Estimating nanoparticle growth rates from size-dependent charged fractions: Analysis of new particle formation events in Mexico City

Kenjiro Iida,1 Mark R. Stolzenburg,1 Peter H. McMurry,1 and James N. Smith2

Received 7 August 2007; revised 16 November 2007; accepted 11 December 2007; published 5 March 2008.

A method to estimate nanoparticle diameter growth rates (GR) during new particle formation (NPF) events from the measured dependence of charged fraction, f, on size, Dp, is introduced. The method is especially useful for observations during intense particle production rates, when the mode in the distribution of newly formed particles does not grow monotonically with time. This method assumes that the observed profile of f versus Dp during the nucleation and growth period is controlled by condensational growth, ion-particle combination/recombination, scavenging by preexisting particles, and coagulation among growing nanoparticles. Values of growth rates obtained by this method (GR) agree well with independently obtained particle growth rates due to gas-to-particle conversion processes (GR_PSD) during regional NPF events. The method was then applied to characterize the NPF events observed at Tecamac, Mexico. These growth rates were found to range from 15–40 nm/h, which is significantly higher than values reported for other urban areas. The production rates for 1 nm particles calculated from the estimated growth rates and measured Fuchs surface area (J_1nm = 1900–3000 particles/cm² s) are comparable to those recently observed in New Delhi. Because critical nuclei are likely close to 1 nm in size, J_1nm should provide a reasonable estimate for nucleation rates.


1. Introduction

The formation and growth of atmospheric aerosols has recently received much attention because of its potential climate and health-related effects. New particle formation (NPF) has been observed at a number of sites around the world over the last decade [Kulmala et al., 2004b], including in the free troposphere [Hoppe et al., 1994; Clarke et al., 1998; Weber et al., 1999; Twyoh et al., 2002], in rural areas [Weber et al., 1997; Birmili et al., 2003], in urban areas [Woo et al., 2001; Dunn et al., 2004; Wehner et al., 2004, 2006; McMurry et al., 2005; Stolzenburg et al., 2005; Shi et al., 2007], the remote boreal forest [Mäkelä et al., 1997; Kulmala et al., 2004a; Dal Maso et al., 2005], over exposed coastal zones [Bates et al., 1998; O’Dowd et al., 1998, 2002; Berresheim et al., 2002; Ulevicius et al., 2002] and elsewhere. The nucleation mechanisms and the species responsible for the growth of newly formed particles are not yet completely understood.

This paper discusses a new approach for estimating the growth rates (GR) of newly formed particles when GR cannot readily be determined using established approaches.

Copyright 2008 by the American Geophysical Union. 0148-0227/08/2007JD009260

[Weber et al., 1997; Kulmala et al., 2004b; Dal Maso et al., 2005; Fiedler et al., 2005; Stolzenburg et al., 2005]. Growth rates are important because they determine the time required for a freshly nucleated particle to grow to a size that is large enough to serve as a cloud condensation nucleus (CCN). Growth rates also affect the probability that a newly formed particle will grow to a CCN before it is lost by coagulation with a preexisting particle [Weber et al., 1997; Kerminen and Kulmala, 2002; McMurry et al., 2005]. Also, the product of GR times the distribution function at a given size (dN/dDp) equals the particle current past that size, J [Friedlander, 2000]. Empirical information on GR and J is needed to establish models for NPF in the atmosphere. Measured values of J are often significantly higher than values predicted by existing theories for multicomponent nucleation that includes sulfuric acid vapor [Weber et al., 1996, 1997; Clarke et al., 1998; Kulmala et al., 1998; O’Dowd et al., 1999; Birmili and Wiedensohler, 2000; Fiedler et al., 2005; Stolzenburg et al., 2005; Wehner et al., 2005]. Atmospheric observations show that J ~ [H2SO4]², 1 < p < 2, which is a significantly weaker dependence than is predicted by classical nucleation theories [Weber et al., 1996, 1997; Kulmala et al., 2006; Sihto et al., 2006; Kuang et al., 2008; Riipinen et al., 2007]. Several groups are pursuing studies aimed at explaining this observation.

Charged fractions can provide information as to whether ion-induced or homogeneous nucleation is the dominant mechanism. Ion-induced nucleation occurs when...
the growth of ion clusters is activated by other condensable species. It has been observed that the charged fraction of atmospheric nanoparticles, \( f(D_p) \), matches reasonably well with the theoretical stationary state values in the absence of growth, external generation, or electrostatic scavenging [Laakso et al., 2004; Iida et al., 2006; Vana et al., 2006]. Measurements of \( f(D_p) \) of freshly nucleated ultrafine particles are sometimes significantly above or below theoretical stationary state values, indicating that in some cases ion-induced nucleation is important while in other cases nucleation of neutral species is dominant [Hörrak et al., 1998; Tamm et al., 2001; Laakso et al., 2004; Vana et al., 2004, 2006; Iida et al., 2006]. Recent modeling studies have analyzed the evolution of \( f(D_p) \) during nucleation and growth [Tamm et al. and Kulmala, 2005; Yu, 2006], and data inversion schemes to calculate the fractional contributions of ion-induced and neutral nucleation from the measured charged fraction and growth rates have been developed [Iida et al., 2006; Laakso et al., 2006].

[5] In this study, our previous data inversion scheme [Iida et al., 2006] is simplified and extended to estimate the diameter growth rates of freshly nucleated particles from the measured profile of \( f(D_p) \) in the 3.7–25 nm range. This approach is particularly useful if particle production persists at high rates througho
day, so that the mode in the distribution of nucleated particles is not readily apparent. Such NPF events were frequently observed at Tecamac, Mexico during the MILAGRO campaign in March 2006. In principle, this approach enables estimates of \( GR \) from a single measurement of size-dependent charged fractions assuming all the processes affecting the charged fractions are in steady state within a moving air parcel; therefore the method may also be useful for interpreting data for NPF events that are not uniform regionally. Most other approaches for determining \( GR \) apply to regional nucleation events, where modal sizes increase monotonically with time. [6] In this paper we first validate this new method for inferring growth rates using our field data for “regional” nucleation events obtained at Tecamac during MILAGRO and in Boulder Colorado during 2005. We then apply it to determine growth rates during more complex nucleation events in Tecamac, Mexico.

