• Dynamic equations for the moments of the distribution(Lee, K.W., 1983)

$$\frac{\partial n}{\partial t} = \frac{1}{2} \int_{0}^{v} \beta(\tilde{v}, v - \tilde{v}) n(\tilde{v}) n(v - \tilde{v}) d\tilde{v} - \int_{0}^{\infty} \beta(v, \tilde{v}) n(\tilde{v}) n(v) d\tilde{v} \beta(v, \tilde{v})$$
$$\beta(v, \tilde{v}) = \frac{2kT}{3\mu} \left(v^{\frac{1}{3}} + \tilde{v}^{\frac{1}{3}} \right) \left(v^{-\frac{1}{3}} + \tilde{v}^{-\frac{1}{3}} \right)$$

Assume aerosol size distribution is log-normal

throughout the coagulation process

$$n(d_p, t) = \frac{N}{\sqrt{2\pi} \ln \sigma_g d_p} \exp \left[-\frac{\left(\ln d_p - \ln d_g \right)^2}{2 \ln^2 \sigma_g} \right]$$

 d_g :geometric mean diameter = CMD \rightarrow count median diameter σ_g :geometric standard deviation







$$M_{k} = \int_{0}^{\infty} v^{k} n(v, t) dv$$
$$M_{0} = \int_{0}^{\infty} n dv = N(t)$$

: total particle number concentration

$$M_1 = \int_0^\infty nv \, dv = V(t)$$

: total particle volume concentration

$$M_2 = \int_0^\infty v^2 n(v,t) \, dv$$

related to the spread of the distribution



$$\int_{0}^{\infty} \text{Dynamics } eq \times v^{k} dv \rightarrow$$

$$\frac{dM_{k}}{dt} = \int_{0}^{\infty} \int_{0}^{v} v^{k} \left(\frac{1}{2}\right) \left(\frac{2kT}{3\mu}\right) \left[2 + \tilde{v}^{\frac{1}{3}}(v - \tilde{v})^{-\frac{1}{3}} + \tilde{v}^{-\frac{1}{3}}(v - \tilde{v})^{\frac{1}{3}}\right] \times n(\tilde{v}, t) n(v - \tilde{v}, t) d\tilde{v} dv$$

$$- \int_{0}^{\infty} \int_{0}^{\infty} v^{k} \left(\frac{2kT}{3\mu}\right) \left[2 + v^{\frac{1}{3}} \tilde{v}^{-\frac{1}{3}} + \tilde{v}^{\frac{1}{3}} v^{-\frac{1}{3}}\right] n(v, t) n(\tilde{v}, t) d\tilde{v} dv$$

$$- \frac{2kT}{3\mu} \left[2M_{0}M_{k} + M_{-\frac{1}{3}}M_{k+\frac{1}{3}} + M_{\frac{1}{3}}M_{k-\frac{1}{3}}\right]$$

$$1^{\text{st}} \text{ term } \int_{0}^{\infty} \int_{0}^{v} d\tilde{v} dv = \int_{0}^{\infty} \int_{v}^{\infty} dv d\tilde{v}$$

$$x = v - \tilde{v}$$

$$v(\tilde{v} \text{ to } \infty) = x(0 \text{ to } \infty)$$





1st terms

$$\frac{2kT}{3\mu} \int_{0}^{\infty} \int_{0}^{\infty} (x+\tilde{v})^{k} n(\tilde{v},t) n(x,t) dx d\tilde{v} + \frac{kT}{3\mu} \int_{0}^{\infty} \int_{0}^{\infty} (x+\tilde{v})^{k} \tilde{v}^{\frac{1}{3}} x^{-\frac{1}{3}} n(\tilde{v},t) n(x,t) dx d\tilde{v}$$

