Chapter 5. Coagulation of nanoparticle aerosols released continuously into a well stirred chamber

5.1. Introduction

The presence of sources of anthropogenic nanoparticles, particularly in the indoor atmosphere of workplaces and schools, is of considerable concern with regard to their impact on human health. One characteristic feature of nanoaerosols is their dynamic evolution with respect to concentration and size distribution during the time of transport from the source to the receptor due to various mechanisms. In a recent study, Schneider et al. (2011) discuss the importance of such modifying factors for the metrics used to estimate the potential hazard of ENPs and, indeed, efforts are increasing to understand how such aerosols evolve in the indoor environment (Seipenbusch et al, 2008, Schneider & Jensen, 2009, Schneider et al, 2011).

The factors responsible for changes in the number concentration and size distribution of an aerosol include homogeneous and heterogeneous coagulation, as well as particle removal due for example to ventilation or wall losses. These mechanisms are linked to the characteristics of a nanoparticle source, interaction with preexisting particles, as well as the transport, mixing and dilution conditions specific to a given environment. Although well understood in principle, it is not at all a trivial task to develop meaningful models and to estimate changes, even the order of magnitude of changes, in aerosol size distribution for a given situation; and it is even more difficult to distill general conclusions which will be relevant for a broader type of situation. For this reason, one often resorts to scenarios.

One such scenario of particular relevance to engineered nanoparticles involves their continuous emission into a confined space or a chamber, from a volume source. Several
analytical and numerical studies have been carried out for a variety of aerosol systems with continuous source injection (Barrett & Mills, 2002; Schneider & Jensen, 2009; Landgrebe & Pratsinis, 1989; Kim et al. 2003). The details of these studies are discussed in the Literature survey section of Chapter 1. While these studies provide general insight into the phenomena to expect, and of course demonstrate that simulation techniques are well established, they do not offer insights into long time system behaviour and interplay of various mechanisms. Also, they fall short of providing general conclusions relevant for workspaces, i.e. large enclosed volumes of air with constant aerosol sources. It is still of considerable interest to explore the relative influence of various factors driving such systems, and to obtain a better understanding, e.g. of when multimodal aerosol distributions evolve, the relative importance of the modes, etc.

In this context, there exist interesting experimental observations of aerosol evolution for a scenario in which nanoaerosol is continuously injected at different rates into a large, well mixed volume of air, with and without the presence of a background aerosol (Seipenbusch et al, 2008). One such observation is the occurrence of a transient peak in the total number concentration during filling of the chamber, as well as indications of an asymptotic stabilization of the total chamber concentration due to the interplay between freshly injected aerosol and the removal of particles by coagulation or ventilation. It is of considerable practical interest to know under what conditions the concentration would eventually stabilize in the chamber, and how this would depend on source strength and removal rate parameters. Similarly, the conditions for the aerosol to develop a distinct secondary large-particle mode need to be explored because this has a direct impact on the coagulation processes taking place.

Some of the features observed in these experiments are not easily explained or reproduced by straightforward models using constant coagulation kernels, because the dynamics
of such systems must exhibit pronounced size dependent features. It is therefore necessary to extend the simulation to realistic coagulation kernels and also examine other effects such as changes in collision radius of particles due to the formation of large fractal aggregates. Given these motivations, the application of a discrete numerical simulation covering the entire particle size regime to investigate solutions to the general dynamic equation with a constant source term and a constant removal term by ventilation is described. Coagulation is treated on the basis of the practically relevant Fuchs kernel and allowing for the growth of fractal particles. A two-group analytical model is developed to assess the asymptotic behaviour of the nanoparticles injected into a closed chamber. Laboratory experiments are carried out to validate these models.

5.2. Formulation of the problem

Let us consider a scenario adapted to the experiments described by Seipenbusch et al. (2008) in which nanoparticles are released continuously into a large volume. The aerosol system evolves by continuous injection of particles at a constant rate, by coagulation, and by removal / dilution with clean air at a constant rate. It must be pointed out that spatial inhomogeneity (Kasper, 1984) is more of a rule than an exception when particles are released from localized sources, and the complexity of addressing these problems has been discussed in previous chapters. Particularly, the effect of spatial inhomogeneity on the size distribution is discussed in the section 4.5 of the chapter 4. However, if the aerosol is mixed rapidly through mixing elements such as fans or induced ventilation, one may, to a first approximation, treat the aerosol concentration as spatially homogeneous at all times. Then the rate of change of aerosol concentration in the chamber is given by

$$\frac{\partial n(u,t)}{\partial t} = S(u,t) + \frac{1}{2} \int K(u',u-u') n(u',t) n(u-u',t) du'-n(u,t) \int_{0}^{\infty} K(u',u) n(u',t) du'$$

$$- \{\lambda_c + \lambda_d(u)\} n(u,t)$$  \hspace{1cm} (5.1)
where $K(u, u')$ is the coagulation kernel (m$^3$s$^{-1}$) between particles of volumes $u$ and $u'$, $n(u, t)$ is the number concentration (m$^{-3}$), $\lambda_v$ is the ventilation rate (s$^{-1}$), $\lambda_d(u)$ is the removal rate due to wall/surface deposition processes, $S(u,t) = (\dot{V}_s/V)Q$ is the particle number injection rate of the source (m$^3$s$^{-1}$), $\dot{V}_s$ is the source volume flow rate to the chamber (m$^3$s$^{-1}$), $V$ is the volume of the chamber (m$^3$), and $Q$ is the number concentration at the source (m$^{-3}$). The initial number concentration in the chamber is assumed to be zero ($n(u, 0) = 0$). The first term in the RHS of Eq.(5.1) represent continuous source injection, the second and third terms represent coagulation, and the fourth for ventilation and size dependent removal processes.

Supposing, for the sake of simplicity, one makes an assumption that the coagulation coefficient may essentially be approximated by an effective constant, i.e. $K(u, v) = K$. Further we assume that the removal rate due to deposition is negligible as compared to ventilation. Then, one obtains the following nonlinear equation from Eq.(5.1) for a constant source term:

$$\frac{dN(t)}{dt} = S - \frac{K}{2} N^2(t) - \lambda N$$

where, the total number concentration is defined as, $N(t) = \int_0^\infty n(u,t) du$. For the initial condition $N(0) = 0$, the solution to this equation may be easily obtained by quadrature as follows:

$$N(t) = -\frac{\lambda}{K} + \left(\frac{2A}{K}\right)^{1/2} \left[ \frac{\exp(\sqrt{2AK} t)}{\sqrt{4AK + 2\lambda^2}} - \frac{\exp(-\sqrt{2AK} t)}{\sqrt{4AK - 2\lambda^2}} \right]$$

where, $A = S + \frac{\lambda^2}{2K}$.

At large times, the above expression tends to a steady-state given by,

$$N(\infty) = -\frac{\lambda}{K} + \frac{\lambda^2}{K^2} + 2S^{1/2}$$
In the absence of removal processes, the solution of the Eq. (5.2) is given by,

$$N(t) = \left( \frac{2S}{K} \right)^{1/2} \frac{\exp(\sqrt{2SK} t) - 1}{\exp(\sqrt{2SK} t) + 1}$$

(5.5)

This leads to a steady-state concentration, $N(\infty) = \left( \frac{2S}{K} \right)^{1/2}$. This is an interesting result that deserves attention. In the absence of ventilation removal, one expects the mass concentration to diverge to infinity after sufficiently long time because of the continuous injection of particles. However, the presence of the coagulation manages to limit the number concentration to a finite value for constant kernel. This raises a question as to whether a finite number concentration will be sustained for size dependent kernels?. The assumption of a constant kernel is reasonable for homogeneous problems involving one time injection of monodisperse particles. In contrast, under continuous injection, the number concentration will be dictated by the fact that the injected nanoparticles will be scavenged by the coagulated large particles and the rate of this scavenging increases with particle size. Constant kernel is a too simplistic an assumption to handle this effect and to address the question raised above, it is necessary to go for the next level of approximation, achieved by formulating the two-group model.

