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Recent Development of Analytical Solutions to Brownian Aerosol Coagulation in Different Particle Size Regimes

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Abstract

The log-normal size distribution theories developed recently for aerosol coagulation are reviewed. The analytical solutions to Brownian coagulation developed recently for various particle size regimes are reviewed. In order to describe the evolution of the size distribution of a coagulating aerosol over the entire size range, the analytical solutions developed individually for the free-molecule regime, the transition regime, the near-continuum regime, and the continuum regime have been combined. The work described here represents the first analytical solution to the aerosol coagulation problem covering the entire particle size range.

Key words : aerosol, Brownian motion, coagulation

1. INTRODUCTION

Individual particles suspended in the air collide and stick together through various mechanisms such as random Brownian motion of particles, differential settling velocities, flow turbulence, and by velocity gradients in laminar flow. Among these mechanisms, coagulation due to Brownian motion is an important particle growth mechanism in situations where small aerosol particles at a high concentration are concerned or where long-time behavior of suspended particles is of interest. The time evolution of particle size distribution for a coagulating aerosol is of fundamental interest in many applications such as atmospheric science, industrial hygiene, and nuclear safety analysis, because many properties such as toxicity, radioactivity, electrostatic charging, and light scattering of the suspended particles depend upon their size distribution.

A complete particle size distribution of a polydisperse aerosol undergoing coagulation is governed by the following integro-differential equation (Müller, 1928):

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta(v-\bar{v},\bar{v})\,n(v-\bar{v},t)\,n(\bar{v},t)\,d\bar{v} - n(v,t)\int_0^\infty \beta(v,\bar{v})\,n(\bar{v},t)\,d\bar{v} \qquad (1)$$

where $n(v, t)$ is the particle size distribution function at time, t, and $\beta(v, \bar{v})$ is the collision kernel for two particles of volume v and $\bar{v}$. Thus the first term of the right-hand side represents the production rate of particle size v by collision of particles of size $v-\bar{v}$ and $\bar{v}$, and the second term gives the disappearance rate of particles having volume v by collision with particles of all sizes. The exact solution to Eq. (1) coupled with the particle size dependent β does not exist to date due to the complexity involved in the integro-differential equation.

The problem of Brownian coagulation retaining the size-dependent collision kernel was treated comprehensively by Friedlander and Wang (1966), Wang and Friedlander (1967), and Lai *et al.* (1972). Using the similarity transform for the particle size distribution function, a series of solutions were provided for the self-preserving size distributions that coagulating aerosols attain after sufficient time elapses. Brownian coagulation in the continuum (Friedlander and Wang, 1966), the near-continuum (Wang and Friedlander, 1967), and the free-molecule (Lai *et al.*, 1972) regimes were treated. The solutions are in a form that is much simpler than the original governing equation although the results are generally in numerical or tabular form. The self-preserving size distribution theory played a very important role for researchers in understanding the coagulation mechanism. For this reason, the theory has been of extensive interest for numerous theoretical and experimental studies. The discovery that the size distribution of an aerosol undergoing Brownian coagulation in certain cases eventually attains an asymptotic form of the size distribution is indeed very significant and useful theoretically and experimentally. One shortcoming of the theory is its inability to resolve the size distribution for the time period before an aerosol attains the self-preserving size distribution. Therefore, it was still necessary to resort to numerical calculations.

Lately, we took another approach to obtain simple analytical solutions that provide the size distribution over the entire time period of coagulation for various size regimes (Otto *et al.*, 1999; Park *et al.*, 1999; Lee *et al.*, 1997; Lee *et al.*, 1990; Lee *et al.*, 1984; Lee, 1983). The approach we have taken is based on the use of a time-dependent log-normal function for depicting the size distribution of a coagulating aerosol. Through suitable simplifications, the Müller equation was solved analytically providing a simple solution. Due to both the simplicity in concept and the straightforward approach taken in the studies, the results have also been of interest in recent experimental and theoretical studies (Otto *et al.*, 1994; Vemury *et al.*, 1994; Rosner, 1989; Pratsinis, 1988; Lee, 1985; Lee and Chen, 1984). The purpose of this paper is to review those analytical solutions and to give a guideline for use of the solutions.

