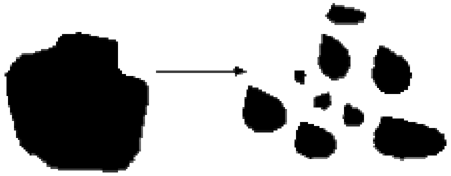
Chapter 4. Formation and Growth of Nanoparticles - Theories

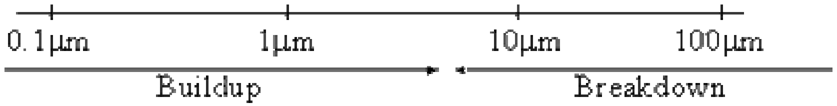
4.1 Introduction

- Breakdown (Disintegration) : by crushing, milling, spraying

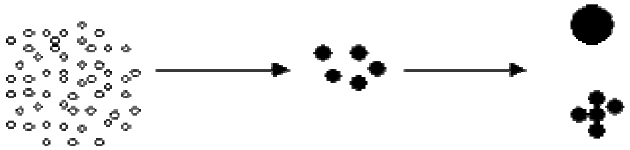
**"Wall of 3µm"*



Bulk   *fine particles*

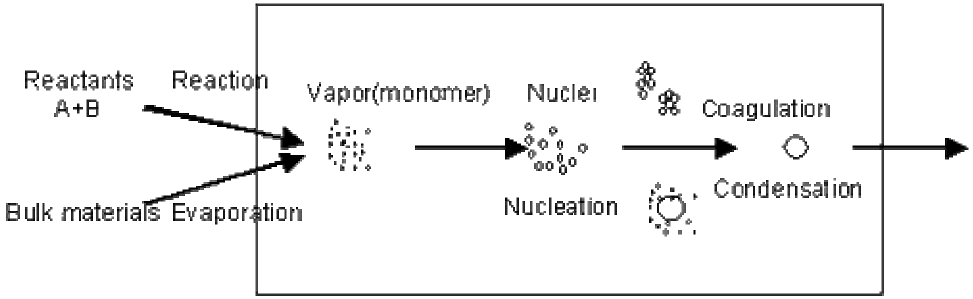


- Buildup (Growth) : nucleation and growth (condensation, coagulation)



Atoms or molecules   *Nuclei*   *Nanoparticles*

*



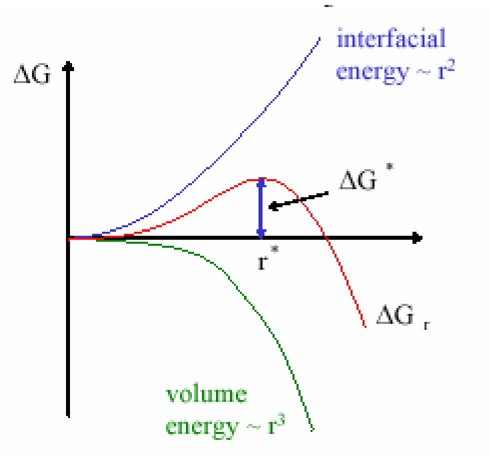
4.2 Birth of Nanoparticles: Nucleation

Formation of nuclei: new-born particles

(1) Homogeneous nucleation

- *Gibbs free energy change for a droplet from monomer molecules*

$$\Delta G = \underbrace{\pi d_p \sigma}_{\text{interfacial energy}} - \underbrace{\frac{\pi d_p^{\,3}}{6}\Delta G_v}_{\text{volume energy}}$$



where $$\Delta G_v = \frac{kT}{v_m}\ln S$$

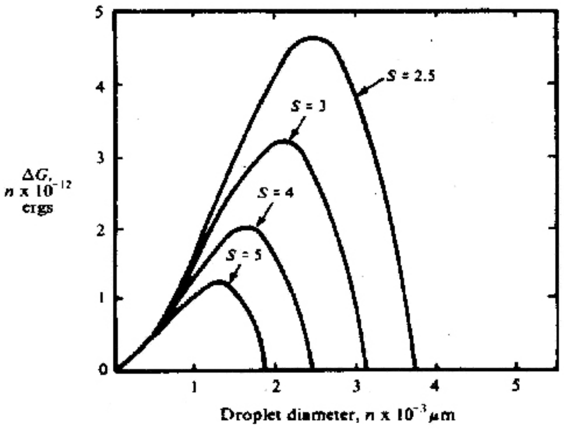
v_m: *molecular mass*

- *Saturation ratio*

For solution-to-particle: $S = \dfrac{c}{c_0}$

For vapor-to-droplet or particle: $S = \dfrac{p}{p_0}$

where c_0, p_0*: equilibrium solubility, vapor pressure*



Gibbs free energy change for water droplet formation

- *Critical nuclei*

From $$\frac{d\Delta G}{dd_p} = 0$$

$$d_p{}^* = -\frac{4\sigma}{\Delta G_v} = \frac{4\sigma v_m}{kT \ln \frac{P}{P_0}}$$