+ $\frac{kT}{3\mu} \int_{0}^{\infty} \int_{0}^{\infty} (x+\tilde{v})^{k} \tilde{v}^{-\frac{1}{3}} x^{\frac{1}{3}} n(\tilde{v},t) n(x,t) dx d\tilde{v}$
 $k = 0: \frac{2kT}{3\mu} M_{0}^{2}, \quad \frac{kT}{3\mu} M_{\frac{1}{3}} M_{-\frac{1}{3}}, \quad \frac{kT}{3\mu} M_{\frac{1}{3}} M_{-\frac{1}{3}}$
 $\therefore \frac{dM_{0}}{dt} = -\frac{2kT}{3\mu} \left[M_{0}^{2} + M_{\frac{1}{3}} M_{-\frac{1}{3}} \right] \left(\frac{dN}{dt} = -\frac{2kT}{3\mu} 2N^{2} \right)$
 $k = 1 \frac{dM_{1}}{dt} = 0 \quad \} M_{1} = \text{const} = V \text{(total volume is constant)} \quad k = 2 \frac{dM_{2}}{dt} = -\frac{4kT}{3\mu} \left[M_{1}^{2} + M_{\frac{4}{3}} M_{\frac{1}{3}} \right]$
 $k = 1 \frac{2kT}{3\mu} 2M_{0} M_{1} + \frac{kT}{3\mu} \left(M_{\frac{2}{3}} M_{\frac{1}{3}} + M_{\frac{4}{3}} M_{-\frac{1}{3}} \right) + \frac{kT}{3\mu} \left(M_{\frac{4}{3}} M_{-\frac{1}{3}} + M_{\frac{2}{3}} M_{\frac{1}{3}} \right)$
 $\int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} (x+\tilde{v}) n(\tilde{v}) n(x) dx d\tilde{v} = M_{1} M_{0} + M_{0} M_{1}$



Moments for log-normal distribution

$$M_{k} = \int_{0}^{\infty} v^{k} n(v,t) dv = \frac{N}{3\sqrt{2\pi} \ln \sigma_{g}} \int_{0}^{\infty} v^{k-1} \exp\left[-\frac{\left(\ln v - \ln v_{g}\right)^{2}}{18 \ln^{2} \sigma_{g}}\right] dv$$

change of variable

$$u = \ln v, \quad \bar{u} = \ln v_g, \quad \sigma_u = \ln \sigma_g$$

$$M_k = \frac{N}{3\sqrt{2\pi}\sigma_u} \int_{-\infty}^{\infty} e^{ku} \exp\left[-\frac{\left(u - \bar{u}\right)^2}{18\sigma_u^2}\right] du = N v_g^{\ k} \exp\left(\frac{k^2}{2} \left(3\ln\sigma_g\right)^2\right) (12)$$

$$= M_1 v_g^{\ k-1} \exp\left(\frac{9}{2} (k^2 - 1)\ln^2\sigma_g\right) (13)$$



For example

$$k \qquad M_k$$

 $0 \qquad M_1 v_g^{-1} \exp\left(-\frac{9}{2}\ln^2 \sigma_g\right)$
 $\frac{1}{3} \qquad M_1 v_g^{-\frac{2}{3}} \exp\left(-4\ln^2 \sigma_g\right)$
 $M_{\frac{4}{3}} M_{\frac{2}{3}}^2 = M_1^2 \exp\left(\ln^2 \sigma_g\right)$
 $\frac{dM_0}{dt} = -\frac{2kT}{3\mu} M_1^2 \left[\frac{1}{v_g^2} \left(\exp\left(-9\ln^2 \sigma_g\right) + \exp\left(-8\ln^2 \sigma_g\right)\right)\right]$
 $\frac{dM_2}{dt} = \frac{4kT}{3\mu} M_1^2 \left[1 + \exp\left(\ln^2 \sigma_g\right)\right]$



Differentiation of eq(13) gives:

$$\frac{dM_0}{dt} = M_1 \exp\left[-\frac{9}{2}\ln^2\sigma_g\right] \left(-\frac{1}{v_g}\right) \left[9\ln\sigma_g\frac{d\ln\sigma_g}{dt} + \frac{d\ln v_g}{dt}\right]$$
$$\frac{dM_2}{dt} = M_1 \exp\left[\frac{27}{2}\ln^2\sigma_g\right] v_g\left[\frac{d\ln v_g}{dt} + 27\ln\sigma_g\frac{d\ln\sigma_g}{dt}\right]$$

