Coagulation Theory and The Smoluchowski Equation:

Coagulation is defined as growth of particles by collisions among particles. It is usually associated with dense, 3-d growth, in contrast to **aggregation** which leads to low dimension, branched structures. The process of coagulation usually is associated with sintering and coalescence of particles by Gibbs-Thompson maturing and through strong van der Waals bonding of the particles. Then the result of coagulation is usually considered a solid 3-d particle. **Agglomeration** is similar to coagulation but, for the most part, does not include coalescence of the particles so that an agglomerate can be "broken down" in to the units of which it is made while a coagulated particle can not be broken down exactly into the subparticles from which it grew.

In aerosol and other gas phase growth the time rate of change of particle size distribution is of primary interest. In a general sense we can consider two types of particles, with volumes, v_i and v_j. The rate of collision between i and j particles is N_{ij}. For spherical particles, each diameter of particles has a unique volume. The collision of two particles leads immediately to the growth of a new particle with the summed volume of the two contributing particles. The concentration of particles "i" is n_i and that of "j" is n_j. We can define the **collision frequency function**, β_{ij}, by,

$$N_{ij} = \beta_{ij}(v_i, v_j, T, P, \text{etc.})\, n_i\, n_j$$

For one such collision, a new particle, "k", is formed of volume $v_k = v_i + v_j$. The rate of formation of "k" particles is,

$$\frac{1}{2} \sum_{i+j=k} N_{ij}$$

The rate of loss of particles "k" due to collision with other particles is,

$$\sum_{i=1}^{\infty} N_{ik}$$

Then,

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} N_{ij} - \sum_{i=1}^{\infty} N_{ik} = \frac{1}{2}\sum_{i+j=k}\beta(v_i,v_j)n_i n_j - n_k \sum_{i=1}^{\infty}\beta(v_i,v_k)n_i$$

This is the Smoluchowski equation (1917). The equation converts the problem of the determining the evolution of a spectrum of particle sizes to the problem of determining the collision frequency function, β_{ij}. The functional form for β_{ij} depends on the transport mechanisms at play in the system. The equation is based on instantaneous bonding of particles after collision.

Determination of β_{ij} for Brownian Motion of Particles:

For nanoparticles (particles smaller than 1 μm) Brownian motion governs the collision frequency. For a spherical particle of radius a_i with a coordinate system fixed on its center, and particles, a_j, surrounding it and subjected to Brownian motion, the a_j particles diffuse to the surface of a_i. a_i is a perfect sink since the particles bond by van der Waals interactions. We consider that $n_j = 0$ at $a_i + a_j$. Fick's second law for the spherical particle, a_i, is given by,

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

We have at $r = a_i + a_j$, $n_j = 0$ for all t, and for $r > a_i + a_j$, at time $t = 0$, $n_j = n_\infty$. Fick's second law can be rewritten in terms of the dimensionless parameters,

$$x = \frac{r - \left(a_i - a_j\right)}{a_i - a_j} \qquad w = \frac{n_\infty - n}{n_\infty}\quad\frac{r}{a_i + a_j} = \frac{n_\infty - n}{n_\infty}\left(x + 1\right)$$
and

so

$$\frac{\partial n}{\partial t} = \left(1 - x\right)\frac{\partial w}{\partial t}$$

$$\frac{\partial x}{\partial r} = \frac{1}{a_i - a_j}$$

$$\frac{\partial w}{\partial r} = -\frac{\left(x - 1\right)}{n_\infty}\frac{\partial n}{\partial r} + \frac{n_\infty - n}{n_\infty}\frac{\partial x}{\partial r} = \frac{n_\infty - n}{\left(a_i + a_j\right)n_\infty} + \frac{\left(1 - x\right)}{n_\infty}\frac{\partial n}{\partial r}$$

$$\frac{\partial^2 w}{\partial r^2} = -\frac{1}{\left(a_i + a_j\right)n_\infty}\frac{\partial n}{\partial r} + \frac{\left(1 - x\right)}{n_\infty}\frac{\partial^2 n}{\partial r^2} - \frac{1}{n_\infty}\frac{\partial x}{\partial r}\frac{\partial n}{\partial r}$$

