Journal of Colloid and Interface Science **231,** 129–135 (2000)
doi:10.1006/jcis.2000.7102, available online at http://www.idealibrary.com on IDEAL®

Brownian Coagulation of Fractal Agglomerates: Analytical Solution Using the Log-Normal Size Distribution Assumption

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Received March 10, 2000; accepted July 17, 2000

An analytical solution to Brownian coagulation of fractal agglomerates in the continuum regime that provides time evolution of the particle size distribution is presented. The theoretical analysis is based on representation of the size distribution of coagulating agglomerates with a time-dependent log-normal size distribution function and employs the method of moments together with suitable simplifications. The results are found in the form that extends the spherical particle solution previously obtained by K. W. Lee (*J. Colloid Interface Sci.* 92, 315–325 (1983)). The results show that the mass fractal dimension has a significant effect on the size distribution evolution during coagulation. When the obtained solution was compared with numerical results, good agreement was found. The self-preserving size distribution of nonspherical agglomerates is discussed.

Key Words: **Brownian coagulation; fractal agglomerates.**

INTRODUCTION

Many industrial aerosols generated at high temperatures are composed of individual primary particles forming irregular fractal-like structures (1–3). The behavior of these agglomerates is considerably different from that of their spherical counterparts (4). The volume of the agglomerates can be related to their collision radius by a power law exponent that varies between 1 and 3 (5). This exponent has been termed the mass fractal dimension.

The coagulation of nonspherical aerosol agglomerates is one of the most important processes in industrial and environmental systems affecting the time evolution of the size distribution of agglomerates. The mass fractal dimension influences coagulation rates due to the effects of agglomerate morphology on collision diameter (2, 6).

One of the earliest models of agglomerate growth through coagulation was developed by Vold (7) and Sutherland (8). In this model, cluster growth was treated as a series of random collisions between primary particles and agglomerates. Meakin (9) and Kolb *et al.* (10) independently developed the cluster–cluster aggregation model in which clusters as well as single particles diffuse. This model provided a more realistic description of the agglomeration processes. Mountain *et al.* (11) simulated the coagulation of fractal agglomerates by following the trajectory of every cluster. This method enabled straightforward comparison with the kinetics of a real system. They showed that the agglomerates can be described as a fractal, at least with regard to the power law relationship between mass and size, with a dimensionality of 1.7 to 1.9.

Although Brownian coagulation is well understood, the integro-differential coagulation equation is too complex to solve exactly. Typically, a numerical integration method is used to resolve the time-dependent size distribution (1, 3, 6, 12). Lee (13) used the moment method to obtain a simple analytical solution that provides the size distribution over the entire time period of coagulation. This approach is based on the use of a time-dependent log-normal function for depicting the size distribution of coagulating particles. The solution, however, is valid only for spherical particles.

The only analytical study on the coagulation of fractal agglomerates was done by Jain and Kodas (14) only for the asymptotic value of the spread of the agglomerate size distribution. However, their study could not provide the time evolution of the entire particle size distribution. The purpose of this study is to present an analytical solution for the time evolution of size distribution of agglomerates by Brownian coagulation using the assumption that the agglomerates can be described by a log-normal distribution.

THEORY

The particle size distribution of an aerosol undergoing coagulation is governed by the integro-differential equation (15)

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

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 $\bar{v}$.

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0021-9797/00 $35.00

The collision kernel of agglomerates, $\beta(v, \bar{v})$, covering the continuum regimes is represented by the expression (11)

$$\beta(v, \bar{v}) = K\left(v^{1/D_f} + \bar{v}^{1/D_f}\right)\cdot\left(\frac{1}{v^{1/D_f}} + \frac{1}{\bar{v}^{1/D_f}}\right), \quad [2]$$

where K is the collision coefficient [$=2k_B T/3\mu$], k_B is the Boltzmann constant, T is the absolute temperature, μ is the gas viscosity, and D_f is the mass fractal dimension. It is assumed in this study that the entire growth process can be described by a constant mass fractal dimension.