Critical nuclei diameter

Kelvin equation

$$\Delta G^* = \frac{16\pi\sigma}{(3\Delta G_v)^2}$$

Energy barrier for nucleation

- *Rate of nucleation*

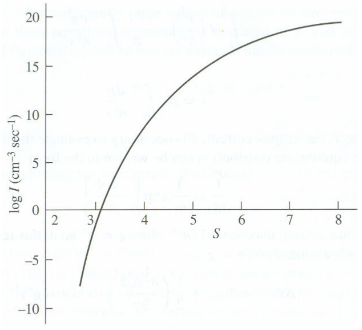
J(nuclei/(s)(cm^3))=(frequency of collision) (species concentration) (probability)

Solution-to-particle $$J = \frac{kT}{3\pi d\mu} n_m \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Vapor-to-droplet or particle $$J = \frac{p}{(2\pi mkT)^{1/2}} (\pi d_p{}^{*2}) n_m \exp\left(-\frac{\Delta G^*}{kT}\right)$$

n_m: number concentration of the species

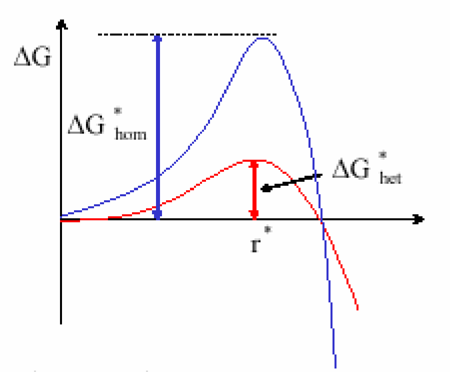
- *Critical saturation, S_{crit}*: S at J=1*

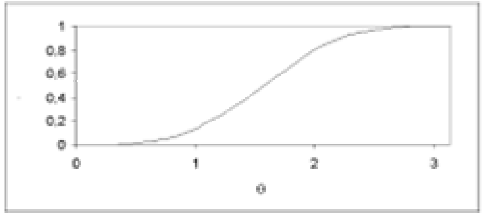


Nucleation rate of water droplets at 300K

(2) Heterogeneous nucleation

$$\Delta G_{het}{}^{*} = f\Delta G^{*} = \frac{(2+\cos\theta)(1-\cos\theta)^{2}}{4}\Delta G^{*}$$





