A criterion for new particle formation in the sulfur-rich
Atlanta atmosphere

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[1] A simple dimensionless parameter, L, is shown to determine whether or not new particle formation can occur in the atmosphere on a given day. The criterion accounts for the probability that clusters, formed by nucleation, will coagulate with preexisting particles before they grow to a detectable size. Data acquired in an intensive atmospheric measurement campaign in Atlanta, Georgia, during August 2002 (ANARChE) were used to test the validity of this criterion. Measurements included aerosol size distributions down to 3 nm, properties and composition of freshly nucleated particles, and concentrations of gases including ammonia and sulfuric acid. Nucleation and subsequent growth of particles at this site were often dominated by sulfuric acid. New particle formation was observed when L was less than ~1 but not when L was greater than ~1. Furthermore, new particle formation was only observed when sulfuric acid concentrations exceeded 5 x 10^5 cm^-3. The data suggest that there was a positive association between concentrations of particles produced by nucleation and ammonia, but this was not shown definitively. Ammonia mixing ratios during this study were mostly in the 1 to 10 ppbv range.


1. Introduction

[2] Atmospheric measurements carried out over the past decade have shown that new particles are often formed by nucleation from the gas phase. A recent review of the literature identified about 100 journal articles that report observations of nucleation throughout the troposphere [Kulmala et al., 2004]. Particle formation occurs in the continental boundary layer, in polluted urban areas, in industrial plumes that contain sulfur dioxide, in the outflows of convective clouds, and over exposed tidal zones. Nucleation is typically observed in the morning or near midday, suggesting that it is photochemically driven.
Table 1. Summary of ANARCHES Measurements Pertinent to Nucleation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Technique</th>
<th>Sampling Interval</th>
<th>Measurement Uncertainty</th>
<th>Reference</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2</td>
<td>pulsed fluorescence</td>
<td>5 min</td>
<td>~25%</td>
<td>[Eisele and Berresheim, 1992]</td>
<td>NCAR, ARA</td>
</tr>
<tr>
<td>H2SO4</td>
<td>SICIMSa</td>
<td>7.5 s or 30 s</td>
<td>±40% to ±60%</td>
<td>[Fehsenfeld et al., 2002; Nowak et al., 2002]</td>
<td>NCAR, NOAA, GaTech</td>
</tr>
<tr>
<td>NH3</td>
<td>CIMSa</td>
<td>1 s, 4 s</td>
<td>±20%</td>
<td>[Wang and Flagan, 1990; Woo et al., 2001]</td>
<td>UMN</td>
</tr>
<tr>
<td>Particle size distributions: 3–40 nm, 20–250 nm, 0.1–2 μm</td>
<td>Nano SMPS, SMPS, Lasair model 1002, OPC</td>
<td>5 min</td>
<td>depends on size and concentration</td>
<td>[Sakurai et al., 2005]</td>
<td>UMN</td>
</tr>
<tr>
<td>Nanoparticle volatility and hygroscopicity: 4–10 nm</td>
<td>Nano TDMA^d</td>
<td>~5 min</td>
<td>size changes measured to within ~5%</td>
<td>[Smith et al., 2005]</td>
<td>NCAR, UMN</td>
</tr>
<tr>
<td>Nanoparticle composition: 6–15 nm</td>
<td>TDCIMS^e</td>
<td>occasional</td>
<td>~≤50%</td>
<td>[Hansen et al., 1984]</td>
<td>ARA</td>
</tr>
<tr>
<td>BC^f</td>
<td>aethalometer</td>
<td>5 min</td>
<td>±0.1 μg/m^3 or ±15%, whichever is greater</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a(SICIMS: (Select Ion) Chemical Ion Mass Spectrometry.
^bSMPS: Scanning Mobility Particle Sizer.
^cOPC: Optical Particle Counter.
^dNano TDMA: Nanometer Tandem Differential Mobility Analyzer.
^eTDCIMS: Thermal Desorption Chemical Ionization Mass Spectrometer.
^fBC: black carbon.

