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# Self-Preserving Theory for the Volume Distribution of Particles Undergoing Brownian Coagulation

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**In this paper, the self-preserving theory of coagulating aerosols is presented in a new way: the logarithmic volume (or mass) distribution of an aerosol undergoing coagulation stays invariant in shape at long times. This is shown for both the free molecular and continuum regime collision frequency functions as well as the constant collision frequency function. In addition, new simple approximate forms are presented for the self-preserving distributions, based on numerical solutions to the discrete coagulation equation.** © 2001 Academic Press

## INTRODUCTION

Prediction of the size distribution of a coagulating aerosol has been a continuing interest in aerosol physics. Analytical solutions have been obtained only in certain special cases, corresponding to simplified forms of the collision frequency function (CFF) and/or the initial particle size distribution (1–6). For real systems, an important discovery was made by Friedlander and Wang (3) for coagulation in the continuum regime: by use of a similarity transformation to the size distribution function, one can find an asymptotic form, the self-preserving distribution (SPD), after long times that is independent of the initial conditions. This was later (7) shown to apply also for the free molecular particle size regime. Vemury *et al*. (8) studied the time to reach the SPD for various initial distributions and found that, especially, if the initial distribution is narrow the time lag to reach the SPD is very short.

In this paper, we present the self-preserving theory in a new convenient way, i.e., that the logarithmic volume (or mass) distribution of an aerosol undergoing coagulation is invariant in shape when the size variable axis (in this case particle volume) is scaled logarithmically. This is actually a standard way to present aerosol particle size distributions (9–11). This will be done first for the simple constant CFF, starting from Schmoluchowski's (1) analytical solution of the discrete coagulation equation, and then for the continuum and free molecular CFF, using the similarity transformation of Friedlander and Wang (3). In addition, we will present simple analytical approximations to the shape of the volume distributions, obtained by fitting to numerical solutions of the coagulation equation.

## THEORY

Let $n(v,t)dv$ be the particle number concentration per unit mass of gas in a volume range between $v$ and $v+dv$ at time $t$. Then the coagulation equation for the number concentration function is (11)

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

Here the first term on the right-hand side is the rate of formation of particles of size $v$ by smaller particles of sizes $u$ and $v-u$. The factor 1/2 must be introduced since collisions are counted twice in the integral. The second term is the rate of loss of particles of size $v$ by collisions with all other particles. The term $\beta(u,v)$ is the collision frequency function, which can be written as

$$\beta(u,v) = \begin{cases} \dfrac{2KT}{3\mu}\left(\dfrac{1}{u^{1/3}}+\dfrac{1}{v^{1/3}}\right)\left(u^{1/3}+v^{1/3}\right), & \text{continuum regime;} \\ \left(\dfrac{3}{4\pi}\right)^{1/6}\left(\dfrac{6KT}{\rho_p}\right)^{1/2}\left(\dfrac{1}{u}+\dfrac{1}{v}\right)^{1/2}\left(u^{1/3}+v^{1/3}\right)^2 & \text{free molecular regime.} \end{cases} \qquad [2a,b]$$

Friedlander and Wang (3) pointed out that if the collision frequency function is a homogenous function of particle volume, that is if

$$\beta(\lambda u, \lambda v) = \lambda^n \beta(u,v), \qquad [3]$$

then the transformation

$$\eta = \frac{v}{\bar{v}(t)} \qquad \bar{v}(t)n(v,t) = N(t)\psi(\eta) \qquad [4a,b]$$

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reduces the coagulation equation [1] to an ordinary integro-differential equation for $\psi$ of $\eta$. This solution is called the self-preserving solution of the coagulation equation. It is an asymptotic solution $\psi(\eta)$ toward which all systems converge, regardless of the initial distribution. It is easily checked that the collision frequency functions for the free molecular and continuum regimes are homogenous functions, which means that asymptotic solutions exist.

In this paper, we focus on the logarithmic volume distribution $\phi^{\log}(v)$, instead of the number distribution,

$$\phi^{\log}(v) = \frac{d\Phi}{d(\log v)} = v(\phi)(v) = v^2 n(v), \qquad [5]$$

in which $\Phi$ is the cumulative volume distribution function and $\phi$ the volume distribution function (10). We will show that this distribution will stay constant in shape for a coagulating aerosol in the free molecular or continuum regime as well as for a constant collision frequency function.

