Impactor Apparatus for the Study of Particle Rebound: Relative Humidity and Capillary Forces

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The effect of relative humidity (RH) on the adhesion of particles colliding with a hard surface was studied for submicron particles of liquid oleic acid, solid ammonium sulfate, and solid polystyrene latex (PSL). For this purpose, a three-arm impactor was designed and constructed. The three arms consisted of one impactor having an uncoated impaction plate (i.e., a rebound arm), one impactor having a viscous-liquid-coated impaction plate (i.e., a capture arm), and one impactor having no impaction plate (i.e., a null arm). The particle number concentrations downstream of each arm were measured by condensation particle counters (CPCs). Data were analyzed to obtain the particle rebound fraction. Use of ambient upstream pressure allowed measurements from 5 to 95% RH at the impaction plate. Particle rebound depended strongly on RH, even for non-hygroscopic PSL particles. The rebound fraction for PSL particles dropped monotonically from nearly unity at 50% RH to 0.5 at 70% RH. The decreased rebound at higher RH was explained by the formation of a water meniscus. The resulting capillary forces inhibited particle detachment. A model, taking into account the impact kinetic energy compared to the contact adhesion energy arising from van der Waals and capillary forces, captured the observations well. The reduced rebound arising from increased adhesion at high RH, independent of particle water content, potentially confounds a recent assumption that non-rebounding atmospheric particles are liquid.

[Supplementary materials are available for this article. Go to the publisher’s online edition of Aerosol Science and Technology to view the free supplementary files.]

1. INTRODUCTION

Impactors are widely used in aerosol science for particle collection as well as for particle sizing (Hinds 1999; Kulkarni et al. 2011). Particles are more massive than the surrounding gas molecules and so their trajectories can separate from the fluid streamlines around an obstacle, possibly resulting in collision of the particles with the surface of the obstacle. A typical geometry of an impactor is a small orifice (i.e., a nozzle) positioned over a flat plate such that the impinging fluid makes a 90° turn. Particles of sufficiently large inertia collide with the plate. In this way, provided that adhesion occurs on collision, particles of large aerodynamic diameter $d_a$ are removed and absent in the outflow from the impactor. The setpoint aerodynamic diameter $d_{50}^*$ of the impactor, denoting a particle transmission function $\Omega$ of 50% (i.e., $\Omega(d_{50}^*) = 0.5$), is controlled by the number of nozzles, the nozzle diameter, and the fluid flow velocity, among other factors (Marple and Willeke 1976; Hinds 1999).

Early studies of impactor performance noted that not all particles colliding with a plate adhered (Pouchet 1860; Marple 2004). Particles of sufficient kinetic energy to overcome the adhesive interactions at the surface rebounded (Dahneke 1971; Winkler 1974). Particle rebound was regarded as a technical problem because a nonrepresentative mass on an assayed impaction plate led to systematic error in the reported mass-diameter distribution of a particle population (i.e., particles were incompletely collected) (Dzubay et al. 1976; Markowski 1984). The coating of impaction plates with an oil or grease was one solution for increasing particle adhesion (Turner and Hering 1987). Other solutions included operating the impactor at a flow sufficiently slow such that the threshold kinetic energy for particle rebound was not exceeded (Cheng and Yeh 1979; Markowski 1984; Wang and John 1987), using an impaction cavity rather than a flat surface to collect rebounded particles (Xu and Willeke 1993; Chang et al. 1999; Lai et al. 2008), or increasing the relative humidity (RH) of the flow above 70% (Winkler 1974; Stein et al. 1994; Chen et al. 2011). Understanding the physics of particle rebound has been an active area of theoretical and computational study (Dahneke 1971, 1972, 1973; Esben et al. 1978; Cheng and Yeh 1979; U 1983; Rogers and Reed 1984; Wang and John 1987; Tsai et al. 1990; Wall et al. 1990; Dahneke 1995; John 1995; Qin and Pletcher 2011; Miyakawa et al. 2013). The reduced rebound at elevated RH was attributed to increased
adhesion because of capillary forces associated with adsorbed water on the particle and the impaction plate, thereby increasing the threshold impact kinetic energy for particle rebound (Jordan 1954; Winkler 1974; Wang and John 1987). No quantitative estimate, however, was made of the associated capillary forces.

