A SIMPLE MOMENT MODEL TO STUDY THE EFFECT OF DIFFUSION ON THE COAGULATION OF NANOPARTICLES DUE TO BROWNIAN MOTION IN THE FREE MOLECULE REGIME

by

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In the study a simple model of coagulation for nanoparticles is developed to study the effect of diffusion on the particle coagulation in the one-dimensional domain using the Taylor-series expansion method of moments. The distributions of number concentration, mass concentration, and particle average volume induced by coagulation and diffusion are obtained.

Key word: *nanoparticles, coagulation, diffusion, moment method*

Introduction

Nowadays, aerosol particles gradually become one of the most common unhealthy components of air pollution [1]. Particle size and concentration affect not only the environment but also the health of human beings. Researches have already shown that there is a strong correlation between mortality and particle size, with specific reference from nanoparticles (<50 nm) to fine particles (<2.5 μm) [2].

The evolution of nanoparticles is controlled by the general dynamic equation (GDE), which is a non-linear partial differential equation [3]. The GDE is capable of describing the particle evolution under all kinds of processes (*i. e.*, convection, diffusion, coagulation, nucleation, surface growth and other physical or chemical phenomena, *etc*.). However, it is difficult to solve the equation mainly because of its dependence on the particle volume. As a compromise, several scientific methods have been developed to cover this shortcoming, including the sectional method and nodal method [4, 5], the method of moment (MOM) [6-8]. Recently Yu and Lin proposed a Taylor-series expansion method of moment (TEMOM) [9-11]. The developed TEMOM method has no prior requirement for the particle size distribution (PSD), and it is a promising method to approximate the aerosol general dynamics equation.

In the present study, a simple model is built to simulate the effect of diffusion on the coagulation of nanoparticles due to Brownian motion in the free molecule regime. The

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TEMOM model is utilized to approximate the aerosol general dynamic equation; and the fraction moment in the diffusion terms is expressed explicitly and closed by the recurrence relationship with the first three particle moments. To avoid the numerical diffusion and dispersion, a smaller time step is set to get the steady results. The time advancement is accomplished by means of a fourth-order Runge-Kutta method, and the numerical method is validated by comparison with other known methods over large evolution time.

Mathematical modeling

The transport of the nanoscale particles dispersed through the fluid is governed by the aerosol general dynamics equations (GDE). In the present study, the Brownian coagulation in the free molecule regime is solely considered, and the 1-dimensional GDE without convection can be written as:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D_n \frac{\partial n}{\partial x} \right) + \left[\frac{\mathrm{d}n}{\mathrm{d}t} \right]_{coag} \tag{1}$$

where $[\mathrm{d}n/\mathrm{d}t]_{coag}$ represents the effects of particle-particle interactions resulting in coagulation and is given by:

$$\left[\frac{\mathrm{d}n}{\mathrm{d}t} \right]_{coag} = \frac{1}{2} \int_0^v \beta(\upsilon, \upsilon - \upsilon_1) n(\upsilon_1, t) n(\upsilon - \upsilon_1, t) \mathrm{d}\upsilon_1 - \int_0^v \beta(\upsilon_1, \upsilon) n(\upsilon, t) n(\upsilon_1, t) \mathrm{d}\upsilon_1 \tag{2}$$

where $n(\upsilon,t)$ is the number of particles of volume υ at time t, and β – the collision frequency function for coagulation in free molecule regime, which is given by:

$$\beta = \sqrt[6]{\frac{3}{4\pi}} \sqrt{\frac{6K_b T}{\rho_p}} \sqrt{\frac{1}{\upsilon} + \frac{1}{\upsilon_1}} \left(\sqrt[3]{\upsilon} + \sqrt[3]{\upsilon_1} \right) \tag{3}$$

where K_b is the Boltzmann's constant, ρ_p – the particle density, and D_n – the diffusion coefficient in the free molecule regime, which is given by:

$$D_n = \frac{\sqrt[3]{\frac{3}{4\pi}} K_\mathrm{b} T}{\sqrt[3]{\upsilon^2}\, \rho_p c \left(1 + \frac{\pi \alpha_p}{8} \right)} \tag{4}$$

where c is the mean thermal speed, α_p – the accommodation coefficient, T – the fluid temperature, and the fluid in this study is the air at room temperature. In order to describe the particle field in time and space, a moment is utilized. The k-th order moment M_k of the particle distribution is defined as:

$$M_\mathrm{k} = \int_0^\infty \upsilon^\mathrm{k} n(\upsilon) \mathrm{d}\upsilon \tag{5}$$