2. ANALYTICAL SOLUTIONS

In order to represent a polydisperse aerosol size distribution, the log-normal function, one of the most commonly used mathematical forms for the study of dynamics of particles, is used here. The size distribution density function for particles whose radius is r for the log-normal distribution is written as

$$n(r,t)=\frac{1}{r}\,\frac{N(t)}{\sqrt{2\pi}\,\ln\sigma(t)}\exp\left[\frac{-\ln^2\{r/r_g(t)\}}{2\ln^2\sigma(t)}\right] \qquad (2)$$

where $r_g(t)$ is the geometric number mean particle radius, $\sigma(t)$ is the geometric standard deviation based on particle radius, and $N(t)$ is the total number concentration of particles. For studying the coagulation problem in which two particles collide to become a particle whose volume is the sum of the two volumes, it is convenient to rewrite Eq. (2) in terms of particle volume:

$$n(v,t)=\frac{1}{3v}\,\frac{N(t)}{\sqrt{2\pi}\ln\sigma(t)}\exp\left[\frac{-\ln^2\{v/v_g(t)\}}{18\ln^2\sigma(t)}\right] \qquad (3)$$

where $v_g(t)$ [$=4\pi r_g^3/3$] is the geometric number mean particle volume. If one obtains the time evolution of the three parameters $N(t)$, $v_g(t)$, and $\sigma(t)$, the particle size distribution of the coagulating aerosol of interest for any time, t can be constructed using Eq. (3).

In the following sections, the analytical solutions are introduced for different number regimes where the Knudsen number, $Kn\,[=\lambda/r]$, is the ratio of the mean free path length of the gas molecules, λ to the particle radius, r.

2. 1 Continuum Regime ($Kn < \sim 0.1$)

For the case of coagulation due to Brownian motion in the continuum regime, the collision $\beta(v,\bar{v})$ is written as

$$\beta(v,\bar{v})=K_{co}(v^{1/3}+\bar{v}^{1/3})\left(\frac{1}{v^{1/3}}+\frac{1}{\bar{v}^{1/3}}\right) \tag{4}$$

where K_{co} is the collision coefficient for the continuum regime [$=2k_BT/3\mu$], subscript co designates the continuum regime, k_B is the Boltzmann constant, T is the absolute temperature, and μ is the gas viscosity. Using Eq. (4), Lee (1983) derived the following solutions:

$$\frac{N}{N_o}=\frac{1}{1+\{1+\exp(\ln^2\sigma_o)\}K_{co}N_ot}, \tag{5}$$

$$\ln^2\sigma=\frac{1}{9}\ln\left[2+\frac{\exp(9\ln^2\sigma_o)-2}{1+\{1+\exp(\ln^2\sigma_o)\}K_{co}N_ot}\right], \tag{6}$$

and

$$\frac{v_g}{v_{go}}=\frac{\exp(4.5\ln^2\sigma_o)\,[1+\{1+\exp(\ln^2\sigma_o)K_{co}N_ot]}{\sqrt{2+\{\exp(9\ln^2\sigma_o)-2\}/[1+\{1+\exp(\ln^2\sigma_o)K_{co}N_ot]}} \tag{7}$$

where N_o, σ_o, and v_{go} are the initial values for N, σ, and v_g, respectively.