5.3. Two-group model

In order to provide quantitative insights into the temporal behaviour of the total number concentration, the approach of Jeong and Choi (2003) is followed and a simplified two-group model of the coagulation problem under continuous injection is proposed. Let us assume that essentially the behaviour can be described by the interactions between the particles of two different size groups; the first one corresponds to the mean particle volume of the injected nanoparticles ($v_1$), and the second group to the mean particle volume of the part of the size
spectrum of the already coagulated particles \( (v_2(t)) \) (i.e. excluding the first group). The entire spectrum of the second group is represented by a single effective size determined by mass conservation. This approach is somewhat similar to the two-group model proposed by Jeong and Choi (2003) for the case of coagulation of coalescing particles. Unlike their formulation, we do not consider coalescence. The two-group model results in a purely differential formulation of the coagulation equation which can be easily subjected to mathematical analysis, also at long times. Let \( N_1(t) \) be the number concentration of the particles of the first group having constant size \( v_1 \), and \( N_2(t) \) be the number concentration of the particles of second size group of volume \( v_2(t) \) at any given time \( t \). Then, the total number concentration \( (N(t)) \) is given by,

\[
N(t) = N_1(t) + N_2(t)
\]

(5.6)

The evolution of \( N_1(t) \) and \( N_2(t) \) proceeds via the coagulation processes described by three kernel types, i) the coagulation coefficient \( K_{11}(v_1,v_1) \) among particles of first size group, ii) the coefficient \( K_{12}\{v_2(t),v_1\} \) for the coagulation between first group size particles of volume \( v_1 \) and second size group particles of volume \( v_2(t) \), and iii) the coagulation coefficient \( K_{22}\{v_2(t),v_2(t)\} \) between the second size group particles themselves. The effect of externally maintained ventilation is included by introducing a size independent removal term. With this, one can write down the following equations for the process of evolution of \( N_1(t) \) and \( N_2(t) \):

\[
\frac{dN_1(t)}{dt} = S_1 - K_{11}N_1^2(t) - K_{12}\{v_2(t),v_1\}N_1(t)N_2(t) - \lambda N_1(t)
\]

(5.7)

\[
\frac{dN_2(t)}{dt} = \frac{1}{2}K_{11}N_1^2(t) - \frac{1}{2}K_{22}\{v_2(t),v_2(t)\}N_2^2(t) - \lambda N_2(t)
\]

(5.8)

The evolution equation for the total number concentration (Eq.(5.2)) is now split into two separate evolution equations (Eq.(5.7) & Eq.(5.8)). In Eq.(5.7), the first term on the RHS is the number of particles injected into the study volume per unit time per unit volume, the second term
represents the loss of particles from the first group due to homogeneous coagulation. The loss term will not involve the usual factor 1/2 because of the following reason. There will be 
\[ \frac{1}{2} K_{11} N_1^2(t) \]
coagulation events between the primary particles themselves per unit time and since two particles are lost in each event and the coagulated particle is lost from this group to the higher group, the loss rate in the first group will be 
\[ 2 \times \left( \frac{1}{2} K_{11} N_1^2(t) \right) = K_{11} N_1^2(t) \]. The third term on the RHS represents loss of first-size-group particles due to the interaction with the second-size-group particles. Similarly, in the second equation (Eq.(5.8)), the first term (gain term) in the RHS represents the contribution due to homogeneous coagulation of first size group particles, and the second term in the RHS represents the loss of the second size group particles due to their homogeneous coagulation. Heterogeneous coagulation between the first and second size group particles does not contribute to the change in the concentration of second-size-group particles. These two equations need to be supplemented with the mass conservation law which will provide equation for \( v_2(t) \) as follows:

Let \( \phi(t) \) be the total volume concentration (of both size groups) in the air space (i.e., mass concentration divided by particle density). Since coagulation is a volume (mass) conserving process, \( \phi(t) \) increases linearly with time because of steady and continuous injection satisfying the following equation.

\[
\frac{d\phi(t)}{dt} = v_1 S_1 - \lambda \phi(t)
\]

(5.9)

However, \( \phi(t) \) is related to \( v_2(t) \) and \( v_1 \) through the following closure equation,

\[
\phi(t) = N_1(t)v_1 + N_2(t)v_2(t)
\]

(5.10)

From Eqs. (5.9) and (5.10), one can obtain the following relation for the volume of the second size group,
\[ v_2(t) = \frac{\phi(t) - N_1(t)v_1}{N_2(t)} \] (5.11)

The initial conditions for this model are,

\[ N_1(0) = 0; N_2(0) = 0; v_2(0) = 0; \phi(0) = 0 \] (5.12)

Although the above set of equations is nonlinear and complex, it is attractive because it can be easily solved for any type of kernel using differential equation solver packages such as Mathematica. More importantly these equations are amenable to asymptotic analysis in order to elicit the long time behaviour of the solutions analytically.

5.3.1. Additive coagulation kernel

In order to illustrate the usefulness of the two-group model, we first apply it for a size dependent, yet relatively simple, coagulation kernel such as the \((u+v)\) kernel, which is analytically solvable. The additive coagulation kernel \((u + v)\) kernel arises in the study of cloud droplet coalescence (Bertoin, 2002; Scott, 1968; Berry, 1967; Hidy & Brock,), gravitational clustering in the universe (Sheth & Pitman, 1997), and phase transition for parking (Chassaing & Lochard, 2001). This kernel has the following form,

\[ K(u, v) = \alpha(u + v) \] (5.13)

where, \(\alpha\) is a constant.

By substituting the Eq.(5.13) in Eqs.(5.7) & (5.8), one can obtain,

\[ \frac{dN_1(t)}{dt} = S_1 - 2\alpha v_1 N_1^2(t) - \alpha [v_1(t) + v_2(t)]N_1(t)N_2(t) - \lambda N_1(t) \] (5.14)

\[ \frac{dN_2(t)}{dt} = \alpha v_1 N_1^2(t) - \alpha v_2(t)N_2^2(t) - \lambda N_2(t) \] (5.15)

The evolution equation for total number concentration can be obtained from Eqs.(5.14) & (5.15) by using the relations, \(N(t) = N_1(t) + N_2(t)\), and \(N_2(t)v_2(t) = \phi(t) - N_1(t)v_1\), and is given by,
\[
\frac{dN(t)}{dt} = S_i - \alpha \phi(t)N(t) - \lambda N(t) \quad (5.16)
\]

Let us non-dimensionalise the above equation by introducing the following dimensionless variables,

\[
t' = t / t_c, \quad \text{where}, \quad t_c = (S_i K_{i1})^{1/2}
\]

\[
N^*(t') = N(t) / N_c, \quad \text{where}, \quad N_c = (S_i / K_{i1})^{1/2}
\]

\[
\lambda^* = \lambda / t_c
\]

\[
\phi^*(t') = \alpha \phi(t) / t_c
\]

where, \( K_{i1} = K(v_1,v_1) = 2\alpha v_1 \), from Eq.(5.13). By substituting the parameters defined in Eq.(5.17) in Eqs.(5.16) & (5.9), the following set of equations can be obtained:

\[
\frac{dN^*(t')}{dt'} = 1 - \phi^*(t') N^*(t') - \lambda^* N^*(t') \quad (5.18)
\]

\[
\frac{d\phi^*(t')}{dt'} = \frac{1}{2} - \lambda^* \phi^*(t') \quad (5.19)
\]

Eq.(5.18) and (5.19) together form the complete set of equations for the total number concentration. It may be easily verified that one arrives at the same set of equations starting from the unapproximated coagulation equation (Appendix - D), for the kernel under consideration. In view of this and the fact that the equations are simple to solve, the predictions from this case provide valuable guiding results on the general behaviour for more complex, size dependent kernels. Let us examine the behaviour of this system when \( \lambda^* = 0 \). In this case, the Eq.(5.18) becomes,

\[
\frac{dN^*(t')}{dt'} = 1 - \frac{1}{2} N(t') t'
\]

where, \( \phi^* \) is replaced by \( t' / 2 \). The solution of the Eq.(5.20) is obtained by quadrature and given as,
\[ N^*(t^*) = \int_0^{t^*} \exp \left[ -\frac{1}{4} (t'^2 - t^2) \right] dt' \]  
(5.21)

Let \((t^*-t') = x\), then the Eq.(5.21) can be written as,

\[ N^*(t^*) = \int_0^{t^*} \exp \left[ -\frac{1}{4} x(2t^* - x) \right] dx \]  
(5.22)

Since major part of the contribution to the integral will arise from points near \(x \sim 0\), we may assume \(x \ll t^*\) in the integrand above in which case Eq.(5.22) is reduced to,

\[ N^*(t^*) \approx \int_0^{t^*} \exp \left[ -\frac{t^* x}{2} \right] dx = \frac{2}{t^*} \left[ 1 - \exp \left( -\frac{t^*}{2} \right) \right] \]  
(5.23)

From Eq.(5.23), the asymptotic number concentration (as \(t^* \to \infty\)) is,

\[ N^*(t^*) \approx \frac{2}{t^*} \]  
(for \(\lambda^* = 0\))  
(5.24)

Eq.(5.24) shows an important result that the total number concentration decays as \(t^*^{-1}\) in the absence of removal processes.