By multiplying both sides of the GDE with υ^k and integrating over all particle sizes, a system of transport equations for M_k is obtained. The transport equations for the *k*-th order moment M_k is expressed as:

$$\frac{\partial M_k}{\partial t} = \frac{\partial}{\partial x}\left(\kappa \frac{\partial M_{k-2/3}}{\partial x}\right) + \left[\frac{\mathrm{d}M_k}{\mathrm{d}t}\right]_{coag} \tag{6}$$

where the size-independent diffusivity is $\kappa = D_n \cdot \sqrt[3]{\upsilon^2}$, $[\mathrm{d}M_k/\mathrm{d}t]_{coag}$ – the source term due to the Brownian coagulation and can be expressed as [20] :

$$\left[\frac{\mathrm{d}M_k}{\mathrm{d}t}\right]_{coag} = \frac{1}{2}\int_0^\infty\int_0^\infty \left[\upsilon+\upsilon_1{}^k - \upsilon^k - \upsilon_1^k \right]\beta(\upsilon,\upsilon_1)n(\upsilon,t)n(\upsilon_1,t)\mathrm{d}\upsilon\mathrm{d}\upsilon_1, \quad (k=0,1,2,\cdots) \tag{7}$$

The minimum number of moments required are the first three, M_0, M_1, and M_2. The zero[th] moment M_0 is the total particle number concentration; the first moment M_1 is proportional to the total particle mass; the second moment M_2 is proportional to the total light scattered. According to the prior developed Taylor-series expansion method of moment (TEMOM) [9], the source term in the first three moments can be written in the forms:

$$\left.\begin{aligned}
\left[\frac{\mathrm{d}M_0}{\mathrm{d}t}\right]_{coag} &= \frac{\sqrt{2}B_1 \;\; 65M_C{}^2 - 1210M_C - 9223 \;\; M_0{}^2}{5184\sqrt[6]{\dfrac{M_0}{M_1}}} \\
\left[\frac{\mathrm{d}M_1}{\mathrm{d}t}\right]_{coag} &= 0 \\
\left[\frac{\mathrm{d}M_2}{\mathrm{d}t}\right]_{coag} &= -\frac{\sqrt{2}B_1 \;\; 701M_C{}^2 - 4210M_C - 6859 \;\; M_1{}^2}{2592\sqrt[6]{\dfrac{M_0}{M_1}}}
\end{aligned}\right\} \tag{8}$$

where the dimensionless moment $M_C = M_0M_2/M_1{}^2$. In order to obtain the fractional moments in eq. (8), a Taylor-series expansion technique is used to close the moment equations. In eq. (7), υ^k can be expanded with Taylor-series about the point $\upsilon = V$, and $V = M_1/M_0$ is the mean particle size which is consistent with the expansion point proposed by Yu *et al*. [9]. Then the three fractional moments $M_{-2/3}$, $M_{1/3}$ and $M_{4/3}$ appeared in the first three moment equations can be expressed as:

$$M_{-2/3} = \frac{4+5M_C \;\; M_0\sqrt[3]{\dfrac{1}{V^2}}}{9}; M_{1/3} = \frac{10-M_C \;\; M_0\sqrt[3]{\dfrac{1}{V}}}{9}; \; M_{4/3} = \frac{7+2M_C \;\; M_0\sqrt[3]{\dfrac{1}{V^4}}}{9} \tag{9}$$

