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Deposition and coagulation of polydisperse nanoparticles by Brownian motion and turbulence

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Abstract

Turbulent and Brownian coagulation rates as well as deposition coefficients of polydisperse nanoparticles were measured experimentally. The coagulation rates were obtained from the change in the total number concentration of polydisperse sodium chloride aerosols, with geometric mean diameters ranging from 30 to 120 nm, in a closed chamber at atmospheric pressure. The geometric standard deviations of the experiments were in the range of 1.55–1.65. The experimental coagulation rates took deposition rates into account, because coagulation and deposition occur simultaneously in a closed chamber. As a result of deposition, it was shown that the experimental deposition coefficients of polydisperse aerosols were agreed well with the theoretical data of Park et al. [(2001). Wall loss rate of polydispersed aerosols. *Aerosol Science and Technology*, *35*, 710–717]. It was shown that the effect of the coagulation was much greater than that of the deposition in the high particle number concentration. In addition, the results represented that bigger turbulent coefficients, caused by higher fan rotation speeds, make the turbulent coagulation process become stronger. In the small particle size range, however, the coagulation rates tend to converge though turbulent coefficients are different. In conclusion, it was shown that experimental coagulation rates followed the values of Lee and Chen [(1984). Coagulation rate of polydisperse particles. *Aerosol Science and Technology*, *3*, 327–334], which were calculated for polydispere aerosols in the gas-slip regime and free-molecule regime.

Keywords: Deposition; Turbulent coagulation; Brownian coagulation; Polydisperse aerosols; Coagulation rate

1. Introduction

Particle deposition to the walls in a stirred vessel is of importance in many chemical processes including aerosol reactor. Brownian diffusion controls the deposition rate primarily for small particles, whereas gravitational settling plays a significant role for large particles. Coagulation is a process whereby particles collide with one another, due to their relative motions, and adhere to form large particles. Brownian and turbulent coagulations are caused by random Brownian motion and turbulent flow, respectively. Many properties, such as light scattering, electrostatic charges and

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Nomenclature

GMD	geometric mean diameter (nm)
GMD_0	initial geometric mean diameter (nm)
GSD	geometric standard deviation (dimensionless)
GSD_0	initial geometric standard deviation (dimensionless)
k	deposition coefficient (s^{-1})
K_{co}	collision coefficient for the continuum regime (cc particles^{-1} s^{-1})
k_e	constant related to the turbulent energy dissipation rate (s^{-1})
Kn	Knudsen number (dimensionless)
N	total number concentration of particles (particles cc^{-1})
N_0	initial total number concentration of particles (particles cc^{-1})
$\frac{N}{N_0}$	dimensionless number concentration (dimensionless)
PDF	polydispersity factor (dimensionless)
t	time (s)
γ	coagulation coefficient (cc particles^{-1} s^{-1})

toxicity, as well as physical processes, including diffusion, condensation and thermophoresis, depend strongly on the size distribution. Thus, Brownian and turbulent coagulations are of great interest in many applications, including mechanical and chemical engineering, atmospheric science, combustion technology, inhalation toxicology and nuclear safety analysis (Pratsinis, 1998; Reade & Collins, 2000).

Since the pioneering work of Saffman and Turner (1956), many investigators have studied turbulent coagulation (Abrahamson, 1975; Kruis & Kusters, 1997). Pratsinis (1989) and Xiong and Pratsinis (1991) simulated the change in the size distribution of solid powders undergoing turbulent and Brownian coagulations. Park, Kruis, Lee, and Fissan (2002) numerically studied the evolution of particle size distributions due to Brownian and turbulent coagulations. Numerous studies have been concentrated on the theoretical turbulent coagulation, but very few have focused on the experimental studies. In addition, most of the experimental studies on coagulation have focused on Brownian coagulation only. Experimental works of Brownian coagulation have been conducted by many investigators, such as Wagner and Kerker (1977) and Kim, Park, Song, Kim, and Lee (2003). Therefore, the experimental studies of turbulent coagulation are still needed.

In this study, turbulent and Brownian coagulation rates as well as deposition coefficients of polydisperse nanoparticles were measured experimentally. The experimental coagulation rates took deposition rates into account, because the coagulation and deposition occur simultaneously in a closed chamber. The deposition and coagulation rates were obtained from the change in the total particle number concentration of test aerosols in a closed chamber at atmospheric pressure. Therefore, experiments for both the coagulation and deposition were carried out for the accurate measurement of the turbulent and Brownian coagulation rates.