For nonzero \(\lambda^*\), the analytical solution is not very convenient as it involves higher mathematical functions. In view of this, Eqs.(5.18) & (5.19) are solved together using the numerical solver of Mathematica. For various removal rates, the temporal variation of total number concentration is plotted in Fig. 5.1. One notes that for \(\lambda^* = 0\), the concentration falls monotonically with time. A fit to the graph for large times shows that \(N^* \sim 1/t^*\), which is in agreement with analytical theory (Eq.(5.24)). When a slight ventilation removal is present, the concentration tends to approach a nonzero steady state. The value of this steady state increases with ventilation for \(\lambda^* = 0.01, 0.1, 0.6\) and decreases for higher ventilations (e.g. \(\lambda^* = 2.0, 10.0\)). This is an interesting result that predicts a critical ventilation parameter for which the steady-state particle concentration will be maximum.
In order to understand this somewhat intriguing result, we solve the equation analytically for the special case of steady-state (i.e., $d/dt^* = 0$). The following steady-state solutions may easily be obtained from Eq.(5.18, 5.19):

$$N^* = \frac{2\lambda^*}{1 + 2\lambda^*} \quad \text{(Steady-state number concentration)} \quad (5.25)$$

$$\phi^* = \left(\frac{1}{2\lambda^*}\right) \quad \text{(Steady-state volume/mass concentration)} \quad (5.26)$$

This example clearly demonstrates in a simple way that the steady-state concentration is achievable only in the presence of removal processes as shown in the Eq.(5.25). From Eq.(5.25), it can be shown that steady-state concentration attains a peak value for a removal rate $\lambda^* = \left(\frac{1}{\sqrt{2}}\right) = 0.707$. This removal rate is called as critical ventilation rate. Beyond the critical
ventilation rate, the concentration decreases as expected (Fig.5.2). Considering the practical
importance of this result in ventilation design for removal of high particle concentration in
workplace environments, it is pertinent to explore the consequence for other kernels. More
detailed discussion on this topic is presented in Section 5.5.1.4 (for the case of Fuchs coagulation
kernel).

![Graph](image)

**Fig. 5.2:** Steady-state number concentration vs. removal rate in the case of \((u + v)\) type kernel

### 5.3.2. Fuchs coagulation kernel

Fuchs coagulation kernel is very often used in the study of Brownian coagulation process,
and it is applicable for the entire particle regime (from free-molecular regime to continuum
regime). Since the Fuchs kernel has a form of complex function unlike the additive kernel
mentioned above, the analysis is carried out by numerical methods to obtain complete solution of
Eqs.(5.7) & (5.8). However, the asymptotic behaviour of this system is obtained analytically as follows:

Since the particle sizes of the first group (primary) do not change with time, the homogeneous coagulation coefficient will be a constant quantity, say $K_{11} = \sqrt{\frac{16\pi k T r_0^4}{\rho v_0^2}} 2^{d_f} v_1^{1/2}$, given by the free-molecular limit of the Fuchs kernel. Here, $d_f$ is the fractal dimension, $k$ is the Boltzmann constant, $T$ is the temperature, $\mu$ is the air viscosity, $r_0$ is the radius of the individual spherule of volume $v_0$, and $\rho$ is its density. In the asymptotic limit of long times, the characteristic volume $v_2(t)$ of the second group particles will be large and hence the Fuchs kernel corresponding to their mutual coagulation will approach the continuum Smoluchowski kernel $(K_{22}\{v_2(t), v_2(t)\} = \frac{8kT}{3\mu})$ which will be again a constant regardless of time. On the other hand, the heterogeneous coagulation coefficient $(K_{12})$ between first group and second group particles will be time dependent according to the formula,

$$K_{12} \{v_2(t), v_1\} = \frac{2kT}{3\mu} \left[v_2^{1/d_f} (t) + v_1^{1/d_f} \left[\frac{1}{v_2^{1/d_f} (t)} + \frac{1}{v_1^{1/d_f}} \right] \right] \approx \text{const} \left(\frac{v_2(t)}{v_1}\right)^{1/d_f} \quad (5.27)$$

To render the equation more transparent for mathematical analysis, it is advantageous to introduce non-dimensional variables (some of them as in the text) as follows:
\[ t^* = \frac{t}{t_c}, \quad \text{where, } t_c = \left( \frac{S_i K_{ii}}{K_{ii}} \right)^{1/2} \]
\[ \left\{ N^*_1(t^*), N^*_2(t^*) \right\} = \left\{ N_1(t), N_2(t) \right\}/N_c, \quad \text{where, } N_c = \left( \frac{S_i}{K_{ii}} \right)^{1/2} \]
\[ u(t^*) = \frac{v_2(t^*)}{v_1} \]
\[ k_1 = \frac{1}{u} \frac{K_{12}}{K_{11}} \]
\[ k_2 = \frac{K_{22}}{K_{11}} \]
\[ n = d_v^3 \]

(5.28)

With these notations and by using the appropriate asymptotic limits of the Fuchs kernel, Eqs. (5.7-5.11) may be written in the following simpler form:

\[ \frac{dN^*_1(t^*)}{dt^*} = 1 - \left[ N^*_1(t^*) \right]^2 - k_1 \left[ u(t^*) \right]^2 \left[ N^*_1(t^*) \right] N^*_2(t^*) \]

(5.29)

\[ \frac{dN^*_2(t^*)}{dt^*} = \frac{1}{2} \left[ N^*_1(t^*) \right]^2 - \frac{1}{2} k_2 \left[ N^*_2(t^*) \right]^2 \]

(5.30)

\[ u(t^*) = \frac{t^* - N^*_1(t^*)}{N^*_2(t^*)} \]

(5.31)

Let us now hypothesize that, after sufficiently long time, the concentrations \( N^*_1(t^*) \) and \( N^*_2(t^*) \) vary according to the following power laws:

\[ N^*_1(t^*) = a t^{\alpha}, \quad (\alpha < 1) \]

(5.32)

\[ N^*_2(t^*) = b t^{\beta} \]

(5.33)

as \( t^* \rightarrow \infty \)

where, \( a, b \) are positive quantities. We do not impose any restriction on \( \alpha, \beta \) (they are positive or negative depending on whether \( N^*_1(t^*), N^*_2(t^*) \) are increasing or decreasing) except that \( N^*_1(t^*) \) cannot increase faster than linearly (i.e. \( \alpha < 1 \)) so that \( u(t^*) \) in Eq. (5.31) (the size of the
secondary group) always remains a positive quantity. This implies, from Eq. (5.31), that asymptotically,

\[ u(t^*) \sim b^{-1} t^{s^{\beta}} \quad \text{as} \quad t^* \to \infty \tag{5.34} \]

Upon using Eqs. (5.31)-(5.33), Eqs. (5.29) and (5.30) transform to the following equations:

\[ a\alpha t^{s^{\alpha-1}} \sim 1 - a^2 t^{2\alpha} - a b^{1-n} k_{1} t^{s^{\alpha+n-\alpha n}} \quad , \quad (\alpha < 1) \tag{5.35} \]

\[ b\beta t^{s^{\beta-1}} \sim \frac{1}{2} a^2 t^{2\alpha} - \frac{1}{2} k_{2} b^{2} t^{2\beta} \tag{5.36} \]

Let us first argue that \( \alpha \) cannot be greater than \( \beta \). Supposing the opposite were true, (i.e. \( \alpha > \beta \)), then the first term on the RHS of Eq. (5.36) will dominate over the second term at large times. In that case,

\[ b\beta t^{s^{\beta-1}} \sim \frac{1}{2} a^2 t^{2\alpha} \tag{5.37} \]

and upon matching the exponents one obtains,

\[ 2\alpha = \beta - 1. \tag{5.38} \]

Similarly, matching the pre-factors of both sides of Eq. (5.37), one obtains

\[ \frac{a^2}{2b} = \beta \tag{5.39} \]

But the condition \( \alpha > \beta \) implies that \( 2\alpha > 2\beta \) which together with the condition obtained in Eq. (5.38) yields the constraint

\[ \beta < -1. \tag{5.40} \]

But \( \beta \) cannot be negative since it violates the constraint (Eq. (5.39)) on the pre-factor requirement which should be positive. Hence, \( \alpha \) cannot be greater than \( \beta \). One can also arrive at the same conclusion by plugging Eqs. (5.38) and (5.39) in Eq. (5.35) and examining the condition under
which exponent of the leading term (third term on RHS of Eq.(5.35)) matches with the exponent (0) of the source term.