2. Experiments

[7] Measurements were performed from 15 to 31 March 2006 during the MILAGRO field sampling campaign. Our sampling site, Tecamac, Mexico, is located 35 km NW of the center of Mexico City. Aerosol size distributions from 3 nm to 5 \( \mu \)m were measured using a pair of scanning mobility particle sizers (SMPS) and an optical particle counter [McMurry et al., 2000; Woo et al., 2001]. The mobility distributions of small and intermediate ions in the 0.5–6.3 nm range were measured using the Inclined Grid Mobility Analyzer (IGMA) [Tamm et al., 2002]. Small ions are defined as those having electrical mobility ranging from 0.5 to 3.2 cm\(^2\)/V-s; their corresponding geometrical diameters [Tamm et al., 1995] range from 1.6 to 0.4 nm. The electrical mobility and diameter ranges of the intermediate ions are 0.05–0.5 cm\(^2\)/V-s and 6.3–1.6 nm, respectively. The Radial SMPS system shown in Figure 1 was used to measure the charged fractions of 2.5–25 nm particles. The system consists of a Radial Differential Mobility Analyzer (RDMA) [Zhang et al., 1995] and a TSI 3785 Water-based Condensation Particle Counter (WCPC) [Hering et al., 2005].

[8] During operation atmospheric aerosols at 2 LPM constantly flow through the \(^{210}\)Po neutralizer and the geometrically identical dummy neutralizer which samples in parallel. It is important to maintain steady flow through the neutralizer since particles formed by radioactive decay inside the \(^{210}\)Po neutralizer accumulate under stagnant conditions (see Appendix A). A three-way valve selects particles that flow either through the \(^{210}\)Po neutralizer or the dummy neutralizer. The aerosol that passes through the \(^{210}\)Po neutralizer is assumed to reach the stationary state charge distribution [Fuchs, 1963; Hoppel and Frick, 1986; Reischl et al., 1996]; therefore the total population for a given size can be calculated. Aerosol that passes through the dummy neutralizer has the same charge state as the ambient air. The charged fraction for a given size and polarity is calculated by taking the concentration ratio of charged to total (charged plus neutral) particles.

[9] Figure 2 shows the experimentally evaluated transport efficiency through the \(^{210}\)Po neutralizer, the dummy neutralizer, and radial DMA, as well as the detection efficiency of the WCPC. As shown in Figure 2, the losses through the

Figure 1. Schematic of the Radial SMPS system.
210Po neutralizer and the dummy neutralizer are nearly equal. The condenser and saturator temperature of the WCPC were changed to 72°C and 15°C, respectively, to lower the size detection limit. We found that by increasing the temperature difference of the TSI 3785 condenser and saturator, the 50% cutoff size \(D_{P50}\) for detecting NaCl test aerosol is extended down to 2.2 nm. A recent study showed that \(D_{P50}\) for this instrument is strongly material-dependent and that its detection efficiency for atmospheric particles increases with increasing particle hygroscopicity [Hering et al., 2005; Kulmala et al., 2007]. Because our measured charged fractions equal the ratio of charged to total concentrations, the effects of transport losses and composition-dependent CPC counting efficiencies cancel out and do not affect our results.

3. Results

During the campaign, evidence of nucleation was clearly observed on 13 out of 17 days. We categorized these nucleation events into two types, which are illustrated in Figures 3 (type I) and 4 (type II). Type I and II events share several common features. The elevated concentrations of 10–50 nm particles observed between 0400 and 0700 local time (LT) in Figures 3 and 4 appear to be associated with rush hour traffic, and Figures 3b and 4c show that \(H_2SO_4\) vapor concentrations remained low during these periods. As shown in Figures 3a and 4a, new particle formation typically occurred sometime between 0700 and 1200 LT, and was accompanied by significantly elevated concentrations of \(H_2SO_4\) and sub-5 nm particles. Type I and II nucleation events are distinctly different in the following three respects. First, the evolution of modal diameter of freshly nucleated particles is readily apparent for type I but not for type II events. Most previous analyses of new particle formation and growth rates have focused on type I events [Weber et al., 1997; Kerminen and Kulmala, 2002; Kulmala et al., 2004b; Dal Maso et al., 2005; Stolzenburg et al., 2005]. Second, a parameter that can quantitatively distinguish between type I and II events are the scavenging rate of freshly nucleated 3–6 nm particles, \(\Gamma_{3–6nm}\), given by

\[
\Gamma_{3–6nm} = \frac{1}{4} c_P A_{Fuchs} N_{3–6nm}
\]

Figure 2. Measured transport efficiencies through the neutralized path, dummy path, and radial DMA and the detection efficiency of the WCPC. Shown here are parameterized curves fitted to experimental data. CPC detection efficiencies drop rapidly to zero for sizes below 2.2 nm.

Figure 3. Example of a type I nucleation event. Measurements were obtained on 22 March 2006 at Tecamac, Mexico. (a) Contour plots of the particle number distributions measured by the SMPS system (\(\Delta N/\Delta \log D_p\)) and (b) concentration of \(H_2SO_4\) vapor and 3–6 nm particles.
where \( c_p \) is the mean thermal velocity at the geometric mean size of 3–6 nm size bin, \( A_{\text{Fuchs}} \) is the Fuchs aerosol surface area of preexisting aerosol. Figure 5 shows the frequency distribution of the value of \( G_{3-6nm} \) during the new particle formation period analyzed in this study. Data for type I events also includes five additional type I NPF events obtained in Boulder, Colorado, during 2005 since the amount of type I data obtained during the MILAGRO campaign is limited. As shown in Figure 5 two distributions are distinctly separated by about two orders of magnitude. The geometric mean values of the distributions are 1.0 cm\(^{-3}\) s\(^{-1}\) and 150 cm\(^{-3}\) s\(^{-1}\) for type I and II events, respectively, suggesting that the particle production rates at 3–6 nm are also expected to be in the same order of magnitude. Third, as shown in Figure 4c concentrations of freshly nucleated 3 to 6 nm particles during type II events, \( N_{3-6nm} \), are significantly higher and remain high for a longer time period. As a result, it is difficult to follow the peak of the evolving particle size distribution in time; therefore it is difficult to obtain the modal diameter growth rate. Type II events account for five out of thirteen events during the measurement period while type I events account for only three. The remaining five events are associated with inhomogeneities in air transported to our sampling site (plume impacts, etc.), and are neither of type I or II. Since type II events led to high concentrations of nucleated particles, it is important to have an approach for analyzing such data.