and

$$\frac{\partial w}{\partial x} = \frac{n_\infty - n}{n_\infty} - \frac{\left(x + 1\right)}{n_\infty}\frac{\partial n}{\partial x}, \quad\text{and,}\quad \frac{\partial^2 w}{\partial x^2} = -\frac{2}{n_\infty}\frac{\partial n}{\partial x} - \frac{\left(x + 1\right)}{n_\infty}\frac{\partial^2 n}{\partial x^2}$$

and

$$\frac{\partial w}{\partial t} = -\frac{\left(x + 1\right)}{n_\infty}\frac{\partial n}{\partial t} = -D\frac{\left(x + 1\right)}{n_\infty}\frac{\partial\left(r^2\, \partial n/\partial r\right)}{r^2\, \partial r} = -D\frac{\left(x + 1\right)}{n_\infty}\left[\frac{2}{r}\frac{\partial n}{\partial r} + \frac{\partial^2 n}{\partial r^2}\right]$$

$$= -D\frac{\left(x + 1\right)}{n_\infty}\left[\frac{2\left(a_i - a_j\right)}{x\left(a_i - a_j\right) + \left(a_i - a_j\right)}\frac{\partial n}{\partial x} + \left(a_i - a_j\right)\frac{\partial^2 n}{\partial x^2}\right] = -D\frac{\left(x + 1\right)}{n_\infty}\left[\frac{2}{\left(x + 1\right)}\frac{\partial n}{\partial x} + \frac{\partial^2 n}{\partial x^2}\right]$$

$$= -D\frac{2}{n_\infty}\frac{\partial n}{\partial x} - D\frac{\left(x + 1\right)}{n_\infty}\frac{\partial^2 n}{\partial x^2} = \frac{D}{\left(a_i + a_j\right)^2}\frac{\partial^2 w}{\partial x^2}$$

The boundary conditions become $x = 0$; $w = 1$ for all t and $x > 0$; $t = 0$, $w = 0$. This is a 1-d diffusion equation so the solution is,

$$w = 1 - erf \frac{x(a_i + a_j)}{2(Dt)^{1/2}} \quad \text{or} \quad \frac{n - n}{n} = \frac{a_i + a_j}{r} \left[1 - erf \frac{(r - (a_i + a_j))}{2(Dt)^{1/2}} \right]$$

The steady state solution is obtained at $t \Rightarrow$, $w \Rightarrow 1$, so

$$\frac{n - n}{n} \quad \frac{a_i + a_j}{r}$$

Fick's first law can be used to calculate the flux of a_j particles to a_i (at $r = a_i + a_j$),

$$J = -D \left. \frac{n_j}{r} \right|_{r = a_i + a_j}$$

and the rate of collision, $F(t)$, is given by,

$$F(t) = -4 \ D \ r^2 \left. \frac{n_j}{r} \right|_{r = a_i + a_j}$$

From the expression for n above,

$$F(t) = 4 \ D(a_i + a_j)n \left[1 + \frac{(a_i + a_j)}{(\ Dt)^{1/2}} \right]$$

At steady state, $t \gg (a_i + a_j)^2/D$,

$$F(t) = 4 \ D(a_i + a_j)n$$

which is minimum value of the time function since "j" particles have, for the most part diffused away or coagulated.

We must also consider Brownian diffusion of the "i" particle which was fixed in the previous assessment. The Einstein equation gives the relative displacement of "i" and "j" particles,

$$D_{ij} = \frac{\langle (x_i - x_j)^2 \rangle}{2t} = \frac{\langle (x_i)^2 \rangle}{2t} + \frac{\langle (x_i x_j) \rangle}{2t} + \frac{\langle (x_j)^2 \rangle}{2t} = \frac{\langle (x_i)^2 \rangle}{2t} + \frac{\langle (x_j)^2 \rangle}{2t} = D_i + D_j$$

since the two particles are not correlated in motion, i.e. the motion is random.

The collision frequency function, $_{ij}(v_i, v_j)$,

$$_{ij}(v_i, v_j) = 4 \ (D_i + D_j)(a_i + a_j)$$

for steady state. For 0.1µm particles the time constant deciding steady state is about 1×10^{-3} sec allowing for this approximation.