Now, let us similarly argue that \( \alpha \) cannot be less than \( \beta \). If the converse is true (i.e. \( \alpha < \beta \)), the second term on the RHS in Eq.(5.36) will dominate over the first term, and hence,

\[
b \beta t^\beta - 1 \sim -\frac{1}{2} k_2 b^2 t^{2\beta}
\]

(5.41)

The exponent and pre-factor matching implies that

\[
\beta = -1
\]

\[
b = \frac{2\beta}{k_2} = \frac{2}{k_2}
\]

(5.42)

and the sign of the pre-factor (\( b \)) is positive which is acceptable. However, the above result \( \beta = -1 \) is not consistent with Eq.(5.35). The first term (i.e. unity = \((t^*)^0\)) on the RHS of Eq.(5.35) can only be matched by the third term providing

\[
\alpha + \beta + n - n\beta = 0
\]

(5.43)

With the result \( \beta = -1 \), one can obtain (from Eq.(5.43)) the relation \( \alpha = 1 - 2n \) which implies that \( \alpha > -1 \) (since \( n = (t/d_f) < 1 \)). This violates the starting premise that \( \alpha < \beta \), i.e. \( \alpha < -1 \).

Hence by contradiction, \( \alpha \) cannot be less than \( \beta \).

In view of the above, the only possibility is that \( \alpha = \beta \). In order to determine this value, match the source term in Eq.(5.35) with the remaining terms which lead to Eq.(5.43). With \( \alpha = \beta \), this immediately yields the result

\[
\alpha = \beta = -\frac{n}{2 - n} = -\frac{1}{2d_f - 1}
\]

(5.44)

The corresponding pre-factor from Eq.(5.35), yields

\[
ab^{1-n}k_1 = 1
\]

(5.45)
and from Eq.(5.36),
\[ a^2 = b^2 k \]  
(5.46)

Eq.(5.44) determines uniquely the power of the leading terms in the asymptotic behaviour of \( N_1(t^*) \), \( N_2(t^*) \). The total number concentration may be given by,
\[ N^*(t^*) = N_1^*(t^*) + N_2^*(t^*) \sim (a + b) t^{-b/(2d_f - 1)} \]  
(5.47)

This completely determines the law of asymptotic behaviour of the number concentration of particles for the problem of coagulation with continuous injection in the absence of removal.

From Eq.(5.44), for the case of a fractal dimension \( d_f = 1.75 \), the value of the exponent \( \alpha = \beta \) works out to be -0.4 and hence the total number concentration is expected to decay as
\[ N^*(t^*) \sim \text{const.} t^{-0.4}, \text{ for } d_f = 1.75 \]  
(5.48)

Hence for the Fuchs kernel too, the number concentration will approach zero in the absence of removal, albeit more slowly (exponent of -0.4 instead of unity) as compared with \((u+v)\) kernel.

This effect has been validated by the numerical simulation of the original integro-differential coagulation equation (Eq.(5.1)), as discussed in the next section.

### 5.4. Numerical model

The evolution of the size distribution is simulated by the nodal method as described in Section 2.3.1.1. The discrete form of the coagulation part of Eq.(5.1) is given by
\[
\frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{j=1}^{k-1} \chi_{ijk} K_{i,j} n_j n_{k-j} - n_k \sum_{i=1}^{k-1} K_{i,k} n_i
\]  
(5.49)

\( K_{ij} \) is the coagulation kernel for the interacting particles of size \( i \) and \( j \), and \( \chi_{ijk} \) is the size-splitting operator given by
$$
\chi_{ijk} = \begin{cases} 
\frac{u_{k+1}-(u_i+u_j)}{u_{k+1}-u_k}; & u_k \leq u_i + u_j \leq u_{k+1}, \\
\frac{(u_i+u_j)-u_{k-1}}{u_k-u_{k-1}}; & u_{k-1} \leq u_i + u_j \leq u_k, \\
0; & \text{otherwise.}
\end{cases}
$$

(5.50)

where, \(u_i\) is the volume of the particle at the \(i^{th}\) node, and \(i, j\) and \(k\) are the corresponding particle sizes. At every coagulation step, the size-splitting operator redistributes the particles back to nodes to conserve the mass. The aerosol size distribution of the freshly injected nanoparticles (the source) is described by a log-normal distribution in terms of a series of discrete particle nodes, with the number of particles in each node representing the particle number concentration integrated between two consecutive nodes.

The most widely used Fuchs coagulation kernel \(K(r_i, r_j)\) that accounts for transition regime effects is employed. It is given by,

$$
K(r_i, r_j) = \frac{4\pi(r_i + r_j)(D_i + D_j)}{(r_i + r_j) + \sqrt{\delta_i^2 + \delta_j^2} + \frac{4(D_i + D_j)}{\sqrt{\delta_i^2 + \delta_j^2}(r_i + r_j)}}
$$

(5.51)

wherein \(r_i\) is the radius of the particle of size \(i\), \(D_i\) is the particle diffusion coefficient, \(\delta\) is the mean distance from the centre of a sphere reached by particles leaving the sphere’s surface and traveling a distance of particle mean free path \(\lambda_i\), and \(v_i\) is the mean thermal speed of a particle. These parameters are given by

$$
\delta_i = \frac{(2r_i + \lambda_i)^{1/2} - (4r_i^2 + \lambda_i^2)^{1/2}}{6r_i \lambda_i} - 2r_i; \quad \lambda_i = \frac{8D_i}{\pi v_i}; \quad D_{\text{air}} = \frac{kT}{6\pi r_i \eta_a} \quad G_i
$$

(5.52)

where, \(k\) is the Boltzmann constant, \(T\) is the temperature, \(\eta_a\) is the air viscosity, and \(G_i\) is the slip-flow correction which further depends on the Knudsen number of the particle.
Implicit in the traditional derivation of rate kernels for clusters is the assumption that they are compact objects, which may be approximated by equivalent spheres. This is no longer found to be true. Fractal-like agglomerates are formed due to coagulation of solid primary particles. Experimental studies on the structure of metal smoke indicated that particle aggregates may be better described by fractal geometry. Fractals are self-similar objects; a small part, when magnified, appears exactly like the original cluster. Also, the clusters are spongy, having voids on all length scales. For real aggregates, self-similarity breaks-down at length scales of the order of the monomer size. Hence, the fractal description is adequate for clusters which are much larger than their constituent monomers. In brief, fractal clusters differ from compact clusters in the following important aspect. For a compact cluster, one can assign a constant density ($\rho$) such that its mass ($M$) is related to its radius ($R$) by

$$M = \rho R^3$$  \hspace{1cm} (5.53)

Compact objects can have voids; but these give rise to size independent porosities and hence size independent effective densities. For fractals, on the other hand, the porosity monotonically increases (the effective density decreases) with the cluster size. The mass therefore scales as a fractional power of the size, i.e.,

$$M = \text{constant} \ R^{d_f}$$  \hspace{1cm} (5.54)

where, $d_f$ is the fractal dimension of the cluster ($d_f <= 3$). For metal smoke, $d_f = 1.74$. The above equation implies that the effective density of the cluster decreases as

$$\rho = \text{constant} \ R^{(3-d_f)}.$$  \hspace{1cm} (5.55)

Two important models, viz., diffusion-limited aggregation (DLA), and cluster-cluster aggregation (CCA) models have been put forward in order to understand the origin of fractality. In the DLA model valid at low monomer concentrations, a given seed particle grows by the
successive accretion of monomers. The probability of a monomer being added at a given surface site is proportional to the Fickian flux, $\nabla C \cdot \hat{n}$, where, $C$ is the monomer concentration field satisfying the Laplace’s equation $\nabla^2 C = 0$ outside the aggregate, with the irreversible sticking condition, $C = 0$ on the surface. Since the Fickian flux is higher at points having greater curvature, tips formed due to fluctuations tend to grow more rapidly than the shallower regions of the cluster. This leads to a progressive increase in the fractional void space as the cluster builds up, giving rise to a fractal object. Computer simulations of this model yield a fractal dimension of 2.5, which agrees with that obtained in laboratory experiments with colloids. It has been shown that the electrical charge on monomers has no effect on the cluster structure.

In the cluster-cluster aggregation model, many clusters are formed simultaneously in the suspension and the clustering of these clusters occurs. This is more like what happens in a high-density aerosol as is implied in the coagulation equation. The inter-penetrability between a cluster and another cluster is much less than that between a monomer and a cluster, and hence larger voids are left in CCAs than in DLAs. Therefore, CCAs are far more ramified objects. In this case, the computer simulations give a fractal dimension of 1.78 which is close to that observed for smoke aggregates.