Note also that during the particle production periods shown in Figures 3 and 4, the time lags between changes in \( \text{H}_2\text{SO}_4 \) and \( N_{3-6nm} \) are short or negligible. Previous studies in remote or rural environments have shown that the growth
rates of freshly nucleated particles can be estimated from the time lag between the time profile of H$_2$SO$_4$ vapor and N$_{3–6nm}$ [Weber et al., 1997; Dal Maso et al., 2005; Sihto et al., 2006; Kuang et al., 2008; Rimpinen et al., 2007]. The absence of a time lag in our data qualitatively implies that the growth rates from the size of initial nuclei (~1 nm) to 3–6 nm in Tecamac, Mexico, are higher than those typically observed in rural or remote environments. As is shown below, growth rates observed in Tecamac, Mexico are significantly higher than have been reported for other sites.

4. Analysis

4.1. Estimating Diameter Growth Rates From Size-Dependent Charged Fractions

[12] As mentioned previously, it is often not possible to estimate the diameter growth rates for type II events using conventional approaches. In this section, a method is introduced to estimate the diameter growth rate from the measured charged fraction of 3.7 to 25 nm particles observed during such events. The method tries to find diameter growth rate, $GR_p$ that reproduces the measured size-dependent charged fraction, $f$ versus $D_p$, by simulating condensational growth, ion-particle combination/recombination, coagulation among growing nanoparticles, and scavenging by preexisting particles. To simplify analysis, we make the following four assumptions:

[13] 1. The size distributions of freshly nucleated nanoparticles in the 3.7–25 nm range are equal for positively and negatively charged particles

$$n_p \approx n_n = n_i,$$  \hspace{1cm} (2)

where $n_p$ and $n_n$ are the particle size distribution, $dN/dD_p$, of positively and negatively charged particles, respectively, and $n_i$ is used to represent $dN/dD_p$ of positively or negatively charged particles. Since the fraction of charged particles are calculated by taking the concentration ratio of charged to total (charged plus neutral) particles, it follows that the fractions of positively and negatively charged particles are equal:

$$f_p \approx f_n = f$$  \hspace{1cm} (3)

where $f_p$ and $f_n$ are the fraction of positively and negatively charged particles, respectively. We use $f$ to represent the charged fraction of positively or negatively charged particles

$$f = \frac{n_p}{2n_1 + n_0} = \frac{n_i}{n_{tot}},$$  \hspace{1cm} (4)

where $n_0$ and $n_{tot}$ are the particle size distribution of electrically neutral and total particles, respectively. This assumption is consistent with the charged fractions of 3.7–25 nm particles measured with the Radial SMPS system for all the NPF events analyzed and is also consistent with recent measurements in Hyv"{a}ti"{a}, Finland, for particles larger than 5 nm [Vana et al., 2006]. This assumption is also consistent with the theoretical analysis of Hoppel and Frick [1986, 1990] which states the ratio of negatively to positively charged fractions approaches unity under relatively high ion depletion rate to the aerosols and low ion production rate in the atmosphere. The measured values of $n_i$ are obtained by taking the average values between measured $n_i$ and $n_{-}$. 

[14] 2. The concentrations and electrical mobilities of positive and negative small ions are equal.

$$c_{+ion} \approx c_{-ion} = c_{ion} \hspace{1cm} (5a)$$

$$Z_{+ion} \approx Z_{-ion} = Z_{ion} \hspace{1cm} (5b)$$

where, $c$ and $Z$ are concentration and electrical mobility of small ions, respectively. We define small ions as those having electrical mobility ranging from 6.3 to 0.5 cm$^2$/V-s. The corresponding range of sizes is 0.4 to 1.6 nm. As seen in the IGMA data taken after 0700 LT in Figure 4b these small ions are always present in the atmosphere. The representative concentration and electrical mobility of positive or negative small ions ($c_{ion}$ and $Z_{ion}$) are obtained by taking the average values of positive and negative small ions measured by the IGMA: $c_{ion} = \text{Average}(c_{+ion}, c_{-ion})$, $Z_{ion} = \text{Average}(Z_{+ion}, Z_{-ion})$. We have confirmed that values of growth rates obtained using this assumption do not change significantly if the electrical mobilities and concentrations of small positive and negative ions measured by the IGMA are both used to simulate interactions between small ions and particles. Results are shown only for the average values of mobility and concentration, since this significantly simplifies the discussion.

[15] 3. The diameter growth rates of 3.7–25 nm particles during a NPF event are independent of charge state. The effect of particle charge on condensation rates can be estimated from the permanent and induced dipole moments of the condensing vapor [Nadykto and Yu, 2003; Tammet and Kulmala, 2005]. For sulfuric acid, the enhancement factor is less than 1.05 for sizes above 3.5 nm [Tammet and Kulmala, 2005]; therefore the effect of charge-enhanced growth is likely negligible for particles larger than 3.7 nm.

[16] 4. The time dependences of all simulated processes that affect the size-dependent charged fractions during growth from 3.7 to 25 nm are neglected. These processes include condensational growth, ion-particle combination/recombination, coagulation among growing nanoparticles, and scavenging by preexisting particles. This assumption simplifies the determination of $GR_p$ by the least squares scheme. In section 5 we will estimate the error in diameter growth rate caused by this assumption. The results suggests that errors are less than 10% during the middle part of NPF events and increase up to 20–30% near the beginning and end of the NPF event.