In this study the size distribution of a coagulating aerosol is represented with a time-dependent log-normal size distribution that is written as

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

where $N(t)$ is the total number concentration of particles, $\sigma(t)$ is the geometric standard deviation, and $v_g(t)$ is the geometric number mean particle volume. This approach has been widely employed for representing the size distribution of particles both theoretically and experimentally. Kaplan and Gentry (4) have shown that log-normally distributed agglomerates maintain their log-normal distribution a long time after coagulation begins.

The kth moment of the particle size distribution is written as

$$M_k = \int_0^\infty v^k n(v, t)\, dv, \quad [4]$$

where k is an arbitrary real number. According to the properties of a log-normal function, any moment can be written in terms of M_1, v_g, and σ as follows

$$M_k = M_1 v_g^{k-1}\exp\left\{\frac{9}{2}(k^2-1)\ln^2\sigma\right\}. \quad [5]$$

In the next section, an analytical solution for the time evolution of particle size distribution of fractal agglomerates by Brownian coagulation is derived using the properties of the log-normal function.

DERIVATION OF ANALYTICAL SOLUTION AND RESULTS

Substituting Eq. [2] into Eq. [1] and integrating from 0 to ∞, one can obtain the following equations using Eq. [4]:

$$\frac{dM_0}{dt} = -K\left(M_0^2 + M_{-1/D_f}M_{1/D_f}\right), \quad [6]$$

$$\frac{dM_1}{dt} = 0, \quad [7]$$

and

$$\frac{dM_2}{dt} = 2K\left\{M_1^2 + M_{(D_f-1)/D_f}M_{(D_f+1)/D_f}\right\}. \quad [8]$$

Eq. [7] merely indicates that $M_1 = const.$ Differentiating Eq. [5] with respect to t for $k = 0$ and 2, and using Eq. [7], we have

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

and

$$\frac{dM_2}{dt} = M_1 v_g \exp\left(\frac{27}{2}\ln^2\sigma\right)\left\{\frac{d(\ln v_g)}{dt} + \frac{27}{2}\frac{d(\ln^2\sigma)}{dt}\right\}. \quad [10]$$

Substituting Eqs. [5], [9], and [10] into Eqs. [6] and [8], and eliminating dt thereafter, we obtain

$$d(\ln v_g) = \frac{9\{1 - 3\exp(9\ln^2\sigma)/2\}}{\exp(9\ln^2\sigma) - 2}\, d(\ln^2\sigma). \quad [11]$$

Integrating Eq. [11], we obtain the following relation

$$\frac{v_g}{v_{g0}} = \frac{\exp(9\ln^2\sigma_0) - 2}{\exp(9\ln^2\sigma) - 2}\exp\left\{\frac{9}{2}(\ln^2\sigma_0 - \ln^2\sigma)\right\}, \quad [12]$$

where σ_0 and v_{g0} are the initial values of σ and v_g, respectively. Substituting Eqs. [11] and [12] into Eq. [9] or [10], and using Eq. [5], we have

$$\frac{-9\{\exp(9\ln^2\sigma_0) - 2\}\exp(9\ln^2\sigma)d(\ln^2\sigma)}{\{\exp(9\ln^2\sigma) - 2\}^2\left\{1 + \exp\left(9\ln^2\sigma/D_f^2\right)\right\}} = KN_0\, dt, \quad [13]$$

where N_0 is the initial value of N [$=M_0$]. Noting that the quantity $\{1 + \exp(9\ln^2\sigma/D_f^2)\}$ appearing in the denominator of the left-hand side of Eq. [13] generally would vary to a much lesser extent than $\{\exp(9\ln^2\sigma) - 2\}^2$ for a typical value of σ, say between 1.0 and 2.5, we approximate that quantity by setting $\sigma = \sigma_0$. This type of approximation proves to be quite reasonable. As will be shown from the results, the fact that σ does not diverge but always converges to a certain value further justifies this approximation. With it, the following expression for σ is obtained by integrating Eq. [13].

$$\ln^2\sigma = \frac{1}{9}\ln\left[2 + \frac{\exp(9\ln^2\sigma_0) - 2}{1 + \left\{1 + \exp\left(9\ln^2\sigma_0/D_f^2\right)\right\}KN_0 t}\right]. \quad [14]$$