In place of considering particle rebound as a technical problem, a subdiscipline has recently emerged that takes advantage of rebound as a scientific indicator of liquid or solid phase state (Virtanen et al. 2010). The phase state directly influences elasticity and hence particle rebound (Saukko et al. 2012a,b). The assumption is that solid to semisolid particles rebound whereas liquid particles adhere. Possible limitations on the accuracy of this assumption, however, have not been thoroughly assessed. Moreover, the most thorough study to date in this emerging subdiscipline employed impactors having upstream pressures significantly below ambient pressure (Saukko et al. 2012a,b), implying an upper limit of approximately 65% RH for RH-dependent studies of particle rebound (Table 1). In light of the importance of capillary forces at elevated RH and a dynamic phase state of particles with RH (Martin 2000), the capability to carry out studies to higher RH is desirable.

In the present study, a new three-arm impactor apparatus is presented and employed to study particle rebound up to 95% RH. The study is motivated in part by the need for a better understanding of the impaction technique as a probe of particle phase state. The designed impactor apparatus has no upstream pressure drop, thereby allowing study at high RH. The three-arm design is a parallel nulling configuration that increases the precision and accuracy of the measurement of rebound fraction. It also allows continuous measurements at a temporal resolution of approximately 1 s, which can be important for atmospheric applications in which the chemical composition and number concentration of the particle population can change continuously. The study presents datasets on the effect of RH on the adhesion of particles colliding with a hard surface for submicron particles of liquid oleic acid, solid ammonium sulfate, and solid polystyrene latex (PSL). A model is developed to take into account the impact kinetic energy compared to the contact adhesion energy arising from van der Waals and capillary forces. The model predictions are compared to the datasets.

2. EXPERIMENTAL

2.1. Description and Design of Impactor

The three-arm impactor apparatus (Figure 1) is built from three single-stage impactors operated in parallel. Two different single-stage impactors (labeled α and β), each consisting of a nozzle plate, an impaction plate, and a housing and differing by their nozzle characteristics (Table 1), were used in the experiments. A technical diagram is presented in Figure S1 of the online supplemental information (SI). The impactors were characterized in the absence of particle rebound by the aerodynamic diameter \( d_a \) at which half of the particles pass through, that is, a transmission function \( \Omega \) of 0.5 at that diameter (called setpoint diameter). The term \( d_{sp}^* \) denotes a measured setpoint diameter, the term \( d_{sp}^\alpha \) denotes a setpoint diameter estimated using semiempirical design equations, and...
the term $d_0^*$ denotes a setpoint diameter based on computational fluid dynamics (CFD) numerical simulation.

The semi-empirical design setpoint aerodynamic diameter $d_0^*$ satisfying $\Omega(d_0^*) = 0.5$ is given by the following equation (Section S1 in the SI):

$$C_\alpha(d_0^*) (d_0^*)^2 = 9 \eta \text{Stk} \frac{D}{\bar{v} \rho_0}$$

Terms include the Cunningham slip correction factor $C_\alpha$, the dynamic viscosity $\eta$ of the fluid, the Stokes number $\text{Stk}$, the diameter $D$ of the nozzle, the average velocity $\bar{v}$ of the fluid, and the particle reference material density $\rho_0$. Values of these quantities are listed in Tables 1 and 2 for the $\alpha$ and $\beta$ impactors. Design values $d_0^*$ of 92.9 and 293.4 nm are obtained for the $\alpha$ and $\beta$ impactors, respectively, using Equation (1).

For comparison, design parameters are also listed in Table 1 for stages of two commercially available cascade impactors having similar $d_0^*$ as the $\alpha$ and $\beta$ impactors (Marple et al. 1991; Marjamaki et al. 2000). These stages have been used to study particle rebound, either in cascade operation (Virtanen et al. 2010, 2011; Chen et al. 2011) or as single stages (Stein et al. 1994; Saukko et al. 2012a,b). For the study of particle rebound at high RH, an advantage of the designed impactors compared to the commercially available ones is the absence of an upstream pressure drop (Section S2 in the SI). A pressure drop must be maintained for the commercial impactors listed in Table 1 to avoid shifts in flow rates that would otherwise cause shifts in the setpoint aerodynamic diameter.

For $d_a \neq d_0^*$, the transmission function $\Omega(d_a)$ has no well-accepted formulation (Hinds 1999). Detailed numerical modeling of the fluid flow and the associated particle trajectories in the impactor is required (Marple and Liu 1974; Marple et al. 1974). Limiting conditions in the absence of particle rebound are that $\Omega(d_a) = 1$ for $d_a < d_0^*$ and $\Omega(d_a) = 0$ for $d_a > d_0^*$. For a well-designed impactor, an empirical sigmoid function (Figure 2a) can typically represent the transition of $\Omega$ from 1 to 0 for $d_a$ near $d_0^*$, as follows (Kwon et al. 2003):

$$\Omega(d_a) = \frac{1}{1 + \exp((d_a - d_0^*)/\delta)} \tag{2}$$

for width parameter $\delta$. A typical example of a well-designed impactor has $\Omega(d_a) = 0.7$ for $d_a = 0.9 d_0^*$ and $\Omega(d_a) = 0.3$ for $d_a = 1.1 d_0^*$, implying a width parameter $\delta = 0.118 d_0^*$ (Hillamo and Kauppinen 1991; Marple et al. 1991; Marjamaki et al. 2000). The width parameter is related to the steepness parameter $\chi$, defined as $\chi = d_0^* \Omega = 0.3/d_0^* \Omega = 0.7$, as $\delta = 1.180 d_0^* (\chi - 1)/ (\chi + 1)$ (Hillamo and Kauppinen 1991).