[17] Using the assumptions 1 through 3, the rates of change of the particle size distribution functions of electrically charged and neutral particles are given by

$$\frac{\partial n_0}{\partial t} + \frac{\partial n_0}{\partial D_p} = -2\beta_0 c_{ion} n_0 + 2\beta_1 c_{ion} n_1 + r_0 \hspace{1cm} (6a)$$

$$\frac{\partial n_1}{\partial t} + \frac{\partial n_1}{\partial D_p} = \beta_0 c_{ion} n_0 - \beta_1 c_{ion} n_1 + r_1 \hspace{1cm} (6b)$$
where $n_0$ and $n_1$ are particle size distributions, $dN/dD_p$, of electrically neutral and singly charged particles, respectively. The "current" of particles with charge state $q$ past size $D_p$, $J_q$, is given by $J_q = n_q GR_p$, where $GR_f$ is the diameter growth rates of electrically neutral or charged particles obtained from this approach. Theory of Fuchs is used to evaluate the ion-particle combination coefficients, $\beta_b$, for collisions between small ions and charged particles and ion-particle recombination coefficients, $\beta_1$, for collisions between small ions and charged particles having opposite polarity [Reischl et al., 1996]. Other production or depletion mechanisms of charged and neutral particles, primarily loss to preexisting particles and intramodal coagulation, are represented by $r_1$ and $r_0$, respectively.

[18] Equations (6a) and (6b) can be combined using the following relations

$$J_1 = n_1 D_p = f n_{tot} D_p = f J_{tot},$$  \hspace{1cm} (7a)$$

$$J_{tot} = J_0 + 2J_1,$$  \hspace{1cm} (7b)$$

$$r_{tot} = r_0 + 2r_1,$$  \hspace{1cm} (7c)$$

where, $J_{tot}$ and $r_{tot}$ are the particle current and the production/depletion rate of total particles, respectively. The resulting equation is

$$\frac{df}{dt} + GR_f \frac{df}{dD_p} = c_{ion} \beta_b \left(1 - \frac{f}{f_{stationary}}\right) + \frac{(r_1 - f r_{tot})}{n_{tot}}.$$  \hspace{1cm} (8)$$

The stationary state charged fraction, $f_{stationary}$, is given by

$$f_{stationary} = \frac{\beta_b}{\beta_1 + 2\beta_0}.$$  \hspace{1cm} (9)$$

This expression gives accurate values for sizes below 25 nm based on assumptions 1 and 2. Under steady-state conditions, equation (8) simplifies to:

$$GR_f \frac{df}{dD_p} = c_{ion} \beta_0 \left(1 - \frac{f}{f_{stationary}}\right) + \frac{(r_1 - f r_{tot})}{n_{tot}}.$$  \hspace{1cm} (10)$$

In this study we use a least squares method to determine $GR_f$ from equation (10). Measured values for $f(D_p)$, $c_{ion}$, temperature and particle size distributions are used when calculating $GR_f$. Estimates of error caused by neglecting the time dependence of $f$ are included in section 5.

[19] Scavenging of growing nanoparticles by larger preexisting particles is the most important depletion mechanism, and coagulation of smaller particles is an important production mechanism at a given size. Equation (10) can be rewritten to explicitly show the scavenging and coagulation terms:

$$GR_f \frac{df}{dD_p} = c_{ion} \beta_0 \left(1 - \frac{f}{f_{stationary}}\right) - (\Gamma_1 - \Gamma_{tot}) f + K_1 - f K_{tot}.$$  \hspace{1cm} (11)$$

where $K$ and $\Gamma$ are the coagulation rate and scavenging rates, respectively, and the expressions for $K$ and $\Gamma$ are given in the notation section. The scavenging rate for total particles, $\Gamma_{tot}$, is generally evaluated assuming that growing nanoparticles and preexisting particles are electrically neutral [Weber et al., 1997; Dal Maso et al., 2002; Kerminen and Kulmala, 2002; McMurry et al., 2005]. In order to calculate the scavenging rate of charged particles, $\Gamma_1$, we assumed the stationary state distribution for the preexisting particles and accounted for the effects of charge on scavenging rates. Note that $f$ is not affected by scavenging if electrostatic interactions with the preexisting particles are neglected, $\Gamma_1 = \Gamma_{tot}$. $K_1$ is the coagulation rate between charged and neutral particles that accounts for enhancements in collision rates due to image forces. In order to analyze the effect of charge-enhanced coagulation the measured size-dependent charge fraction ($f$ versus $D_p$) and size distributions of total particles were extrapolated to sizes below 3.7 nm to 1 nm assuming a power law relationship between $dN/dD_p$ versus $D_p$ [McMurry et al., 2000] and, similarly, $f$ versus $D_p$. We found it is unnecessary to decompose $K_{tot}$ into $K_0 + 2K_1$ since the separation has negligible effects on the obtained $GR_f$. Therefore $K_{tot}$ was calculated assuming that all particles are electrically neutral. Our further analyses showed that the effects of scavenging and coagulation on $GR_f$ for type I NPF events analyzed in this paper are generally insignificant, while those effects were significant for type II NPF events. A detailed analysis of this subject is given in section 5.

4.2. Validation of the Method

[20] Before applying the method introduced in the previous section to type II events observed in Tecamac, the method is verified by applying it to type I events where growth rates can be evaluated independently from growth of the particle size distribution when the modal diameter is evolving from below 10 nm to around 60 nm. Stolzenburg et al. [2005] showed that both intra and inter modal coagulation cause the observed modal growth rates to be higher than the growth rates of particles due to gas-to-particle conversion processes, $GR_{PSD}$; therefore the observed modal growth rates were corrected for these effects. Additionally, the particle current, $J$, passing toward larger sizes through both upper and lower size boundaries of the growing mode decreases the modal growth rate [Iida, 2008]; therefore the observed modal growth rates were corrected for these effects. In this section, data obtained in Boulder, Colorado, during 2005 are also used to validate this approach for determining growth rates since the amount of type I data obtained during the MILAGRO campaign is limited. The same instruments were used for the Boulder and MILAGRO studies.