Correction term f vs. the contact angle in radian

* *Critical supersaturation ratio (S_{crit})*

If $S > S_{crit} \Rightarrow$ *Homogeneous nucleation*

$S < S_{crit} \Rightarrow$ *Heterogeneous nucleation*

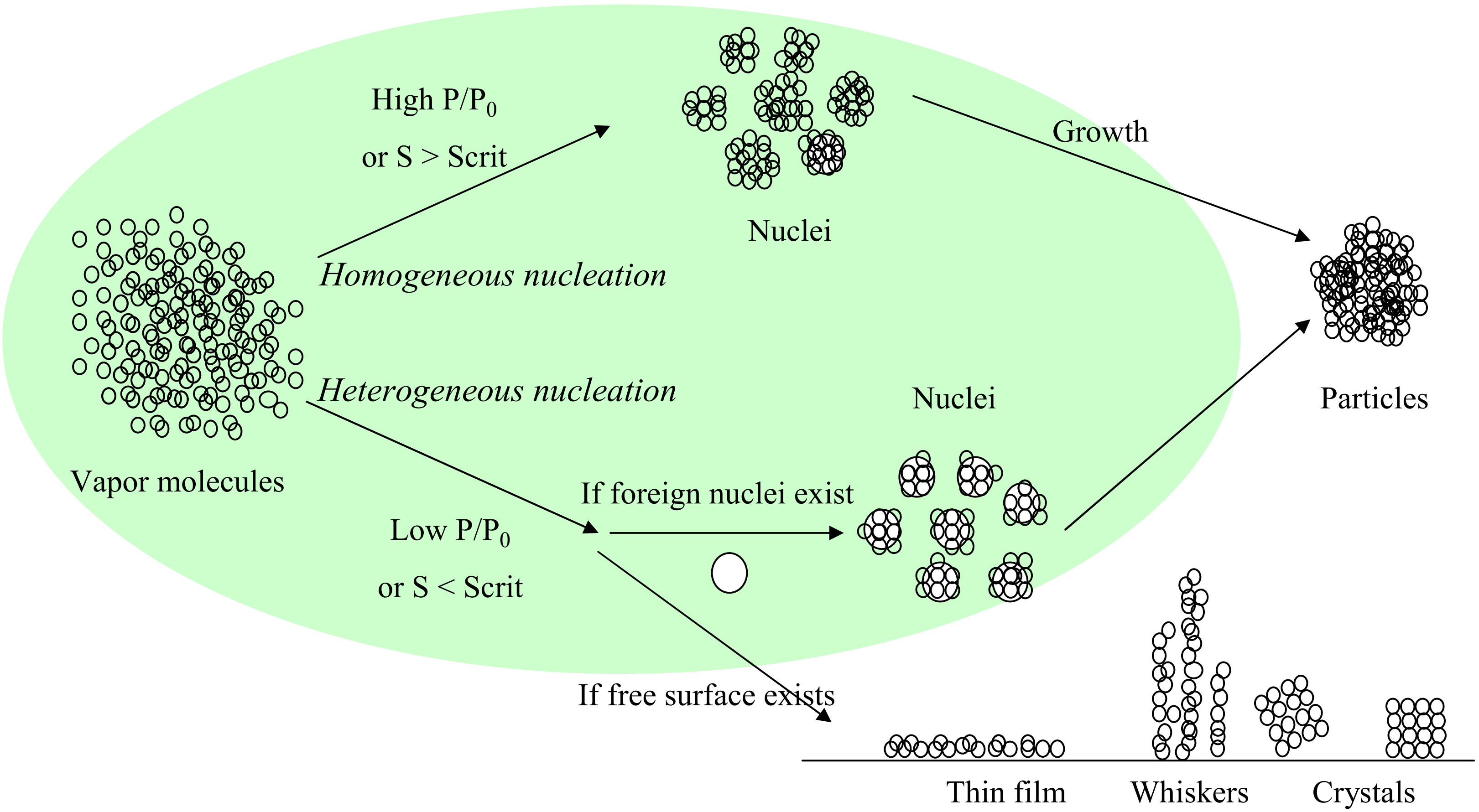
* *Used for formation of artificial rain (seed: AgCl, AgI)*

Core-shell particles

Monodisperse particles

Films

* *Particles or Films?*



High P/P_0

or $S > S_{crit}$

Homogeneous nucleation

Nuclei

Growth

Particles

Vapor molecules

Heterogeneous nucleation

Nuclei

If foreign nuclei exist

Low P/P_0

or $S < S_{crit}$

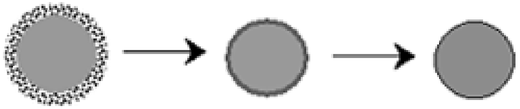
If free surface exists

Thin film

Whiskers

Crystals

4.3 Condensational Growth of Nanoparticles



Growth of particles by collision followed by sticking

- *Rate of condensation*

http://www.eng.uc.edu/~gbeaucag/Classes/Nanopowders/

	Gas phase	*Liquid phase*
Diffusion limited	$d_p \ll \lambda_{gas}$ $\quad \frac{dd_p}{dt} = \frac{2v_m(p_1 - p_2)}{(2\pi mkT)^{1/2}}$ $d_p \gg \lambda_{gas}$ $\quad \frac{dd_p}{dt} = \frac{4Dv_m(p_1 - p_2)}{d_p kT}$	$\frac{dd_p}{dt} = \frac{4Dv_m(n_1 - n_2)}{d_p}$
Surface reaction limited	$\frac{dd_p}{dt} = \frac{2k_r \alpha v_m p_1}{(2\pi mkT)^{1/2}}$	$\frac{dd_p}{dt} = 2k_r v_m n_1$
Droplet phase reaction limited	$\frac{dd_p}{dt} = \frac{d_p}{3}\rho_p\left(\sum_{i=1}^{R} M_i \nu_i\right)r$	