The Stokes-Einstein equation gives $D = kT/(3\mu d_p)$ for the continuum regime, so

$$\beta_{ij}\left(v_i, v_j\right) = \frac{2kT}{3\mu}\left[\frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}}\right]\left(v_i^{1/3} + v_j^{1/3}\right) \qquad \text{Continuum Range}$$

In the free molecular regime the functions described in the previous section are used for D and,

$$\beta_{ij}\left(v_i, v_j\right) = \left(\frac{3}{4}\right)\left(\frac{6kT}{\rho_p}\right)^{1/2}\left[\frac{1}{v_i} + \frac{1}{v_j}\right]^{1/2}\left(v_i^{1/3} + v_j^{1/3}\right)^2 \qquad \text{Free Molecular Range}$$

which is based on the kinetic theory of gasses.

An interpolation function can be found in Fuchs, NA *Mechanics of Aerosols*, Pergamon Press, NY (1964). This function shows a maximum collision frequency for $Kn \approx 5$. Collision frequency is highest for particles with widely separated sizes, favoring monomer cluster growth for instance.

Development of a Particle Size Distribution by Coagualtion:

For a monodisperse system undergoing coagulation, initially $v_i = v_j$,

$$\beta_{ij} = K = \frac{8kT}{3\mu} \qquad \text{Continuum Range, Monodisperse}$$

This can be inserted in to the Smoluchowski equation to yield,

$$\frac{dn_k}{dt} = \frac{K}{2}\sum_{i+j=k} n_i n_j - Kn_k\sum_{i=1} n_i$$

The total number of particles per unit volume, $N = \sum n_i$. The Smoluchowski equation can be written for the rate of change for the total particle number per unit volume,

$$\frac{dN}{dt} = \frac{K}{2}\sum_{k=1}\sum_{i+j=k} n_i n_j - KN^2 = -\frac{K}{2}N^2$$

so,

$$N = \frac{N(t=0)}{1 + \left(KN(t=0)t/2\right)} = \frac{N(t=0)}{1 + (t/\tau)}$$

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The discrete size distribution can be obtained by considering the solution to the kinetic growth equations for a series of sizes, for k = 1,

$$\frac{dn_1}{dt} = -Kn_1N \quad \text{or} \quad n_1 = \frac{N\ (t=0)}{\left(1+t/\ \right)^2}$$

and for k = 2,

$$\frac{dn_2}{dt} = \frac{Kn_1^2}{2} - Kn_2N \quad \text{or} \quad n_2 = \frac{N\ (t=0)(t/\ )}{\left(1+t/\ \right)^3}$$

In general,

$$n_k = \frac{N\ (t=0)(t/\ )^{k-1}}{\left(1+t/\ \right)^{k+1}}$$

Continuum range, Constant Collision Frequency from Monodisperse System

where $\ = 2/(K\ N\ (0)) = 3\mu/(4kT\ N\ (0))$. For k > 1 the distribution has a maximum in time as shown in the figure from Smoluchowski (in Friedlander's book) below. For higher k the peak occurs at longer times. Since particles are growing, the total number decays with time.

This model is appropriate for small t/ , where the particle size distribution is close to monodisperse. This might be applicable to a batch system, or a plug flow reactor.