When rebound occurs, $\Omega(d_a) = 1$ for $d_a < d_0^*$, $\Omega(d_a) = 0$ for $d_a > d_0^*$, and $\min(\Omega(d_a))$ occurs for $d_a \approx d_0^*$ (Cheng and Yeh 1979). The minimum occurs because intermediate-sized particles are large enough to separate from the fluid streamlines and hit the impaction plate yet small enough to do so with a sufficiently small normally incident kinetic energy that they adhere (i.e., glancing impact). An empirical double sigmoid function (Figure 2b) can typically represent $\min(\Omega(d_a))$ for $d_a$ near $d_0^*$, as follows:

$$\Omega(d_a) = \frac{1}{1 + \exp((d_a - d_0^*)/\delta)}$$

$$f(d_a) \frac{\Omega(d_a)}{1 + \exp((d_a - d_0^*)/\delta)} \tag{3}$$
for a particle rebound fraction $f(d_a)$ for the second sigmoid function.

### 2.2. Measurement of Rebound Fraction

Test aerosols of liquid oleic acid, solid ammonium sulfate, and solid PSL were produced and conditioned to low RH (Section S3). The particle population upstream of the impactor was described by a lognormal probability density function $n(d_a)$ of the number-diameter distribution. In one arm of the apparatus, impaction plates were clean (i.e., uncoated). In a second arm, impaction plates were coated with high-vacuum grease (Dow Corning) (Section S4). The uncoated plates allowed particle rebound to occur if favorable to do so, whereas the coated plates eliminated particle rebound (Marple and Willeke 1976; Turner and Hering 1987; Marple et al. 1991).

In a non-size-resolved protocol (Figure 1, gray boxes bypassed), 3 Lpm of aerosol passed through a Nafion RH conditioner and directly into the apparatus. In this protocol, $n(d_a)$ had a width much greater than $\delta$. The number concentration $N$ measured by a condensation particle counter (CPC, TSI model 3010; 1 Lpm) after each impactor was a convolution of the transmission function (Equation (2) or (3)) and the particle size distribution, as follows:

$$N = \int_0^\infty \Omega(d_a) n(d_a) \, d(\log_{10} d_a) \tag{4}$$

By using the same $n(d_a)$ while comparing $\Omega(d_a)$ measured between uncoated and coated impaction plates in a parallel configuration (Figure 1), a non-size-resolved measurement of the rebound fraction of the particle population was obtained, at least for those particles of $d_a \cong (1 - \delta) d_a^\ast$ and larger. This measurement, though not size resolved, had high accuracy because of the high particle number concentrations ($>1000$ cm$^{-3}$). Care was taken to ensure that the particle loadings on the surfaces of both the coated and uncoated plates were sufficiently low during the course of the measurements to avoid particle-on-particle collisions (Section S4).

In a size-resolved protocol (Figure 1, use of gray boxes), 1 Lpm of the aerosol passed through a radioactive source (TSI model 3077) and then into a differential mobility analyzer (DMA; TSI model 3085; 10:1 sheath-to-sample flow) by selection by electric mobility $Z$. Exiting the DMA, the aerosol was mixed with 2 Lpm of dry air, passed through the Nafion RH conditioner, and then into the apparatus. Particle diameter growth at elevated RH was accounted for in the analysis by using the hygroscopic growth factors from Biskos et al. (2006) for ammonium sulfate particles and a hygroscopic growth factor of unity for PSL spheres (Ye et al. 2009; Tan et al. 2013) (Section S5).

Considering just the singly charged particles, $n(d_{a+1}; Z)$ exiting the DMA had a width less than $\delta$. Figure 3 shows graphically the width of the DMA transfer function compared to the width of the impactor transfer function. The data analysis herein effectively assumes that the particle population exiting the DMA is monodisperse.