The governing equations are non-dimensional to simplify the treatment and analysis of the particle coagulations. It can be accomplished using the following relations:

$$t^* = \frac{t}{\dfrac{L}{c}}; \quad x^* = \frac{x}{L}; \quad M_k{}^* = \frac{M_k}{M_{k0}} \tag{10}$$

where t is time, and the characteristic length L – the length of the domain contained with particles at initial time, the characteristic velocity, c – the mean thermal velocity, and M_{k0} – the initial value of the k-th moment. Substituting the relations given in eq. (10) into eq. (6) yields the non-dimensional equations for the first three moment equations (for briefly, the star symbol '$*$' is ignored thereafter):

$$\left.\begin{aligned}
\frac{\partial M_0}{\partial t} &= \frac{1}{\mathrm{Re}_T \mathrm{Sc}_M}\frac{\partial^2}{\partial x^2}\left(\frac{4+5M_C}{9}\,M_0\frac{1}{\sqrt[3]{V^2}}\right)+\mathrm{Da}\,\frac{65M_C^2-1210M_C-9223}{5184}\,M_0^2\sqrt[6]{V}\\
\frac{\partial M_1}{\partial t} &= \frac{1}{\mathrm{Re}_T \mathrm{Sc}_M}\frac{\partial^2}{\partial x^2}\left(\frac{10-M_C}{9}\,M_0\sqrt[3]{V}\right)\\
\frac{\partial M_2}{\partial t} &= \frac{1}{\mathrm{Re}_T \mathrm{Sc}_M}\frac{\partial^2}{\partial x^2}\left(\frac{7+2M_C}{9}\,M_0\sqrt[3]{V^4}\right)-\mathrm{Da}\,\frac{701M_C^2-4210M_C-6859}{2592}\,M_1^2\sqrt[6]{V}
\end{aligned}\right\} \quad (11)$$

where the dimensionless number based on the mean thermal velocity is defined as $\mathrm{Re_T} = c\,L/\nu$, which is similar with the flow Reynolds number, and the Schmidt number based on the particle moment is $\mathrm{Sc_M} = \nu/(\kappa/V_0^{2/3})$. The initial mean particle volume V_0 is determined by the reference moment M_{k0} (*i. e.*, $V_0 = M_{10}/M_{00}$) and $M_{c0} = M_{20}M_{00}/M_{10}^2$ is a constant. It should be noted that M_{c0} is the polydispersity index and is unity in monodisperse aerosol. The Damkohler number, $\mathrm{Da} = 2^{1/2} B_1 M_{00} V_0^{1/6}/(c/L)$, represents the ratio of the convective time scale to the coagulation time scale. It is obvious that eqs. (11) is the system of partial differential equations and all terms are denoted by the first three moments M_0, M_1, and M_2, and thus the system can be automatically closed. Under these conditions, the first three moments for describing aerosol dynamics are obtained through solving the systems of partial differential equations. Here, the whole derivation of eqs. (11) for the particle fields does not involve any assumptions for the particle size distribution (PSD), and the final mathematical form is explicitly and much simpler than the method of moment (MOM) [6-8].

Results and discussions

The length of the computational domain is chosen as [–1, 1] based on the dimensionless length; initially, the right domain is free of particles, while the left domain is populated by nanoparticles, as shown in fig. 1. The simulations typically employ a discretization mesh consisting of 129 points in the computational domain. Slip conditions are applied at the left and right boundaries of the control volume, that means the zero gradient boundary condition are applied to the boundaries. Throughout the investigation, the parameters is taken as $\mathrm{Re_T} = 1000$ and $\mathrm{Da} = 1$. The time advancement is accomplished by means of a fourth-order Runge-Kutta method, and the size of

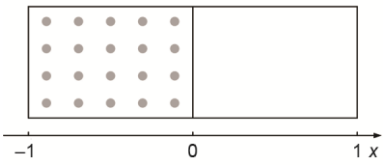

Figure 1. The diagram of particles diffusion in 1-D domain

the time step is set to Δt = 1e – 4, which is small enough to get steady results under the effect of numerical diffusion or dispersion, and each calculation simulated up to a non-dimensional time of t = 100. The initial particle distribution of the present cases is assumed to be the log-normal distribution; then the initial k-th moments for k = 0, 1, 2 are M_{00} = 1, M_{10} = 1, and M_{20} = 4/3 in the particle laden stream, respectively.