At long times the curves shown for particle size as a function of time begin to show a similar shape, although shifted in time and k. This is the source of a *self-preserving* shape to the size distribution. That is, the size distribution, when scaled with dimensionless numbers, retains the same shape, so is called *self-preserving*. For the result of the Smoluchowski equation for constant collision frequency the self-preserving distribution has the form,
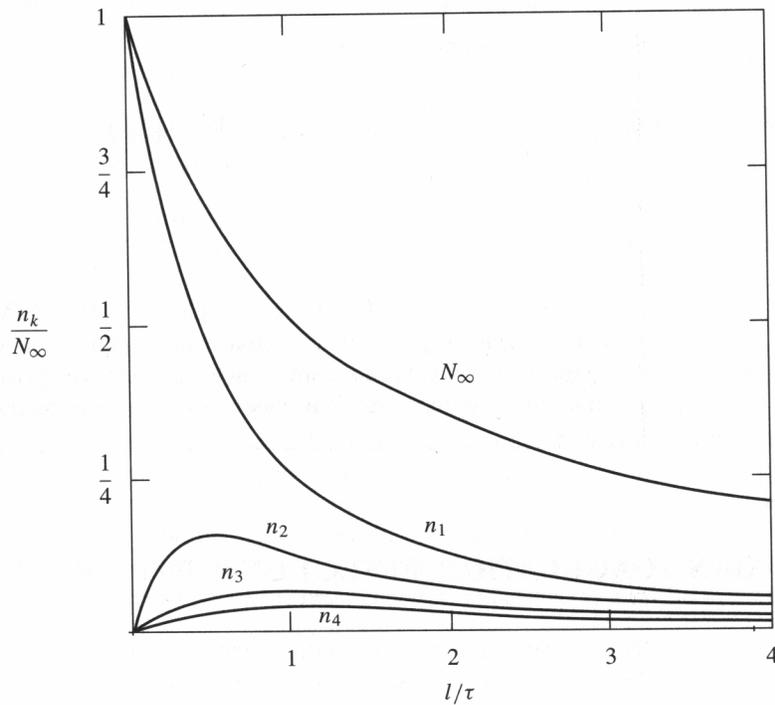
$N_k \sim e^-$

where $\ = k/<k>$ and ,k.$=N\ (0)/N\ (t)$. We can rearrange the size distribution as,

$$\frac{n_k N\ (0)}{N^2} = \frac{(t/\ )^{k-1}}{\left(1+t/\ \right)^{k-1}}$$

$$\frac{n_k N\ (0)}{N^2} = \frac{(t/\ )^{k-1}}{\left(1+t/\ \right)^{k-1}} = \left(1+\frac{\ }{t}\right)^{1-k} = \left(1+\frac{\ }{t}\right)^{t/\ \ (1-k)\ /t}$$

For large t/ ,

Figure 7.2 The variations in N_∞, n_1, n_2, ... with time for an initially monodisperse aerosol. The total number concentration, N_∞, and the concentration of n_1 both decrease monotonically with increasing time. The concentrations of n_2 ... pass through a maximum. (After Smoluchowski, 1917)

Friedlander SK, Smoke Dust and Haze, 2000

$$1 + \frac{-}{t}^{t/} \qquad e$$

and

$$\frac{n_k N(0)}{N^2} = e^{-}$$

since $= \langle k \rangle - 1$, $= (k-1)/(\langle k \rangle - 1)$. Then the asymptotic limit of the size distribution is self-preserving.

Similarity Solutions for Particle Size Distributions due to Coagulation (Self Preserving):

If it is assumed that the fraction of particles in a given size range is a function of the particle volume normalized by the average particle volume then,

$$\frac{n(v,t)N(0)dv}{N} = \frac{v}{\langle v \rangle} d \frac{v}{\langle v \rangle}$$

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where $\langle v\rangle = \ /N$, and is a function describing the particle size distribution which is not time dependent. Since n is the particle number per unit volume both sides of this equation are dimensionless. Since $d(v/\langle v\rangle) = dv/\langle v\rangle = (N\ /\ )dv$,

$$n(v,t) = \frac{N^2}{}\ (\ )$$

where $= v/\langle v\rangle = N\ v/\ ,$ $N = \int_0 n\,dv,$ $= \int_0 nv\,dv,$ $n(v)\ \ 0$ when $v\ \ 0$ or .   An expression for $n_p(d_p, t)$ can also be obtained,

$$n_d(d_p,t) = \frac{N^{4/3}}{^{1/3}}\ _d(\ _d)$$

where $_d = d_p(N\ /\ )^{1/3}$.

For Brownian coagulation we have,

$$_{ij}(v_i, v_j) = \frac{2kT}{3\mu}\ \frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}}\ (v_i^{1/3} + v_i^{1/3})$$

<div align="right">Continuum Range</div>

For a continuous distribution function the coagulation equation is,

$$\frac{\partial n}{\partial t} = \frac{1}{2}\int_0^v (\langle v\rangle,(v - \langle v\rangle)))n(\langle v\rangle)n(v - \langle v\rangle)d\langle v\rangle - \int_0 (v,\langle v\rangle)n(v)n(\langle v\rangle)d\langle v\rangle$$