The size-resolved protocol allowed a mapping out of $\Omega(d_a)$ by systematically varying the diameter selected by the DMA (i.e., by scanning $Z$) while measuring $N(Z)$ that passed through each parallel impactor (Figure 1). The quantity $\Omega(d_a; d_a > d_a^\ast)$ was a direct mobility-resolved measurement of rebound fraction. The relationship between electric mobility and aerodynamic diameter is presented in Section S5. Corrections were made in the data analysis for multiply charged particles $n(d_a; +i, i > 1; Z)$ of larger aerodynamic diameter that also contributed to $N(Z)$ (Section S6).

Both protocols were conducted in a parallel-arms configuration, meaning that the sampled flow of 3 Lpm was divided three ways and flowed into the three separate impactors. The
number concentrations $N_1$, $N_2$, and $N_3$ were recorded by separate CPCs (Figure 1). The first impactor employed the nozzle plate but not an impaction plate, thereby serving as a reference arm. This configuration allowed for counting of the entire particle distribution (i.e., $N_1 = N_A + N_B$ of Figures 2a and b). This reference arm served to compensate for possible particle wall losses and other particle-loss pathways in the two other impactors. The second impactor used the nozzle plate and a grease-coated impaction plate. This configuration eliminated particle rebound and thus counted the particle population constituting $N_A$ in Figures 2a and b, meaning $N_2 = N_A$ (Equation (4)). The third impactor contained a nozzle plate and an uncoated impaction plate. This configuration passed both subpopulation $N_A$ (i.e., that did not hit the impaction plate) as well as some fraction $f$ of subpopulation $N_B$ that rebounded from the impaction plate, meaning $N_3 = N_A$ for Figure 2a and $N_3 = N_A + fN_B$ for Figure 2b.

From the number concentrations measured by the CPCs, the transmission functions $\Omega_2$ and $\Omega_3$ for coated and uncoated plates, respectively, were calculated as follows:

$$\Omega_2 = \frac{N_2}{N_1}, \quad \Omega_3 = \frac{N_3}{N_1}$$  \[5\]

The term $\bar{a}$ is determined using an assumption of adiabatic flow (Hering 1987) (Equation (S2)). The width parameters $\delta$ correspond to steepness parameters $\chi$ of 1.10 and 1.19 for the $\alpha$ and $\beta$ impactors, respectively. The particle Stokes number $Stk^{\dagger}$ of 0.20 is used as the characteristic semiempirical design value for 50% particle transmission through round nozzles (Jurcik and Wang 1995). It can be compared to the measured Stokes number $Stk^*$ that satisfies Equation (1). Values in parentheses indicate the percent difference compared to the measurement.

### 3. RESULTS AND DISCUSSION

#### 3.1. Setpoint Aerodynamic Diameter

Figure 3 (solid lines) shows the size-resolved transmission functions $\Omega(d_a)$ of quasi-monodisperse particle populations of dry ammonium sulfate and oleic acid in the absence of particle rebound for the $\alpha$ and $\beta$ impactors. The values of $d_a^*$ and $\delta$ (Equation (2)) and the associated one-sigma uncertainties are listed in Tables S1 and S2. For comparison, the $d_a^*$ values expected from semiempirical design (Equation (1)) are shown as solid symbols. The size-resolved transmission functions simulated numerically (Figures S2–S5) and assuming no particle rebound are shown as the dashed lines (Section S7). The steepness and general shape of the simulated transmission functions capture well the measurements. The experimental, designed, and simulated values of the setpoint aerodynamic diameters of the two impactors agree within 20% (Table 2). This range is within that expected by Arffman et al. (2011) in a more generalized performance-simulation comparison of impactors, for reasons stated therein. The greater resolution (i.e., steepness) of the $\beta$ compared to the $\alpha$ impactor can be explained by the tighter distribution of the normally incident particle impact velocities of the former (Figure S5). A narrower velocity distribution is favored by a smaller $T/D$ ratio (Arffman et al. 2012) (Table 1).

#### 3.2. Particle Rebound for Dry Conditions

Figure 4 shows the transmission functions $\Omega_2(d_a)$ and $\Omega_3(d_a)$ (Equation (5)) using a test aerosol of ammonium sulfate and uncoated and grease-coated impaction plates for the $\alpha$ and $\beta$ impactors. Figure 5 shows the rebound fraction $f(d_a)$ obtained by analysis (Equation (6)) of the size-resolved data of Figure 4. Results are shown for <5% up to 95% RH. The discussion in Section 3.2 is restricted to dry conditions (i.e., RH < 5%). As quantified in the caption of Figure 4, the presented datasets are slightly shifted along the abscissa to compensate for differences among impaction and nozzle plates as well as for the effects of grease coating (Section S8).
FIG. 4. Transmission functions $\Omega(d_a)$ of a test aerosol of ammonium sulfate for uncoated compared to grease-coated impaction plates. Results are shown for <5% up to 95% RH. Panels a and b represent data obtained for the $\alpha$ and $\beta$ impactors, respectively. The data points show results using uncoated plates. The lines (data points not shown) represent the results for coated plates. The coated and uncoated datasets have been shifted by up to 4 and 21 nm, respectively, for the $\alpha$ impactors and by 25 and 30 nm, respectively, for the $\beta$ impactors (Section S8) so that the $d_a^*$ values of panels a and b equal those listed in Table 2. The test aerosols were pre-conditioned to <5% RH prior to conditioning to the RH of the experiment. The error bars represent one-sigma uncertainties from error propagation of the CPC measurements (Section 2.2). (Color figure available online.)

