Atmospheric humidity and particle charging state on agglomeration of aerosol particles

He, Yuanping; Gu, Zhaolin; Lu, Weizhen; Zhang, Liyuan; Okuda, Tomoaki; Fujioka, Kentaro; Luo, Hui; Yu, Chuck Wah

Published in:
Atmospheric Environment

Published: 15/01/2019

Document Version:
Final Published version, also known as Publisher’s PDF, Publisher’s Final version or Version of Record

License:
CC BY

Publication record in CityU Scholars:
Go to record

Published version (DOI):
10.1016/j.atmosenv.2018.10.035

Publication details:

Citing this paper
Please note that where the full-text provided on CityU Scholars is the Post-print version (also known as Accepted Author Manuscript, Peer-reviewed or Author Final version), it may differ from the Final Published version. When citing, ensure that you check and use the publisher’s definitive version for pagination and other details.

General rights
Copyright for the publications made accessible via the CityU Scholars portal is retained by the author(s) and/or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights. Users may not further distribute the material or use it for any profit-making activity or commercial gain.

Publisher permission
Permission for previously published items are in accordance with publisher’s copyright policies sourced from the SHERPA RoMEO database. Links to full text versions (either Published or Post-print) are only available if corresponding publishers allow open access.

Take down policy
Contact lbscholars@cityu.edu.hk if you believe that this document breaches copyright and provide us with details. We will remove access to the work immediately and investigate your claim.

Download date: 19/12/2019
Atmospheric humidity and particle charging state on agglomeration of aerosol particles

Yuanping Hea,b, Zhaolin Gua,b,*, Weizhen Lu,b,***, Liyuan Zhanga, Tomoaki Okudad, Kentaro Fujiokad, Hui Luoa,e, Chuck Wah Yua,f

a Department of Earth and Environmental Sciences, Xi’an Jiaotong University, Xi’an, 710049, China
b Department of Architecture and Civil Engineering, City University of Hong Kong, Kowloon Tong, Hong Kong
c Department of Environmental Engineering, Chang’an University, Xi’an, 710064, China
d Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, 223-8522, Japan
e Meteorological Bureau of Xi’an City, Xi’an, 710016, China
f International Society of the Built Environment (ISBE), Milton Keynes, UK

ARTICLE INFO

Keywords:
Haze formation
Aerosol particles
Atmospheric humidity
Particle charging
Liquid bridging forces
Electrostatic interactions
Agglomeration rate

ABSTRACT

Formation of haze is a phenomenon dependent on the relative atmospheric humidity and concentration of aerosol particles. The physical and chemical reactions on particle surfaces would lead to variations in particle sizes. This paper focuses on the physical behaviour of aerosol particles under the influence of atmospheric humidity, which produces liquid bridging forces and electrostatic interactions among particles. By water absorption experiment, a correlation between relative humidity (RH) and water content on particles was obtained. Through theoretical derivation, a relationship between the relative humidity and humidity ratio was established for calculating liquid bridging forces. The findings from experiments on atmospheric particles charging, showed most aerosols were negatively or positively charged and the average charges on these particles was more than one. An extended soft-sphere discrete element method (DEM) was used to simulate the evolution of aerosol particles, encapsulated in water vapour by considering liquid bridging forces, electrostatic interactions and Brownian forces. Results suggest that the agglomeration rate of particles would increase with a rise in the atmospheric humidity due to the increased liquid bridging forces that enhance the agglomeration velocity. The higher humidity would enhance the ionization on particle surfaces, which could affect electrostatic interactions. This paper provides an insight of a mechanism for formation of haze in atmosphere.

1. Introduction

Heavy haze (with visibility less than 2 km and under RH < 80%) is generally attributed to high concentrations of particulate matter (PM) in atmosphere, such as fine (PM2.5, aerodynamic diameter ≤ 2.5 μm) and ultrafine particles (UFPs, diameter ≤ 100 nm) (Chan and Yao, 2008; Yu et al., 2018). According to the Chinese National Ambient Air Quality Standard, GB 3095-2012 standard (http://www.mee.gov.cn/), the daily mean ambient PM2.5 mass concentration should not exceed 75 μg m⁻³. Therefore, ambient concentration exceeding this air quality criterion is recognized as a polluted condition. Many observations have indicated that the occurrence of severe air pollution are characterized by a rise of the number concentration of larger particles (accumulated mode), which is closely related to the agglomeration of ultrafine particles in specific conditions (Cheng et al., 2015; Jayaratne et al., 2011; Shen et al., 2015; Wang et al., 2014). Wang et al. (2014) measured the aerosol number concentration and particle size distribution during different levels of haze in Shanghai in 2009. The results showed that as haze events become more severe, the number concentration of particles smaller than 50 nm was decreased, but there was an increase in particles of 50–200 nm and 0.5–1 μm.