<div align="center">Continuous Distribution</div>

which becomes,

$$\frac{1}{N^2}\frac{dN}{dt}\ \ 2\ +\ \frac{d}{d}\ = \frac{kT}{3\mu}\int_0 (\langle\rangle)\ (\ -\langle\rangle)[\langle\ \rangle^{1/3} + (\ -\langle\rangle)^{1/3}]\frac{1}{\langle\ \rangle^{1/3}} + \frac{1}{(\ -\langle\rangle)^{1/3}}d\langle\ \rangle$$

$$-\frac{2kT}{3\mu}\ (\ )\int_0 (\langle\ \rangle)[\ ^{1/3} + \langle\ \rangle^{1/3}]\frac{1}{^{1/3}} + \frac{1}{\langle\ \rangle^{1/3}}d\langle\ \rangle$$

when the similarity form is substituted (4'th equation above).

For a continuous distribution the change in total number concentration with time is,

$$\frac{dN}{dt} = -\frac{1}{2}\int_0\int_0 (v,\langle v\rangle)n(v)n(\langle v\rangle)dv\,d\langle v\rangle$$
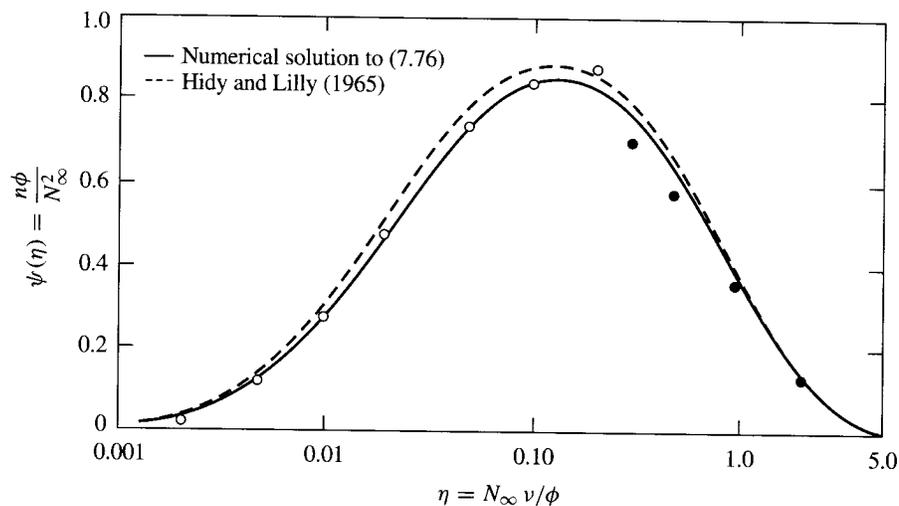
<div align="center">Continuous Distribution</div>

By substitution of the similarity distribution for n(v,t) and the continuum definition of , we obtain,

$$\frac{dN}{dt} = -\frac{2kT}{3\mu}(1+ab)N^2 \quad \text{where } a = {}^{1/3}d_0 \text{ and } b = {}^{-1/3}d_0 \qquad \text{Continuum Regime}$$

This has the same functionality as Brownian coagulation from a monodisperse system,
$$\frac{dN}{dt} = -\frac{K}{2}N^2$$
. This expression can be used in the continuous distribution function above (long function) and an ordinary intergrodifferential equation for in terms of results. This means that the similarity solution for Brownian coagulation is a possible particular solution. The solution can be found using the integral definitions of N and given above. The function is solved for the upper and lower ends of the distribution and then the complete distribution can be obtained numerically using these limits. The numerical solution is shown below (from Friedlander's book)

Similarity Solution for Brownian Coagulation **213**

Figure 7.8 Self-preserving particle size distribution for Brownian coagulation. The form is approximately lognormal. The result obtained by solution of the ordinary integrodifferential equation for the continuous spectrum is compared with the limiting solution of Hidy and Lilly (1965) for the discrete spectrum, calculated from the discrete form of the coagulation equation. Shown also are points calculated from analytical solutions for the lower and upper ends of the distribution (Friedlander and Wang, 1966).