[21] In order to quantitatively evaluate the method, we compared $GR_f$ and $GR_{PSD}$. Since observed $GR_{PSD}$ is constant no size dependence in $GR_f$ is included in the analysis. Although the Radial SMPS starts scanning from 2.5 nm, charged fractions measured below 3.7 nm were disregarded in the analysis since the values measured below ~3.0 nm were occasionally affected by the particles formed inside the $^{210}$Po neutralizer. This artifact was also investigated during the MILAGRO campaign, as discussed in Appendix A. In order to obtain $f$ versus $D_p$ data in the 3.7 to 25 nm size range, we used data from the MILAGRO and type II events observed in Tecamac.
range is divided into four equal logarithmic intervals. Charged fractions for size interval \( j \), \( f_j \), were evaluated by

\[
\frac{f_j}{f} = \frac{\int_{D_p} f_n dD_p}{\int_{D_p} n_{as} dD_p}
\]

where integration is over size interval \( j \). \( GR_f \) is obtained for each NPF period by solving equation (11) by iteratively adjusting the values of \( GR_r \) and of \( f \) at the lowest size boundary until the calculated profile of \( f \) versus \( D_p \), matched measurements. Figure 6 shows a typical example of measured and fitted profiles of \( f \) versus \( D_p \). It was generally found during this study that measured and fitted profiles of \( f \) versus \( D_p \) matched well without including the size dependence of \( GR_r \) in equation (11) suggesting that actual diameter growth rates within the 3.7–25 nm range were reasonably constant during type I and II events analyzed in this study. Table 1 summarizes the six type I NPF events analyzed, and Figure 7 compares \( GR_f \) and \( GR_{PSD} \) for those same events. The correlation coefficients between \( GR_f \) and \( GR_{PSD} \) is 0.94 and most observations of \( GR_f \) and \( GR_{PSD} \) agree to within estimated uncertainties, supporting our argument that charged fractions in the 3.7 to 25 nm diameter range can be used to estimate growth rates.

4.3. Application of the Method: Analysis of Type II Nucleation Events in Mexico City

The method introduced in the previous section was applied to the three type II events during which the SMPS, Radial SMPS, and the IGMA were working properly. The diameter growth rates \( GR_r \) were obtained by solving equation (11), which includes the effects of scavenging and coagulations. Figure 8 shows an example of \( GR_r \) obtained during type II new particle formation events observed on 16 March 2006. Figures 8a and 8b show the contour plots of the particle number distributions (\( \Delta N/\Delta \log D_p, \text{cm}^{-3} \)) measured by the SMPS system and positive small-intermediate ions measured by the IGMA, respectively. Estimated diameter growth rate, \( GR_f \), and concentration of \( \text{H}_2\text{SO}_4 \) are shown in Figure 8c. The values of \( GR_f \) correspond well with the concentration of \( \text{H}_2\text{SO}_4 \) although they are obtained by independent measurement techniques indicating that \( \text{H}_2\text{SO}_4 \) plays an important role in particle growth within the 3.7–25 nm range. Properties and composition of the freshly nucleated nanoparticles were also measured with the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) on 16 March 2006 [Smith et al., 2008]. That study showed that organics were responsible for about 90% of the growth while sulfates accounted for only about 10%. Independent calculations based on measured concentrations of sulfuric acid vapor concentrations produce the consistent result that sulfuric acid condensation could account for only about 10% of the observed growth rate, \( GR_r \). [21] Table 2 shows the average value and standard deviation among the estimated values of \( GR_r \) for three type II events. The number of analyzed size-dependent charged fractions and the duration of the analyzed time in hours are also given in Table 2. The average and standard deviation among the values of \( GR_f \) among all three days are 24 nm/h and 11 nm/h, respectively. The estimated diameter growth rates are higher than the values observed in other polluted areas: 3–22 nm/h in Atlanta [Stolzenburg et al., 2005], 6.7 ± 4.8 nm/h in St. Louis [Shi et al., 2007], 0.1–13.5 nm/h in Beijing [Wehner et al., 2006], 11.6–18.1 nm/h in New Delhi [Kulmala et al., 2005; Mönkkönen et al., 2005].

[24] Once the growth rate is available, the particle formation rate at 1 nm, \( J_{1nm} \), can be estimated using the following expression [Weber et al., 1997; McMurry et al., 2005]:

\[
J_a = J_b \exp \left( \frac{1}{2} \frac{A_{Fuchs}}{GR} \left[ \frac{48k_BT}{\pi^2 \rho} \right]^{1/2} \left[ D_{pa}^{1/2} - D_{pb}^{1/2} \right] \right)
\]

where \( \rho \) is particle density. The subscripts \( a \) and \( b \) indicate the initial size (1 nm in this work) and the representative size at which new particle formation rates were measured, respectively. In our case the size b (4.7 nm) corresponds to the geometric mean of the smallest size interval for the Radial SMPS data (~3.7 to ~6.0 nm). The particle current \( J_b \) is equal to the product of particle size distribution \( dN/dD_p \) and \( GR \). Equation (13) describes the particle current along the characteristic growth trajectory when nanoparticle growth rates and scavenging by the preexisting aerosol surface area, \( A_{Fuchs} \), are both constant. Nucleation rates can be reasonably estimated by \( J_{1nm} \) [McMurry, 1983] since the critical size is likely in the vicinity of 1 nm. As shown in Table 2, the estimated nucleation rate \( J_{1nm} \) is on the order of a few thousand per cm\(^3\)-s. Using a similar approach, \( J_{1nm} \) for NPF events in New Delhi were estimated to be ~1300 per cm\(^3\)-s [Kulmala et al., 2005; Mönkkönen et al., 2005].
indicating that the nucleation rates in these mega cities, Mexico City and New Delhi, are comparable.

Previous studies suggest that the diameter growth rates below 3 nm are smaller than the values estimated from the evolution of particle size distributions [Kulmala et al., 2004b; Fiedler et al., 2005]. The slower the diameter growth rates the smaller the fraction of nucleated particles that would survive to the detectable size range (~3 nm). Since the calculated $J_{\text{ion}}$ depends exponentially on the diameter growth rate, slower diameter growth rates would increase the estimated nucleation rate.