In order to validate the numerical method in the present study, it is necessary to have the comparisons the model with other known methods over large evolution time. The evolution of particle moments and mean particle volume without diffusion are shown in fig. 2, all the curves overlap with those of Yu *et al*., and it is difficult to distinguish from one to the other. There exists an asymptotic solution for the distribution of reduced particle number in fig. 2(a), and the increased dimensionless particle moment in fig. 2(c).

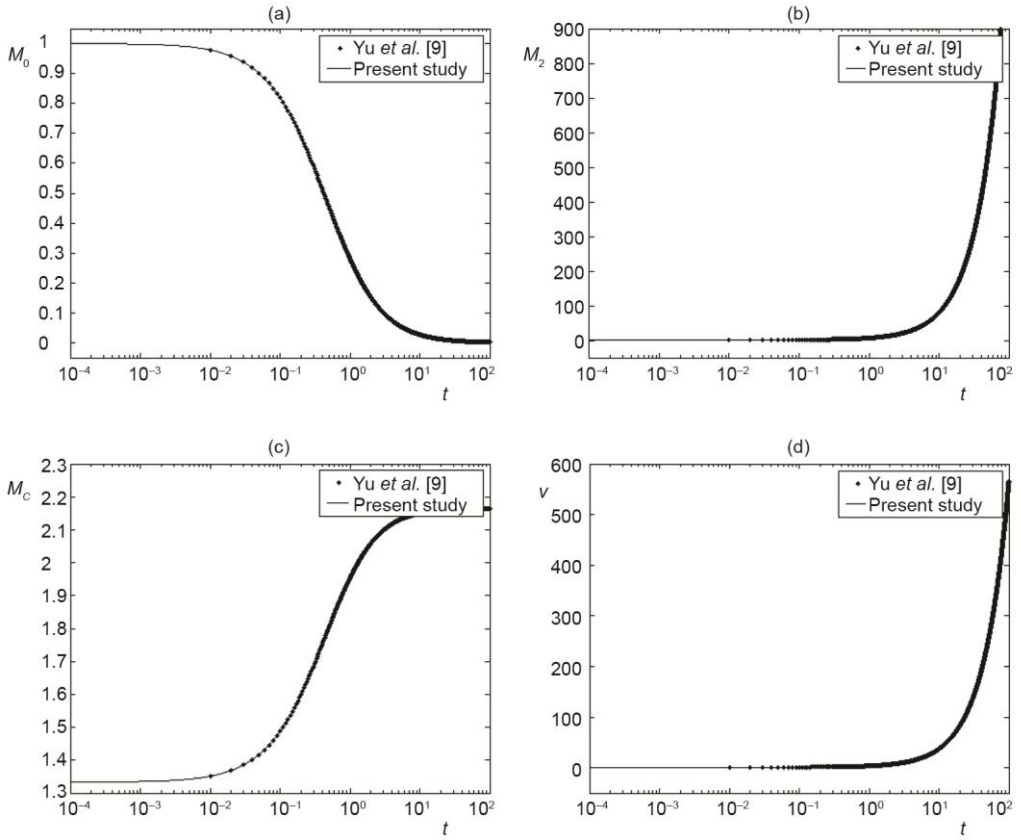

Figure 2. The evolution of particle moments without diffusion

The evolution of particle moments with diffusion in 1-D domain is shown in fig. 3. The results show that total particle number concentration, which is represented by M_0, decreased due to particle coagulation; fig. 2(a) also reveals the decreasing time rate of change in M_0 is about exponentially, which corresponds to the non-linear characteristic of coagulation. At the same time, the value of M_0 in the neighborhood of the interface between the particle laden and particle free domain is greater than that in other places, which is brought out by the combination of coagulation and diffusion, it reveals that the change rate for coagulation is much larger than