## Constant Collision Frequency Function

If the collision frequency function $\beta$ is a constant, then the discrete version (11) of the coagulation equation

$$\frac{dN_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1} \beta(v_i, v_{k-i}) N_i N_{k-i} - N_k \sum_{i=1}^{\infty} \beta(v_i, v_k) N_i \qquad [6]$$

with initial conditions $N_1(t=0) = N_1^0$ and $N_k(t=0) = 0$—i.e., all the particles are assumed to be in the first size class at $t = 0$—has an analytical solution

$$N_k = \frac{N_1^0 \cdot \left(\frac{t}{\tau}\right)^{k-1}}{\left(1+\frac{t}{\tau}\right)^{k+1}}; \quad \frac{1}{\tau} = \frac{\beta N_1^0}{2}. \qquad [7]$$

In this version of the coagulation equation, $N_k$ is the number concentration in size class $k$, and the volumes of the size classes are successive multiples of the first one: $v_k = k v_1$.

In the discrete solution, each size bin is of width $v_1$, and thus, the number distribution density function $n$ is

$$n_k = \frac{N_k}{\Delta v_k} = \frac{N_1^0 \hat{t}^{k-1}}{v_1(1+\hat{t})^{k+1}}, \qquad [8]$$

in which we have defined a dimensionless time $\hat{t} = t/\tau$. In this paper, we are primarily interested in the behavior of the volume (or mass) distribution $\phi$ of the particles. For the coagulation equation with a constant CFF, we have simply

$$\phi_k = v_k n_k = \frac{N_1^0 k \hat{t}^{k-1}}{(1+\hat{t})^{k+1}} = \frac{N_1^0 k}{\hat{t}(1+\hat{t})}\left(\frac{\hat{t}}{1+\hat{t}}\right)^k. \qquad [9]$$

At long times, that is, when $t$ is large, the following approximations apply,

$$\frac{\hat{t}}{1+\hat{t}} \approx \exp\left(-\frac{2}{2\hat{t}+1}\right) \quad \text{and} \quad \hat{t}(1+\hat{t}) \approx \frac{1}{4}(2\hat{t}+1)^2, \qquad [10]$$

and $\phi_k$ becomes

$$\phi_k = \frac{4N_1^0 k}{(2\hat{t}+1)^2} \exp\left(-\frac{2k}{2\hat{t}+1}\right). \qquad [11]$$

For large $k = v/v_1$, the discrete distribution can be approximated with a continuous one,

$$\phi(v) = \frac{d\Phi}{dv} = \frac{4N_1^0 \frac{v}{v_1}}{(2\hat{t}+1)^2} \exp\left(-\frac{2\frac{v}{v_1}}{2\hat{t}+1}\right), \qquad [12]$$

in which $\Phi$ is the cumulative volume distribution. Since $\phi$ is now the continuous number density distribution at long times, we can directly obtain the corresponding logarithmic distribution

$$\phi^{\log}(v) = \Phi_{tot} \frac{\left(2\frac{v}{v_1}\right)^2}{(2\hat{t}+1)^2} \exp\left(-\frac{2\frac{v}{v_1}}{2\hat{t}+1}\right). \qquad [13]$$

The time evolution of the volume corresponding to the peak of the distribution $v_{\text{mode}}$ can be found by differentiating the distribution with respect to $v$ and setting to zero and is

$$v_{\text{mode}} = v_1(2\hat{t}+1). \qquad [14]$$

Thus, we can rewrite the logarithmic distribution function into the following convenient form:

$$\phi^{\log}(v) = \Phi_{tot}\left(\frac{2v}{v_{\text{mode}}(t)}\right)^2 \exp\left(-\frac{2v}{v_{\text{mode}}(t)}\right). \qquad [15]$$

It is now clear that this distribution stays invariant in shape on a logarithmic plot as time evolves, since it is only a function of the ratio $v/v_{\text{mode}}$.

From the distribution, Eq. [15], it is straightforward to further show that the volume (or mass) mean volume is also $v_{\text{mode}}$ and that the number mean volume, or simply the mean volume, is