FIG. 5. Rebound fraction $f(d_a)$ obtained from the size-resolved data of Figure 4. The left and right panels show results for the $\alpha$ and $\beta$ impactors, respectively. The dashed lines represent the simulation results (Section 3.2 for Equation (9) and Section 3.3 for Equation (13)). The error bars represent one-sigma uncertainties from error propagation of the CPC measurements (Section 2.2). (Color figure available online.)
Two features are apparent in the data, both for the \( \alpha \) and \( \beta \) impactors. First, for \( d_a >> d_a^* \) the transmission function shown in Figure 4 is zero for grease-coated plates and close to unity (ca. 0.9) for uncoated plates. This difference is caused by particle rebound. Second, for the uncoated plates, a minimum occurs in the transmission function for \( d_a \approx d_a^* \). Correspondingly, the rebound fraction for dry conditions goes from nearly zero for \( d_a \approx d_a^* \) to nearly unity for \( d_a >> d_a^* \) (Figure 5).

Dahneke (1971) presents a theory of particle rebound upon collision with a surface as a balance between kinetic energy after impact (specifically, the component that is elastically restored in the surface normal direction) and surface adhesion. When the former is greater than the latter, rebound occurs. In the case that van der Waals forces govern the surface-particle interactions, as believed accurate for dry conditions, the adhesion energy \( E_a \) for a spherical particle in contact with a flat surface is given as follows:

\[
E_a = \frac{A d_p}{12 z_0} \tag{7}
\]

in which \( A \) is the Hamaker constant (i.e., describing the strength of van der Waals forces), \( d_p \) is the geometric particle diameter, and \( z_0 \) is the contact distance between the particle and surface.

Taking into account the coefficient \( \epsilon \) of restitution for the particle-surface collision and assuming a spherical nonporous particle, Dahneke (1971) balances the kinetic and adhesion energies to obtain the following equation for a critical velocity \( v_c \) of impact:

\[
v_c d_p = \left[ \frac{A (1 - \epsilon)^2}{\pi z e^2 \rho_p} \right]^{1/2} \tag{8}
\]

Any particle of diameter \( d_p \) having an incident-normal velocity equal to or greater than \( v_c \) rebounds. The term \( \rho_p \) is the material density of the particle. The coefficient of restitution, a measure of the material hardness, is the incident-normal velocity divided by the velocity after impact.

A further version of Equation (8) that isolates the properties of the particle to the LHS and the particle-surface interactions to the RHS is \( v_c d_p (\rho_p/\rho_0)^{1/2} = \xi \) (Cheng and Yeh 1979). By Equation (S14), this equation is written in terms of aerodynamic diameter for spherical nonporous particles as follows:

\[
v_c d_a \left( \frac{C_e(d_a)}{C_e(d_m)} \right)^{1/2} = \xi \tag{9}
\]

The term \( d_m \) is the particle mobility diameter (e.g., as selected by the DMA). The term \( [C_e(d_a)/C_e(d_m)]^{1/2} \) does not differ too much from unity (i.e., 0.82 to 0.94) for the size characteristics of the present study across the abscissa of Figure 5. The lumped parameter \( \xi \) is given by \( \xi = [A (1 - \epsilon)^2/\pi z_0 e^2 \rho_0]^{1/2} \). The analysis herein does not dissect \( \xi \) into \( A, \epsilon, \) or \( z_0 \). For a range of typical physical parameters (0.1 < \( 10^9 \) \( A < 10 \) J, 0.05 < \( e < 0.9, 0.1 < 10^9 z_0 < 0.3 \) m), the expectation is 1 \( \times 10^{-8} < \xi < 3 \times 10^{-5} m^2 s^{-1} \). Semiempirically, 2.5 \( \times 10^{-6} \approx \xi < 9.2 \times 10^{-4} m^2 s^{-1} \) is observed for a range of common particle-surface interactions (Cheng and Yeh 1979).