Implications of fractality to aerosols are manifold. In the coagulation equation, the rate kernels have to be re-derived for fractal clusters. In order to include the effect of particle morphology (i.e. fractality) in Fuchs kernel, the particle radius ($r_i$) in Eq.(5.51) is replaced by the collision radius of the agglomerate of volume $u_i$, which is taken as the fractal radius ($r_{f,i}$) given by (Matsoukas & Friedlander, 1991)

$$r_{f,i} = r_i N_i^{1/d_f}$$  \hspace{1cm} (5.56)
where, \( r_i \) is the volume-equivalent radius defined as radius of a sphere with the same volume and
density as the agglomerate, \( r_s \) is the radius of each individual spherule, \( N_i \) is the number of
individual spherules or primary particles in the agglomerate, and \( d_f \) is the agglomerate fractal
dimension. The particle diffusion coefficient, the Knudsen number, and the mean distance
traveled by the particles (\( \delta i \)) are evaluated at the mobility radius using the prescription proposed

Indoor particles are generally removed by the combined action of wall deposition and
ventilation mechanisms. The former has a complex dependence on size, atmospheric turbulence,
surface characteristics and room geometry, which has been a topic of considerable research
interest in recent years. In contrast, removal by ventilation occurs at a uniform rate for all sizes
and is independent of environmental parameters other than the air-exchange rate or ventilation
rate. (Recall that a well-stirred reactor is assumed at all times.) From the perspective of capturing
the peculiar effects that might arise because of the removal process combined with coagulation
under continuous injection, we consider the simpler case of ventilation removal only.

5.5. Results and Discussion

5.5.1. Evolution of total particle number concentration

The numerical method described in the previous section is used to study the temporal
evolution of total number concentration, particle size distribution, and average particle size
during simulation periods of ten hours each. The following parameter sets are considered to
construct the evolution scenarios:

- 2 fractal dimensions (1.75 and 3.0; i.e. “branched” and “compact”),
- 3 source injection rates \((2 \times 10^8, 2 \times 10^9 \text{ and } 2 \times 10^{10} \text{ m}^{-3} \text{sec}^{-1})\), assumed to be constant in
time,
- 2 initial particle size distributions (count median diameters (CMDs) 15 and 30 nm; constant $\sigma_g$ of 1.3)
- Ventilation rate (0, 0.15, 4 (“normal”), and 10 h$^{-1}$ (“high”)).

Temperature and pressure are fixed at 300 K and 1 atm respectively.

The total particle number concentration is one of the major metrics used to estimate the toxicological hazard of particles in the workplace environment. Its dependency on the above parameter sets is therefore of central interest.

5.5.1.1. Effect of particle fractal dimension on the total concentration

It is by now well established that droplets evolve as compact spheres with $d_f = 3$ while solid particles evolve as more or less branched, fractal aggregates depending on the mode of their generation and the chemical nature of particles. Fractality of particles tends to increase the value of the coagulation kernel thereby enhancing the coagulation rate at a given particle concentration (Maynard & Zimmer, 2003, Jacobson, 2005). In the present study, two extreme cases are considered, one with fractal dimension 3.0 and the other with 1.75, in order to examine the effect of fractal dimension on the evolution of particle characteristics in the absence of any removal process. Although not unique, the choice of 1.75 corresponds to the fractal dimensions seen in cluster-cluster aggregation models (Schneider & Jensen, 2009). This value has been used by other investigators as well. It is further assumed that the fractal aggregates are made up of spherules of 5 nm diameter. The formation of these fractal aggregates takes place at an early stage near the aerosol source before the actual measurements could take place. In the present simulations, the initial particles (measured near the injection point) are assumed to be aggregates comprised of such 5 nm dia. spherules. As mentioned, two initial size spectra of the fractal aggregates, viz., 15 and 30 nm CMDs are examined, and the particle size distribution is assumed
to be lognormal with a GSD of 1.3. The numerical model was suitably modified to take into account the appropriate definitions of the mobility and the area equivalent radii (Jacobson, 2005) required for the Fuchs kernel for fractal agglomerates.

The temporal evolution of the total particle number concentrations for $d_f = 3$ and 1.75, with other parameters fixed as above, are shown in Fig. 5.3. In both cases, the concentration initially increases rapidly as the chamber fills, reaches a peak and then tends to decrease with time as coagulation sets in. The simulation for compact particle morphology ($d_f = 3.0$) shows that the peak concentration of $2.2 \times 10^{12} \text{ m}^{-3}$ occurs after about 50 min. In the case of fractal particles ($d_f = 1.75$), the total number concentration of $1.37 \times 10^{12} \text{ m}^{-3}$ peaks at around 25 min. Apparently both the peak concentration and the time of its occurrence are reduced considerably, in fact nearly cut in half, for fractal particles ($d_f = 1.75$) as compared to compact particle $d_f = 3.0$.

![Figure 5.3](image_url)

**Fig. 5.3.** Effect of particle fractal dimension on the total number concentration. The ventilation rate is zero.
The initial steep increase, which is almost linear in time, is mainly due to steady injection coupled with the fact that significant coagulation is yet to take effect. After some time when the number concentration has increased sufficiently, coagulation sets in. The increase in the coagulation rate decreases the rate of rise of the number concentration. During this time, significant numbers of secondary particles will also be formed due to coagulation. Subsequently, the coagulation process will be dominated by primary-primary, primary-secondary and secondary-secondary particle interactions. Since the coagulation kernel for the primary-secondary interactions increases in value with the size of secondary particles, the injected primary particles will be removed at an increasingly rapid rate as time progresses. Seen in another way, one can visualize an overall increase of the effective coagulation coefficient for the entire size spectrum with time. This mechanism leads to the peak in the number concentration.

The Fuchs kernel which calculates the coagulation rate for the entire size regime is able to capture the peaking effect of the total number concentration; in contrast, a constant coagulation kernel which does not account for size-dependent effects will be unable to produce this kind of system behavior. Although not shown, a similar peaking behaviour is found for most of the commonly used, size dependent kernels including the free-molecular kernel and the continuum kernel.

After peaking, the concentration gradually decreases. In fact, when the ventilation rate is zero – a parameter discussed in more detail later on -, this trend of decreasing concentration appears to continue indefinitely, at least within the simulation time period. This strongly points to a fundamental behavior of coagulating systems, that asymptotically they would tend to zero number concentration, in spite of steady injection, perhaps even regardless of injection rate. As shown in the Section 5.5.1.2, the concentration appears to fall at least as fast as \( \sim t^{-0.33} \) for the
case of $d_f = 1.75$, the exponent being independent of the strength of the source, where $t^*$ is the scaled time. In fact there are strong indications, obtained by analysing a simplified 2-group version of the coagulation model that the long time decay might be $N_0(t^*) \sim t^{-0.4}$.

One may anticipate the conclusion of an ever-decreasing concentration from the fact that in the absence of any removal mechanism, the average secondary particle sizes will increase indefinitely with time and the ever increasing rate of primary-secondary coagulation will dominate the depletion of number concentration. Basically, the effective coagulation coefficient for the entire aerosol system continually increases which cannot be balanced by the source term. However, in the case of constant kernel, the effective coagulation coefficient is a constant and the continuous injection rate balances coagulation rate thereby leading to a non-zero steady state. These results are noteworthy since they advise against the use of a constant kernel throughout the process in cases where the size distribution broadens continuously with time.

5.5.1.2. Effect of source strength on the total concentration

Here we consider different source strengths with otherwise fixed parameters identical to those of the preceding section; in particular the ventilation rate is zero. According to figure 5.4, an increased injection rate both increases the peak in total number concentration and reduces the peaking time sharply. For example, the total number concentration reaches its maximum around 8 minutes for an injection rate $S = 2 \times 10^{10}$ particles per m$^3$ and sec, compared to 80 minutes for a 100 times lower injection rate.


Fig. 5.4: Effect source injection rate on the total number concentration of particles with $d_f = 1.75$. The ventilation rate is zero.

In the following, possibilities of capturing the effect of varying source strengths on the total concentration in a single plot is examined through an appropriate scaling transformation of variables. It must be noted up front that similarity transformations under steady-injection conditions do not exist, even for scaling kernels: hence the question of a similarity transformation does not arise for a non-scaling kernel such as the Fuchs kernel. Nevertheless one may attempt to scale the number concentrations and the time in terms of respective characteristic variables referring to the primary particle sizes. Suppose let us define a characteristic number concentration $N_c = \sqrt{S/K(u_0, u_0)}$ and a characteristic time $t_c = 1/\sqrt{S K(u_0, u_0)}$, where, $u_0$ is the volume of the particle corresponding to the CMD of the size distribution of the source injected.
into the system. We may then obtain a dimensionless number concentration and dimensionless time as follows:

\[ N^* (t^*) = \frac{N(t)}{N_c} \]  \hspace{1cm} (5.57)

\[ t^* = \frac{t}{t_c} \]  \hspace{1cm} (5.58)

Fig. 5.5 shows plots of \( N^* (t^*) \) vs. \( t^* \) for various source injection rates in the absence of any removal processes in the system. Quite interestingly, all the plots for different injection rates in this graph collapse to a single curve. This is a useful result which shows that the prediction of the total number concentration for any source injection rate can be obtained through these scaling parameters, provided all removal processes operating in the system are negligible.

