Validation of Unipolar Diffusion Charging Models for Spherical and Agglomerated Nanoparticles

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Abstract. An ion-jet diffusion charger was used in this study to investigate the diffusion charging of spherical and agglomerated nanoparticles, and validate corresponding theoretical models. Results show that the limiting-sphere model and White’s theory could preferably predict the diffusion charging of spherical particles, compared with other models. As to agglomerated particles, it is affected by primary particle size and sintered morphology to some extent. Especially for loose agglomerate which is point-to-point contact, obviously more charges could be acquired at same mobility diameter in unipolar diffusion charger. In addition, it was validated that all of Chang’s theory, normalized capacitance model and collision kernel model are in good agreement with experiments results. Chang’s theory and normalized capacitance model, however, are more concise and could be used to evaluate diffusion charging of non-spherical particles in real occasions.

1. Introduction

Charging properties of nanoparticles play important roles in particle collection, aerosol purification and measurement [1-3]. In the field of coal-fired and industrial plant, the electrostatic precipitator (ESP) is one of the most popular techniques to remove particles in exhausted gas. For this method, the collection efficiency of nanoparticle largely depends on its diffusion charging in corona discharge, so investigating the charging mechanism is of great significance to the optimization and prediction of collection efficiency [4]. In another field, aerosol measurement, particle charging is used in many instruments, such as electrical low pressure impactor, to classify and characterize particles [5]. Therefore, an appropriate model to evaluate particle charging, including spherical and agglomerated particles, is important for the further development of such instruments.

Given that the complexity of charging process, it is difficult to describe diffusion charging in the whole size range by just utilizing one theoretical model. Diffusion-mobility model, which was first applied in diffusion charging of spherical particles, was reported to have a good accuracy in the continuous regime [6]. Subsequently, Fuchs limiting-sphere theory and BKG model were developed to predict diffusion charging in transition regime, while White’s theory was applied in free-molecule regime [6]. With regard to non-spherical particles, Laframboise [7] first proposed a theoretical model which is based on diffusion mobility theory, analytical solution of electric field near the charged particle and ion flux equation. Afterwards, Chang [8] established a model to be applied in continuous and free-molecule regimes. On this basis, many scholars [9,10] acquired the charge distribution of
primary particles in an agglomerate, which further enriched charging models of non-spherical particles. Gopalakrishnan [11] proposed an ion-particle collision kernel model in the whole range of Knudsen number to solve particle charge distribution, which utilized dimensional analysis, Brownian diffusion dynamics and molecular dynamic methods. However, this model has not been directly verified by experiments. Additionally, Biskos [6] simulated particle diffusion charging by Monte Carlo method and compared with other charging models. Even though popular charging models used in early stage were discussed and analyzed in Biskos’study [6], effective experiments are still needed to verify current theoretical models.

In this study, an ion-jet diffusion charger was used to evaluate and verify the most of charging models for both spherical and agglomerated particles. The charger adopts an ion-particle impingement mode, which minimizes the effect of external electric field on particle charging and loss. By means of this setup, theoretical models for spherical particles were first validated. Afterwards, agglomerated particles were produced in tandem tube-furnace and the influence of furnace temperature on particle charging was expatiated. Finally, multiple non-spherical charging models were validated by experimental results.

2. Theoretical models

2.1. Spherical particle

Diffusion charging models for spherical particle mainly include White’s theory, Fuchs limiting-sphere theory, BKG model and diffusion-mobility theory, which are shown in equation (1) ~ (4), respectively.

\[
\frac{dq_p}{dt} = \frac{\pi}{4} d_p^2 \nu_i \rho_i \exp\left(\frac{-q_i e}{2\pi e_0 d_p kT}\right),
\]

where \(q_p\) is charges carried by single particle, \(t\) is charging time, \(d_p\) is particle diameter, \(\nu_i\) is the thermal velocity of ions, \(\rho_i\) is ion density, \(e_0\) is vacuum dielectric constant, \(k\) is Boltzmann constant and \(T\) is the absolute temperature.