2. Experiment

The aerosol coagulation chamber in this study consisted of a cylindrical acrylic box, with a bottom surface diameter of 60 cm and a height of 60 cm. A 10 cm steel fan was installed near the center for stirring within the chamber. The chamber was the same as the one previously used in the study of Brownian coagulation (Kim et al., 2003). The inner surface of the acrylic chamber was coated with grease to reduce errors, such as particle bouncing, re-flying and electrostatic losses. Polydisperse sodium chloride (NaCl, solid particles, 2.16 g/cm^3) aerosols were used for the experiments. The aerosols were produced by a spray-drying type generator, and followed by their passage through a Kr-85 charge neutralizer. The aerosols generated were introduced into the coagulation chamber, and mechanically stirred for a short time to maintain gentle mixing.

In closed vessels coagulation is always accompanied by deposition. Thus, a deposition experiment was conducted prior to the coagulation experiment under the same experimental conditions. The initial particle number concentration

Table 1
Experimental condition for particle deposition and coagulation

Parameter	Value
Particle size	30–120 nm
GSD	1.55–1.65
Fan rotation speed	0, 300, 500 and 700 rpm
No. of particles	10^3#/cm^3 (for deposition experiment) 10^6#/cm^3 (for coagulation experiment)
Chamber volume	170 L
Sampling volume	2 L (for Figs. 1 and 3) 4.5 L (for Figs. 2 and 5)

of aerosol particles in the deposition experiment was usually about $10^3\ \text{cm}^{-3}$. However, the initial concentration of aerosol particles for the coagulation experiment was usually about $10^6\ \text{cm}^{-3}$, because coagulation is dominant at high aerosol number concentrations. The geometric mean particle diameters were in the range of 30–120 nm.

The particle concentrations were measured using a condensation particle counter (CPC, TSI model 3022), and the sampling was repeated at intervals of 12 min until the aerosol concentration had decayed to less than half the initial value of the deposition experiment. In addition, this experiment was carried out before changing the initial particle size distribution, which was measured with a scanning mobility particle sizer (SMPS, DMA: TSI model 3071 and CPC: TSI model 3022).

The particle number concentration and size distribution were measured to calculate the coagulation rates. Thus, the initial particle number concentration was measured, and then particle concentration was measured again about 3 min later, which was found to be appropriate for the coagulation experiments (Kim et al., 2003). This relatively short time can reduce the experimental errors, as the particle size increases with time. The particle concentrations and size distributions were measured by a CPC and an SMPS, respectively, in the coagulation experiment. All the experiments were carried out at room temperature and atmospheric pressure. The total sampled volumes in the experiments never exceeded 3% of the total chamber volume. Table 1 shows the experimental condition for the nanoparticle deposition and coagulation experiments.

3. Results and discussion

Fig. 1 shows the experimentally determined values of the deposition coefficients as a function of the particle diameter. As a result, it was shown that the experimental deposition coefficients of polydisperse aerosols were agreed well with the theoretical values of Park, Kim, Han, Kwon, and Lee (2001) who studied deposition rates and polydispersity factor (PDF) for polydisperse particles. The deposition coefficient decreased as the particle diameters increased in the particle sizes ranging from 30 to 100 nm. However, the deposition coefficient of 100 nm particles or larger did not decrease with increase of particle size. This figure represented that the experimental deposition coefficients of 300, 500 and 700 rpm as the fan speeds followed the theoretical data with 0.0095, 0.02 and 0.032 s^{-1} as k_e (constant related to the turbulent energy dissipation rate), respectively. A stirring fan rotation speed of 0 rpm indicates Brownian deposition because no turbulent flow occurred. In Fig. 1, the coefficients of Brownian deposition were not compared with the theoretical data of Park et al. (2001), because their theoretical results were obtained under the condition of turbulent effect. The geometric standard deviations (GSDs) in this experiment were in the range of 1.55–1.65.