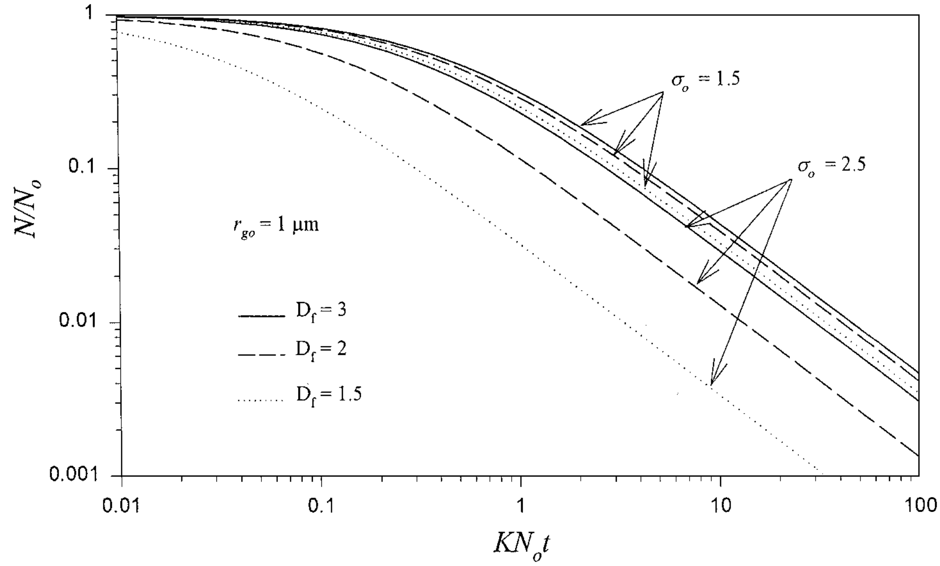

FIG. 1. Number concentration change as a function of σ_0 and D_f.

Substituting Eq. [14] into Eq. [12], v_g subsequently is obtained as a function of time.

$$\frac{v_g}{v_{g0}} = \frac{\exp(9\ln^2\sigma_0/2)\left[1+\left\{1+\exp\left(9\ln^2\sigma_0/D_f^2\right)\right\}KN_0t\right]}{\left[2+\frac{\exp(9\ln^2\sigma_0)-2}{1+\left\{1+\exp\left(9\ln^2\sigma_0/D_f^2\right)\right\}KN_0t}\right]^{1/2}}. \qquad [15]$$

Finally, we obtain Eq. [16] for the decrease in the total number concentration of particles from Eqs. [5], [14], and [15]:

$$\frac{N}{N_0} = \frac{1}{1+\left\{1+\exp\left(9\ln^2\sigma_0/D_f^2\right)\right\}KN_0t}. \qquad [16]$$

With the values of σ, v_g, and N given by Eqs. [14] through [16], it is possible to construct a size distribution for any t using Eq. [3]. The governing equation for coagulation coupled with the collision kernel is a highly nonlinear integro-differential equation. However, the solution just obtained is in a form with which the time-dependent size distribution of coagulating agglomerates can readily be computed. Eq. [16], for example, attains a very simple form, yet it predicts the time-dependent number concentration of coagulating agglomerates while comprehensively taking into account the effects of the initial values of the number concentration, the geometric standard deviation, and the mass fractal dimension.

Figures 1 through 3 are plots of N, v_g, and σ, respectively, as functions of dimensionless time, KN_0t, and of the mass fractal dimension for different σ_0 values. In Fig. 1, it is noted that the mass fractal dimension effects are indeed important. As indicated by prior researchers (3, 4), the number decay is shown to occur at a high rate with decreasing D_f. In addition, the mass fractal dimension effects become more important as σ_0 becomes larger. Figure 2 is a plot of the geometric mean particle volume as calculated by Eq. [15]. The mass fractal dimension effects are again shown to be substantial, particularly for agglomerates having a large σ_0 value. Figure 3 shows the time change of the geometric standard deviation as a function of the initial geometric standard deviation, σ_0, and the mass fractal dimension, D_f. Regardless of the initial value of σ_0, all $\sigma(t)$'s appear to approach a certain value and their approach is accelerated with decreasing mass fractal dimension, D_f. The asymptotic value for σ is discussed further in the next section.