The \( \xi \) values associated with the dataset of Figure 4 are obtained as follows. The aerodynamic diameter at which \( \Omega_1(d_a) \) and \( \Omega_2(d_a) \) diverge from one another represents the onset of particle rebound. For 5% RH, this value is 85.3 ± 5.4 nm for the \( \alpha \) impactor (Figure 4a) and 278.1 ± 3.5 nm for the \( \beta \) impactor (Figure 4b). The associated mobility diameters \( d_m \) are 52.7 ± 3.3 and 191.3 ± 2.4 nm, respectively. The corresponding incident-normal velocities are numerically simulated for every streamline exiting the nozzle (Section S7). The maximum velocity of this simulation is the critical velocity \( v_c \) at which the onset of rebound occurs (Figures S2–S5). For 85.3 ± 5.4 and 278.1 ± 3.5 nm, these velocities are 14.7 ± 7.8 and 3.1 ± 1.0 m s\(^{-1}\). The associated values of \( \xi \) are obtained by Equation (9). Results are listed in Table 3. At 5% RH, \( \xi = 1.0 (\pm 0.6) \times 10^{-6} \) and 0.8 (± 0.3) \( \times 10^{-6} m^2 s^{-1} \) for the \( \alpha \) and \( \beta \) impactors, respectively, implying that they are equal within uncertainty. Equality is expected because the equation for \( \xi \) is independent of particle diameter and impactor flow characteristics, as a first-order approximation. The measured \( \xi \) value on order 1.0 \( \times 10^{-6} m^2 s^{-1} \) is lower than that reported for PSL particles (2.5 to 4.64 \( \times 10^{-6} m^2 s^{-1} \)) and Eosin-Y particles (4.5 to 9.2 \( \times 10^{-6} m^2 s^{-1} \)) also using hard-surface impactors (Cheng and Yeh 1979). The lower value of the present study indicates that ammonium sulfate particles are more prone to rebound, possibly because they are harder and therefore have a higher coefficient of restitution upon impact. Another possibility is that the incident-impact velocities of the present study based on numerical simulation are more accurate than the approximate flow fields used by Cheng and Yeh (1979). Any overestimate of impact velocity leads to an overestimate of \( \xi \).

The \( \xi \) values listed in Table 3 for < 5% RH can be used to model \( f(d_a) \), as follows. For any \( d_a \), there is a probability density function of incident-normal impact velocities (Figure S5), as obtained by modeling of particle trajectories along the flow fields (Section S7). The rebound fraction is the integral of this function from \( v = v_c(d_a) \) to \( v = \infty \). For fixed \( \xi \), Equation (9) constitutes \( v_c(d_a) \). The modeled \( f(d_a) \) by this approach are shown as hatched black regions in Figure 5. For reasons discussed in the next paragraph, the model results which run from 0 to 1 are rescaled for presentation in Figure 5 to the maximum value of the datasets (i.e., 0.9 for <5% RH). Qualitatively, for <5% RH the model captures the dataset of size-resolved rebound fraction, and model-data agreement can be described as good. Quantitatively, in the case of the \( \alpha \) impactor, the model somewhat underpredicts the initial dependence of rebound fraction on \( d_a \) whereas, in the case of the \( \beta \) impactor, it somewhat overpredicts the initial dependence. This difference in model performance might be explained by the use of a single impact velocity (i.e., the maximum value) to
determine $\xi$ rather than taking into account possible secondary impacts and an associated spectrum of impact velocities.

As apparent for Figures 4 and 5, the datasets for <5% RH approach but do not reach unity (ca. 0.9) for $d_a > d_a^*$ for uncoated impaction plates. Under the assumption that 100% of the particles actually do rebound for $d_a > d_a^*$, the explanation for the difference from unity is that approximately 10% of the rebounded particles have secondary losses and do not flow out of the impactor for counting by the CPC. Rebounded particles do not initially follow the gas streamlines and can have secondary impacts. This possibility is addressed to first approximation by the numerical simulation of the trajectories after initial rebound for every streamline exiting the nozzle (Section S7). Figure S6 shows the result that 10% of the particles for <5% RH adhere on second or third impact. According to this simulation for the $\alpha$ impactor, those particles of highest initial impact velocity are also those particles that undergo adhesion on secondary impact. The reason is that they rebound in a nearly normal direction from the surface and do so into a strong downward flow of the gas, leading to secondary impact at reduced velocities (i.e., favoring adhesion). Because of these secondary losses, as a first-order empirical correction, the model results are scaled for presentation in Figure 5 by the maximum value of the datasets. The undulations apparent in the dataset of Figure 5a are also qualitatively captured in the simulation result presented in Figure S6. In the simulation, the undulations arise from the interactions of the bounce field with the flow field.