5. Discussion
5.1. Effect of Neglecting Time Dependence on the Estimated Diameter Growth Rates

In our analysis the steady state assumption (assumption 4) was applied to obtain equation (10). The error caused neglecting unsteady effects can be estimated by including the partial derivative with respect to time $\partial f/\partial t_{D_p}$ in equation (10) and solving for $GR_f$.

$$GR_f = \frac{1}{\partial f/\partial D_p} \left[ \hat{\beta}_f c_{\text{ion}} \left( 1 - \frac{f}{f_{\text{stationary}}} + \frac{(r_l - r_{\text{tot}})}{n_{\text{tot}}} \right) \right]$$

The first term on the RHS equals the steady state growth rate, $GR_f$ estimated by our analysis. Accordingly, the second term is the correction due to unsteady effects.

$$GR_f^{\text{unsteady}} = GR_f^{\text{steady}} + \Delta GR_f^{\text{unsteady}}$$

$$GR_f^{\text{steady}} = \frac{1}{\partial f/\partial D_p^{\text{stationary}}} \left[ \hat{\beta}_f c_{\text{ion}} \left( 1 - \frac{f}{f_{\text{stationary}}} + \frac{(r_l - r_{\text{tot}})}{n_{\text{tot}}} \right) \right]$$

$$\Delta GR_f^{\text{unsteady}} = -\frac{\partial f/\partial D_p^{\text{stationary}}}{\partial f/\partial D_p}$$

The values of measured $f$ and $D_p$ generally vary linearly with correlation coefficients exceeding 0.98 when plotted on log-log scale; therefore the partial derivative $\partial f/\partial D_p^{\text{stationary}}$ in the denominator of $\Delta GR_f^{\text{unsteady}}$ can be expressed as $\partial f/\partial D_p^{\text{stationary}} = f \cdot \kappa / D_p$ where the constant $\kappa$ equals $\partial \ln f / \partial \ln D_p$. Then $\Delta GR_f^{\text{unsteady}}$ is written as

$$\Delta GR_f^{\text{unsteady}} = -\frac{D_p}{\kappa \partial f/\partial D_p^{\text{stationary}}}$$

The values of $\partial f/\partial D_p^{\text{stationary}}$ evaluated using the data obtained at the beginning and end of the NPF events generally have larger fluctuations than those during the middle part of

![Figure 7](image-url)

Figure 7. Comparison of diameter growth rate of particles due to gas-to-particle conversion obtained from the measurement of size-dependent charged fraction, $GR_f$, versus those obtained the evolution of the particle size distribution, $GR_{PSD}$. The vertical error bars are one standard deviation among the values of $GR_f$ for each measured size-dependent charged fraction. The horizontal error bars are one standard deviation in $GR_{PSD}$ caused by correcting the observed modal diameter growth rate for the effects of coagulation, scavenging, and particle current through boundaries of growing mode at given time.
the event. We evaluated $\Delta GR_f^{unsteady}$ at four sizes and used the average of these values when estimating $GR_f$. The error in the diameter growth rate caused by neglecting unsteady effects, $\varepsilon$, can be expressed as

$$\varepsilon = \frac{\Delta GR_f^{unsteady}}{GR_f^{steady}}. \quad (17)$$

The value of $\varepsilon$ is plotted in Figure 8d for data obtained on 16 March. The values of $\varepsilon$ are higher (20–30%) at the beginning and end of the NPF event, while they are low (<10%) during the middle of the event.

5.2. Effect of Scavenging and Coagulation on Estimated Diameter Growth Rates

It is desirable to find conditions in which the effects of scavenging and coagulation can be neglected when obtaining $GR_f$ from the measurements of $f$ versus $D_p$ since the computational time spent for calculating the scavenging and coagulation rates are about 50 times greater than those for that account only for ion-particle combination/recombin-

![Figure 8. Example of diameter growth rates estimated from the size-dependent charged fraction measured during new particle formation events observed on 16 March 2006. Contour plots of (a) the particle number distributions ($\Delta N/\Delta \log D_p$, cm$^{-3}$) measured by the SMPS system and (b) positive small-intermediate ions measured by the IGMA. (c) Estimated diameter growth rate, $GR_f$, and concentration of H$_2$SO$_4$. The noises in $GR_f$ are reduced by performing 30 min running average. (d) Estimated error in $GR_f$ caused by neglecting unsteady effects, $\varepsilon$.](image)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>16 March 2006</th>
<th>18 March 2006</th>
<th>21 March 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of data points</td>
<td>28</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Time duration, hours</td>
<td>2.3</td>
<td>1.2</td>
<td>3.0</td>
</tr>
<tr>
<td>$GR_f$, nm/h</td>
<td>24 (±5.0)</td>
<td>39 (±9.0)</td>
<td>15 (±2.7)</td>
</tr>
<tr>
<td>Fuchs surface area, $A_{\text{Fuchs}}$μm$^2$/cm$^3$</td>
<td>536 (±90)</td>
<td>630 (±111)</td>
<td>365 (±81)</td>
</tr>
<tr>
<td>$J$ at 4.7 nm, cm$^{-3}$ s$^{-1}$</td>
<td>200 (±82)</td>
<td>510 (±200)</td>
<td>140 (±80)</td>
</tr>
<tr>
<td>$J$ at 1 nm, cm$^{-3}$ s$^{-1}$</td>
<td>2600 (±1300)</td>
<td>2800 (±1000)</td>
<td>1900 (±1300)</td>
</tr>
</tbody>
</table>

The values in the parentheses are time variations of a given parameter during the NPF period expressed as one standard deviation.

*Geometric mean size of smallest size regime used in our analysis of Radial SMPS data.*

| Table 2. Summary of the Analysis of Type II Nucleation Events Observed at Tecamac, Mexico* |

*The values in the parentheses are time variations of a given parameter during the NPF period expressed as one standard deviation.*
nation rates. This section theoretically describes these effects on \( GR_f \). On the basis of this analysis we conclude that coagulation and scavenging can be safely neglected during the type I events but not during the type II events that were included in this study.