Atmospheric visibility is mainly related to the number concentration of particles falling within the visible wavelength range of 0.1–1 μm; as well as the scattering and extinction of accumulation mode of particles (Huang and Yang, 2013). So, haze formation could be resulted mainly from an increase in the number concentration of larger-size particles (> 0.1 μm). Therefore, the meteorological conditions and the corresponding physical-chemical processes affecting the increase in...
mass concentration and mean diameter of particles should be further studied.

The increase in the mean diameter (MD) of aerosol particles is mainly dominated by physical agglomeration and chemical growth. Zhang (2017) used a population balance equation to describe the size spectrum of fine particulate matter, and the respective contribution of the physical agglomeration rate and the chemical growth rate. A great difference in contribution of physical and chemical effects can be found in different cities leading to different level of haze. In our previous research, six haze episodes resulting from accumulative-rise of PMs in Xi’an were examined. The chemical and physical effects on the MD have an average value of 9.14% and 90.86%, respectively (Zhang, 2017). In six accumulative-rise haze episodes in Beijing, the chemical and physical effects on the MD have an average value of 19.62% and 80.38%, respectively (Zhang, 2017). Therefore, the physical agglomeration rate has an important effect on the increase in the mean diameter (MD) of aerosol particles during the accumulative-rise process, and the primary emission of particles would have an important role in the rise of aerosol mass concentrations. This paper focuses on the physical effect on aerosol particles.

Humidity is an important factor that can affect the physical-chemical behaviour of aerosol particles, thus triggering haze formation and degrading atmospheric visibility (Malm and Day, 2001; Xiao et al., 2011). During the humidification of atmospheric aerosol, an increase in the size of majority of ultrafine particles to a mid-visible light scattering range occurs; thus increasing the scattering coefficient and reduce visibility in the atmosphere (Lee and Tsai, 1998; Tang, 1997). Ding and Liu (2014) analyzed the long-term variations of haze in China over the past 50 years, and estimated that the mean relative humidity during hazy days is approximately 69%. Tie et al. (2017) also reported that a higher RH, along with a shallow planetary boundary layer, could induce a trapping and a massive increase in PM in the near-surface air. In addition, during an extreme winter pollution event in Beijing, Li et al. (2014) observed an increase in aerosol volume concentration and a decrease in particle number after partial dissipation of fog. Also, a significant increase in water content in the aerosols can occur in a short time.

Previous studies in describing the impact of humidity on haze formation, mainly focused on various water soluble components in airborne particles and their hygroscopic effects (Covert et al., 1972; Tie et al., 2017; Sun et al., 2013). However, there have not been much research on the physical behaviours between particles, which would actually lead to particle evolution. Water molecules adsorbed on surfaces of particles in the atmosphere can play a very complicated role in the process of particle evolution. If a thin water film is present on the surface of suspended aerosol particles, a “liquid bridge” could be formed at the contact interface once particles collide (Li et al., 2011). In addition, the transfer rate of free ions in the surface absorption layer would be affected by the atmospheric relative humidity, and the dissolved ions would be redistributed by the “liquid bridge”, producing charged particles after separation (Gu et al., 2013; Zhang et al., 2016). Furthermore, the condensation or evaporation of water on particle surface are associated with the variation of RH. These processes would lead to the formation of a temperature gradient inside particles, and then a migration of H⁺/OH⁻ ions. The difference in mobility of H⁺/OH⁻ ions would results in a net negative/positive charges on particle surfaces (Latham and Mason, 1961). Okuda et al. (2015) measured the electrostatic charging state of individual ambient aerosol particles by using a Kelvin probe force microscopy (KPFM) and found that the particles were negatively or positively charged. Besides, Jayaratne et al. (2016) measured the number concentration of charged particles (2.8–40 nm) by using a neutral cluster and air ion spectrometer (NAIS) and the results showed that the concentration of charged particles varied during particle formation events. In fact, charges on the surfaces of particles would introduce an electrostatic force between particles, promoting the agglomeration of ultrafine particles, enhancing the formation of secondary chemical reactions, and then further accelerating the growth rate of particle sizes (Petersen and Saykally, 2005; Wei and Gu, 2015). In this paper, humidity and electrical charges on particles are examined as important factors that could cause changes in the physical characteristics of aerosols, including liquid bridging and electrostatic forces.