Shown below is a comparison of experimental measurements on coagulation in tobacco smoke with the predictions of the figure above.
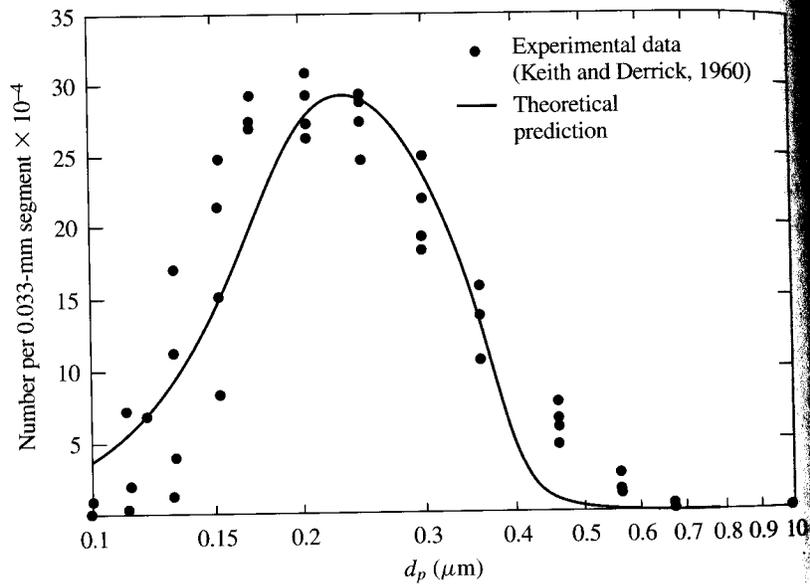
Figure 7.9 Comparison of experimental size distribution data for tobacco smoke with pr[...] based on self-preserving size spectrum theory. $\phi = 1.11 \times 10^{-7}$, $N_\infty = 1.59 \times 10^7$ cm^{-3}. T[...] in the number distribution measured in this way occurs at $d_p \approx 0.2$ μm (Friedlander and Hid[...]

Similarity Solution in the Free Molecular Regime:

Generally, when the collision frequency function, β(v, <v>), is a homogeneous function of v, it can be transformed to an ordinary integrodifferential equation. If an ordinary integrodifferential equation can be made it must also satisfy the integral boundary conditions and constraints. For the free molecular range we have,

$$\beta_{ij}\left(v_i, v_j\right) = \frac{3}{4}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{1}{v_i} + \frac{1}{v_j}\right)^{1/2}\left(v_i^{1/3} + v_i^{1/3}\right)^2 \qquad \text{Free Molecular Range}$$
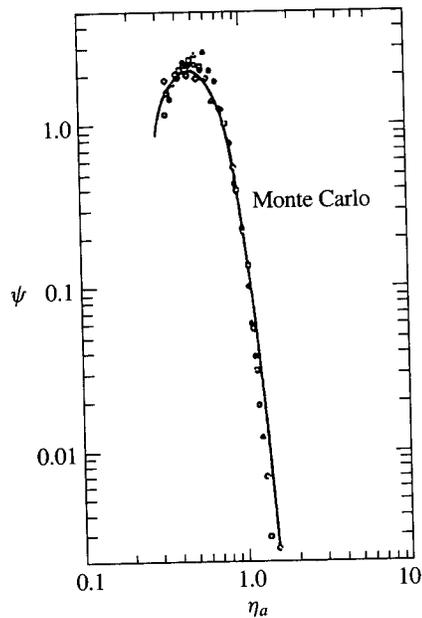
This is a homogeneous function of order 1/6 in particle volume. The similarity transformation can be made and a numerical solution can be found. The rate of change of the total number of particles is given by,

$$\frac{dN}{dt} = -\frac{a}{2}\left(\frac{3}{4}\right)^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2} V^{1/6}N^{11/6}$$

where a is an integral function of τ with a value of about 6.67. An example of numerical simulation (Monte Carlo) versus experimental observation for particle size distribution is shown below from Friedlander's text.