If $p_1 < p_2$, evaporation instead of condensation

For diffusion-controlled condensation

Integration yields

$$d_p^{\,2} = k_D t + d_{p0}^{\,2} \quad (*) \qquad \text{where} \qquad k_D = 8 D v_m (n_1 - n_2)$$

Considering a variation in size $d_p = < d_p > + \delta d_p$ *and* $d_{p0} = < d_{p0} > + \delta d_{p0}$

Substituting these into (*), omitting square term which is small

$$< d_p >^2 + 2 < d_p > \delta d_p = k_D t + < d_{p0} >^2 + 2 < d_{p0} > \delta d_{p0}$$

Since $< d_p >^2 = k_D t + < d_{p0} >^2 \quad (**)$

Then $$\delta d_p = \frac{d_{p0}\delta d_{p0}}{d_p}$$

Substituting (**) $$\delta d_p = \frac{d_{p0}\delta d_{p0}}{\sqrt{k_D t + d_{p0}^{\,2}}}$$

The variation in size decreases as growth proceeds!

For surface reaction-controlled condensation

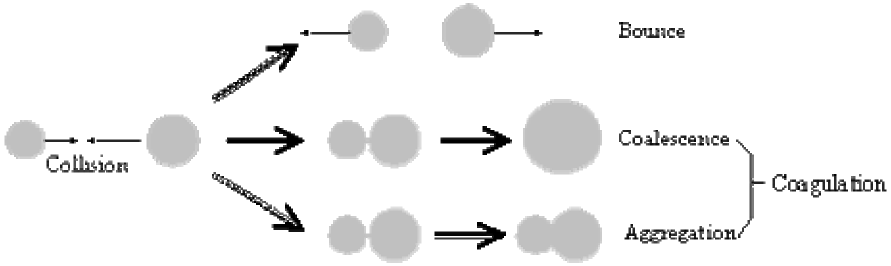
Integration $d_p = k_p t + d_{p0}$ *where* $k_p = 2k_r v_m n_1$

$$\therefore \delta d_p = \delta d_{p0}$$

The variation in size is kept constant but the relative size variation decrease as growth proceeds!

4.4 Coagulation: Coalescence and Aggregation

Growth as a result of collision and subsequent coagulation with other particles.



- *Sources of collision*

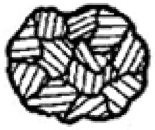
Brownian motion, external force fields, particle-particle interaction (polar, coulombic)

- *Coagulation efficiency*

Comparison of condensation and coagulation

	condensation	*coagulation*
size	*increase*	*increase*
Particle number concentration	*No change*	*decrease*
Total particle mass concentration	*increase*	*decrease*

(1) Shapes of particles coagulated (secondary particles)



Spherical/near-spherical growth

: Liquid-phase or liquid-like growth

- Liquid particles grow by "coalescence"..
- Solid particles grow by "aggregation (agglomeration)" and followed by rapid sintering