A particle-resolved model PartMC-MOSAIC was used to simulate the diversity in per-particle composition and the variation of the aerosol mixing state (Laura et al., 2016; Liu et al., 2011; Ma et al., 2012). A Monte Carlo approach was used in the PartMC model to simulate the stochastic coagulation of particles (Ma et al., 2012). In fact, the Monte Carlo approach does not really track every particle, but determines whether there is collision between particles by using a probabilistic sampling method, so that the system’s macroscopic behaviours cannot be fully predictable (He et al., 2018; Zhou et al., 2015). A discrete element method (DEM) was used for the numerical simulation in this work, in which the motion, collision and adhesion of individual particles are resolved in time and space. Although for macroscopic granular materials, the dynamics are governed mostly by gravity and collisional and frictional forces, for adhesive microparticles the dominant interactions are electrostatic (Coulomb) and van der Waals forces (Aranson and Tsimring, 2006). Recently, a rapid progress on understanding the physics related to the intermolecular and surface forces at the micro-scale (Marshall and Li, 2014) has emerged, which lead to the development of a rational adhesive contact model for our simulation of the behaviour of atmosphere particles.

This research does not consider the various water-soluble components in airborne particles and their hygroscopic effect. The objectives of the study are: (i) to establish a correlation between relative humidity and water content on particles; (ii) to determine the electric charges on aerosol particles; (iii) to simulate the dynamic evolution of aerosol particles, to identify the physical effect of humidity and particle charging state on formation of haze.  

2. Physical mechanisms

2.1. Liquid bridge force

In a humid environment, most aerosol particles are surrounded by a film of aqueous liquid (Marshall and Li, 2014). When two particles collide, their aqueous films coalesce to form a “liquid bridge”, producing a capillary force \( F_{cap} \), that pulls the particles towards each other, leading to an agglomeration of particles. In addition, the aqueous films would confer an enhanced viscous force \( F_{visc} \), between the particles due to the higher viscosity of the aqueous filling of the contact region compared to the surrounding gas. The total liquid bridge force \( F_{液} \) is given by Equation (1).

\[
F_{液} = F_{cap} + F_{visc}
\]  

The capillary force \( F_{cap} \) is given by Equation (2) derived by Maugis (1987),

\[
F_{cap} = 4\pi R\sigma G_f \cos \theta
\]

where \( R \) is the effective particle radius; \( \sigma \) is the liquid surface tension; \( \theta \) is the contact angle, and \( G_f \) is a coefficient defined by Equation (3).

\[
G_f = 1 - \left[ 1 + \frac{\nu_f}{\pi R \theta} \right]^{1/2}
\]

Where, \( h \) is the minimum distance between the particles and \( \nu_f \) is the liquid bridge volume. The humidity ratio is expressed as \( \alpha_{\text{humid}} = V_f / R^2 \).

The definition of the viscous force \( F_{visc} \) was given by Matthews (1988) as describe in Equation (4). This was validated by experimental data for viscous force conducted by Pitois et al. (2000):
\[ F_{\text{visc}} = 6 \pi \mu_q R^2 \frac{1}{h} \frac{dh}{dt} \]  

where \( \mu_q \) is the liquid viscosity.

The critical separation distance \( h_{\text{rupt}} \) of particles at which the bridge ruptures, was proposed by Potois et al. (2001) as described in Equation (5), in their experimental study.

\[ h_{\text{rupt}} = \left(1 + \frac{3}{2} \left(1 + Ca^{1/2}\right) (V_j/4 R^2) \right) \]

where \( Ca = \mu_i |\rho_i n| / \alpha \) is the capillary number, written in terms of the normal component of the relative velocity of particle \( i \) and particle \( j \).