**Fig.5.5:** Non-dimensionalized representation of total concentration \( N^* (t^*) \) vs. time for various source injection rates. The ventilation rate is zero.
A power-law fitting to the tail of Fig. 5.5 shows that for \( d_f = 1.75 \), the concentration appears to fall as \( N^* \sim \text{const.} t^{* -0.33} \) at around \( t^* \sim 20 \). However, since numerical simulation for longer times is computationally very intensive it is difficult to establish whether asymptotic limit has been attained at time \( t^* \) about 20. The exponent is still different from the theoretical prediction of -0.4 (Eq.(5.48)). To understand the origin of this difference, numerical solutions to the set of the simplified equations (5.29-5.31) have also been obtained for the Fuchs kernel using the differential equation solver in Mathematica. These solutions closely agree with the asymptotic predictions of the long-time decay exponents for various \( d_f \)'s ranging from 1.5-3, thereby confirming the formula (Eq.(5.44)). However, it is found that the asymptotic law sets in at very large times, i.e., for scaled times \( t^* \) greater than about 1000. Around \( t^* \sim 20 \), the decay exponent is still about -0.34, hence very close to the value observed in our simulations of the integro-differential equation. Considering that numerical simulation of the original coagulation equation for scaled times beyond 20 becomes increasingly time consuming, the predicted exponents of the simplified differential formulation may be taken as representative of the true asymptotic behaviour of the aerosol number concentration for continuous injection without external removal.

It should be pointed out that the power law \( t^{* -0.4} \) dependence for the monotonic decrease in concentration with continuous injection is far slower than the decrease following a one-time (instantaneous source) injection, which is well known to merge asymptotically into a \( t^{-1} \) dependence. In terms of real variables, the asymptotic number concentration will be \( N(t) \sim \text{const.} S^{0.3} K_{11}^{-0.7} t^{-0.4} \) for continuous injection, and \( N(t) \sim K^{-1} t^{-1} \) for one-time injection. These relations show that the pre-factor for continuous injection will depend upon the source strength, unlike the latter case in which the number concentration after long time no longer
depends upon the initial concentration. This latter property of a rate of decrease independent of initial conditions is sometimes utilized (e.g. Koch et al, 2008) to establish an aerosol concentration standard; i.e., a system with a predictable particle concentration which becomes an inherent property of the aerosol and does not depend on its initial size or concentration. Our finding implies that one cannot generally establish such a standard on the basis of steady injection.

5.5.1.3 Effect of initial particle size on the total concentration

Fig. 5.6 shows the effect of the size of the source particles. The comparison is made between two CMDs, 15 nm and 30 nm, while keeping all other parameters constant; in particular the ventilation rate is zero. For source particles with CMD = 30 nm, the total number concentration peaks earlier ($t = 18$ min) at a peak concentration which is lower by a factor of $\sim 0.7$ as compared to particles with CMD = 15 nm. However, at about 150 minutes, the concentration for 30 nm particles crosses over and thereafter tends to remain higher by about 25%. Thus larger source particles have a greater persistence at long times.
Fig. 5.6: Effect of source particle size on the total number concentration. Source strength and fractal dimension are constant at $S=1.67\times10^9$ m$^{-3}$ s$^{-1}$ and $d_f=1.75$.

5.5.1.4. Effect of the removal rate due to ventilation on the total concentration

Fig. 5.7 compares the temporal evolution of the total particle number concentration at increasing ventilation rates with the case of no removal ($\lambda_r=0$) corresponding to the scenarios of the previous sections. The other parameters are as given earlier.
Most importantly, the figure shows that (within our parameter range) ventilation always causes the total number concentration to reach an asymptotic steady state, while in the $\lambda_v=0$ case there is a continuous decline as discussed earlier. The higher the dilution (applicable for dilution rates above the critical ventilation rate defined later in this section), the lower the final plateau and the less prominent the initial concentration peak. The principal reason for this apparent stabilization of the concentration even at these ventilation rates is the dilution of very large secondary particles. Without dilution, the ageing aerosol contains an increasing number of very large agglomerates (This is discussed on more detail in Section 5.5.2). The ever increasing size and number of these secondary particles leads to a growing loss of freshly injected primary particles due to heterogeneous coagulation in such a way that the total concentration tends to fall.

**Fig. 5.7:** Effect of ventilation rate on the total number concentration. $S = 2 \times 10^8 \text{ m}^{-3} \text{ s}^{-1}$; $d_f = 1.75$
continuously. Thus a small amount of ventilation suffices to remove enough larger particles from the airspace to slow down heterogeneous coagulation sufficiently to balance it with injection of new aerosol. On the other hand, strong dilution appears to also affect the primary particle concentration sufficiently to reduce the asymptotic plateau.

Interestingly, Fig.5.7 shows a cross-over between the cases of $\lambda_v = 0$ and $0.15 \text{ h}^{-1}$, with the low-dilution case leading to higher concentrations after the peak than no dilution at all (Recall that in Fig.5.7 all parameters are kept constant except the ventilation rate). Thus, Fuchs kernel too seems to predict a critical ventilation rate at which the stabilized concentration is maximum, between insufficient suppression of heterogeneous coagulation on the one hand and too much primary aerosol dilution on the other.

This finding has significant implications for control strategies of a nanoparticle leak in the workplace. Introducing a ventilation rate below this critical value may be counterproductive from the point of view of nanoparticle reduction. In fact it is seen from Fig.5.7 that a dilution of $4 \text{ h}^{-1}$ is required at the prevailing source injection rate, in order to maintain the aerosol concentration within about $10^{11} \text{ m}^{-3}$. A higher source injection rate of $2 \times 10^9 \text{ m}^{-3}\text{s}^{-1}$ (curves not shown here), would require a ventilation rate $>15 \text{ h}^{-1}$, amounting to 15 turn-overs of the chamber volume per hour, to bring down the total number concentration. Note that such high ventilation rates would also bring the flow conditions in the chamber close to those of a well-stirred reactor.

5.5.2. Evolution of particle size

5.5.2.1. Evolution of the particle size distribution

The experimental study of Seipenbusch et al. (2008) has clearly established the formation of a bimodal size distribution under continuous aerosol injection. It is interesting to examine model predictions with regard to the effect of various parameters on the evolution of the size
spectrum and in particular on the appearance of the secondary size mode which cannot be generated with constant-kernel coagulation simulations. It is worth to mention here that the bimodal distribution may also be produced near the source due to the effect of spatial heterogeneity (See Section 4.5 of Chapter 4). However, in the present model, we assume that the aerosols released into the chamber is having unimodal (lognormal) size distribution. Further, it is assumed that these aerosols are uniformly mixed well in the chamber. The effect of source strength, choice of fractal dimension and CMD are again investigated.

![Graph of particle size spectrum](image)

**Fig. 5.8:** Evolution of particle size spectrum for compact particles with \( d_f = 3.0 \) (\( S = 2 \times 10^9 \text{ m}^{-3}\text{s}^{-1} \), CMD=15 nm; zero ventilation rate)

Fig.5.8 shows the evolution of particle size spectra for the case of a constant injection rate \( S=2 \times 10^9 \text{ m}^{-3}\text{s}^{-1} \) with compact spherical particles (\( d_f = 3.0 \)) with an initial size of 15 nm. The
simulations are carried out with $\lambda_v = 0$. The size distribution remains unimodal at early times (up to $\sim 1$ hr) and the second mode appears to gradually evolve at a later stage. While the first peak remains nearly stationary at the primary size, a distinct second peak, although of much smaller height as compared to the first mode, appears after about 5 hours and then continues gradually to move to larger sizes. This secondary mode becomes less prominent at lower injection rates (not shown in the figure).

Fig. 5.9: Evolution of particle size spectrum for fractal particles with $d_f = 1.75$. ($S = 2 \times 10^9$ m$^{-3}$s$^{-1}$, CMD=15 nm; zero ventilation rate)

The secondary mode forms earlier if we consider particles of a fractal nature (Fig. 5.9). For $d_f = 1.75$ it appears at $t = 2$ h around the particle diameter of 110 nm. With increasing time, the mode flattens and extends to larger diameters as one would expect from a self-preserving-
size-distribution-like behavior. Another interesting feature of the fractal particles is the continuous decrease of the primary peak with time, while for compact particles (Fig.5.8) the first mode height remains almost unchanged. Also the secondary mode shifts more rapidly to higher sizes for fractal particles. The above features appear more markedly at higher injection rates (Fig.5.10).