Aggregate of TiO2 nanoparticles

Random (fractal) growth

: Solid-phase growth

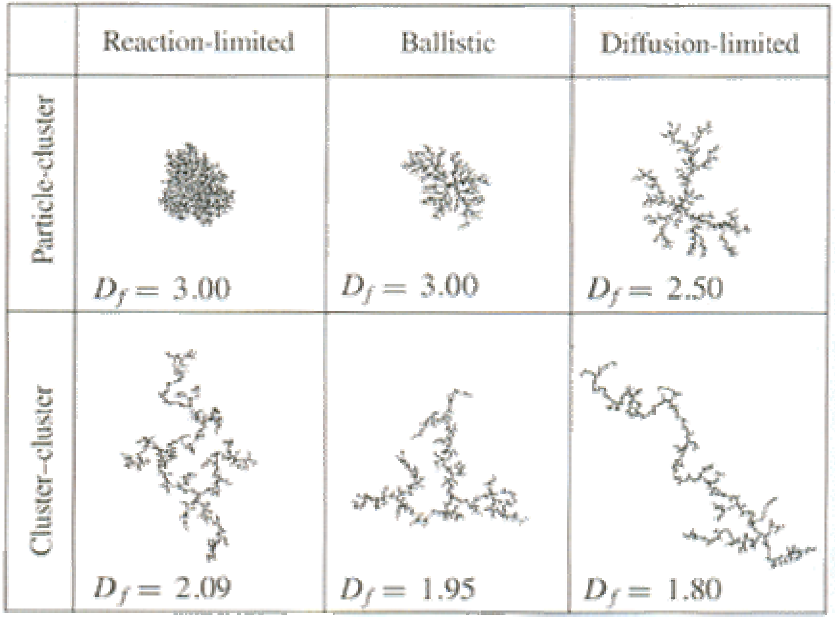
- Fractal representation

$$V \sim l^D$$

where V: solid volume

l: characteristic length of the aggregate

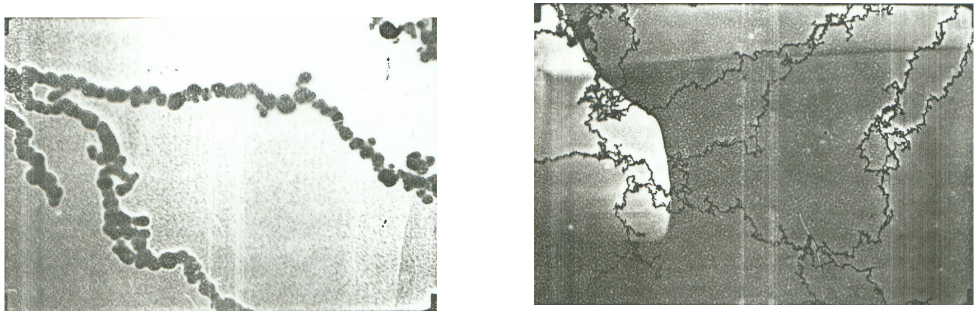
D: fractal dimension($\neq 1, 2, 3$)



<u>*Directional (anisotropic) growth*</u>

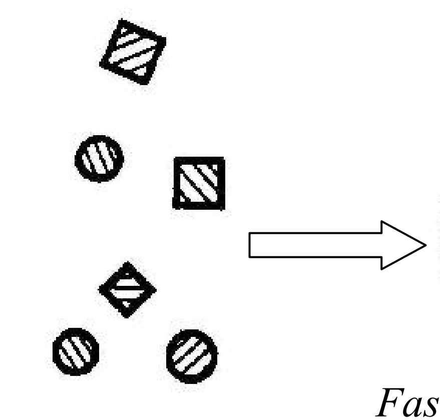
With interparticle forces - electrical or magnetic dipoles

e.g. Smoke particles, iron nanoparticles

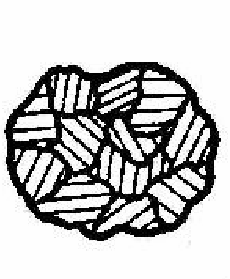


Iron particles

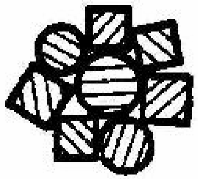
** Solid particle growth*



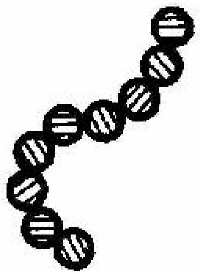
Primary particles



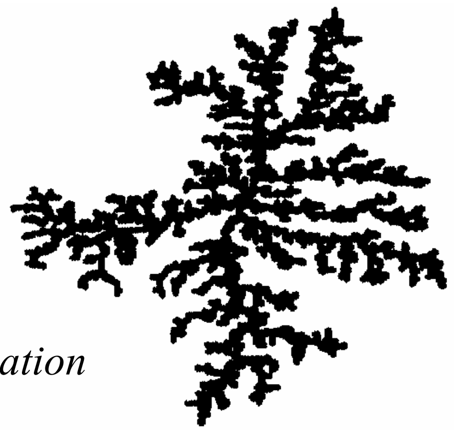
Fast sintering



Slow sintering



Dipole aggregation



Fraction growth

Secondary particles

- Coalescence or Aggregation?