In order to understand the effects of scavenging and coagulation on the size-dependent charged fractions it is helpful to rearrange equation (11) into the following form.

\[
GR_f \frac{df}{dD_p} = A \left( 1 - \frac{f}{f_{\text{asymptotic}}} \right) \tag{18a}
\]

\[
A = \beta_0 c_{\text{ion}} + K_1 \tag{18b}
\]

\[
f_{\text{asymptotic}} = \frac{A}{f_{\text{stationary}} + (1 - \Gamma_{\text{es}}) + K_{\text{tot}}} \tag{18c}
\]

where \( f_{\text{asymptotic}} \) is the asymptotic value of \( f \) that would be achieved in the absence of growth by gas-to-particle conversion (i.e., \( GR_f = 0 \)) when coagulation and scavenging are occurring. Equation (18a) indicates that the charged fraction of particles approaches \( f_{\text{asymptotic}} \) as the particles acquire charge during their growth. Figure 9 shows the profiles of \( f \) versus \( D_p \) measured during two type I and one type II NPF events; measured charged fractions are nondimensionalized by both \( f_{\text{asymptotic}} \) and \( f_{\text{stationary}} \). The initial charge state around 1 nm inferred from the diameter growth rates and measured charged fraction [Iida et al., 2006] suggests that the nucleated particles are initially almost all electrically neutral. Figure 9 shows that the measured charged fraction of particles approaches \( f_{\text{asymptotic}} \) as the particles acquire charge during their growth; our observations are all qualitatively consistent with the trend predicted by the form \( A(1 - f/f_{\text{asymptotic}}) \) in equation (18a). When particle production rates were low, \( f/f_{\text{stationary}} \) and \( f/f_{\text{asymptotic}} \) both approach unity indicating that scavenging and coagulation have negligible effects on the asymptotic trend of \( f \). However, as \( J_{\text{inn}} \) increases, \( f/f_{\text{stationary}} \) deviates further from unity while \( f/f_{\text{asymptotic}} \) consistently approaches unity indicating that the effects of scavenging and coagulation become more important as nucleation rate increases.

Figure 9. Size-dependent charged fractions measured during two type I and one type II NPF events. The values are nondimensionalized by \( f_{\text{asymptotic}} \) and \( f_{\text{stationary}} \).

Figure 10. Frequency distribution of percent errors on \( GR_f \) caused by neglecting (a) the effect of scavenging, (b) coagulation, and (c) both scavenging and coagulation.
Figures 10a–10c show the frequency distributions of errors in $GR_f$ caused by neglecting scavenging, coagulation, and both scavenging and coagulation. As shown in Figure 10a, $GR_f$ is always overestimated if the electrostatic effects on scavenging are neglected ($\Gamma_0 = \Gamma_1$). This occurs because neglecting scavenging increases the value of $f_{\text{asymptotic}}$, thereby increasing the RHS of equation (18a), which in turn leads to a higher value of $GR_f$. Neglecting coagulation ($K_0 = K_1 = 0$) causes $A$ to decrease (equation (18b)) and $f_{\text{asymptotic}}$ to increase (equation (18c)). The net effect is that $GR_f$ is generally underestimated. This effect is stronger for type II events where number concentrations are very high. Figure 10c shows errors that occur when both scavenging and coagulation are neglected. For type I events, the overall error on $GR_f$ is $7.8 \pm 7.4\%$ indicating that the size-dependent charged fractions are determined primarily by the condensation growth and ion-aerosol attachment.

Accordingly, for the type I events the governing equation simplifies to:

$$\frac{df}{dD_p} = \frac{c_{\text{ion}}}{GR_f c_{\text{ion}}} \beta_0 \left(1 - \frac{f}{f_{\text{stationary}}} \right). \quad (19)$$

Since the ion mobility and ion mass estimated by the method of Tammet [1995] do not vary significantly among different nucleation events, the value of $\beta_0$ and $f_{\text{stationary}}$ for a given size also do not vary much. It follows that the dependence of $f$ on $D_p$ depends primarily on the ratio $GR_f / c_{\text{ion}}$. Figure 11 shows the measured charged fraction normalized by the stationary state values, $f / f_{\text{stationary}}$, observed during three type I NPF events in Boulder, Colorado. In order to confirm that the observed trend of $f$ versus $D_p$ is consistent with the trend predicted by equation (19) the actual diamet...
was stopped for several minutes by opening and closing valves 1 and 2, respectively. Figure A2 shows the frequency of counts measured by the ultrafine condensation particle counter, UCPC, when valve 2 was opened and valve 1 was closed simultaneously. Counting rates initially dropped rapidly as particles that had been formed radiolytically during the stagnant period were purged from the neutralizer. After about 2 min, particle concentrations downstream of the neutralizer were found to oscillate, as has been observed previously for aerosol reactors [Friedlander, 2000]. Further experiments showed that the detected particles are almost all electrically neutral, and that the effect of this artifact on the particle size distribution measured by the Radial SMPS system (Figure 1) was negligible within the 2.5–25 nm range as long as air is constantly flowing through the $^{210}$Po neutralizer.

In order to determine the accuracy of our measured charged fractions, this artifact was also investigated during the MILAGRO campaign. A Teflon filter was installed at the aerosol sampling inlet of the Radial SMPS to remove particles without otherwise affecting the composition of the sampled air. Although the flows through $^{210}$Po and dummy neutralizers were continuous, a large number of particle counts was occasionally observed when the sampled air passed through the $^{210}$Po neutralizer, whereas near zero counts were routinely observed through the dummy neutralizer. Figure A3 shows a typical particle size distribution (PSD) obtained when particle formation inside the neutralizer was occurring. A comparison between cases with and without the upstream filter indicates that the artifact contributes significantly to the measured PSD below 4.5 nm. A comparison between 1 LPM and 2LPM cases shows that the effect of radiolytic decay extended to larger sizes at lower flow rates, presumably because the longer residence time through the neutralizer to the classifier inlet provides more time for particles to grow and coagulate. Figure A4 shows the size-dependent concentration ratio of particles downstream of the $^{210}$Po neutralizer with and without the Teflon filter installed, $N_{\text{filter}}/N_{\text{no filter}}$. The ratio shows the fractional contribution of artifact to the measured concentration of total (charged plus neutral) particles. The measured total concentration above 3.5 nm is little affected by the artifact, which supports the accuracy of our measured charged fractions above this size.