### 2.2. Electrostatic force

Identifying the charges on particles is essential for accurately predicting the electrical force on particles. A solid particle would acquire an electric charge in an aerosol system by field charging, diffusion charging or contact charging (Marshall and Li, 2014). Our study focuses on the contact charging induced by relative humidity.

Triboelectric charging is a type of electric charge that can be generated by contact between materials through friction. The electric field induced by triboelectric charging can change the trajectories of particles. Moreover, these charges can influence electric field strength (Gu et al., 2013). The particle charge density is related to relative humidity (Chen et al., 2003), and many chemical reactions involved in the ion migration are accelerated by water. The contact charging mechanism as proposed by Gu et al. (2013) was used in our study to explain the migration of particles at which the bridge ruptures.

According to the contact charging mechanism, the higher mobility of \( H^+ \) relative to that of \( OH^- \) causes high temperature particles to become negatively charged and low temperature particles to become positively charged. The ion/electron flux \( J \), between the contacting particle \( i \) and the particle \( j \), is related to the temperature difference, as given by Equation (6).

\[ J = \alpha_i \alpha_j (\Delta T_i - \Delta T_j) \]

where, \( \Delta T_i \) and \( \Delta T_j \) are the instantaneous temperature difference between particle \( i \) or particle \( j \) and the gas, respectively; \( \alpha_i \) is the electrical conductivity of particles with the absorbed water influenced by the relative humidity and the ambient temperature; \( \alpha_j \) is the coefficient describing the electrical charge flux related to the amount of ions/electrons on the particle surface and the mobility velocity of \( H^+ \) and \( OH^- \).

After the collision, particle \( i \) and particle \( j \) would acquire opposite charges, according to Equation (7):

\[ q_i = \int_{t_i}^{t_j} J dt, \quad q_j = -\int_{t_i}^{t_j} J dt \]

where \( t_i \) and \( t_j \) are the start and end time of the particle-particle collision.

The charges carried on particles \( i \) and \( j \) are the combined effect of field charging, diffusion charging and contact charging. The electrical force can be calculated by the Coulomb’s law, i.e., \( F_E = \frac{k q_i q_j}{r_{ij}^2} \), where \( k \) is Coulomb’s constant \((k = 8.9875 \times 10^9 \text{Nm}^2 \text{C}^{-2}) \), \( q_i \) and \( q_j \) are charges on particles \( i \) and \( j \), and \( r_{ij} \) is the distance between particles.

The humidity, correlated with the electrical conductivity and the charge density, would alter the electrical forces between particles, and accelerate the agglomeration of aerosol particles.

### 3. Experimental measurements

#### 3.1. Water content on particles

The thickness of the water layer on particle surface increases with humidity (Pence et al., 1994), and the humidity ratio \( a_{\text{humid}} \) is closely related to the RH in the atmosphere. Therefore, the humidity ratio can be adjusted to verify the effect of atmospheric humidity on particle evolution. From Equation (8), the humidity ratio is proportional to the capacity of particles to absorb water as follows:

\[ C_w = \frac{m_w}{m_p} = \frac{\rho_w}{\rho_p} \left( \frac{V_w}{r^2} \right) \]

where \( m_w \) and \( m_p \) are the mass of water and particles, respectively; \( \rho_w \) and \( \rho_p \) are the density of water and particles, respectively; \( r \) is the particle radius; and \( V_w \) is the water volume.

To test the capacity of particles to absorb water in different atmospheric humidity, a sample of fine sand taken from Kumtag desert was placed in the oven at 105°C for 6h to completely dry the absorbed water. Then, the sand particles were divided into ten samples, each containing 100g of fine sand, and these samples were placed in a temperature and humidity control box. The temperature inside the box was controlled at 30°C. A humidifier was used to control the humidity inside the box. The weight changes of the sand were recorded at a regular interval. The weight change of sand was assumed to be due to the adsorption of water in the environment. Taking the average weight change of ten samples, a curve showing the capacity of sand particles to absorb water at different humidity levels was established, which is shown in Fig. 1. The water absorption capacity was shown to increase with the RH of the environment. Therefore, the water content and

Fig. 1. The relationship of the relative humidity to water absorbing capacity of sand particles and humidity ratio of the liquid bridging forces.
thickness of the absorbed water on the particle surfaces increased with the RH. Then, through Equation (8), the relationship between the humidity ratio and the atmospheric relative humidity is described.