that due to diffusion under the given conditions. The evolution of M_1 in the same conditions is shown in fig. 3(b), the total particle volume or mass concentration remains unchanged. It should be pointed out that the value of M_1 develops in an asymmetric manner due to coagulation. Without coagulation, the mass increase of particle on a point in the right zones should be equal to the decrease on the spot in the left zones with the same distance to the interface (*i. e*. symmetric). In some place, the value of M_1 is larger than unit slightly, the reason is that the maximum value of M_0 occurs in the neighborhood of the interface due to the competition between coagulation and diffusion as analysis above, and the particles will be transported from higher to lower particle number concentration zones due to diffusion. If the particles were transported to the left zones, the particle volume concentration will increase and exceeds unit. In an initially mono-disperse aerosol, coagulation produces particles of various size and increases the size of each particle. These processes are indicated by the evolution of the second moment, M_2, and the mean volume concentration, V, which are shown in fig. 3(c) and fig. 3(d). As the coagulation proceeds, the value of M_2 and V increased throughout the whole domain.

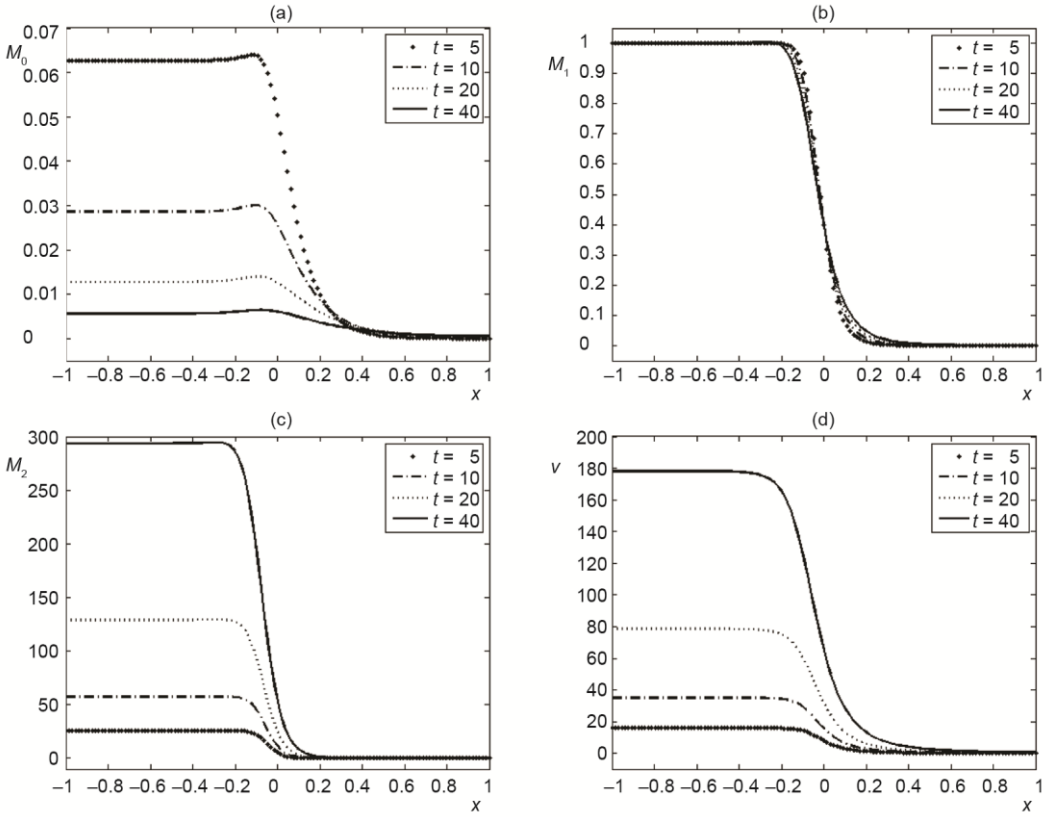

Figure 3. The evolution of particle moments with diffusion in 1-D for Da = 1 and Sc_M = 1

