: fixed n. of clusters
- the supersaturation decreases

$$R^2(t) = R_0^2 + K_1 D t$$

(supersaturation)

3. Coarsening (Ostwald ripening, OR)

- competitive growth: the n. of cluster decreases
- the growth is controlled by the Gibbs-Thomson equation

$$R^3(t) = R_0^3 + K_2 D t$$

(Gibbs-Thomson)

G. De Marchi, G. Mattei, P. Mazzoldi, C. Sada, A. Miotello, J. Appl. Phys. 92 (2001) 4249

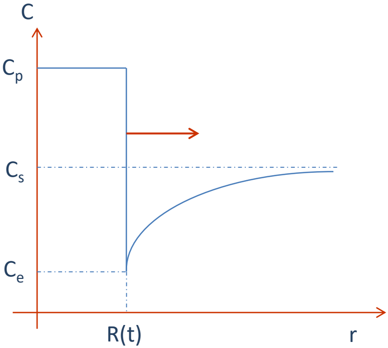
2. Diffusion limited aggregation (DLA)

Balance of the atomic flux at the surface of a cluster with radius R (boundary cluster-matrix):

$$\Phi_\Sigma(\bar{J}) = Flux\Big|_{r=R} = \frac{dN}{dt}\Big|_{out} - \frac{dN}{dt}\Big|_{in}$$

$$\frac{dN}{dt}\Big|_{in} = C_p \frac{d}{dt}\left(\frac{4\pi}{3}R^3\right) = 4\pi R^2 C_p \frac{dR}{dt}$$

$$\frac{dN}{dt}\Big|_{out} = C_e \frac{d}{dt}\left(\frac{4\pi}{3}R^3\right) = 4\pi R^2 C_e \frac{dR}{dt}$$



$$\bar{J} = -D\bar{\nabla}C$$ 1ª Fick's Law (Isotropic diffusion)

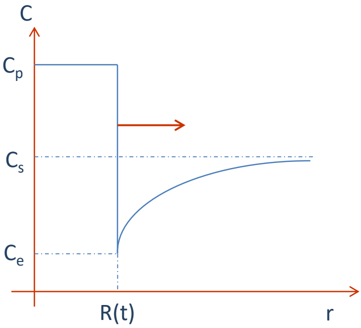
$$\Phi_\Sigma(\bar{J}) = \int_\Sigma \bar{J}\cdot\hat{n}\,d\Sigma = -4\pi R^2 D \frac{\partial C(r,t)}{\partial r}\Big|_{r=R}$$ Net incoming flux (growth)

Substituting:

$$\left.\frac{dN}{dt}\right|_{out} = \left.Flux\right|_{r=R} + \left.\frac{dN}{dt}\right|_{in}$$

$$C_e\frac{dR}{dt} = -D\left.\frac{\partial C(r,t)}{\partial r}\right|_{r=R} + C_p\frac{dR}{dt}$$

$$(C_p - C_e)\frac{dR}{dt} = D\left.\frac{\partial C(r,t)}{\partial r}\right|_{r=R}$$



$\boldsymbol{C = C(r,t)}$ concentration field around the cluster

$\boldsymbol{C_s = C(r,0)}$ concentration in the matrix at $t = 0$

$\boldsymbol{C_p}$ equilibrium concentration in the cluster (density)

$\boldsymbol{C_e}$ equilibrium concentration in the matrix (solubility limit)

Linearizing the gradient:

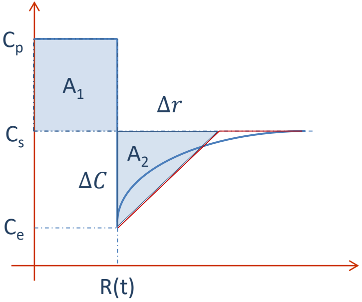
$$\left.\frac{\partial C(r,t)}{\partial r}\right|_{r=R} \approx \frac{\Delta C}{\Delta r} = \frac{(C_s - C_e)^2}{2(C_p - C_s)}\frac{1}{R}$$

$$(C_p - C_e)\frac{dR}{dt} \approx D\frac{(C_s - C_e)^2}{2(C_p - C_s)R}$$

$$R^2(t) = R_0^2 + \frac{(C_s - C_e)^2}{(C_p - C_e)(C_p - C_s)}Dt$$

$$R^2(t) = R_0^2 + K_1 Dt$$

$$K_1 = \frac{(C_s - C_e)^2}{(C_p - C_e)(C_p - C_s)} \approx \frac{{C_s}^2}{{C_p}^2}$$



$A_1 = A_2$

supersaturation

3. Ostwald Ripening (OR)

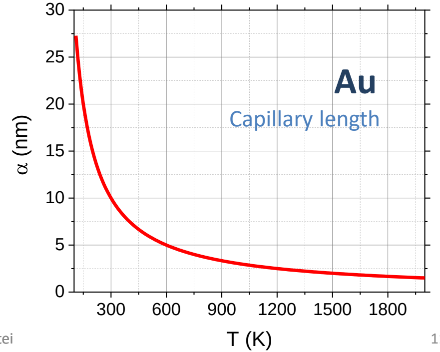
When the supersaturation is decreased: Gibbs-Thomson

$$k_B T \ln \frac{C_e(R)}{C_e(\infty)} = \frac{2\gamma}{\rho R} \qquad C_p \equiv \rho$$

$$C_e(R) = C_e(\infty) \exp\left(\frac{2\gamma}{C_p k_B T}\frac{1}{R}\right) \sim C_e(\infty)\left(1 + \frac{\alpha}{R}\right)$$

$$\alpha \equiv \frac{2\gamma}{C_p k_B T}$$

Capillary length



$C_e(R)$ can be interpreted as the equilibrium solute concentration in the matrix at the cluster surface (it increases by decreasing R)

The atomic flux at the cluster surface is:

$$\frac{dN_{clu}}{dt} = C_p \frac{d}{dt}\left(\frac{4\pi}{3}R^3\right) = 4\pi R^2 C_p \frac{dR}{dt}$$

$$\frac{dN_{clu}}{dt} = \Phi_\Sigma(\bar{J}) = -4\pi R^2 \left(D \left.\frac{\partial C}{\partial r}\right|_{r=R} \right) \approx -4\pi R^2 D \frac{dC_e(R)}{dR} = 4\pi R^2 D \frac{C_e(\infty)\alpha}{R^2}$$

$$\frac{dC_e(R)}{dR} = -C_e(\infty)\frac{\alpha}{R^2}$$

$$\frac{dN_{clu}}{dt} = 4\pi R^2 D \frac{C_e(\infty)\alpha}{R^2}$$

$$\frac{dR}{dt} = D \frac{C_e(\infty)\alpha}{C_p}\frac{1}{R^2}$$

$$R^3(t) = R_0^3 + 3\frac{C_e(\infty)\alpha}{C_p}Dt = R_0^3 + 6\frac{C_e(\infty)\gamma}{C_p^2 k_B T}Dt$$

$$R^3(t) = R_0^3 + K_2 Dt$$