DISCUSSION

The solution was given in analytical form. Thus we have examined two limiting cases with the solution:

(1) For $D_f = 3$. If D_f is set to 3 as a limiting case, it is evident that Eqs. [16], [14], and [15] reduce, respectively, to

$$\frac{N}{N_0} = \frac{1}{1+\{1+\exp(\ln^2\sigma_0)\}KN_0t}, \qquad [17]$$

$$\ln^2\sigma = \frac{1}{9}\ln\left[2+\frac{\exp(9\ln^2\sigma_0)-2}{1+\{1+\exp(\ln^2\sigma_0)\}KN_0t}\right], \qquad [18]$$

and

$$\frac{v_g}{v_{g0}} = \frac{\exp(9\ln^2\sigma_0/2)\lfloor 1+\{1+\exp(\ln^2\sigma_0)\}KN_0t\rfloor}{\left[2+\frac{\exp(9\ln^2\sigma_0)-2}{1+\{1+\exp(\ln^2\sigma_0)\}KN_0t}\right]^{1/2}}. \qquad [19]$$

Eqs. [17] through [19] represent the solution for the spherical particles ($D_f = 3$) that was given by Lee (13).

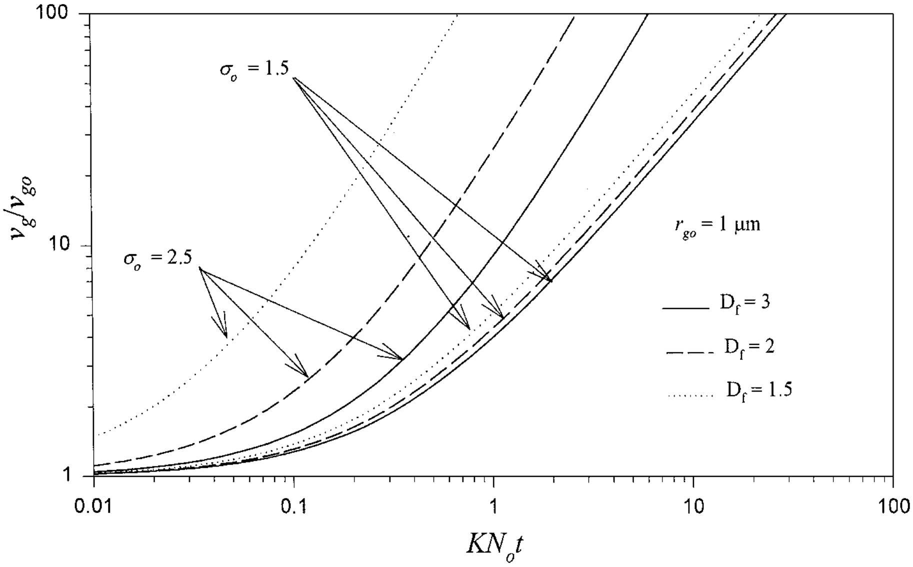

FIG. 2. Increase in the geometric mean particle volume as a function of σ_0 and D_f.

(2) For $t \to \infty$. As coagulation proceeds for a sufficiently long time, one finds from Eq. [14] that

$$\exp(9\ln^2\sigma) = 2 \quad \text{or} \quad \sigma_\infty \cong 1.32, \qquad [20]$$

where σ_∞ is the asymptotic value of σ for $t \to \infty$. This value is identical to that for the self-preserving log-normal size distribution obtained by Lee (13) for spherical particles. These identical values indicate that the spread of log-normally preserving size distribution in the continuum regime does not depend upon the mass fractal dimension of the agglomerates. This fact was presented previously by Jain and Kodas (14).

To verify the analytical expressions derived, comparisons with a numerical model were performed in Figs. 4 and 5 using an aerosol with $r_{go} = 1\ \mu$m, $\sigma_0 = 1.5$, and $D_f = 2.0$, where r_{go} is the initial value of the geometric mean particle radius, r_g. For the comparisons we used as a reference model the sectional code of Landgrebe and Pratsinis (16), which did not assume any functional form for a particle size distribution. In the sectional model, 1.18 was used for the section spacing factor. Figures 4 and 5 demonstrate that the analytical solution obtained in this study is in good agreement with the numerical calculation. These investigations show that the analytical solution derived in this study is a robust tool to describe the time evolution of a size distribution of nonspherical particles due to Brownian coagulation.