### 3.3. Particle Rebound for Humid Conditions

The effects of RH on particle rebound are significant. The transmission functions (Figure 4) and rebound fractions (Figure 5) have no difference within experimental uncertainty for <5% RH and 25% RH. At 50% RH, however, particle transmission and rebound decrease for $d_a > d_a^*$. The trend continues for 70% RH. In addition, compared to dry conditions, the onset of particle bounce, as represented by the point of divergence between curves $\Omega_2$ and $\Omega_1$ of Figure 4, shifts to greater diameters for 50% and 70% RH. These observations of the effects of RH hold for both the $\alpha$ and $\beta$ impactors. For RH of 80% and greater, ammonium sulfate deliquesces, and the liquid particles do not rebound, as is apparent in the data of Figures 4 and 5 for $d_a > d_a^*$.

The RH-dependent nominal values of $\xi$ are obtained from the dataset of Figure 4 using Equation (9) (Section 3.2). Results are listed in Table 3. The nominal $\xi$ values increase from 1.0 ($\pm 0.6$) $\times 10^{-6}$ m$^2$ s$^{-1}$ for dry conditions (5% and 25% RH) up to 2.4 ($\pm 1.0$) $\times 10^{-6}$ m$^2$ s$^{-1}$ at 70% RH for both the $\alpha$ and $\beta$ impactors. Under the assumption that the particles do not soften or otherwise change $\epsilon$ for increasing RH, the implication of the increase in nominal $\xi$ is that the adhesion energy of Equation (7) based on van der Waals interactions is systematically too low compared to actual adhesion energies at high RH. An additional physical mechanism should be invoked to contribute to the adhesion energy (viz. capillary forces; vide infra) that presents itself as an increase in nominal $\xi$ values.

Given that ammonium sulfate is a hygroscopic salt, an additional set of experiments was conducted using PSL spheres to test the generality of the observations of RH on rebound fraction. Compared to ammonium sulfate, polystyrene is water insoluble and more hydrophobic. The comparative datasets are shown in Figure 6. PSL particles have an apparent rebound fraction of 0.9 under dry conditions, presumably representing 100% rebound in actuality when taking into account secondary losses (Section 3.2). Above 60% RH, the rebound fraction monotonically drops, reaching 0.4 at 95% RH. Although the RH-dependent rebound

### Table 3

Physical parameters defining the effects of relative humidity (RH) on the rebound characteristics of ammonium sulfate (Sections 3.2 and 3.3).

| Relative humidity (RH) (%) | $\rho_p$ (kg m$^{-3}$) | $d_a$ (nm) | $v_c$ (m s$^{-1}$) | $d_m$ | $\xi$ ($10^{-6}$ m$^2$ s$^{-1}$) |
|---------------------------|------------------------|------------|-------------------|------|-----------------|
| 5                         | 1770                   | 85.3 ± 5.4 | 14.7 ± 7.8        | 52.7 | 1.0 ± 0.6       |
| 25                        | 1770                   | 85.7 ± 5.4 | 15.1 ± 7.8        | 53.0 | 1.1 ± 0.6       |
| 50                        | 1770                   | 88.3 ± 5.6 | 17.5 ± 8.1        | 54.7 | 1.3 ± 0.6       |
| 70                        | 1747                   | 101.3 ± 8.9| 28.7 ± 12.1       | 64.2 | 2.4 ± 1.0       |
| $\alpha$ Impactor         |                        |            |                   |      |                 |
| $\beta$ Impactor          |                        |            |                   |      |                 |
| 5                         | 1770                   | 278.1 ± 3.5| 3.1 ± 1.0         | 192.9| 0.8 ± 0.3       |
| 25                        | 1770                   | 276.7 ± 3.5| 2.8 ± 1.0         | 192.1| 0.7 ± 0.3       |
| 50                        | 1770                   | 278.7 ± 3.8| 3.2 ± 1.1         | 192.9| 0.8 ± 0.3       |
| 70                        | 1747                   | 304.4 ± 5.7| 8.5 ± 1.6         | 226.9| 2.4 ± 0.5       |

Term $\rho_p$ is determined a priori according to RH (Section 3.3). Term $d_a$ is determined by inspection of Figure 4 at point of divergence between the coated and uncoated curves. Term $d_m$ is determined by Equation (S14) for a spherical nonporous particle. Term $v_c$ is determined by the maximum simulated incident-normal impaction velocity associated with $d_m$ (Section 3.2). Term $\xi$ is determined by use of Equation (9).
behavior of PSL is qualitatively similar to that of ammonium sulfate, meaning a drop in rebound fraction above a threshold RH, the results are quantitatively different in that threshold RH is at a lower RH for ammonium sulfate than for PSL. The implication is that a specific and quantitatively different interaction of water with each material should underlie any explanation for quantitative differences in the RH-dependent bounce fraction.