Fig. 2 shows the particle number concentration ratio (N/No) with elapsed time. The initial geometric mean diameter (GMD) and GSD in this experiment were 50 nm and 1.6, respectively. The results in this figure were measured simultaneously at intervals of 270 s. The data points for the deposition in Fig. 2 were expressed from Equation (2) of Kim et al. (2003) using the deposition coefficients in Fig. 1. The deposition coefficients of the larger particle sizes were applied to the graph in Fig. 2 as the coagulation time increased. The deposition rates changed due to the growth in size caused by the particle coagulation with each other. Thus, the corrected deposition coefficients, which were the same as those of bigger particles, were applied whenever the particle size increased by 10%. The data points of the sum of the deposition and coagulation (total in Fig. 2) were plotted from the raw experimental data. The data points for the coagulation were attained by subtracting the deposition values from the raw experimental data. The particle number

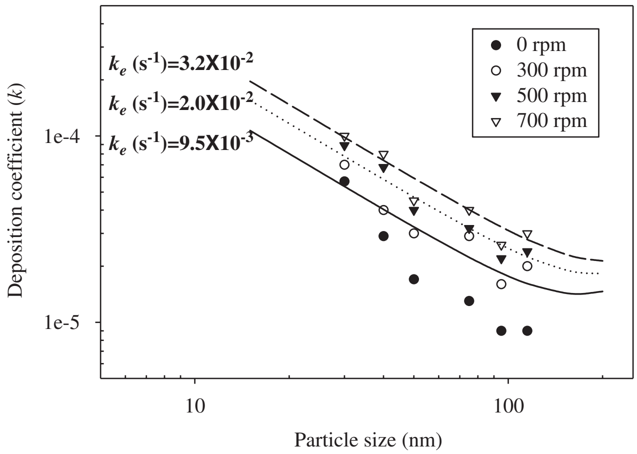

Fig. 1. Comparison of deposition coefficient values from this experiment with theoretical curves for best-fit values of k_e (s^{-1}). Symbol: experimental results, line: theoretical data.