Fuchs limiting-sphere theory assumes that the outer space of a particle is divided into two parts by a concentric sphere. In the gap of hypothetical sphere and particle surface, the movement of gas ions is dominated by thermal diffusion and ion-particle interaction potential, while it is controlled by macroscopic diffusion-mobility theory in the outer space of hypothetical sphere. Based on similar flux theory, BKG model and diffusion-mobility theory are formulated as equation (3) and (4), respectively.

\[
J = \frac{\pi \nu_i \delta^2 \rho_i \exp(-\phi(\delta)kT)}{1 + \exp(-\phi(\delta))\nu_i \delta^2 / 4D \int_{\infty}^{1/r^2} \exp(-\phi(r)kT) dr},
\]

\[
J = \frac{\pi \nu_i \delta^2 \rho_i e_0}{4(1 + \lambda E_i / 2\sqrt{\pi} E_0)},
\]

\[
J(r) = -4\pi \delta^2 (D \frac{d\rho_i}{dr} - Z \rho_i E(r))
\]

where \(\gamma\) is the probability of ions that enter into the hypothetical sphere and transfer charges to the particle, \(\delta\) is the radius of hypothetical sphere, \(\phi(\delta)\) is the potential at the location, \(\delta\). \(D\) is ion diffusion coefficient, \(E_0\) is the zeroth-order correction of molecule-flux flux, \(E_i\) is first-order correction, and \(\lambda\) is the self-defined parameter. In equation (4), \(Z\) is ion mobility, \(E(r)\) is the field strength at the distance \(r\) from particle.

2.2. Agglomerated particle

Diffusion charging models for agglomerated particle primarily involve Laframboise’s theory [7], Chang’s theory [8], normalized capacitance model [9] and ion-particle collision model [11], which are formulated in equation (5), (6) ~ (8), (9) and (10), respectively. Laframboise’s theory was also
established based on flux theory, while the normalized capacitance model was acquired by dimensionless surface potential and self-defined normalized capacitance. For Chang’ theory, equation (6) and (7) are applicable to the continuous regime, whereas the equation (8) corresponds to free-molecule regime. Additionally, Monte Carlo method could be also applied to the calculation of particle charging in diffusion charger, and its effectiveness is also validated in section 4.2.3.

\[
J = 4\pi \rho q_p \frac{L}{\ln(2L/ \ln(1 - \exp(-\varphi_p)))} \exp(-\varphi_p),
\]

(5)

\[
q_p = \frac{C_p \rho C_p \rho \beta_{p,i}}{\varepsilon_0 (\phi_p < 0.1)},
\]

(6)

\[
q_p = \frac{2C_p kT}{e^2} \left[ (\frac{e^2}{kT} \rho C_p \rho \beta_{p,i}) + 1 \right]^{0.5} - 1, (\phi_p < 1),
\]

(7)

\[
q_p = \frac{2C_p kT}{e^2} \ln(1 + e^2 \rho C_p \rho \beta_{p,i} S_p t),
\]

(8)

\[
q_p = \frac{\varphi_p kT}{e^2} C_p = \frac{\varphi_p kT}{e^2} 2\pi \varepsilon_0 d_p C_p',
\]

(9)

\[
\frac{dq_p}{dt} = R_{p,i} - R_{p,i} = \rho_p \beta_{p,i} n_p - \beta_{p,i} n_p
\]

(10)

where \(L\) is the ratio of polar radius to midline radius, \(\varphi_p\) is dimensionless surface potential, \(Kn_i\) is the effective Knudsen number, \(C_p\) is particle capacitance, \(C_p'\) is normalized capacitance, \(S_p\) is particle geometric surface area, \(R_{p,i}\) is the charging rate of a particle carried with \(p\) elementary charges, \(\beta_{p,i}\) and \(\varepsilon_0\) are corresponding collision kernel and particle number concentration, respectively.