-Depends on the characteristic times of collision and coalescence

(2) Mathematical expression for coagulation

$N_{i,j}$: Number of collisions occurring per unit time per unit volume between the particles having diameters (volumes) $d_i(v_i)$ and $d_j(v_j)$ respectively.

$$N_{i,j} = b_{i,j} n_i n_j$$

n_i, n_j: number concentration of colliding particles v_i, v_j, respectively.(no./cm^3)

i, j: number of basic units making particles (e.g. i-mer and j-mer)

In terms of continuous size distribution

$$N(v_i, v_j) = b(v_i, v_j) n(v_i) n(v_j) dv_i dv_j$$

where $b_{i,j}$: collision frequency function

"coagulation coefficient"

Increase in size

$$v_{new} = v_i + v_j$$

$$d_{p,new} = \left(d_{pi}^{\ 3} + d_{pj}^{\ 3}\right)^{1/3}$$

- *Change in number concentration of the particles, v*

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} N_{i,j} - \sum_{i=0}^{\infty} N_{i,k} = \frac{1}{2}\sum_{i+j=k} b_{i,j} n_i \overset{\text{or}}{n_j} - n_k \sum_{i=0}^{\infty} b_{i,k} n_i$$

$$\frac{dn(v)}{dt} = \frac{1}{2}\int_0^v b(v', v-v')n(v')n(v-v')dv' - n(v)\int_0^\infty b(v,v')n(v')dv'$$

Input by coagulation Output by coagulation

- *For Brownian coagulation*

For continuum regime $b(v,v') = \left(\frac{2kT}{3\mu}\right)\left(\frac{1}{v^{1/3}} + \frac{1}{v'^{1/3}}\right)\left(v^{\frac{1}{3}} + v'^{\frac{1}{3}}\right)$ *or*

$$b(v,v') = \left(\frac{2kT}{3\mu}\right)\left(\frac{1}{d_{pi}} + \frac{1}{d_{pj}}\right)\left(d_{pi} + d_{pj}\right)$$

- *For polydisperse particles*

When $d_i > d_j$, $b_{i,j} > b_{i,i}$ *or* $b_{j,j}$

- *Different-size coagulation occurs faster than that between similar-size coagulation.*

Monodisperse particles becomes polydisperse…

Polydisperse particles becomes monodisperse…

∴*Self preserving model: distribution converges to* $\sigma_g = 1.4$

- For monodisperse particles

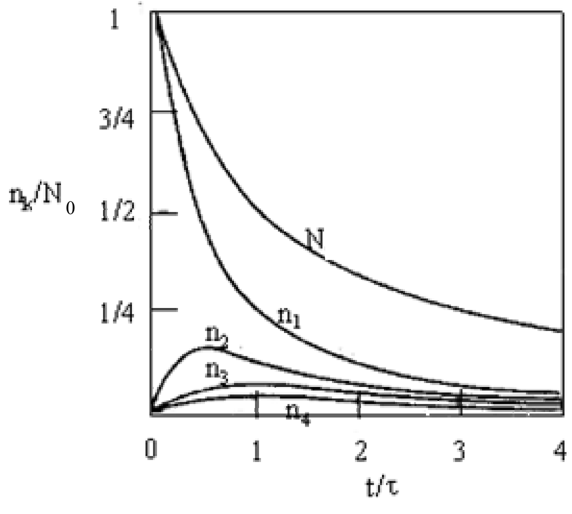
$$b = \frac{8kT}{3\mu} = K = 3.0\times10^{-16} C_c m^3 / s$$

Under standard conditions

$$\frac{dn_k}{dt} = \frac{K}{2}\sum_{i+j=k} n_i n_j - K n_k \sum_{i=0}^{\infty} n_i$$