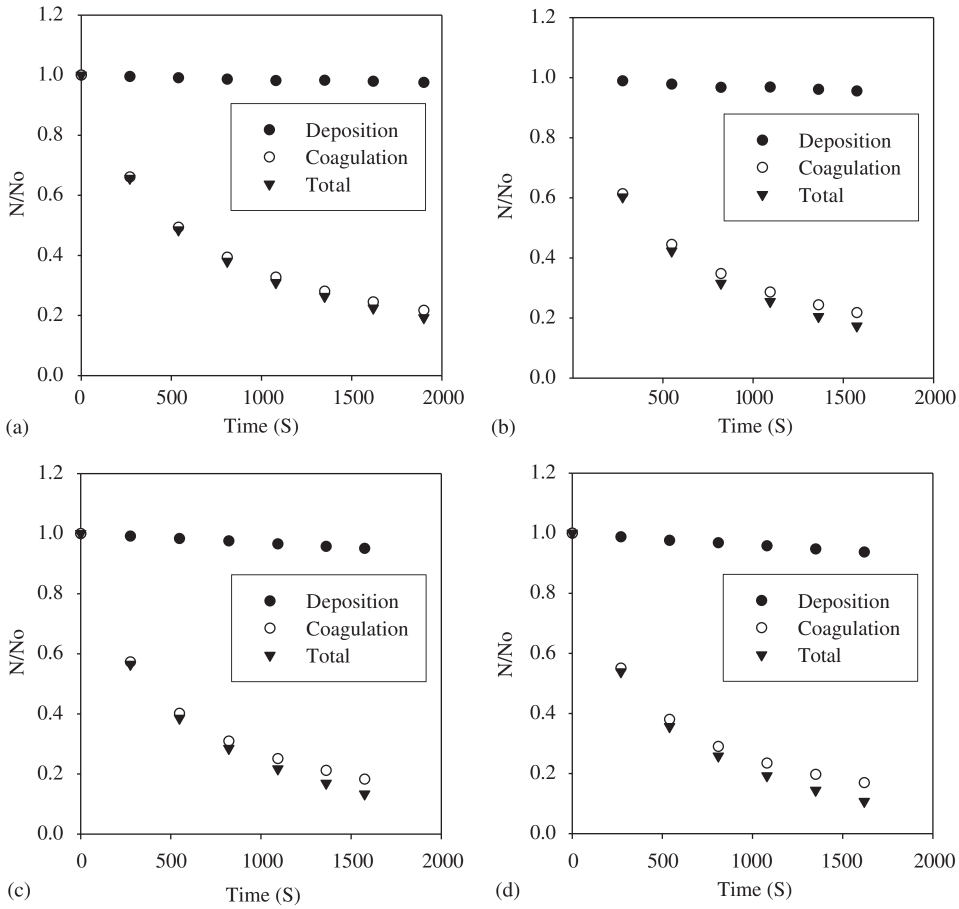

Fig. 2. Change of particle number concentration ratio with elapsed time. The initial geometric mean diameter and geometric standard deviation were 50 nm and 1.6, respectively. (a) 0 rpm, (b) 300 rpm, (c) 500 rpm and (d) 700 rpm.

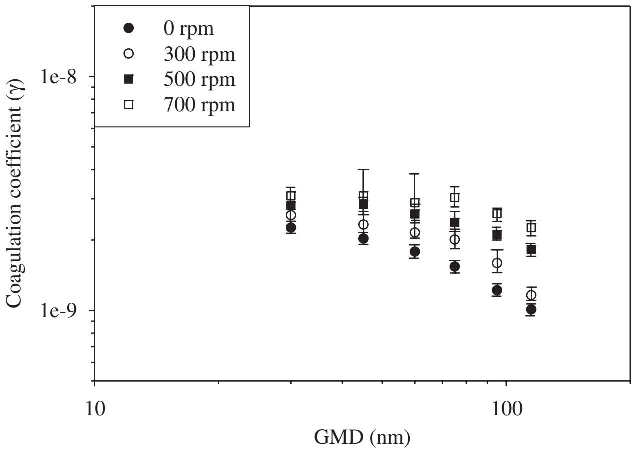

Fig. 3. Coagulation coefficients for different geometric mean diameters and fan speeds (rpm).

concentrations were reduced by coagulation and deposition over time. As shown in Fig. 2, the decrease in the particle concentration caused by coagulation was much higher than that by deposition. It is our belief that the aerosol particles generated in the experiment were about 10^6 #/cm^3, and so the effect of the coagulation was much greater than that of the deposition.

In this figure, the particle number concentration ratio decreased more rapidly when the fan rotation speed was increased. It can be assumed that the bigger turbulent coefficients, caused by higher fan rotation speed, made the turbulent coagulation process stronger.

Fig. 3 shows the coagulation coefficients as a function of the GMD. The coagulation coefficients were calculated from the experimental results using Equation (6) of Kim et al. (2003). A stirring fan rotation speed of 0 rpm indicates Brownian coagulation in this figure. Other fan rotation speeds (300, 500 and 700 rpm) meant that coagulation due to Brownian motion and turbulent flow occurred with different intensities. This result showed that overall, the coagulation coefficients were small in the large initial particle size and increased with decrease of the initial particle size. The coagulation coefficients tend to converge in the smaller particle size range, though fan rotation speeds are different. It means that the smaller particle size, the smaller turbulent coagulation (Park et al., 2002). In the large particle size range, however, higher fan rotation speeds yield higher coagulation coefficients because high rotation speeds cause high turbulent mixing and high turbulent coagulation, as mentioned above.

Fig. 4 shows the comparison of experimentally determined Brownian coagulation coefficients (at the fan rotation speed of 0 rpm) with the theoretical data of Lee and Chen (1984). The theoretical values were calculated from the equations of Lee and Chen (1984), who studied coagulation rates of polydisperse aerosols theoretically. The result showed that experimental coagulation rates followed the values of Lee and Chen in the gas-slip regime and decreased a little near free-molecule regime. However, experimental values were somewhat higher than theoretical data. It is believed that this small difference came from experimental errors, which were turbulent flow and eddy caused by sampling flow. In this figure, the GSD of theoretical data was 1.6. However, GSD of this experiment was in the range of 1.55–1.65 as mentioned above. Therefore, experimental values were corrected by PDF. The PDF is defined as the ratio of the actual coagulation parameter for the polydisperse system to that of a monodisperse aerosol, with particle size equal to the mean radius of the polydisperse system (Lee & Chen, 1984; Otto, Fissan, Park, & Lee, 1999; Park, Lee, Otto, & Fissan, 1999). The polydispersity effects were obtained from the works of Lee and Chen (1984). They concluded that the coagulation rate for polydisperse aerosols is substantially higher than that for monodisperse aerosols.