$$\bar{v} = \frac{v_{\text{mode}}}{2}. \qquad [16]$$

Thus, the logarithmic volume distribution function can also be

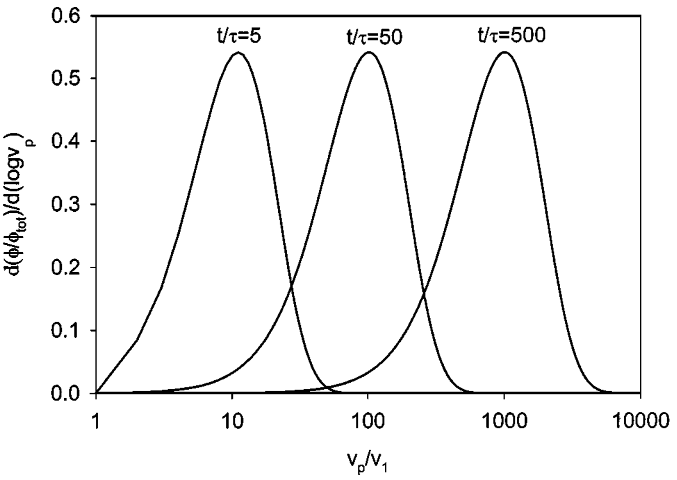


**FIG. 1.** Dynamics of the logarithmic volume distribution for coagulation with a constant CFF. The distributions are the exact analytical solutions at $t/\tau =$ 5, 50, and 500 for the coagulation equation, Eq. [5].

written as

$$\phi^{\log}(v) = \Phi_{tot}\left(\frac{v}{\bar{v}}\right)^2 \exp\left(-\frac{v}{\bar{v}}\right). \qquad [17]$$

From this distribution, one can retrieve the number distribution function directly, and it is

$$n(v) = \frac{N_{tot}^2}{\Phi_{tot}} \exp\left(-\frac{v}{\bar{v}}\right), \qquad [18]$$

which agrees with the solution by Mulholland and Baum (5) for a similar problem, but using a Junge distribution as the initial distribution.

The evolution of the shape of the volume distribution with time, i.e., the exact solution to Eq. [6], is illustrated in Fig. 1. It is clear that a self-preserving form is indeed obtained, and furthermore, this form is reached very quickly. Already at $t/\tau = 5$, when $v_{\text{mode}}/v_1 = 11$ or $\bar{v}_1/v_1 = 5.5$, the distribution appears to be very similar in shape to that at long times.

### Free Molecular and Continuum Regimes

For the free-molecular and continuum regime collision frequency functions [2a,b] there is no analytical solution available for the coagulation (Eq. [1] or [6]). However, the logarithmic volume (or mass) distribution can be proven to remain invariant by just analyzing the similarity transformation [4a,b].

Since

$$n(v,t) = \frac{N_{tot}{}^2}{\Phi_{tot}}\psi(\eta) = \frac{N_{tot}}{\bar{v}}\psi(\eta), \qquad [19]$$

$$\phi(v,t) = v n(v,t) = N_{tot}\eta\psi(\eta) \qquad [20]$$

and

$$\phi^{\log}(v,t) = v\phi(v,t) = \Phi_{tot}\eta^2\psi(\eta). \qquad [21]$$

This means that the shape of the logarithmic volume (or mass) distribution has an asymptotic form, which is independent of time, and the functional form is presented as in Eq. [21], in which $\eta = v/\bar{v}$ and $\psi$ is the self-preserving distribution function introduced by Friedlander and Wang (1966) for the continuum regime or by Lai *et al*. (1972) for the free molecular regime.

The functions $\phi^{\log}$ are presented graphically in Figs. 2–4 for the constant, free molecular, and continuum collision frequency functions, respectively. They have been obtained numerically by solving the discrete coagulation equation until an asymptotic form is reached. In Figs. 2a, 3a, and 4a the $y$-axis is linear and in 2b, 3b, and 4b logarithmic. Since the particle size spectrum that has to be spanned is quite large, it is impractical to use the linear spacing $v_k = kv_1$. Instead, we divide the size axis