2. 2 Near-continuum Regime ($\sim 0.1 < Kn < \sim 1$)

For particles whose Knudsen number is larger than 0.1, slippage of gas molecules around particles influences the coagulation rate. The collision kernel for this regime is:

$$\beta(v,\bar{v})=K_{co}(v^{1/3}+\bar{v}^{1/3})\left\{\frac{C(v)}{v^{1/3}}+\frac{C(\bar{v})}{\bar{v}^{1/3}}\right\} \tag{8}$$

where C is the slip correction factor. The following Cunningham slip correction factor was utilized in Lee *et al.* (1997).

$$C=1+A\cdot Kn \tag{9}$$

where $A=1.591$. Using Eq. (8) coupled with Eq. (9), Lee *et al.* (1997) derived the following solutions:

$$K_{co}N_ot=\frac{3}{p}\left[\frac{1}{3}\left\{\left(\frac{N}{N_o}\right)^{-1}-1\right\}-\frac{s}{2p}\left\{\left(\frac{N}{N_o}\right)^{-2/3}-1\right\}+\left(\frac{s}{p}\right)^2\left\{\left(\frac{N}{N_o}\right)^{-1/3}-1\right\}-\left(\frac{s}{p}\right)^3\ln\left\{\frac{p+s(N/N_o)^{1/3}}{(p+s)(N/N_o)^{1/3}}\right\}\right], \tag{10}$$

$$\ln^2\sigma=\frac{1}{9}\ln\left[2c+\left(\frac{N}{N_o}\right)\{\exp(9\ln^2\sigma_o)-2c\}\right], \tag{11}$$

and

$$\frac{v_g}{v_{go}}=\frac{\exp(4.5\ln^2\sigma_o)\,(N/N_o)^{-1}}{\sqrt{2c+(N/N_o)\,\{\exp(9\ln^2\sigma_o)-2c\}}} \tag{12}$$

where $p=1+\exp(\ln^2\sigma_o)$, $s=A\cdot Kn_o\{\exp(\ln^2\sigma_o/2)+\exp(5\ln^2\sigma_o/2)\}$, $Kn_o(=\lambda/r_{go})$ is the Knudsen number based on r_{go}, and $c=\dfrac{p+s\exp(-3\ln^2\sigma_o)(N/N_o)^{1/3}}{p+s(N/N_o)^{1/3}}$.

2. 3 Free-molecule Regime ($Kn > \sim 50$)

In the free-molecule regime, where particle sizes are much smaller than the mean free paths of gas molecules, λ, the collision kernel has the following form obtained by the kinetic theory:

$$\beta(v,\bar{v})=K_{fm}(v^{1/3}+\bar{v}^{1/3})^2\left(\frac{1}{v}+\frac{1}{\bar{v}}\right)^{1/2} \tag{13}$$

where K_{fm} is the collision coefficient for the free-molecule regime coagulation [$=(3/4\pi)^{1/6}(6k_BT/\rho)^{1/2}$], subscript fm designates the free-molecule regime, and ρ is the particle density. Using Eq. (13), the following solutions were derived by Lee *et al.* (1990) and Park *et al.* (1999):

$$\frac{N}{N_o}=\left(1+\frac{5K_{fm}Hb_ov_{go}^{1/6}N_ot}{6}\right)^{-6/5}. \tag{14}$$

$$\ln^2\sigma=\frac{2}{15}\ln\left[2+\frac{\exp(7.5\ln^2\sigma_o)-2}{1+5K_{fm}Hb_ov_{go}^{1/6}N_ot/6}\right], \tag{15}$$

and

$$\frac{v_g}{v_{go}}=\frac{\exp(4.5\ln^2\sigma_o)\,[1+5K_{fm}Hb_ov_{go}^{1/6}N_ot/6]^{6/5}}{[2+\{\exp(7.5\ln^2\sigma_o)-2\}/(1+5K_{fm}Hb_ov_{go}^{1/6}N_ot/6)]^{3/5}} \tag{16}$$

where $H=\exp(\ln^2\sigma_o/8)+2\exp(5\ln^2\sigma_o/8)+\exp(25\ln^2\sigma_o/8)$ and $b_o=1+1.2\exp(-2\sigma_o)-0.646\exp(-0.35\sigma_o^2)$.