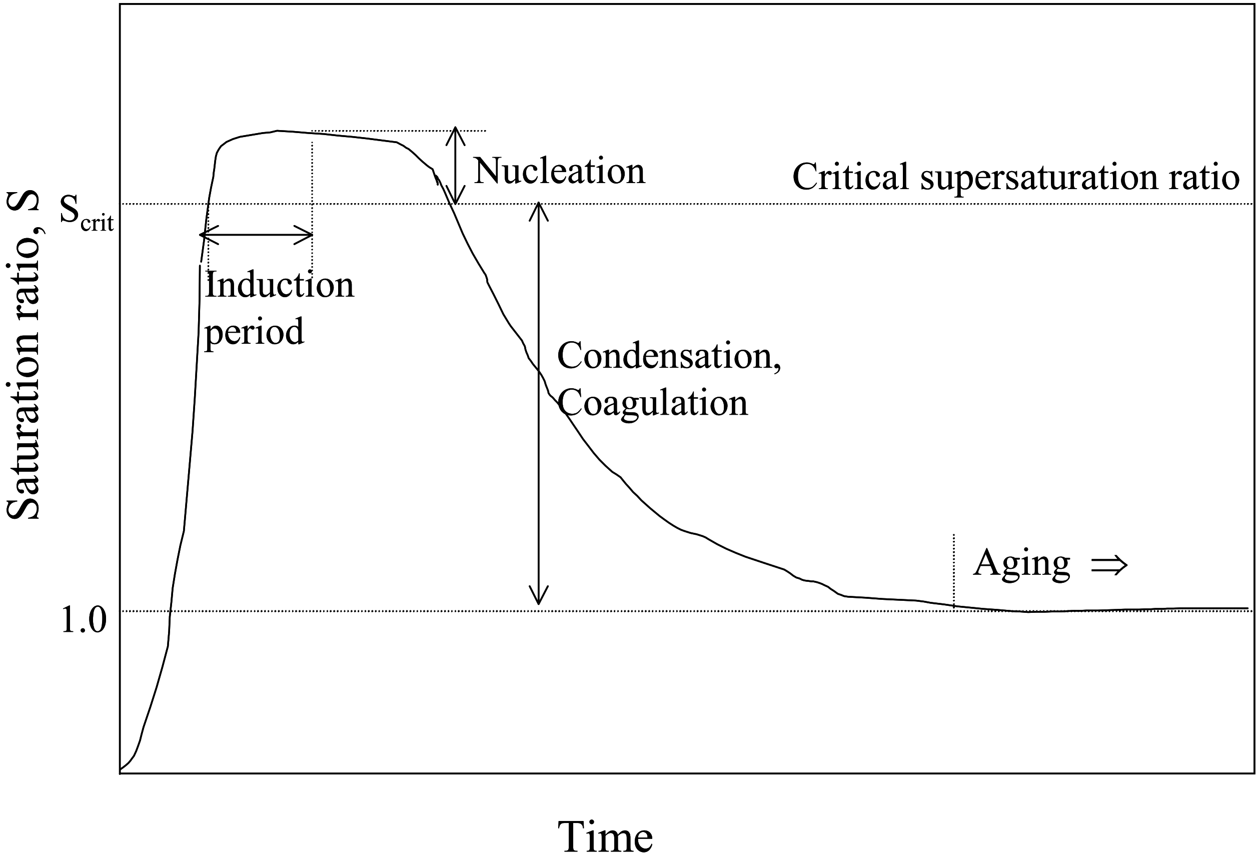
Solving for total number concentration of particles, N and average diameter of the particles, d

$$N(t) = \frac{N_0}{1+N_0Kt} \quad and \quad \frac{d(t)}{d_0} = \left(\frac{N_0}{N(t)}\right)^{1/3}$$



4.5 Some Comments on Particle Growth

(1) Overall growth



(2) *Growth mechanisms and particle size distribution*

- *Nucleation*
  - *increase of particle number concentration*
  - *may cause accelerating the rate of coagulation*
  - *gives delta function in particle size distribution in given condition*
- *Condensation*
  - *No effect of particle number concentration*
  - *results in monodisperse size distribution.*
- *Coagulation*
  - *Decreases in particle number concentration*
  - *gives polydisperse size distribution in growth process*

- *Matijevic's method*

(3) Preparation of monodisperse particles

- *Maintain low rate of nucleation*
  - *using low supersaturation*
  - *inducing heterogeneous nucleation*
- *Allow the same growth time for all the particles by shortening the time of nucleation*
- *Suppress coagulation*
  - *Using electrostatic repulsion (electrical double layer)*
  - *Using adsorption of surfactants and macromolecules*
  - *Rapid cooling and dilution*

(4) Composite particles

** Mixed –phase particles from mixtures of precursors:*

Since reaction (or evaporation), critical supersaturation, saturation: different for each component,

- *Different history of nucleation*
- *Possible occurrence of heterogeneous nucleation*
- *Different condensation rate*
- *uniform distribution of components within each particle: unexpected*

"Composition gradient"

- *Confined growth: preferred*

e.g. spray-pyrolysis, emulsion, in-pore and in-layer growth

** Core-shell composite particles*

coating of existing particles

start with heterogeneous nucleation and subsequent growth