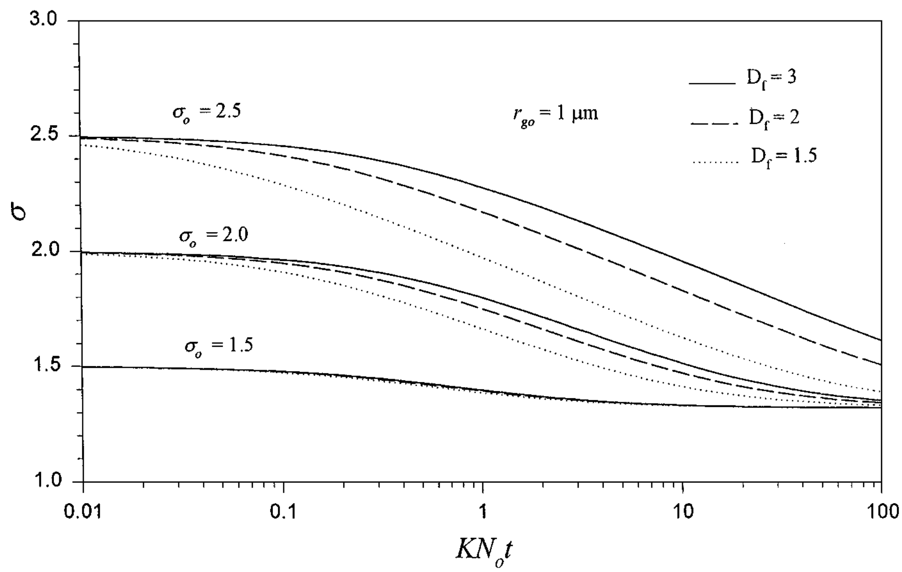

FIG. 3. Change in the geometric standard deviation as a function of σ_0 and D_f.

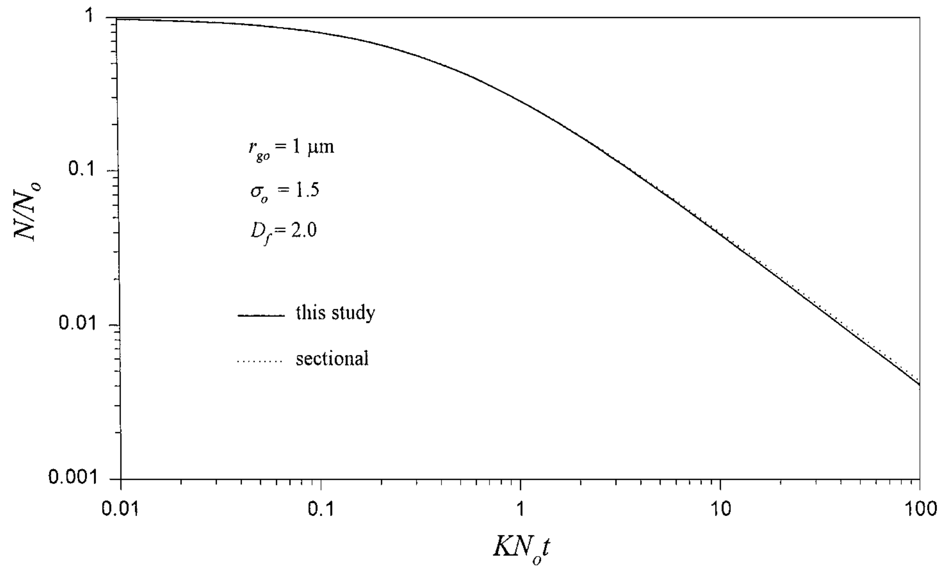

FIG. 4. Comparison with a numerical calculation for the number concentration decay.