2. 4 Transition Regime ($\sim 1 < Kn < \sim 50$)

In the transition regime the coagulation rate is described neither by the continuum theory nor by simple kinetic theory. Since Fuchs (1934) found a semi-empirical solution of the coagulation kernel using the so called flux-matching theory, several similar solutions have been suggested (Pratsinis. 1988; Dahneke, 1983; Fuchs and Sutugin. 1971; Wright. 1960). Otto *et al.* (1999) compared all those solutions and concluded that the harmonic mean kernel (Pratsinis, 1988) is simplest to use while the more complicated Dahneke's kernel is also much easier than other solutions yielding only 1% relative error in maximum. Therefore, in this study the harmonic mean kernel and Dahneke's kernel are to be considered.

In the flux-matching approach, the coagulation kernel for the transition regime is expressed as follows:

$$\beta(v, \bar{v}) = \beta_{nc}(v, \bar{v}) \cdot \frac{1 + B_1 Kn_D}{1 + B_2 Kn_D + B_3 Kn_D^2} \quad \text{with}$$

$$Kn_D = \frac{\beta_{nc}(v, \bar{v})}{2\beta_{fm}(v, \bar{v})} \tag{17}$$

where subscript *nc* designates the near-continuum regime. For the harmonic mean kernel, $B_1 = 0$, $B_2 = 2$, and $B_3 = 0$ and for the Dahneke's kernel. $B_1 = 1$. $B_2 = 2$, and $B_3 = 2$.

2. 4. 1 Harmonic Mean Kernel

Using the harmonic mean kernel, Park *et al.* (1999) derived the following solutions:

$$K_{co} N_o t = \frac{6K_{co}}{5K_{fm} Hb_o v_{go}^{1/6}} \left\{ \left(\frac{N}{N_o}\right)^{-5/6} - 1 \right\} + \frac{3}{p}\left[\frac{1}{3}\left\{ \left(\frac{N}{N_o}\right)^{-1} - 1 \right\} - \frac{q}{2p}\left\{ \left(\frac{N}{N_o}\right)^{-2/3} - 1 \right\} + \left(\frac{q}{p}\right)^2 \left\{ \left(\frac{N}{N_o}\right)^{-1/3} - 1 \right\} - \left(\frac{q}{p}\right)^3 \ln\left\{ \frac{p + q(N/N_o)^{1/3}}{(p+q)(N/N_o)^{1/3}} \right\} \right], \tag{18}$$

$$\ln^2 \sigma = \frac{1}{9} \ln\left[2d + \left(\frac{N}{N_o}\right) \{\exp(9\ln^2 \sigma_o) - 2d\} \right], \tag{19}$$

and

$$\frac{v_g}{v_{go}} = \frac{\exp(4.5\ln^2 \sigma_o)(N/N_o)^{-1}}{\sqrt{2d + (N/N_o)\{\exp(9\ln^2 \sigma_o) - 2d\}}} \tag{20}$$

where $q = A \cdot Kn_o \exp\{1.5(\ln^2 \sigma_\infty - \ln^2 \sigma_o)\}\{\exp(\ln^2 \sigma_o/2) + \exp(5\ln^2 \sigma_o/2)\}$, $d =$

$$\frac{K_{co}(N/N_o)^{1/6}/(K_{fm} Hb_o v_{go}^{1/6}) + 1/\{p + q(N/N_o)^{1/3}\}}{K_{co}(N/N_o)^{1/6} \exp(-1.5\ln^2 \sigma_{\infty,fm})/(K_{fm} Hb_o v_{go}^{1/6}) + 1/\{p + q\exp(-3\ln^2 \sigma_\infty)(N/N_o)^{1/3}\}},$$

σ_∞ (= 1.320) is the asymptotic value of σ for the continuum regime as given by Lee (1983), and $\sigma_{\infty,fm}$ (= 1.355) is the asymptotic value of σ for the free-molecule regime as given by Lee *et al.* (1984).

2. 4. 2 Dahneke's Kernel

Using Dahneke's kernel, Otto *et al.* (1999) developed another solution. The solution is somewhat similar to that obtained by Park *et al.* (1999) in the form, yet it is more complicated. Details on the derivation and the results can be referred to Otto *et al.* (1999).