The significant effects of RH on particle rebound can arise from the adhesion energy contributed by capillary forces. At elevated RH, multiple layers of water adsorb to surfaces. A water meniscus forms between the particle and the surface at elevated RH, multiple layers of water adsorb to surfaces. A contact angle θ between the surface and water. The contact angle θ1 for water against ammonium sulfate is 25° (Hakala et al. 2013). The contact angle θ2 for water on aluminum (i.e., the impaction plate) is 35° (Gentleman and Ruud 2010). Although these contact angles can vary with surface preparation, the stated values are used in the calculations herein.

The modeling framework to assess the RH dependence of rebound fraction is as follows:

$$E_k,0 = E_{\text{rest}} + E_{a,v} + E_{a,m} + E_{k,\text{rest}} \tag{11}$$

The normally incident kinetic energy $E_{k,0}$ of an incoming particle is balanced by energy dissipation $E_{\text{rest}}$ associated with restitution, van der Waals adhesion energy $E_{a,v}$, meniscus adhesion energy $E_{a,m}$, and residual kinetic energy $E_{k,\text{rest}}$ (if any). Particle rebound occurs in the case that $E_{k,\text{rest}} > 0$. Possible additional effects such as particle flattening, local asperity deformation, and plastic deformation are not included in the present analysis (Tsai et al. 1990; Miyakawa et al. 2013). The van der Waals and restitution interactions are assumed in the analysis to change insignificantly with RH, meaning that they are accounted for by Equation (9) using the value $\xi (<5\% \text{RH})$. Equation (9) implies that a kinetic energy associated with $v_r$ is removed by these interactions or more precisely that $E_{\text{rest}} + E_{a,v} = m v_r^2 / 2$ where $m$ is particle mass given by $m = \pi \rho_p d_p^3 / 6$. For nonporous spherical particles, $d_p = d_m$ (Section S5).

After substitution of Equations (9) and (10) into Equation (11), the result is as follows:

$$E_k,0 = \frac{1}{2} m v_0^2 + E_{a,m} + E_{k,\text{rest}}$$

$$= \frac{\pi}{12} \frac{d_m^3}{d_a^3} C_v (d_m) \rho_p \xi^2_{<5\% \text{RH}}$$

$$- \left(\frac{8 \pi \sigma^2 V_m}{RT}\right) \left(\frac{c^2 d_p}{\ln(\text{RH}/100)}\right) + E_{k,\text{rest}} \tag{12}$$

The normally incident velocity $v_0$ at impact and hence $E_{k,0}$ (i.e., $E_{k,0} = m v_0^2 / 2$) for each streamline of the nozzle is determined from numerical simulation (Section S7). The governing equation for the model of RH-dependent rebound is thus obtained (i.e., the term $E_{k,\text{rest}}$ is positive and rebound thus occurs) by satisfying the following inequality:

$$d_m^2 \left(\frac{v_0^2}{v_r^2} - \frac{C_v (d_m)}{C_v (d_a)} \frac{1}{d_a^3}\right) > - \frac{96 \sigma^2 V_m c^2}{\rho_p RT \xi^2_{<5\% \text{RH}} \ln(\text{RH}/100)} \tag{13}$$

The LHS term varies with particle diameter whereas the RHS term is invariant for fixed RH. By application of this equation as a test across all streamlines, the rebound fraction $f(d_a; \text{RH})$ of
In the case of ammonium sulfate, model results are shown only up to 80% RH because deliquescence occurs at that point. An expanded model to treat deliquescence would need to include an additional term in Equation (11) to account for energy dissipation by deformation of liquid particles (Miyakawa et al. 2013).

A more generalized simulation of rebound fraction, as dependent both on diameter and RH, is presented in Figure 7 for PSL particles in the $\alpha$ impactor. The curvature in rebound fraction apparent in the false-color plot arises from capillary forces. For fixed RH and sufficiently small diameters, the particle population adheres. For sufficiently large diameters, the particle population rebounds. The implication is that care should be taken in an interpretation of a dataset-based on particle adhesion concerning whether particle phase state is solid or liquid: for sufficiently high RH and sufficiently small particle diameter, a population of solid particles can adhere when impacting a hard surface. This effect arises in large part because small particles have small normally incident impact kinetic energies. For a fixed setpoint diameter, this effect becomes more important at higher RH. Conversely, though not observed for the material, have small normally incident impact kinetic energies. For a fixed setpoint diameter, this effect becomes more important at higher RH. Conversely, though not observed for the material, have small normally incident impact kinetic energies.
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