In order to reveal the effects of the diffusion on the particle moments' evolution, simulations for various Schmidt number (Sc_M = 0.5, 1, 2) are performed. The spatial distribution of the moments and the mean volume are presented in fig. 4. In the right zones, the particle moments, M_0, M_1, and M_2, and the mean particle volume, V, grow faster at smaller Schmidt numbers, which is the consequence of greater contribution of diffusion. In the neigh-

borhood of the interface, the concentration of particles shows little variation between different Schmidt numbers. The plot shows again the asymmetric pattern for various particle moments under the completion effect of diffusion and coagulation. The differences for different Schmidt number under the effect of diffusion mainly focus on the neighborhood of the interface; far away the interface the effect of diffusion can be ignored.

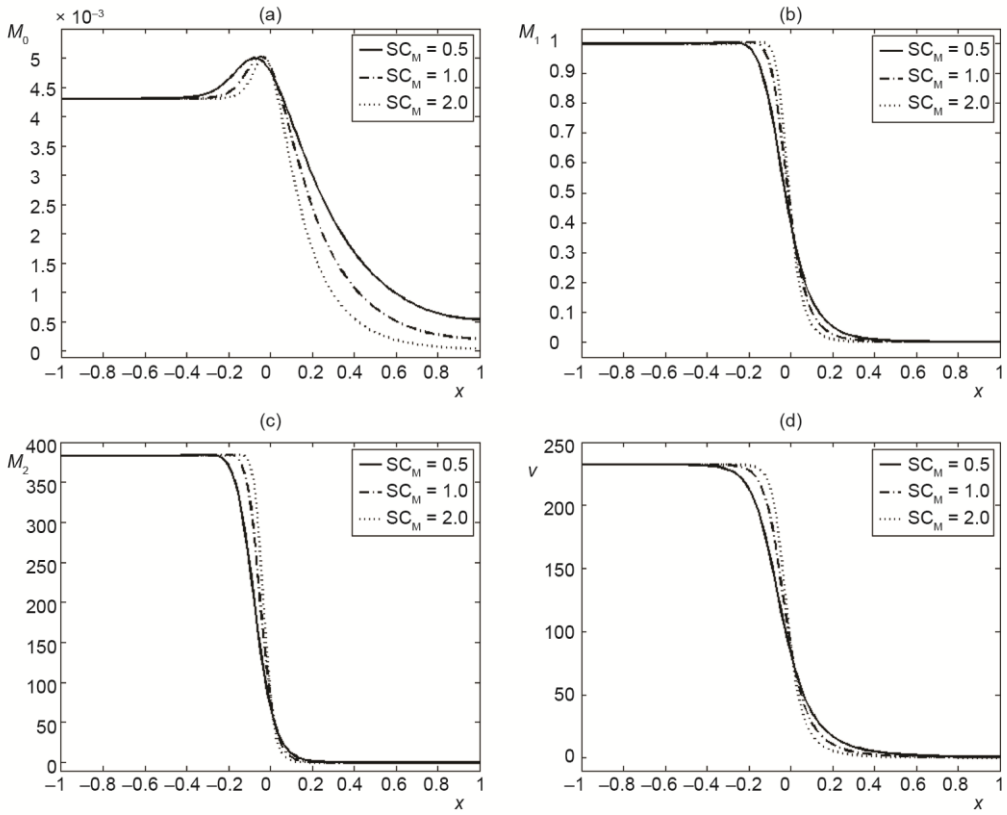

Figure 4. The effect of diffusion on the particle coagulation for Re_T = 1000 and Da = 1 at t = 50

Conclusions

In the present study, a simple 1-D model is built to simulate the effect of diffusion on the coagulation of nanoparticles due to Brownian motion. The Taylor-series expansion method of moment (TEMOM) is utilized to approximate the coagulation of nanoparticles in aerosol general dynamic equation. Generally, the particle number concentration decreases, and total particle volume remains unchanged, and the second particle moment and mean particle volume increase as the particles collide and coagulate.

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