There have been many studies reporting liquid water content of submicron aerosols measured using the humidified tandem differential mobility analyzer (HTDMA), the differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP) and the tandem humidified-nephelometers (Shingler et al., 2016; Titos et al., 2016). The comparison of reported measurement results given by these instruments with our experimental results would be an item for our future work. Considering the sand particle is relatively simple in chemical composition, the study of the relationship between humidity ratio and atmospheric relative humidity would be useful in elucidating the charging behaviour in particles. The humidity ratio is related to the liquid bridge force, and would be useful for numerical modelling for computing.

3.2. Electric charges on atmospheric particles

The charge characteristics of atmospheric particles using particle separator setup with parallel plate electrode is shown in Fig. 2. The plate electrodes were 10 cm width, 20 cm length, and their distance was 5.0 mm, which are the same size as that was used by Okuda et al. (2015). The same inlet airflows were used, to enable a laminar flow to be formed inside the parallel plate electrode, so that the aerosol particles would flow out at the middle outlet. The clean air was obtained by filtering an airflow from the ambient environment and drawn into the parallel plate via the clean air inlets. The middle inlet was the aerosol inlet, where the airflow with particles were directly drawn from the ambient environment.

In this study, a direct current voltage of 800 V was used, based on the calculation of fluid dynamics and deflection properties of particles inside the parallel plate electrode (Okuda et al., 2015). Three optical particle sizeers (OPS, model 3330) having the same airflow rate of 0.06 m³·h⁻¹ were used to sample aerosols at the outlets. Meanwhile, another OPS was directly applied to measure the number concentration of charged particles. OPS1 was used as a benchmark to allow adjustment of the instrumental error of all OPSs, ranging from −7.4% to +14.3%. A TSI DustTrak (desktop aerosol monitor, model 8533) was used to monitor PM₂.₅ concentration in the particle size range from 0.1 to 2.5 μm.

When without power, all particles carried by the middle airflow could flow out from the middle outlet and captured by OPS2. When the electrode plate was powered, the charged aerosol particles would change their tracks and flow out from other outlets. Considering the differences in mass and charges on different sized particles, the particle flow at the inlet of the middle layer were divided into 5 layers above and below, and the deflected distance of particles of different particle sizes in different charge states was calculated. Then, the charge distribution of particles at different size segment was obtained, based on the particle number concentration distribution measured by 3 OPSs (up to 16 channels). The average particle charge was obtained by summing up the charge quantity of particles of different particle sizes which was then divided by the total number of particles measured by another OPS (OPS4).

The experiment was carried out on the roof of the west 4th building at the Qujing Campus of Xi’an Jiaotong University, at approximately 20 m above the ground level. Fig. 3(a) and Fig. 3(b), respectively, show the time series of RH and PM₂.₅ mass concentration during 27–28 December 2017. An obvious rise in the mass concentration of PM₂.₅ was shown with an increase rise in RH. When the humidity reached a high level, over 55%, the mass concentration of PM₂.₅ stopped rising and started a slight decline. Fig. 3(c) shows the ratio of charged particles in all particles (0.3–2.5 μm), indicating that most of atmospheric particles were negative or positive charged, which would affect the physical behaviour of airborne particles. Comparing Fig. 3(b) with Fig. 3(c), a growing number of aerosol particles were with charges at the early stage of this abrupt-rise haze episode, and there was a decline during the development of severe haze. The wind was weak between 22:00–3:00 (< 1.5 m s⁻¹), and this decline could be due to the agglomeration of lots of ultrafine particles under the influence of electrostatic interactions, so that many charges were neutralized leading to a decline in the proportion of charged particles.

4. Numerical simulations

4.1. Model description

The study used an extended soft-sphere discrete element method (DEM) to simulate the evolution of wet particles, the variation of particle size distribution and particle number concentration. In this extended model, adhesive and Brownian forces were considered to examine the agglomeration of fine-particle in static atmosphere. The atmospheric background was set as a three-dimensional structure and the boundaries were cyclic.