 $\frac{dM_0}{dM_2}$ obtained from two methods should be the same:

$$d(\ln v_g) = 9 \left[\frac{1 - \frac{3}{2} \exp(9 \ln^2 \sigma_g)}{\exp(9 \ln^2 \sigma_g) - 2} \right] d(\ln^2 \sigma_g)$$
(22)



$$\frac{d(\ln v_g)}{dt} \text{ and } \frac{d(\ln^2 \sigma_g)}{dt}$$

$$\rightarrow \text{ Integration gives the time variation of } \ln v_g \text{ and } \ln^2 \sigma_g$$
(assuming $1 + \exp(\ln^2 \sigma_g) \square (1 + \exp(\ln^2 \sigma_0))) \quad \text{Eq(24)}$

$$\ln^2 \sigma_g = \frac{1}{9} \ln \left[2 + \frac{\exp(9\ln^2 \sigma_0) - 2}{1 + \left[1 + \exp(\ln^2 \sigma_0)\right] K N_0 t} \right] \quad (25) \quad (B)$$

$$\frac{v_g}{v_{g0}} = \cdots \quad (26)$$
And we know that $M_0 = M_1 \frac{1}{v_g} \exp\left(-\frac{9}{2}\ln^2 \sigma_g\right)$



$$N_{0} = M_{1} \frac{1}{v_{g0}} \exp\left(-\frac{9}{2}\ln^{2}\sigma_{0}\right)$$

$$\frac{N}{N_{0}} = \frac{1}{1 + \left[1 + \exp(\ln^{2}\sigma_{0})\right] \frac{2kT}{3\mu} N_{0}t} \quad (27)$$
(compare with $\frac{N}{N_{0}} = \frac{1}{1 + 2 \times \frac{2kT}{3\mu} N_{0}t}$

← Smoluchowski(Z. Phys. Chem. Vol.92, 1917) 2 versus $(1 + \exp(\ln^2 \sigma_0))$ show polydispersity and size dependence.





FIG. 1. Decrease in total number of particles, N/N_0 , as a function of dimensionless time, KN_0t , for several initial geometric standard deviations, σ_0 .



As $t \to \infty$ ((B)로 부터) $\exp(9\ln^2 \sigma_g) = 2$ or $\sigma_\infty \square 1.32$ (independent of initial distribution) Asymptotic Behavior Similarity solution





FIG. 2. Change in the geometric standard deviation σ as a function of dimensionless time, KN_0t , for several initial geometric standard deviations, σ_0 .





FIG. 3. Increase in the number median particle volume, v_g/v_{g0} , as a function of dimensionless time, KN_0t , for several initial geometric standard deviations, σ_0 .











FIG. 5. Comparison of size distributions calculated using present results with numerical integrations by Jordan *et al.* (16) ($\sigma_0 = 2.0$).





FIG. 6. Comparison of the predicted decay in the total number of particles in the asymptotic behavior regime with that given by Friedlander (17).









Condensation and Evaporation

- Condensation and evaporation can change the particle size, but cannot change the number concentration (while coagulation changes both size and concentration of particles).

- Condensation and evaporation can be considered as a collision process between the particles and the vapor molecules (while coagulation is a collision process between particles).

- Condensation needs "super saturation". (evaporation occurs when the vapor partial pressure is less than its saturation value).

- Saturation means "equilibrium between liquid and vapor", therefore, Supersaturation (vapor partial pressure is larger than saturation pressure) is needed for vapor molecules to condense on the particle.



saturation ratio $= \frac{P}{P_s} P_s$:saturation vapor pressure for a plane liquid surface

Vapor

liquid → We call the vapor pressure as "saturation pressure" when mass equilibrium exists, i.e., when evaporation is balanced with condensation

For the case of water,

$$\log_{10} P_s = 8.11 - \frac{1750}{T + 235}$$

 $T(^{\circ}C) P(mmHg)$ (empirical relation)

 $\frac{dP_s}{dT} = \frac{\Delta H}{T\Delta v}$

: clausius-clapeyron equation $(T\uparrow, P_s\uparrow)$



When saturation ratio is greater than one \rightarrow super saturated When saturation ratio is less than one \rightarrow unsaturated super saturation can occur ① adiabatic expansion