3. DISCUSSION AND CONCLUSIONS

In this review article, a series of analytical solutions to time evolution of the particle size distribution of a coagulating aerosol in different size regimes were introduced. Consequently, a solution to the coagulation problem covering the entire particle size regime is presented. It is noticed that due to the complex nature of the coagulation problem, some of the derived solutions, Eq. (10) and Eq. (18), are in an implicit form. In this case, one needs to compute the time (t) it takes to obtain a desired number concentration decay (N/N_o) instead of computing explicitly the number concentration decay for a given time. Thereafter, it is possible to compute the geometric standard deviation (σ) and the geometric mean particle volume (v_g) for the corresponding coagulation time.

To verify the analytical solutions introduced, we compared the results in a wide parameter range with numerical log-normal method (Otto *et al.*, 1994). In addition, we compared the results with a sectional model (Landgrebe and Pratsinis, 1990) which does not assume a particular size distribution during the coagulation. In Fig. 1, the evolution of the size distribution is compared with the numerical results. The initial parameters for the comparison calculation in this figure were

$N_o = 10^9$ particles/cm^3, $r_{go} = 47$ nm, $\sigma_o = 1.8$,
$T = 300$ K, and $\rho = 1$ g/cm^3.

Fig. 1 shows that the result in this study is in good agreement with that obtained by the numerical methods.

Fig. 2 shows the change in the geometric standard deviation σ as a function of time as the particle size distribution moves from the free-molecule regime to

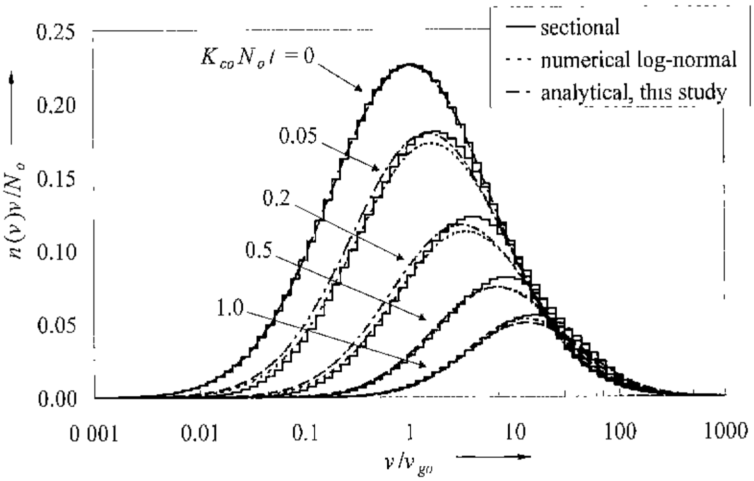

Fig. 1. Comparison of the change in particle size distributions with numerical results.