In the DEM, the fine-particle velocity v and rotation rate Ω were obtained from the solution to the linear and angular momentum equations of the particle, given by Equation (9).

\[
\frac{dv}{dt} = F_A + F_U + F_E + F_E + F_B
\]

Where, v is the particle velocity, m is the particle mass, d is the particle diameter, I = (1/10)md² is the particle moment of inertia, and d/dt is the derivative of the moving particle. The terms on the right of the linear equation are the forces acting on the particle. The elastic collision force, van der Waals attraction force and liquid bridging force, are altogether denoted as Fₐ. The other forces are gravity (Fₐ), fluid force (Fₐ), electrical force (Fₐ) and Brownian force (Fₐ). In the angular momentum equation, Mₐ denotes the sum of the collision torque, van der Waals adhesion torque and liquid bridging torque on particles. Mₐ is the fluid force torque.

The forces and torques acting on particles were decomposed into
four parts: (i) acting along the line normal to the particle centres, (ii) resistance to sliding, (iii) twisting, and (iv) rolling of one particle over another.

Two spherical particles of radii $r_i$ and $r_j$, of velocities $v_i$ and $v_j$, with angular rotation ratios $\Omega_i$ and $\Omega_j$, are in contact, and the collision force and torque with adhesion on particle $i$ can be described by Equation (10), as

$$F_i = F_{ni} + F_{ti}, \quad M_i = \tau_i E_i (\mathbf{n} \times \mathbf{v}) + M_i (t_i \times \mathbf{n}) + M_i \mathbf{n}$$

$F_n$ is the normal force, $F_t$ is the tangential force and $t_i$ is the direction of relative motion of particle surfaces at the contact point projected into the contact plane (the plane orthogonal to $\mathbf{n}$); $t_i$ is the direction of the rolling velocity; $M_i$ is the rolling torque and $M_i$ is the twisting torque.

The normal force ($F_n$) is composed of three parts as shown by Equation (12), the elastic deformation of particles ($F_{ne}$), energy losses during the normal particle impact ($F_{nd}$) and adhesion interactions ($F_{adh}$).

$$F_n = F_{ne} + F_{nd} + F_{adh} = -k_{adh} \delta_i - n_i (v_i \cdot n) + F_{adh}$$

Herein, the adhesive forces include the van der Waals attraction force $F_{vdw}$ and the liquid bridging force $F_{liq}$ as defined by Equation (13).

$$F_{adh} = F_{vdw} + F_{liq} \quad \text{(13)}$$

The sliding force, twisting force, rolling resistance and the corresponding torques, were considered and described by Marshall (2009). The mathematical equations of the electrical ($F_E$), gravity ($F_G$), fluid ($F_F$) and Brownian forces ($F_B$) are given in Table 1; and these are the typical forces acting on particles. The particle diameter $D_p$ is twice the effective particle radius (ie. 2R).

4.2. Computational conditions

In the computational simulations, periodic boundary conditions were applied to the computational domain with 1 mm (L) × 1 mm (W) × 1 mm (H), which could both accurately model the atmosphere and accelerate the calculation. Atmospheric aerosol particles cover a wide size range, but only two particle sizes are considered here. Different sized particles, in the same temperature-humidity varying environment, could carry different charges according to the thermoelectric theory. To study various kinds of interactions between particles and simplify the computation model, we consider two kinds of sizes. Besides, atmospheric adhesive particles would introduce challenges in the modelling of particles interaction forces, and they could also introduce an additional short time scale, typically much smaller than the particle advection time scale, which would serve to enhance the
4.3. Results and discussion

The charge on aerosol particles could be evaluated from the experiment on atmospheric particles charging. Fig. 4 shows the average amount of charges on aerosol particles, giving the absolute values of the negative charges on particles. This result indicates that the number of elementary charges of atmospheric particles was more than one. Besides, considering that the charges on particles vary in proportion with the surface area, the particles in larger sizes would be more likely to carry positive charges (Marshall and Li, 2014). The elementary charges of particles of 200 nm and 100 nm sizes were assumed as +4e and −1e, respectively.

Fig. 5 shows the evolution of particles in this simulated 3D domain at different times when RH was 60%. Fig. 6 shows the particle number size distribution at 4 moments, t = 1s, t = 5s, t = 10s, t = 15s, respectively. As time moves on, large amounts of ultrafine particles ceaselessly collided and agglomerated, and the size distribution spectra moved to the right. The number of particles \( N_p \) included new agglomerates formed by several particles, original single-particles and single-particles, and these were generated from broken agglomerates as shown in Fig. 5. Fig. 7 shows the effect of humidity on the agglomeration rate of particles. When RH was 0, no aqueous liquid bridging force was acting on particles, and the agglomerates become slightly reconstructed and broken-up with time. As the humidity ratio was increased, the increased liquid bridging force enhanced the agglomeration velocity. When the relative humidity was very high, over 80%, the difference in agglomeration velocity was reduced in different humidity.