3. Experiments

Figure 1 shows the setup diagram for unipolar diffusion charging, which involves aerosol generation for both spherical and agglomerated particles, particle classification and measurement, unipolar charging and detection. Spherical particles are first produced in a collision-type atomizer and subsequently flow into a diffusion dryer and a neutralizer. 0.01% K₂SO₄ solution and Di-Ethyl-Hexyl-Sebacate (DEHS) liquid are individually filled in the atomizer to produce polydisperse salt-particles and oil-particles, respectively. After moisture absorption in dryer and charge neutralization in neutralizer, polydisperse particles are classified into monodisperse particles by a DMA (TSI, 3081) followed by a neutralizer and a CPC (TSI, 3776). For non-spherical particles, tandem furnaces and an agglomeration chamber were used to produce agglomerate and aggregate in different fractal dimensions. Firstly, solid silver is placed in the centre of first tube-furnace with 1150°C, then gaseous silver is produced continuously at this temperature. At the exit of first tube-furnace, gaseous silver gradually condenses into a larger number of nanoparticles due to the decrease of gas temperature. Secondly, these nanoparticles collide into loose agglomerates in agglomeration chamber by random Brownian diffusion. After that, loose agglomerates are sintered in the second tube-furnace (25°C~600°C) into aggregates in different fractal dimensions and neutralized to reach Boltzmann equilibrium distribution in a neutralizer.

Aerosol flow produced by atomizer or tandem furnaces is then divide into two branches after classification by a DMA. The one flows into a CPC to detect particle concentration while the other enters into a unipolar charging system. At the inlet of this system, the aerosol is split into two portion again. One portion of 1.5L/min directly flows into a mixing chamber while the other portion of 1L/min is filtered and introduced into a diffusion charger. In this charger, needle electrode is connected to the positive potential (+2.5kV), then a large number of positive ions are produced and carried into the mixing chamber. Injected ions within this mixing chamber impinge with particles, so that particles could acquire charges. After that, charged particles exit from mixing chamber and pass through a
needle-tube ESP (20V) followed by an electrometer to detect induced electric current. Charges carried by single particle could be calculated by equation (11):

$$q_p = I / ef \cdot f c$$

(11)

where $I$ is electric current detected by the electrometer, $f$ is the aerosol flowrate and $c$ is particle number concentration.

Figure 1. Setup diagram used in this study

Figure 2. Validation results for spherical particles (a) particle size distribution, (b) comparison with multiple theoretical models

4. Results and discussion

4.1. Spherical particle

Particle size distribution and charges carried by single particle in diffusion charging are shown in figure 2(a) and 2(b), respectively. Similar distribution, peak size and absolute concentration for K$_2$SO$_4$ and KCl aerosols could be seen in figure 2(a), just expect for material composition. In figure 2(b), diffusion charges carried by single particle increase with mobility diameter, which is because particle surface area is an important factor in diffusion charging at same charging time and ion concentration. As a contrast, material composition has a marginal effect on diffusion charging, which agrees well
with limiting-sphere theory and shin’s study [12]. In order to validate current charging models, Figure 2(b) also shows the comparison of theoretical models with experimental results. Major parameters used in models include the product of ion concentration and charging time \( (\rho t = 2.5 \times 10^{13} \text{s/cm}^3) \) and ion mobility \( (Z_i = 1.15 \text{cm}^2/\text{V×s}) \). For all theoretical models, both Coulomb force and image force are considered in the process of ion-particle collision. Compared with experimental results, all models predict a reasonable charging trend with mobility diameter. However, gaps for absolute level also occur in figure 2(b). BKG model and diffusion-mobility theory slightly deviate from testing results while limiting-sphere theory and White’s theory are in accordance with experimental results.

4.2. Agglomerated particle

4.2.1. Effect of evaporation temperature on agglomerate diffusion-charging. Effects of evaporation temperature on agglomerate size distribution and diffusion charging are shown in figure 3(a) and 3(b), respectively. Unimodal distribution trend could be seen in figure 3(a) and the peak size gradually increases with temperature, stating that average diameter also increases with temperature of the first furnace. A reasonable explanation for this phenomenon is that the amount of gaseous silver would quickly increase once evaporation temperature is improved, so that both size and number of primary particle produced by condensation increase [13]. As a result, these primary particles coalesce into the larger agglomerate with point-to-point structure. Figure 3(b) shows that charges acquired by agglomerates just slightly increase with evaporation temperature at same mobility diameter, suggesting that the primary particle in this study has a marginal effect on diffusion charging of agglomerate. According to Chang’s theory [8], particle surface area and capacitance are crucial factors in diffusion charging. Whereas increasing evaporation temperature could not change agglomerate structure in a large extent, so just minor increase occurs in figure 3(b).