Fig. 5 represents the GMD ratios (GMD/GMD0) with increase in time. The GMD ratio at fan rotation speeds of 300, 500 and 700 rpm had a very similar tendency to that at 0 rpm. However, the result at 700 rpm had the greatest GMD ratio. This meant that the coagulation rate at 700 rpm was higher than that of any other fan rotation speed. When the fan rotation speed was 700 rpm, the turbulent mixing was greater than that at any other case, because the coefficients of the eddy diffusivity were evaluated from the turbulent energy dissipation rate. Thus, the turbulent coagulation at 700 rpm would be higher than that at 300 or 500 rpm.

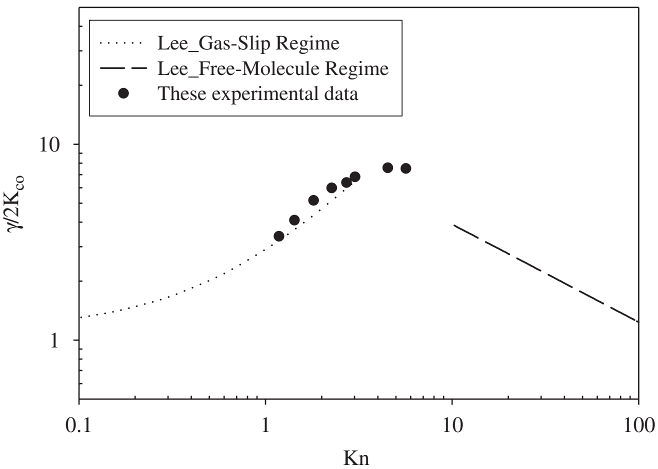

Fig. 4. Comparison of the experimental coagulation rate with the theoretical data of Lee and Chen (1984) for GSD = 1.6.

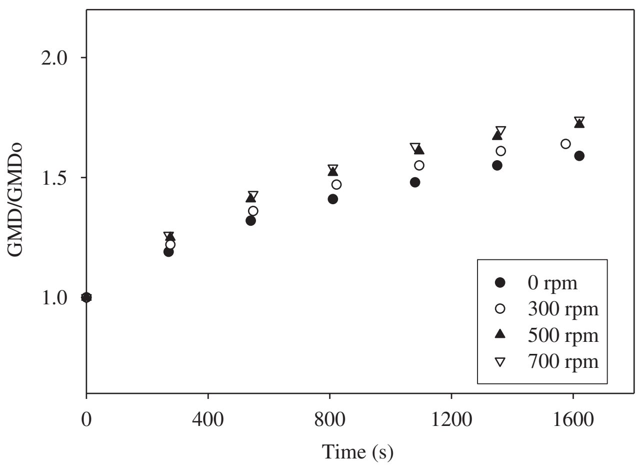

Fig. 5. Comparison of geometric mean diameters under different fan speed conditions. The initial geometric mean diameter and geometric standard deviation were 50 nm and 1.6, respectively.

4. Conclusion

In this study, the turbulent and Brownian coagulation rates for polydisperse nanoparticles were measured experimentally. The size of the particles used ranged from 30 to 120 nm as the geometric mean diameter (GMD) and geometric standard deviation (GSD) in this experiment in the range of 1.55–1.65.

As a result, it was shown that the experimental deposition coefficients of polydisperse aerosols were agreed well with the theoretical values of Park et al. (2001). Fig. 1 represented that the experimental deposition coefficients of 300, 500 and 700 rpm as the fan speeds followed the theoretical data with 0.0095, 0.02 and 0.032 s^{-1} as k_e, respectively. In addition, the results showed that the effect of the coagulation was much greater than that of the deposition at the higher particle number concentration, and the bigger turbulent coefficients caused by a higher fan rotation speed made the turbulent coagulation process stronger. In the small particle size range, however, the coagulation rates tend to converge though turbulent coefficients are different. As a result of coagulation experiment, it was shown that experimental coagulation rates followed the values of Lee and Chen (1984), which were calculated for polydisperse aerosols in the gas-slip regime and free-molecule regime.

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