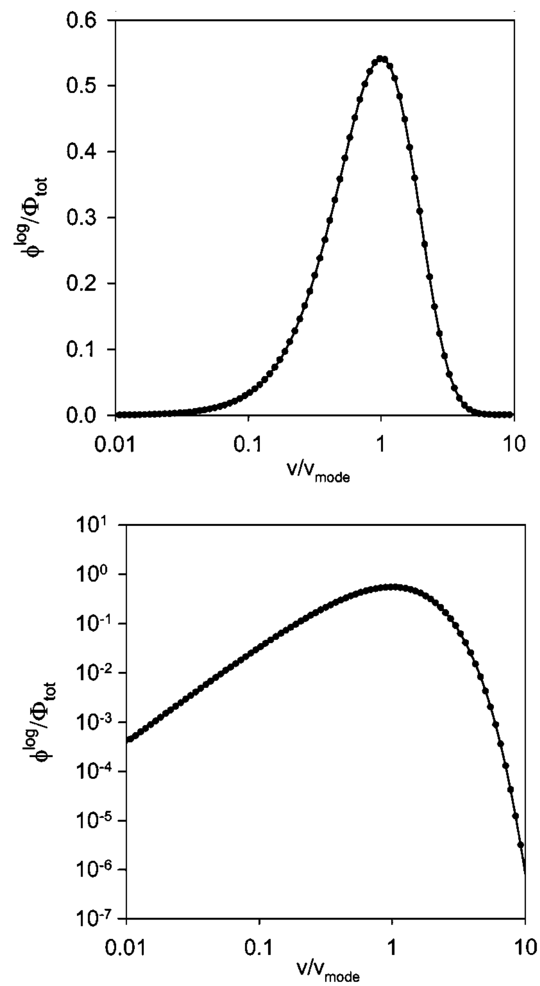


**FIG. 2.** Self-preserving logarithmic volume distributions for constant CFF coagulation, with (a) a linear and (b) a logarithmic $y$-axis. The circles are the result from the numerical solution, and the lines are least-squares curve fits of the form $\phi^{\log}/\Phi_{tot} = \xi^a \exp(-\xi^b)$, in which $\xi = v/v_{\text{mode}}$.

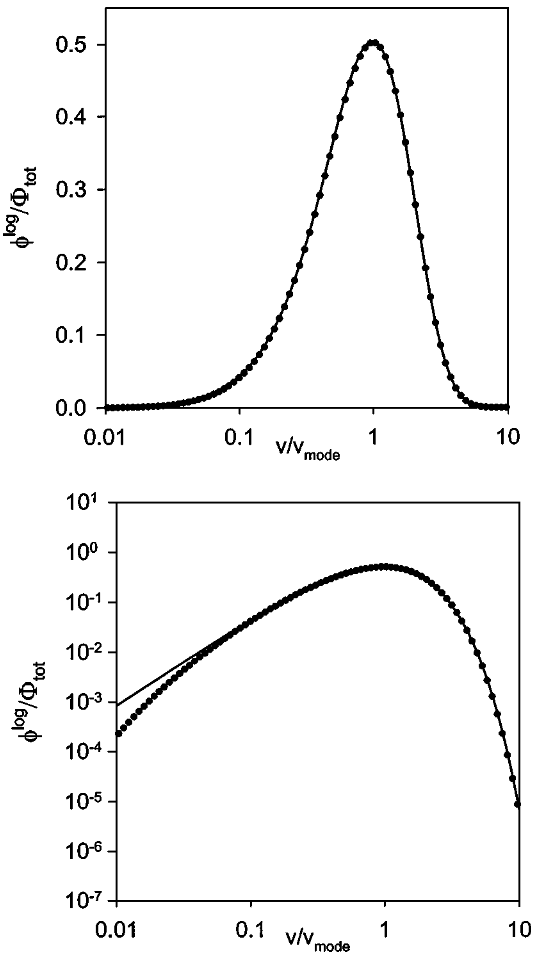


**FIG. 3.** Self-preserving logarithmic volume distributions for free molecular regime coagulation, with (a) linear and (b) logarithmic $y$-axis. The circles are the result from the numerical solution, and the lines are least-squares curve fits of the form $\phi^{\log}/\Phi_{tot} = \xi^a \exp(-\xi^b)$, in which $\xi = v/v_{\text{mode}}$.

into size sections geometrically: $v_k = b^k v_1$. Thus, the discrete coagulation equation must be written as

$$\frac{dN_k}{dt} = \frac{1}{2}\sum_{i,j} \chi_{ijk}\beta_{ij}N_iN_j - \sum_i \beta_{ik}N_iN_k, \qquad [22]$$

in which

$$\chi_{ijk} = \begin{cases} \dfrac{v_{k+1} - (v_i + v_j)}{v_{k+1} - v_k}; & \textit{if } v_k \le v_i + v_j < v_{k+1} \\ \dfrac{(v_i + v_j) - v_{k-1}}{v_k - v_{k-1}}; & \textit{if } v_{k-1} \le v_i + v_j < v_k \\ 0; & \textit{otherwise.} \end{cases} \qquad [23]$$

The function $\chi_{ijk}$ is a size-splitting operator, which divides particles in correct proportions (number and mass are conserved) into size classes, when two particles collide and the resulting particle does not fall exactly into a size class. In generating the distributions of Fig. 2 the logarithmic spacing $b = 2^{1/3}$ was used.