P

$$L V \longrightarrow \frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/\gamma-1} \leftarrow \text{by adiabatic expansion}$$

 $\gamma: \text{ Gamma : specific heat ratio}$
T

(2) mixing(for example, stack gas) \rightarrow cooling(that is advantageous for supersaturation) + dilution(that is a opposite effect for super saturation)



Kelvin Effect

Smaller number of molecules exist underneath the droplet than the case of plane interface, therefore, attractive force grabbing interface molecules should become smaller. Consequently, for given temperature and pressure, smaller droplets can be more easily evaporated.



- P_d : Saturation pressure for a system having curved interface : for droplet
- P_s : Saturation pressure for a system having plane interface

$$\frac{P_d}{P_s} = \exp\left(\frac{4\sigma v_m}{d_p kT}\right)$$

0

 $v_m : \frac{\bar{v}}{N_{av}} / N_{av}$ (volume per molecule of liquid) \rightarrow Kelvin relation

 $\frac{P_d}{P_s}$ region growth 1.0 $< 0.1 \ \mu m$ "Super saturation" is need to maintain liquid droplet For example, if $d_p = 0.05 \mu m$ (water), 104.4% saturation ratio is needed.

For given d_p , If Partial pressure > $P_d \rightarrow$ condensation \rightarrow particle growth Partial pressure < $P_d \rightarrow$ evaporation \rightarrow particle evaporation

For given P, droplets having d_p^* corresponding to Pd remain as it is, droplets having d_p less than d_p^* will be evaporated, and droplets having d_p larger than d_p^* will grow due to codensation



Change of Gibbs free energy during condensation of *n* vapor molecules

$$\Delta G = (\phi_b - \phi_a)n + \pi d^2 \sigma$$

If n_b molecules become liquid and n_a molecules still remain vapor, then

$$G = \phi_a n_a + \phi_b n_b + \pi d^2 \sigma$$
 (originally $G_0 = (n_a + n_b)\phi_a$)

 ϕ_a : free energy potential per molecule in the vapor phase ϕ_b : free energy potential per molecule in the liquid phase

$$d\phi_a = V_a dp \qquad d\phi_b = V_b dp \qquad V_a >> V_b$$
$$d\phi_b - d\phi_a = -V_a dp \approx -\frac{kT}{p} dp$$



$$dg = vdp - SdT$$

$$g = h - TS$$

$$\therefore \phi_b - \phi_a = -kT \ln \frac{P}{P_s(T)} = -kT \ln S$$

$$n = \frac{N_a}{M} \frac{\pi}{6} \rho_p d_p^{-3}$$

$$\therefore \Delta G = \pi d_p^{-2} \sigma - kT \ln S \frac{N_a}{M} \left(\frac{\pi}{6} \rho_p d_p^{-3}\right)^3$$





$$\frac{d\Box G}{dd_p} = 0$$

$$2\pi d_p \sigma - kT \ln S \frac{N_a}{M} \frac{\pi}{2} \rho_p d_p^2 = 0$$

$$d_{p}^{*} = \frac{4\sigma M}{\rho_{p} RT \ln S} \quad \leftarrow \text{Kelvin equation}$$
$$\frac{P_{d}}{P_{s}} = \exp\left(\frac{4\sigma v_{m}}{d_{p} kT}\right)$$



$$d_p > d_p^*$$
, particles grow.

 $d_p < d_p^*$, particles are evaporated and finally disappear.

For given S,
$$d_p^* = \frac{4\sigma M}{\rho_p RT \ln S}$$

designates " critical size " from which we can consider as a stable particle. Droplets less than this critical size are unstable and considered as molecular clusters (not particles).



Homogeneous Nucleation

Questions :

-For given supersaturation ratio S, how many particles can be nucleated from pure vapor per unit time per unit volume ?

-Regardless of generation mechanism of vapor (physical or chemical), you need supersaturation of vapor in order to nucleate "particles" from molecular clusters. This means that you need to generate "stable molecular cluster ", or, "molecular clusters having critical size, or "smallest size of particle".