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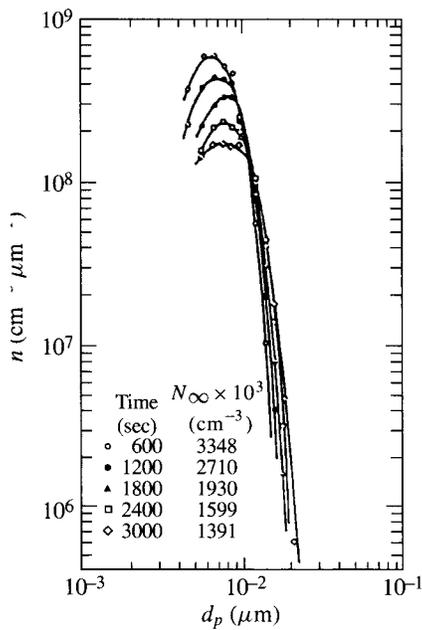
Figure 7.11 Coagulation of aerosol particles much smaller than the mean free path. Size distribution measured with the electrical mobility analyzer (Husar 1971).

The plot legend:

Time (sec)	$N_\infty \times 10^3$ (cm^{-3})
○ 600	3348
● 1200	2710
▲ 1800	1930
□ 2400	1599
◇ 3000	1391

Axes: n (cm^{-3} μm^{-1}) versus d_p (μm)

Figure 7.12 Size distribution data of Fig. 7.11 for coagulation of small particles plotted in the coordinates of the similarity theory. Shown also is the result of a Monte Carlo calculation for the discrete spectrum (Husar, 1971).

Monte Carlo

Axes: ψ versus η_a

The self-preserving distribution can be approximated by a log-normal distribution function with $\sigma_g = 1.44$ for the continuum regime and $\sigma_g = 1.46$ for the free molecular regime. If the initial distribution of particles is also a log-normal distribution, the time to reach the self-preserving distribution (SPD), t_{sp}, is a function of the initial distribution, σ_{g0},

$$t_{sp} = {}_{f}\left[\left(\frac{3}{4}\right)^{1/6}\left(\frac{6kT}{p}\right)^{1/2}v_0^{1/6}N(0)\right]^{-1}$$

Free Molecular

which is due to Vemury, S and Pratsinis, SE (1995)J. Aerosol Sci. **21**, 175. For 1 nm particles at 1800 K the SPD is reached in on the order of 1 microsecond. The figure below from Vemury (Friedlander) shows this behavior. The dip corresponds to the SPD geometric standard deviation.
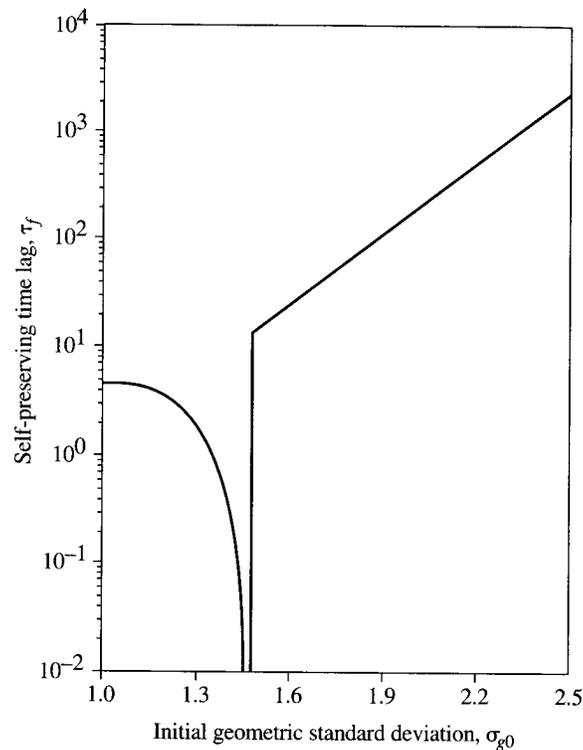
Figure 7.13 Dimensionless time to reach the SPD for initially lognormal size distribution function of σ_{g0}. (After Vemury et al., 1994.) The sharp minimum corresponds to the value of an initially self-preserving free molecule aerosol.

For initially monodisperse distributions the time to reach SPD was also calculated by Vemury/Pratsinis,

$$t_{sp} = 5\left[\left(\frac{3}{4}\right)^{1/6}\left(\frac{6kT}{p}\right)^{1/2}v_0^{1/6}N(0)\right]^{-1}$$

Free Molecular Range

$$t_{sp} = 13\left[\frac{2kTN(0)}{3\mu}\right]^{-1}$$

Continuum Range