![Image of particle size spectrum](image_url)

**Fig. 5.10:** Evolution of particle size spectrum for fractal particles at a higher injection rate of $S = 2 \times 10^{10}$ m$^{-3}$s$^{-1}$. ($d_f - 1.75$, CMD=15 nm; zero ventilation rate)

In Fig. 5.11 the effect of a larger primary particle size (30 nm) for the case of a fractal kernel is also examined. Compared to Fig. 5.11, the 30 nm case shows a more prominent secondary mode. On the whole, it appears that lower fractal dimensions lead to a more distinctive secondary peak (which it is further enhanced for larger primary particle sizes) due to
the increased value of the coagulation kernel. This is perfectly consistent with the more rapid decline in concentration for \( d_f = 1.75 \) already observed in Fig. 5.3 – although there for zero ventilation rate. The impact of the secondary peak on the overall spectrum will be discussed in more detail in the following section.

Fig. 5.11: Evolution of particle size spectrum for a larger initial particle size CMD=30 nm. \((S = 2 \times 10^9 \text{ m}^{-3}\text{s}^{-1}, d_f = 1.75, \text{zero ventilation rate})\)

5.5.2.2. Evolution of the mean particle size

Fig. 5.12 shows the evolution of average particle diameter for a variety of cases discussed in the preceding sections. Although the mean particle size has only limited value in characterizing bimodal particle systems as they are encountered here, it does provide information about the prominence of the secondary size peak compared to the primary aerosol injected into
the chamber. The figure illustrates how widely the mean particle diameter can differ over the course of 10 h, depending on the scenario. All the simulations shown in Fig.5.12 are with zero ventilation except the fourth curve from the top.

![Graph showing the evolution of mean particle diameter with time for various combinations of parameters.](image)

**Fig.5.12:** Evolution of mean particle diameter with time for various combinations of parameters.

Not surprisingly, the particle diameter increases more rapidly with source injection rate, lower ventilation (up to a point!) and for particles of lower fractal dimension. For example, an increase of the source injection rate by a factor of 10 (from $2 \times 10^8$ to $2 \times 10^9$) is easily outweighed by a reduction in $d_f$ from 3 to 1.75. When comparing the two lowest curves of Fig. 5.12, the respective size increases are about 3-fold for the spherical particles vs. nearly 9-fold for the fractal particles. For the fractal particles, an increase of the source injection rate by a factor of
100 (from $2 \times 10^8$ to $2 \times 10^{10}$) increases the final size after 10 h by about 50x, from roughly 130 nm to 800 nm.

5.5.2.3. Evolution of the surface area concentration

As pointed out by Schneider et al (2011), the surface area concentration is another important metric apart from the number and mass concentrations. For solid particles evolving as fractal aggregates, the total surface area will be conserved in the same way as the mass of the aggregate during the coagulation process. As a result, the total surface area concentration ($A(t)$) may be expressed in terms of the total volume concentration $\phi(t)$ as follows:

$$A(t) = \frac{a_1 \phi(t)}{\nu_1}$$ (5.59)

Similarly for instantly coalescing droplets the surface area concentration can be estimated by the formula

$$A(t) = (36\pi)^{1/3} \int_0^{\infty} v^{2/3} \nu(v,t) dv = a_1 N_1(t) + a_1 N_2(t) \left( \frac{v_1(t)}{\nu_1} \right)^{2/3}$$ (5.60)

where, $a_1$ is the surface area of the primary mode particles.

In both these cases, the surface area metric is not an independent quantity, but is related to the particle number concentration and mean sizes, which in turn may be obtained from the simplified equations given in the two-group model.

Jeong and Choi (2003) considered a general case of change of surface area concentration in systems having finite coalescence time ($\tau$) originally formulated by Koch and Friedlander (1990). Within their framework the two situations mentioned above pertain to $\tau = \infty$ (solid particles), and $\tau = 0$ (liquid droplets). For a general case, one is required to establish a separate equation for $A(t)$ in addition to those for $N_1(t)$ and $N_2(t)$. Non-zero and finite coalescence times
are important for aerosols injected into a high temperature reactor system; however, these may not be quite relevant to particles injected into ambient environment. In view of this, the formulae given above are sufficient to estimate $A(t)$ for practical purposes of releases to workplace and ambient environments.

5.5.3. Comparison with experimental results

5.5.3.1. Experiment carried out by Seipenbusch et al (2008)

When allowing for a fractal nature of particles, the present numerical simulations reproduce some of the salient features of the experimental observations of Seipenbusch et al. (2008). The most significant of these is the peaking effect in the total number concentration. We compare the observed value of the peak number concentration and the time of occurrence of the peak with that predicted by the simulations. The source emission rate measured in the experiments is $1.67 \times 10^8 \#/(\text{m}^3\text{sec})$ of platinum nanoparticles and the estimated size of the primary particles (as seen by their first mode) is 15 nm. Since the chamber volume is 2 m$^3$, the emission rate of the platinum hot wire generator is estimated to be $3.34 \times 10^8 \#/$sec. Upon combining this data with the simulation results (Fig.5.5) showing the variation of the scaled concentration as a function of scaled time, we may calculate the peak concentration to be $2.6 \times 10^{11} \#/$m$^3$ and the time of occurrence of this peak to be 50 minutes. This is fairly in agreement with the experimental value of the peak concentration of $2.1 \times 10^{11} \#/$m$^3$ occurring after 30 minutes in Seipenbusch et al. (2008, Fig.(4)). In the simulations, we have used the primary particle density as the platinum density (21450 kg m$^{-3}$) and the agreement improves if one uses lower densities, as is expected if the primary particles are not fully compact.

Similarly, Seipenbusch et al. (2008) obtained a value of about 1.5 for the ratio of the peak number concentration to that attained after about 250-minutes (nearly steady-state). For a
ventilation rate of 0.15 per hour used in their experiments, the simulation also yields a value of 1.5 for this ratio. Although the exact agreement may be fortuitous, it may be stated with confidence that the model predictions compare reasonably well with the experimental data for the total number concentration.

The simulation results also provide qualitative support to the occurrence of a bimodal size distribution demonstrated in the experimental studies cited above. However, the experimental results have shown a secondary mode peak comparable in magnitude to the first peak at an injection rate of $\sim 10^8$ particles/(m$^3$sec) after about 120 minutes, which is not supported by simulations. Similarly, the experiments have shown a more rapid decrease in the primary mode concentration than the simulations, and the secondary mode is larger than the first mode during the early stages (up to 2 hrs). Although it is not possible to reconstruct the reasons for this disagreement, certain non-ideal factors such as the finite time required for the expansion and mixing of the plume during injection into the chamber could have played a role in accentuating the modal results. Possibly, the injection of unimodal particles in the form of a spatially inhomogeneous plume can also lead to a bimodal distribution. In fact, we have noted that in a spatially inhomogeneous aerosol plume, the particles at the centreline of the plume will grow to larger sizes than at the periphery due to coagulation (Chapter 4), which can result in pronounced bimodality as the plume gets mixed subsequently due to increased turbulence in the chamber. As this effect may add to the prominence of the second mode in experimental systems, it needs to be examined separately.

5.5.3.2. Experiments carried out using Nichrome hot wire generator

In this section, we present experimental results of the study of aerosol evolution in a closed chamber with continuous source. The experimental setup is shown in Fig. 5.13. An
important requirement of this setup is a continuous nanoparticle generator; other requirements are such as narrow size distribution, and stability of the source during many hours (constant emission rate). This is satisfied by using a hot wire generator. It was widely used as an aerosol generator for the calibration of particle counters (Liu et al, 1975, Trueblood et al, 2000), and for nucleation studies (Vali et al, 1978) which produces narrow, approximately log-normal size distributions with a peak particle diameter of 24 nm. The particle number concentrations could be varied over two orders of magnitude by adjusting the voltage (or heating current).