-What is the rate of formation of such critical size of particles ? The particle formation rate may be different from the generation rate of vapor molecules owing to chemical reaction or physical evaporation.



Homogeneous Nucleation

Questions :

-If we can assume the critical size or smallest particle size to be the single molecule, then the formation rate of particle should be the same of the generation rate of molecules due to chemical reactions or physical evaporation.

-To find out "nucleation rate", you need to know the generation rate of "stable molecular cluster ", or, " molecular clusters having critical size, or " smallest size of particle"



Homogeneous nucleation theory (Becker and Doring. 1935)

-Consider the generation of g-mers with assumption that the rate of g-mers formation is equal to the rate of formation of g+1-mers

-Consider the collisional process of molecules assuming dominant molecular cluster governing this process is monomers

-To become " particle", clusters should overcome del G.

-Now this theory is receiving a lot of criticism without "alternative established new theory ".

$$I = \left[\frac{p_1}{\left(2\pi m_1 kT\right)^{\frac{1}{2}}} \left[\frac{2\sigma^{\frac{1}{2}}v_l}{\left(kT\right)^{\frac{1}{2}}}\right] N_1 \exp\left(-\frac{16\pi\sigma^3 v_l^2}{3(kT)^3(\ln S)^2}\right)\right] \text{ Eq.(10-16) [\#/cm3sec]}$$



Heterogeneous Condensation

- condensation takes phase on the existing particles \rightarrow cloud formation $d_p >> \lambda$

$$\frac{\partial n}{\partial t} = \frac{D\partial r^2}{r^2 \partial r} \left(\frac{\partial n}{\partial r}\right) = 0$$

n : molecular concentration of the condensing speices

$$r = \frac{d_p}{2} \qquad n = n_d \text{ :concentration in equilibrium}$$

$$r \to \infty \qquad n = n_1$$

$$\frac{n - n_d}{n_1 - n_d} = 1 - \frac{d_p}{2r}$$



The rate of diffusional condensation

$$F = D \frac{\partial n}{\partial r} \Big|_{r=\frac{d_p}{2}} \pi d_p^2 = 2\pi d_p D(n_1 - n_d)$$
$$= 2\pi d_p D \frac{(p_1 - p_d)}{kT} \quad \text{#/sec}$$
$$\frac{dv}{dt} = \frac{2\pi d_p D}{kT} v_m(p_1 - p_d)$$
From $v = \frac{1}{6} \pi d_p^3$, you can obtain $\frac{dd_p}{dt}$



(ii) free molecular region

$$F = \frac{1}{4}n\bar{c}\pi dp^{2} = \frac{1}{4}\frac{p_{1}}{kT}\sqrt{\frac{8kT}{\pi m_{i}}}\pi dp^{2} \quad \therefore \frac{dv}{dt} = \alpha \frac{\pi d_{p}^{2}v_{m}(p_{1}-p_{d})}{\sqrt{2\pi m_{1}kT}}$$

if accommodation coefficient = 1 $\alpha = 1$

Inter-polation formula for the entire range (Fuchs & Sutugin, 1971)

$$F = 2\pi d_p D(n_1 - n_d) \left\{ \frac{1 + kn}{1 + 1.71kn + 1.333kn^2} \right\}$$
$$kn = \frac{\lambda}{a_p}$$
$$p_1 - p_d = p_1 - p_s \exp\left[\frac{4\sigma v_m}{d_p kT}\right]$$



 General Dynamic Equation Including nucleation and condensation and coagulation

$$\frac{dn_{k}}{dt} = \frac{1}{2} \sum_{i+j=k}^{\infty} \beta(v_{i}, v_{j}) n_{i} n_{j} - n_{k} \sum_{i=1}^{\infty} \beta(v_{i}, v_{k}) n_{i}$$

if evaporation is included, define e_k : rate of escape of monomers form a *k*-mer \therefore The rate of formation of *k*-mers by evaporation = $(1+\delta_{1,k})e_{k+1}n_{k+1}(t)$ $k \ge 1$ if k = 1, dimer becomes two monomers If $k \ge 2$, $k+1 \rightarrow k$ -mer 가 된다. $(\delta_{1,k} = 0)$ $\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1}\beta_{j,k-j}n_jn_{k-j} - n_k\sum_{i=1}^{\infty}\beta_{k,j}n_j - e_kn_k + e_{k+1}n_{k+1}$ $k \ge 2$