Under a higher humidity, the ionization on the particle surfaces enhances and increases the electrostatic interactions. To further identify the effect of atmospheric water on particle evolution, the increment charging on particles due to water action was considered. \( Q_1 \) denotes particles of 200 nm size that carried four positive charges +4e and particles of 100 nm size that carried one negative charge −1e, when RH was 60%. \( Q_2 \) denotes particles having charges of +5e and –2e under a RH of 90%. The other parameters are consistent with the previous simulation. The particle number over time for particles with different charges is shown in Fig. 8. When compared with Fig. 7, there are higher charges on particles under 60% and 80% RH, with an obvious rise in the agglomeration rates was shown. Electrostatic interactions would play an important role in particle collision and agglomeration. Atmospheric

### Table 1

Typical forces.

<table>
<thead>
<tr>
<th>Forces</th>
<th>Mathematical equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity</td>
<td>( F_G = \frac{9}{2} \rho_p \pi r^4 \left[ 1 - \frac{r}{R} \right] )</td>
</tr>
<tr>
<td>Fluid force</td>
<td>( F_f = \frac{-m_p v}{t_p} ) (Wei and Gu, 2015)</td>
</tr>
<tr>
<td>vdW force (non-contact)</td>
<td>( F_{vdW} = \frac{2m_p \pi (\zeta v)^2}{\left( \frac{v}{2} \right)^2} ) ( v = 2y = \frac{b}{2} )</td>
</tr>
<tr>
<td>Coulombic force</td>
<td>( F_C = \frac{2}{\pi} \rho_p ) (Brilliantov et al., 2007)</td>
</tr>
<tr>
<td>Liquid bridging force</td>
<td>( F_{lb} = e \rho_p g \gamma \cos \theta ) ( G_1 = 1 - \left( 1 + \frac{\text{molecular} \gamma}{\text{final} \gamma} \right)^{-1/2} ) (Maugis, 1987)</td>
</tr>
<tr>
<td>Brownian force</td>
<td>( F_B = \frac{2}{3} \rho_p \pi r^3 \left( \frac{s}{2} \right) ) ( \beta = \frac{2 \nu s^2}{\pi} ) (Ilie and Ahmadi, 1999)</td>
</tr>
</tbody>
</table>

4.3. Results and discussion

The charge on aerosol particles could be evaluated from the experiment on atmospheric particles charging. Fig. 4 shows the average amount of charges on aerosol particles, giving the absolute values of the negative charges on particles. This result indicates that the number of elementary charges of atmospheric particles was more than one. Besides, considering that the charges on particles vary in proportion with the surface area, the particles in larger sizes would be more likely to carry positive charges (Marshall and Li, 2014). The elementary charges of particles of 200 nm and 100 nm sizes were assumed as +4e and −1e, respectively.

Fig. 5 shows the evolution of particles in this simulated 3D domain at different times when RH was 60%. Fig. 6 shows the particle number size distribution at 4 moments, t = 1s, t = 5s, t = 10s, t = 15s, respectively. As time moves on, large amounts of ultrafine particles ceaselessly collided and agglomerated, and the size distribution spectra moved to the right. The number of particles \( N_p \) included new agglomerates formed by several particles, original single-particles and single-particles, and these were generated from broken agglomerates as shown in Fig. 5. Fig. 7 shows the effect of humidity on the agglomeration rate of particles. When RH was 0, no aqueous liquid bridging force was acting on particles, and the agglomerates become slightly reconstructed and broken-up with time. As the humidity ratio was increased, the increased liquid bridging force enhanced the agglomeration velocity. When the relative humidity was very high, over 80%, the difference in agglomeration velocity was reduced in different humidity.