**Fig. 5.13:** Experimental setup to study the aerosol evolution in a well-stirred chamber

In the present study, a small coil of nichrome is used to generate nanoparticles on-line by an evaporation/condensation method. When the electric current passes through this coil, it gets
heated to higher temperature. Due to this, the material evaporates from the surface thus producing vapour continuously. Then, the vapour emitted by the coil condenses and nucleates to produce nanoparticles (primary source particles). The nichrome coil is placed inside a cubical chamber of volume 0.512 m$^3$ with dimensions 0.8 m x 0.8 m x 0.8 m, and it is connected to a variable power supply. The chamber has inlet or outlet ports distributed over the chamber walls as shown in Fig. 5.13. The inlet ports are used for the electrical connection to the nichrome coil placed inside the chamber, and ventilation. Small sample flows (0.3 lpm) are extracted from outlet ports located in the chamber walls for the purpose of monitoring the aerosol size distribution, and concentration as functions of time. The chamber is also equipped with an external pump to flush it with filtered air in order to obtain a particle-free environment. Two small fans are operated inside the chamber to homogenise the concentration. The quality of mixing is tested by simultaneously measuring the temporal evolution of aerosol from two different sampling ports (one at the top, and other at the bottom of the chamber).

The particle number concentrations are measured using Grimm Aerosol Spectrometer (model 1.108) and Grimm Scanning Mobility Particle Sizer (SMPS 5.403) which covers the size ranges 0.3–20 μm and 9.8–874.8 nm, respectively. The size distributions measured by SMPS consists of a Condensation Particle Counter (CPC, Grimm Series 5.400) and an intermediate length DMA (Grimm Vienna/Reischl type). The aerosol spectrometer works on the principle of scattering of light by the particles. The light source is a solid state laser and the scattering is measured using a set of compact photo-diodes having an effective area of the order of 0.12–0.5 mm$^2$ which have high sensitivity, high speed and a response over a spectral range of 320–1060 nm. The sample flow rate of this system is 1.2 lpm. The GRIMM SMPS was used for the measurement of particles in the fine sizes. In this system, the size-classification is based on the
mobility of the particles in an applied electric field and the counting of particles is by CPC where they undergo condensational growth until they are sufficiently large to be detected optically (diameter growth factor −100 to 1000). These larger sized particle droplets cross a laser beam where each droplet scatters light onto a photo-diode. These signals are continuously counted, stored and converted to particles/cm$^3$ which are displayed on the screen. The sampling flow rate of this model is 0.3 lpm. It should be noted, however, that the chemical nature of the particles has no importance for the present investigation because aerosol dynamic properties are governed entirely by size and concentration.

The release scenario represents the release of nanoparticles from a moderately strong aerosol source (>10$^6$ cm$^3$) into the well-stirred chamber continuously for ~ 2 hours. The voltage applied to the nichrome coil in the present experiment is 8.9 V. The voltage applied to the coil is verified at constant intervals to confirm whether the release rate is a constant or not. The size distribution is monitored over the entire duration of the experiment by SMPS (Fig. 5.14) from a sampling port located at top corner of the chamber. The SMPS takes 8 minutes to complete a single scan of the entire size spectrum. Since our SMPS measuring range starts from 9.85 nm, we are unable to measure the primary particle size emitted by the source. The first spectrum at $t = 8$ min (3:37:39 PM curve in Fig. 5.14) shows that the primary particle spectrum lies below the lower detection limit, and hence the primary particle size at the source is assumed to be less than 9.85 nm. A secondary peak at 15 nm due to the homogeneous coagulation of primary particles appears after eight minutes as shown in the next size distribution (3:45:15 PM curve). Subsequent measurements at a time interval of 8 min show the rapid emergence of a secondary peak which moves towards larger particle sizes. But their concentration (mode of the second peak) continuously decreases with time as shown in Fig.5.14. The formation of the secondary
peak is due to the homogeneous coagulation mechanism between the primary particles injected into the chamber as discussed in the Section 5.5.2.

Fig. 5.14: Temporal evolution of particle size spectrum (Each curve was obtained at an interval of ~8 minutes)

The evolution of the total number concentration and mean particle diameter are shown in figures 5.15 and 5.16. From the Fig. 5.15, it is observed that the total number concentration increases rapidly to a peak value and then decreases slowly. The time taken to reach the peak concentration is 633 seconds. During this period, the number concentration increases linearly due to the source injection. The coagulation process is weak during this time period since the number concentration is low. Once the chamber attains sufficiently high aerosol number concentration,
significant rate of coagulation is initiated since the coagulation rate is proportional to the square of the number concentration.

**Fig. 5.15:** Evolution of total number concentration in the 0.5 m³ chamber - comparison of experimental results with numerical simulation

Fig. 5.15 shows that the theoretical predictions compares well with the experimental results during the initial period (upto 1500 seconds). After this duration, the experimental results show faster decay of total number concentration as compared to simulated results. This may be due to the increase in the coagulation rate. The coagulation rate increases because of the particle growth by vapour condensation (vapour being continuously emitted by the source) in addition to the coagulation. Also, the observed multiple peaks suggest that the nucleation bursts are taking place whenever the vapour concentration reaches above the saturation value in this system.
These processes (nucleation and condensation) are not accounted in the present numerical model, and hence the deviation of the predicted values from the experiments in the later part.

Fig. 5.16: Temporal evolution of particle diameter (geometric mean) in the 0.5 m³ chamber

From the experimental measurements, one can predict the source emission rate using the non-dimensional variables defined in Eq.(5.28). Using the peak concentration and the time to reach peak concentration ($3.98 \times 10^5 \#$/cm³ and 633 seconds respectively) from the experiments and the characteristic concentration ($N_c = N_p/N^*$) and time ($t_c = t_p/t^*$) from simulations, we estimated the source emission rate ($S = N_c/t_c$) as $\sim 1.2 \times 10^9 \#/$(m³ sec). Then, the primary particle emission rate of this hot wire generator is estimated at $\sim 6.0 \times 10^8 \#$/sec. This result is in comparison with typical particle generation rates observed in hot-wire based particle generators (for example, the particle generation rate reported by Seipenbusch et al, 2008 is about $3.4 \times 10^8 \#$/s). This study demonstrates that the theory is useful in characterising particle emission rates
from sources using transient concentration buildup data in closed chambers. This opens up the possibility of an important application for assessing the particle emission rates of variety of fossil fuel based combustion sources used in domestic environments which are responsible for large scale indoor air pollution in rural areas.

5.6. Summary

A non-dimensional form has been found for the concentration decay $N^*(t^*)$ in the limit $t^* \to \infty$ of a coagulating system with constant source term. Simulations combined with analytical results using two-group model (Fuchs coagulation kernel) indicate an asymptotic decay of number concentration in the form $N^*(t^*) \sim t^{* -0.4}$ which is in marked contrast with the well known $t^{-1}$ behavior for systems with a one-time aerosol injection.

The detailed numerical study brings forth several important features of coagulation of particles injected continuously into an air space:

Fractal dimension, initial particle size, injection rate, and ventilation are identified as key variables that influence the evolution of particle characteristics. It is shown that, indeed, the number distribution of this system gradually assumes a bimodal shape, with the larger mode attaining prominence more rapidly for fractal particles and at higher injection rates. In general, the overall concentration of a coagulating system with a constant source term attains a peak soon after nanoparticle emission starts, and then tends toward an asymptotic steady-state limit. An asymptotic law ($t^* \to \infty$) for the decay of number concentration is derived using an analytical model (two-group model).

The number concentration attains a peak when the air space is sufficiently filled with particles, followed by a gradual concentration, which is more pronounced for fractal aggregates
as compared to compact particles. Peaking occurs more rapidly at higher concentrations when source injection rate is increased. For the total number concentration these features agree well even quantitatively, with the experimental data observed by Seipenbusch et al. (2008).

Ventilation of the air space, even a small amount of ventilation, causes the particle concentration to stabilize (i.e. converge toward a finite asymptotic value), as opposed to no ventilation which always seems to lead to an asymptotic concentration of zero regardless of source strength. Particle concentrations may thus be larger at low ventilation rates as compared to an unventilated space. Also, there appears to exist a concentration maximum for a certain ventilation rate. Little ventilation may therefore be a worse prevention measure for nanoaerosols than no ventilation at all.

A prominent effect of applying coagulation dynamics to rapidly mixed systems having continuous injection, is the shift of aerosol mass from the nanoparticle regime into micrometer sized particles. This shift is stabilized by the presence of ventilation rate. The stabilizing effect of ventilation is due to dilution of the secondary particle concentration, which would - without this continued dilution - continue to grow with time in both concentration and particle size, thereby leading to an ever increasing rate of coagulation between the primary and secondary modes. Note that this very relevant feature of aerosol dynamic behavior in a workplace cannot be reproduced by simulation with a size-independent collision kernel.

It was further found that the secondary mode occurs more prominently for fractal particles having larger initial sizes. Several of these results are qualitatively consistent with the experimental observations, but do not match quantitatively, possibly due to the presence of initial inhomogeneity of the aerosols during source injection.