**Figure A1.** Experimental setup for testing particle formation inside the $^{210}$Po neutralizer.

**Figure A2.** Frequency of counts measured by the UCPC after the stagnant air inside the $^{210}$Po neutralizer was suddenly released.

**Figure A3.** Particle size distribution of nucleated particles downstream of a $^{210}$Po neutralizer. The data were taken during late morning on 18 March 2006 at Tecamac, Mexico, during the MILAGRO campaign.

**Figure A4.** Size-dependent ratio of filtered to unfiltered concentrations downstream of the $^{210}$Po neutralizer.
The reaction of SO2 with OH formed by the radioactive H2SO4 is formed inside the 210Po neutralizer, possibly by the reaction of SO2 with OH formed by the radioactive decay. Several laboratory studies have shown that the addition of an OH radical scavenger such as methanol, isopropanol [Leong et al., 1983] or propane [Hanson, 2005] suppresses such nucleation. We added these scavengers at levels ranging from tens of ppm to a few percent but did not succeed in suppressing particle formation inside the 210Po neutralizer. It is possible that the reagents we used as radical scavengers contained trace impurities that themselves contributed to nucleation. Additional work with purer reagents than were readily available in the field is needed.

**Notation**

- \( A_{Fuchs} \): Fuchs aerosol surface area, (area/volume)
- \( A_{Fuchs} = \frac{4\pi}{3} \int \left( \frac{Kn + Kn^2}{1 + 1.71Kn + 1.33Kn^2} \right) D_p^2 n_{pre-exist} dD_p' \)
- \( c_{ion} \): average concentration of positive and negative small ions (number/volume).
- \( D_p \): particle diameter.
- \( f \): fraction of charged particles at size \( D_p \).
- \( f_{asymptotic} \): asymptotic value of \( f \) that would be achieved at size \( D_p \) in the absence of growth by gas-to-particle conversion when coagulation and scavenging are occurring.
- \( f_{stationary} \): stationary state charged fraction of positively or negatively charged particles at size \( D_p \).
- \( GR_f \): diameter growth rate of particles due to gas-to-particle conversion obtained from the measurement of size-dependent charged fraction (size/time).
- \( GR_{PSD} \): diameter growth rate of particles due to gas-to-particle conversion obtained directly from the growing particle size distribution (size/time).
- \( J_{D_p,q} \): current of particles with charge state \( q \) and size \( D_p \) (number/time).
- \( K_{tot} \): coagulation rate among total (charged + neutral) particles at size \( D_p \) [Seinfeld and Pandis, 1998] normalized by the particle size distribution of total particles \( n_{tot}(D_p) \) (time\(^{-1} \)).
- \( K_{tot(D_p)} = \frac{D_p^2}{n_{tot}(D_p)} \int \frac{1}{D_p'} dD_p' \)
- \( D''_p = \sqrt{D_p^2 - D_p^3} \)
- \( D_{ps} \equiv 1 \text{nm} \)
- \( K_1 \): coagulation rate of singly charged particles with neutral particles (time\(^{-1} \)).
- \( K_{1(D_p)} = \frac{D_p^2}{n_{tot}(D_p)} \int \frac{1}{D_p'} dD_p' \)
- \( Kn \): Knudsen number 2\(\lambda/D_p\).
- \( N \): total particle concentration at size \( D_p \).
- \( n_q \): number distribution of particles with charge state \( q \) and size \( D_p \) (d\(n_{pre-exist}(q,D_p)\)/d\(D_p\)).
- \( \phi_{pre-exist}(q,D_p) \): particle size distribution of preexisting particles with charge state \( q \), (d\(n_{pre-exist}(q,D_p)\)/d\(D_p\)).
- \( r_q \): production or depletion rate of particles with charge state \( q \) and size \( D_p \) by any mechanisms other than ion-aerosol attachment and recombination (number/volume-time-size).
- \( T \): gas temperature.
- \( W_{(q,q')}(D_p,D_p') \): the collision enhancement factor due to electrostatic interaction between a particle with charge state \( q \) and size \( D_p \) and a particle with charge state \( q' \) and size \( D_p' \) [Seinfeld and Pandis, 1998]
- \( \beta_0 \): attachment coefficient for ions and electrically neutral particles of size \( D_p \) (volume/time).
- \( \beta_1 \): recombination coefficient for ions and singly charged particles at size \( D_p \) (volume/time).
- \( \beta_{(D_p,D_p')} \): coagulation coefficient between electrically neutral particles of size \( D_p \) and \( D_p' \) (volume time\(^{-1} \)).
- \( \Gamma_q \): scavenging rate of nanoparticles with charge state \( q \) and size \( D_p \) with preexisting particles (time\(^{-1} \)).
- \( \lambda \): gas mean free path.
- \( \rho \): particle density.
- \( \phi_{(q,q')}(D_p,D_p') \): the electrostatic potential between centers of two conductive particles: a particle with charge state \( q \) and diameter \( D_p \) and a particle with charge state \( q' \) and radius \( D_p' \) [Iida et al., 2006].

**Acknowledgments.** We greatly appreciate S. Sjostedt, D. Tanner, and L. G. Facu at School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA, for sharing their H2SO4 data shown in Figures 3 and 4. Support for this research was provided primarily by DOE grant DE-FG-02-05ER63997.
References


Hanson, D. R. (2005), Mass accommodation of H2SO4 and CH3SO3H on water-sulfuric acid solutions from 6% to 97% RH, J. Phys. Chem. A, 109(31), 6919–6927.


Kulmala, M., K. E. J. Lehtinen, and A. Laaksonen (2006), Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulfuric acid concentration, Atmos. Chem. Phys., 6, 787–793.


McMurry, P. H. (1983), New particle formation in the presence of an aerosol, particles, time scales, and the “threshold” of 0.01 micrometer size distributions, J. Colloid Interface Sci., 95(1), 72–80.


---

K. Iida, P. H. McMurry, and M. R. Stolzenburg, Particle Technology Laboratory, University of Minnesota, 111 Church St. SE, Minneapolis, MN 55455, USA. (iida@me.umn.edu)

J. N. Smith, Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307, USA.