Under a higher humidity, the ionization on the particle surfaces enhances and increases the electrostatic interactions. To further identify the effect of atmospheric water on particle evolution, the increment charging on particles due to water action was considered. \( Q_1 \) denotes particles of 200 nm size that carried four positive charges +4e and particles of 100 nm size that carried one negative charge −1e, when RH was 60%. \( Q_2 \) denotes particles having charges of +5e and –2e under a RH of 90%. The other parameters are consistent with the previous simulation. The particle number over time for particles with different charges is shown in Fig. 8. When compared with Fig. 7, there are higher charges on particles under 60% and 80% RH, with an obvious rise in the agglomeration rates was shown. Electrostatic interactions would play an important role in particle collision and agglomeration. Atmospheric

![Fig. 4. Time series of the average charges on aerosol particles measured in Xi'an.](image-url)
Fig. 5. Particle positions at different times under 60% RH.

Fig. 6. Particle size distribution at (a) $t = 1s$, (b) $t = 5s$, (c) $t = 10s$ and (d) $t = 15s$.

Fig. 7. Variation of particle numbers ($N_p$) over time under four RH.
water content not only introduces an aqueous liquid bridging force, but also increases electrostatic interactions. These interactions would lead to agglomeration of large amounts of ultrafine particles and give rise to larger mean diameter of aerosol particles. The rise in number concentration of particles in the size range from 0.1 to 1 μm would give rise to haze with a reduced visibility in the atmosphere.

The numerical model shows the relationship between atmospheric humidity and particle evolution and this would provide a useful tool and reference for further research on haze formation. However, the present experiment and simulation require a further improvement. In the experiment of water absorbing capacity, large-size fine sand particles instead of aerosol fine particles were adopted. Using sand for the experiment could provide a rough estimate of the correlation of relative humidity with water absorption capacity of aerosol particles, but the validity of this correlation remains to be proven. For the validity of the numerical simulation, the simulating domain would need to be extended and more particles would be involved. Further improvement of the model would need to consider various factors affecting the simulations requiring a higher capacity performance of a computer.

There have been a lot of research on the source analysis of aerosols and chemical reactions of secondary aerosols (Chan and Yao, 2008; Kota et al., 2018; Tie et al., 2017; Cao, 2014). However, the dynamic evolution of aerosol particles (e.g. collision, agglomeration and growth) are actually due to the physical and chemical interactions of particles. Further work might consider the effect of dynamic fluctuation in humidity on the abrupt rise of PM concentration. Besides, in view of the importance of homogeneous/heterogeneous interactions on particle surfaces, our future work will extend a kinetic multi-layer model to study gas-particle interactions in aerosols that would include gas phase diffusion, reversible adsorption, surface reactions, bulk diffusion and reaction, condensation, evaporation and heat transfer.

5. Conclusions

Through laboratory investigation of the water absorbing capacity of particles under different relative humidity conditions, the correlation between the relative humidity and water content of particles was established. Also, through the theoretical derivation, the relationship between the relative humidity and humidity ratio was obtained for calculation of the liquid bridging force.

The findings of the experiment on particle charging show that most atmospheric particles would carry negative or positive charges. The number of elementary charges of atmospheric particles in this study was more than one. A strong relationship between the mass concentration of PM$_{2.5}$ and the number of charges on particles implied that the haze formation could partly be attributed to the variation of particles’ charging state, which might be related to meteorological conditions.

The results from the extended soft-sphere DEM simulation of the evolution of wet particles illustrate an enhancement in the agglomeration rate of particles corresponding to the atmospheric humidity; and due to the increased aqueous liquid bridging force. The higher humidity (> 80%) would enhance the ionization on particle surface, giving rise to higher electrostatic interactions. These interactions would lead to agglomerations of large amounts of ultrafine particles and consequently affect the size of agglomerated particles, and thus affect the size distribution of PM in the atmosphere. Therefore, the dynamic evolution of particles is actually and additionally, attributed to the physical effects of aerosol particles in the atmosphere, together with chemical effects on particle surfaces.

Acknowledgments

The authors appreciate the constructive comments and suggestions of Professor Daizhou Zhang (Prefectural University of Kumamoto). The work was partially supported by the Key State Science and Technology Projects (No. 2016ZX05011-003-007), the National Natural Science Foundation of China (No. 11872295), the Key R&D Projects of Shaanxi Province (No. 2018ZDCXL-SF-02-06) and the Strategic Research Grant of City University of Hong Kong (No. SRG-7004637).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2018.10.035.

References