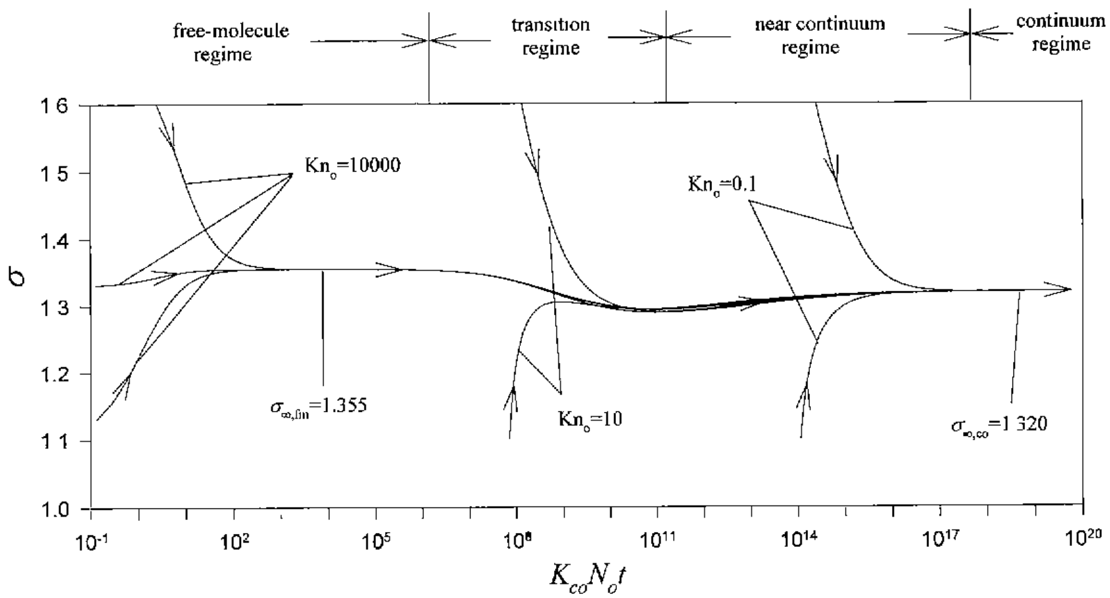

Fig. 2. Change in the geometric standard deviation σ as a function of time as the particle size makes a transition from the free-molecule regime to the continuum regime.

the continuum regime. It is seen that in a late stage within the free-molecule regime, σ approaches 1.355, which is the asymptotic value given previously by Lee *et al.* (1990) for the free-molecule regime coagulation. As coagulation progresses further, particles move into the transition regime in which σ decreases following the quasi-self-preserving values (Otto *et al.*, 1994). As coagulation proceeds further, coagulating particles are seen to enter the continuum regime. In this regime σ approaches 1.320, which is the asymptotic value given by Lee (1983) for the continuum regime coagulation. It is interesting to note that regardless of what size regime an aerosol originates from, the geometric standard deviation of all the aerosols quickly joins the asymptotic σ curve shown in the middle in Fig. 2 and then follows the curve before finally attaining the value of 1.320.

Nomenclature

A	constant (=1.591) [−]
b_o	defined in Eqs. (14) through (16) [−]
B_1, B_2, B_3	variables used for the coagulation coefficient in the transition regime [−]
c	defined in Eqs. (11) and (12) [−]
C	Cunningham slip correction factor [−]
d	defined in Eqs. (19) and (20) [−]
H	defined in Eqs. (14) through (16) [−]
K_{co}	collision coefficient for the continuum regime [m³/particles/sec]
K_{fm}	collision coefficient for the free-molecule regime [$m^{5/2}$/particles/sec]
k_B	Boltzmann constant [kg m²/sec²/K]
Kn	Knudsen number [−]
Kn_D	defined in Eq. (17) [−]
N	total number concentration of particles [particles/m³]
n	particle size distribution density function [particles/m³/m³]
p	defined in Eq. (10) [−]
q	defined in Eq. (18) [−]
r	particle radius [m]
r_g	geometric mean particle radius [m]
s	defined in Eq. (10) [−]
t	time [sec]
T	absolute temperature [K]
v, $\bar{v}$	particle volume [m³]
v_g	geometric mean particle volume [m³]
β	collision kernel [m³/particles/sec]
σ	geometric standard deviation based on particle radius [−]
μ	gas viscosity [kg/m/sec]
λ	mean free path of gas molecules [m]
ρ	particle density [kg/m³]

Subscripts

o	refers to initial condition
∞	refers to condition at $t \rightarrow \infty$
∞, fm	refers to asymptotic condition within free-molecule regime
co	refers to the continuum regime
nc	refers to the near-continuum regime
fm	refers to the free-molecule regime

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여러 입자크기영역에서의 브라운 응집에 대한 해석해에 관한 고찰

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초 록

본 연구에서는 브라운 응집문제에 적용되는 대수정규분포이론에 대하여 최근에 개발된 여러 입자크기영역에 대한 해석해들을 중심으로 고찰하였다. 모든 입자크기영역에서 일어나는 에어로졸의 응집에 의한 입자크기분포의 변화를 설명하기 위해 자유분자영역, 전이영역, 근연속체영역 및 연속체영역에서의 해석해들을 종합적으로 검토하였다. 본 연구의 결과는 전 입자크기영역에서의 브라운응집문제에 대한 첫 해석해이다.

주제어 : 에어로졸, 브라운운동, 응집