The shape of the volume distribution with a constant CFF (Fig. 2) is exactly the one predicted by Eq. [15]. Furthermore, the curve representing continuum regime coagulation (Fig. 4) falls almost perfectly on this same curve. The free molecular regime volume distribution function (Fig. 3) is clearly different. All three curves can be very well approximated with the functional form

$$\frac{\phi_{\log}}{\Phi_{tot}} = \xi^a \exp(-\xi^b), \qquad [24]$$

in which $\xi = 2v/v_{\text{mode}}$ and the least-squares fits for $a$ and $b$ give $a = 2$, 1.804, and 2.005 and $b = 1$, 0.9512, and 1.002 for constant, free-molecular, and continuum CFFs, respectively. The fits are practically perfect for large particle sizes. In the lower end, there is some deviation, which can be seen from the logarithmic plots (Figs. 2–4b). The linear plots (Fig. 2–4a) illustrate nicely the deviation from the lognormal shape.

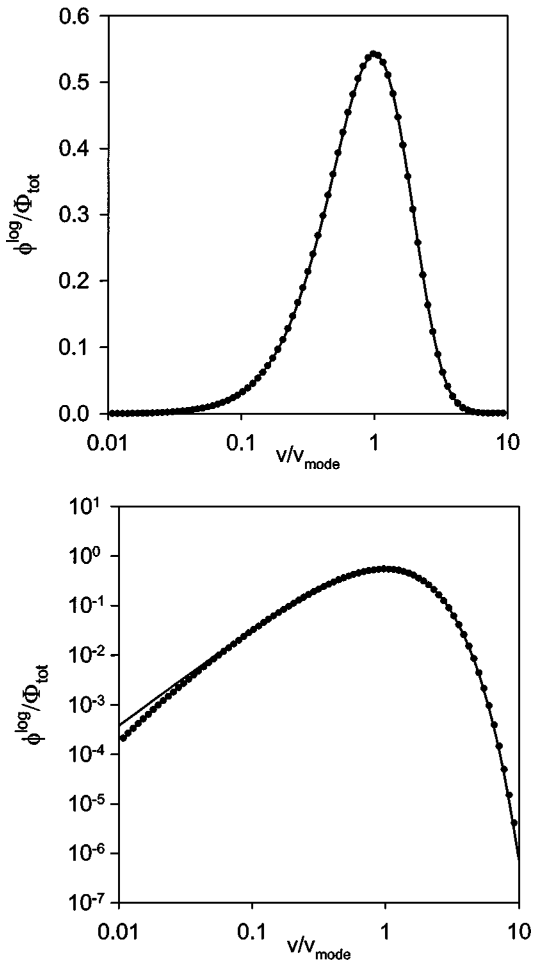


**FIG. 4.** Self-preserving logarithmic volume distributions for continuum regime coagulation, with (a) a linear and (b) a logarithmic $y$-axis. The circles are the result from the numerical solution, and the lines are least-squares curve fits of the form $\phi^{\log}/\Phi_{tot} = \xi^a \exp(-\xi^b)$, in which $\xi = v/v_{\text{mode}}$.

The numerically generated self-preserving distributions were also used to calculate the asymptotic relationship between $v_{\mathrm{mode}}$ and $\bar{v}$ for continuum and free molecular regime coagulation:

$$\frac{v_{\mathrm{mode}}}{\bar{v}} = \begin{cases} 2.10 & \textit{for free-mol.} \\ 1.94 & \textit{for continuum.} \end{cases} \qquad [25]$$

These relationships enable one to use Eq. [24] to generate the distributions by using the mean particle volume instead of the peak volume, if desired.

## CONCLUSIONS

In this paper, we have presented the self-preserving theory of a coagulating aerosol in a new way. We have shown that the logarithmic volume (or mass) distribution is invariant in shape when the size axis (in this case particle volume) is scaled logarithmically. We have tested this approach for the case of a constant collision frequency function for which an analytical solution to the self-preserving distribution is obtained. We have also tested this approach for both free molecular and continuum regime coagulation against a sectional solution to the coagulation equation. In all cases we recover the correct shapes for the self-preserving distributions when compared against either the analytical and numerically derived solutions for the three cases.

This analysis presented provides a very simple and fast solution to coagulation problems: the evolution of the mean particle size is obtained from the well-known self-preserving theory of Friedlander and the shape of the size distribution from the analytical approximations presented in this work.

Also, this way of presenting the classical self-preserving theory is in our view much easier to grasp for students of aerosol science than the “standard” way, presented in many well-known books. The fact that the logarithmic mass distribution stays constant in shape is both easy to remember and simple to use in quick estimates.

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