![Figure 3](image-url)

Figure 3. Effect of evaporation temperature on size distribution and diffusion charging (a) particle size distribution, (b) charges acquired in diffusion charger.

4.2.2. Effect of sintering temperature on agglomerate diffusion-charging. Effects of sintering temperature on particle size distribution and diffusion charging are shown in figure 4(a) and 4(b), respectively. With an increase of sintering temperature, peak size in figure 4(a) shifts from 80nm to 55nm and the size range becomes narrow. In room temperature, particles produced by tandem furnaces are regarded as loose agglomerates with fractal dimension of 1.78 [14]. When sintered in high temperature, agglomerates gradually become dense ellipsoid or nearly spherical particles, meanwhile the fractal dimension increases from 1.78 to 3 approximately. As particle morphology varies, the drag force applied to the particle and mobility diameter selected by DMA also change, which agrees well with experiment in this study. In figure 4(b), sintering temperature has a significant influence on particle charges acquired in diffusion charger, with more charges in the higher temperature. In a specific charger, particle charges in steady stage depend on collision frequency of ion-particle and
corresponding adsorption efficiency. It is generally assumed that charges transfer to conductive particle immediately once the event of ion-particle collision occurs in a diffusion charger [11]. Consequently, only ion-particle collision probability is the main parameter to determine unipolar diffusion charging. At same mobility diameter, loose structure of agglomerate could reduce the distance of ion-particle collision to some extent, meanwhile the large surface area could increase the collision probability and storage more charges. Therefore, the geometric structure of particle itself is the one of important factors to affect diffusion charging, and large surface area could significantly promote ion adsorption on particle surface.

![Figure 4. Effect of sintering temperature on size distribution and diffusion charging (a) particle size distribution, (b) charges acquired in diffusion charger.](image)

![Figure 5. Comparison with multiple theoretical models.](image)

**4.2.3 Comparison with theoretical models.** Figure 5 shows the comparison of experimental data with modeling results predicted by multiple theoretical models. It should be noted that experimental data in figure 5 correspond to charges carried by loose agglomerates which are assumed in most of models. In a contrast, results provided by Monte Carlo simulation are quite different from that of other models as well as experiment. However, it should be attributed to the modeling rectangular particle in Monte Carlo simulation to some extent. For this shape, the surface area just varies a little at different mobility diameters but the aspect ratio changes considerably. Compared with other models, it could be found that the aspect ratio has a significant effect on diffusion charging, which is mainly because aspect ratio affects the potential energy distribution on particle surface and probability of ion-particle collision. As an overall comparison in figure 5, Chang’s theory, normalized capacitance method and collision kernel model could provide a good prediction on diffusion charging. Ulteriorly, collision kernel model
can describe the charging process in detail, while Chang’s theory and normalized capacitance model are more concise to be applied in real conditions.

5. Conclusion

An ion-jet diffusion charger was adopted in this study to investigate the diffusion charging of both spherical and agglomerated particles, and validate multiple theoretical models. Results show that charges acquired by spherical particles in diffusion charger increase with an increase of mobility diameter. This experiment also verifies that Fuchs limiting-sphere theory and White’s theory could provide a good prediction for spherical particles. For agglomerated particles, diffusion charging is mainly affected by particle morphology and primary particle number while primary particle size is the secondary factor. With increasing sintering temperature, particle fractal dimension also increases, whereas charges acquired by particles decrease. Similarly, multiple theoretical models were validated by experiments in this study, indicating all of Chang’s theory, normalized capacitance model and collision kernel model agree well with testing data. Further, Chang’s theory and normalized capacitance model are more concise and applicable to real occasions.

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