To further investigate the self-preserving feature of coagulating agglomerates, we compared the solution derived with the previous numerical model of Vemury and Pratsinis (3), who used the sectional code to obtain self-preserving size distribution. Conventionally, in the self-preserving formulation, the dimensionless particle volume is defined as

$$\eta = v/\tilde{v} \quad [21]$$

and the dimensionless size distribution density function is defined as

$$\Psi = n\tilde{v}/N, \quad [22]$$

where $\tilde{v}$ [$=V/N$] is the arithmetic mean particle volume, and V ($=M_1$) and N ($=M_0$) are the total particle volume and number concentrations, respectively. Because the plot of Ψ against a log scale of η does not provide direct information on the size distribution, a plot of $\Psi\eta$ versus η was used in this study so that the area under the curve represents more accurately the particle size distribution.

Figure 6 compares the analytical solution derived in this study with the numerical model of Vemury and Pratsinis (3). It is interesting to note, as is different from the analytical result, that in the numerical results the self-preserving size distribution actually depends on the mass fractal dimension. The difference

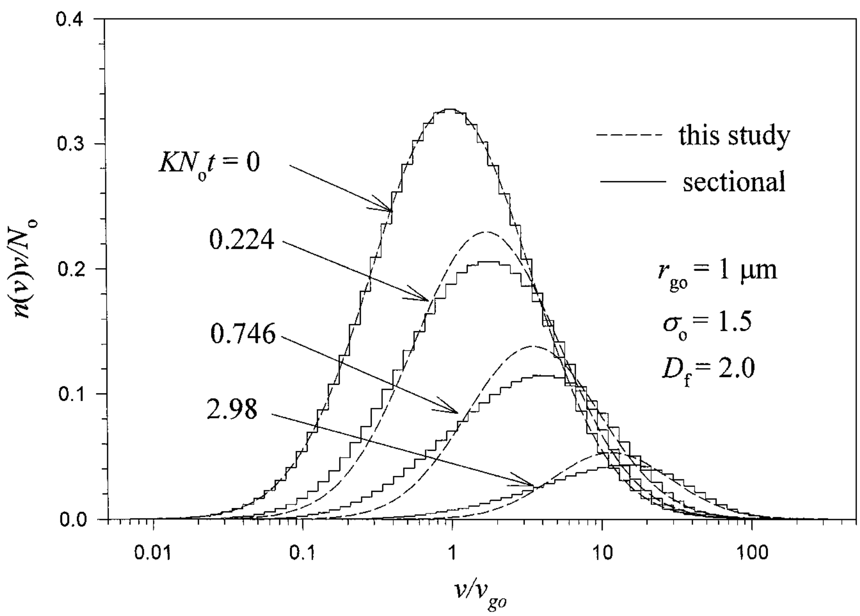

FIG. 5. Comparison with a numerical calculation for the particle size distribution change.