+ condensation (addition of monomers)



 $p_{k}(/\text{sec}): \text{frequency with which a monomer collides with a k-mer.}$ $\frac{dn_{k}}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} \beta_{j,k-j} n_{j} n_{k-j} - n_{k} \sum_{j=1}^{\infty} \beta_{k,j} n_{j} - e_{k} n_{k} + e_{k+1} n_{k+1} + p_{k-1} n_{k-1} - p_{k} n_{k}$

• Stable nucleus (particle)

→ Should have a minimum number of monomers : g*>>2→ super saturation → homogeneous nucleationJ₀(t) ← g* nucleus (#/cm³ · sec)k ≥ g* $<math display="block"> \frac{dn_k}{dt} = \frac{1}{2} \sum_{j=g^*}^{k=g^*} \beta_{j,k-j} n_j n_{k-j} - n_k \sum_{j=g^*}^{\infty} \beta_{k,j} n_j + p_{k-1} n_{k-1} - (p_k + e_k) n_k + e_{k+1} n_{k+1} + J_0(t) \delta_{k,g^*}$ $k = g^*, g^* + 1, \cdots$



continuous form

dv

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2} \int_{v_0}^{v-v_0} \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)n(\tilde{v},t)d\tilde{v} - \int_{v_0}^{\infty} \beta(\tilde{v},v)n(v,t)n(\tilde{v},t)d\tilde{v} - \frac{\partial}{\partial v} [I_0(v)n(v,t)] + \frac{\partial^2}{\partial v^2} [I_1(v)n(v,t)] + J_0(v)\delta(v-v_0)$$

 $v = k \Box v$, $\Box v$:monomer volume, $v_0 = g^* \Box v$, $I_0(v) = \Box v(P_k - e_k)$

$$I_{1}(v) = \frac{\Box v^{2}}{2} (P_{k} + e_{k})$$

$$\left(\frac{\partial}{\partial v} (\Box v(P_{k} - e_{k})n(v,t)) = \frac{(P_{k+1} - e_{k+1})n_{k+1} - (P_{k-1} - e_{k-1})n_{k-1}}{2}$$

$$\frac{\partial^{2}}{\partial v^{2}} (I_{1}n) = \frac{(P_{k+1} + e_{k+1})n_{k+1} + (P_{k-1} + e_{k-1})n_{k-1} - 2(P_{k} + e_{k})n_{k}}{2}$$

$$\therefore -\frac{\partial(I_{0}n)}{dv} + \frac{\partial^{2}(I_{1}n)}{dv^{2}} = e_{k+1}n_{k+1} + P_{k-1}n_{k-1} - (P_{k} + e_{k})n_{k}$$



assumption $v_0 \to 0, \ n(v,0) = n_0(v) = 0 \ v < v_0$ and no partices of volume $v < v_0$ can be produced for t > 0 $\frac{\partial^2(I_1n)}{\partial v^2} \rightarrow \text{can be neglected.}$ Brock(1972) "Condensational Growth of Atmospheric Aerosols"

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$$\therefore \frac{\partial n(v,t)}{\partial t} + \frac{\partial}{\partial v} (I(v,t)n(v,t))$$

$$= \frac{1}{2} \int_{0}^{v} \beta(v - \tilde{v}, \tilde{v})n(v - \tilde{v}, t)n(\tilde{v}, t)d\tilde{v}$$

$$-n(v,t) \int_{0}^{\infty} \beta(v, \tilde{v})n(\tilde{v}, t)d\tilde{v} + J_{0}(t)\delta(v - v_{0})$$
: continuous General Dynamics Equation
$$I = \Box v(p_{k} - e_{k}): \text{rate of change of the volume of}$$
a particle size $v = k \Box v$

$$I = \frac{dv}{dt} = G$$