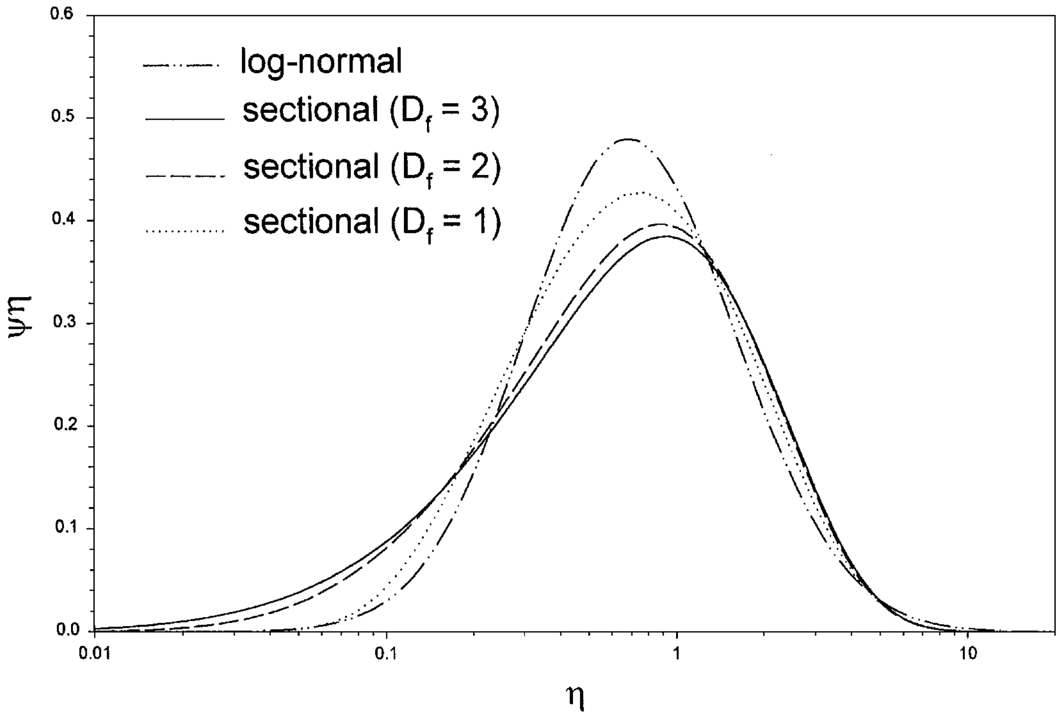

FIG. 6. Comparison with a numerical calculation for the self-preserving particle size distribution.

between the analytical and the numerical models results from the symmetrical assumption of the log-normal size distribution (17). Further, this figure shows that, as the particle shape deviates from the sphere (with the smaller D_f value), the self-preserving size distribution is predicted better by the solution derived in this study. Numerically predicted asymptotic σ values for $D_f = 3.0$, 2.0, and 1.0 were 1.444, 1.405, and 1.338, respectively, whereas the analytical solution obtained in this study gave the value of 1.32.

The time it takes for a distribution to reach the asymptotic distribution is of interest for many applications. To derive an expression for this time, let us assume that σ has reached σ_∞ if $1.9 < \exp(9\ln^2\sigma) < 2.1$ compared with Eq. [20]. This means if σ reaches in a range of 1.306 to 1.333, a distribution will be assumed to have attained the asymptotic distribution. With the above criterion, we obtain the following expression from Eq. [14] for the required time to approach the asymptotic distribution, t_∞,

$$t_\infty = -\frac{\pm 10\{\exp(9\ln^2\sigma_0) - 2\} - 1}{KN_0\{1 + \exp(9\ln^2\sigma_0/D_f^2)\}}, \qquad [23]$$

where the sign convention may be used for $\sigma_0 > \sigma_\infty$ and $\sigma_0 < \sigma_\infty$ in that order. According to Eq. [23], the times required to reach such an asymptotic distribution, t_∞, for various σ_0's and for various D_f's are presented in Table 1. It is shown in this table that t_∞ decreases with decreasing $|\sigma_0 - \sigma_\infty|$ and with decreasing D_f. This trend is repeated in Fig. 3.

TABLE 1
KN_0t_∞ for Various σ_0 and D_f Values

σ_0	$D_f = 3.0$	$D_f = 2.0$	$D_f = 1.0$
1.0	5.50	5.50	5.50
1.32	0	0	0
1.5	10.5	9.36	4.25
2.0	280	186	9.59
2.5	5760	2510	9.98

CONCLUSIONS

A theoretical analysis of Brownian coagulation for agglomerates was performed by correlating the size distribution with a time-dependent log-normal function. Using this approach, it was possible to obtain an analytical solution for the size distribution of coagulating agglomerates as a function of time. The assumptions and the simplifications employed in the present study proved to be reasonable when the limiting cases were examined and the results were compared with numerical calculations. The results of this study show that the mass fractal dimension has a significant effect on the subsequent time evolution of the size distribution. The smaller the mass fractal dimension is, the faster coagulation occurs. The self-preserving feature of coagulating agglomerates was also investigated. It was found that the self-preserving size distribution is approximated better by the solution derived in this study for lower mass fractal dimension value. The time required to reach log-normally self-preserving size distribution was shown to decrease with decreasing mass fractal dimension.

ACKNOWLEDGMENT

This work was supported by the Brain Korea 21 program from the Ministry of Education through the Graduate Program for Chemical and Environmental Engineering at Kwangju Institute of Science and Technology.

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