[1] While much has been learned about nucleation over the past decade, it is not yet possible to predict, a priori, rates at which particles are formed and grow, or even to know with certainty which species are involved [Kulmala et al., 2004]. Binary nucleation of sulfuric acid and water [Doyle, 1961; Kulmala et al., 1998] was the first atmospherically relevant process for which a theory was developed, and some atmospheric observations are consistent with theoretical predictions for this process [Clarke et al., 1999; Weber et al., 1999; Clement et al., 2002]. However, it is often found that new particle formation rates are orders of magnitude higher than are predicted by the binary theory, especially when nucleation is observed near ground level [Weber et al., 1996, 1999]. These observations have led researchers to conclude that nucleation may involve a species in addition to sulfuric acid and water [Weber et al., 1997]; a leading candidate for this species is ammonia [Kulmala et al., 2000; Napari et al., 2002b; Birmili et al., 2003]. Evidence has also been reported that ion-induced nucleation of sulfuric acid may play a widespread role in the upper troposphere and lower stratosphere [Lee et al., 2003; Lovejoy et al., 2004], that the oxidation of organic iodine compounds may be responsible for nucleation over exposed surf zones [Jimenez et al., 2003] and that complexes of sulfuric and aromatic acids reduce the energy barrier for nucleation [Zhang et al., 2004]. Species that are responsible for the growth of freshly nucleated particles may be different from those that participate in nucleation. Measurements have shown that condensation of sulfuric acid vapor (and its associated water and ammonia) often accounts for only a fraction of the observed growth [Weber et al., 1997, 1998a; Birmili et al., 2003]. Measurements suggest that organic compounds may be responsible for much of the nanoparticle growth during nucleation events in the boreal forests of Finland [O’Dowd et al., 2002].

[4] This paper analyzes data collected during the Aerosol Nucleation and Real Time Characterization Experiment (ANARCHES), which took place in the city of Atlanta during August 2002. The Jefferson Street sampling site, where these measurements were carried out, is described by Solomon et al. [2003]. In this paper we focus on conditions that lead to new particle formation, and also examine the sensitivity of nucleated nanoparticle concentrations to concentrations of gas phase ammonia.

2. Experiment

[5] A summary of parameters measured during ANARCHES that are pertinent to this paper is shown in Table 1. Most details of the measurement techniques are discussed in the cited references. It should be pointed out that in this study, an active control system was used to maintain the relative humidities of particles at 40% during measurement of size distributions. The control system made use of a Permapure Model MD-110-24S Nafion semipermeable membrane [Woo, 2003]. Properties and composition of the freshly nucleated nanoparticles were measured with the Nano TDMA and the TDCIMS. Results of those measurements are discussed in companion papers [Sakurai et al., 2005; Smith et al., 2005]. Measurements were carried out around the clock in a field sampling laboratory that was installed for the study.

3. Theory

[6] “Nucleation” occurs when stable molecular clusters are formed spontaneously from the gas phase. These clusters may contain a single or multiple species. The current thinking about photochemically driven nucleation in the atmosphere is that stable nuclei contain sulfuric acid and water, or sulfuric acid, water, and ammonia, although this has not been demonstrated definitively and, as was discussed above, alternative hypotheses have been suggested. “New particle formation” occurs if nucleated particles grow to a size that can be detected. The minimum detectable size for aerosol particles is currently about 3 nm [Stolzenburg and McMurry, 1991]. Some nucleated particles will be lost by coagulation with preexisting particles before they grow to this size. If this loss rate is sufficiently high, new particle formation would not be observed even if nucleation were taking place. The distinction between nucleation and new particle formation was discussed originally by McMurry and Friedlander [1979].
[7] A simple, limiting criterion for determining whether or not new particle formation will occur in an aerosol that is undergoing nucleation driven by gas phase chemical reactions can be determined by comparing rates at which stable nuclei are lost by coagulation to preexisting particles and grow by condensation. Assuming accommodation coefficients of unity and using kinetic theory, the ratio of these rates, \( L_j \), can be expressed as:

\[
L_j = \frac{\frac{dN_j}{dt}}{\frac{dN}{dt}} \text{loss to preexisting particles} = \frac{\tau_j N_j A_{\text{Fuchs}}}{\beta_{ij} N_j} = \frac{\tau_j A_{\text{Fuchs}}}{4\beta_{ij} N_1} \equiv Lf(j)
\]

where

\( \tau_j \) = mean thermal speed of clusters of size \( j \)
\( N_j \) = concentration of clusters that contain \( j \) molecules
(Note that \( N_1 \) is the concentration of the condensing vapor)
\( A_{\text{Fuchs}} = \frac{4\pi}{3} \int_{D_p \text{ min}}^{D_p \text{ max}} \left( \frac{Kn + Kn^2}{1 + 1.71Kn + 1.33Kn^2} \right) n(D_p) dD_p \)

\[Kn = \frac{2\lambda}{D_p}\]

Cluster Knudsen number
\( D_p \) = diameter of preexisting particle
\( D_p \text{ min} \) = diameter above which most surface area is found (10 nm in this study)
\( \beta_{ij} \) = collision frequency function of condensing vapor and clusters of size \( j \)

\[f(j) = \frac{4\sqrt{2}}{\sqrt{j} \left( 1 + \frac{1}{j} \right)^{1/2}} \left( 1 + \frac{\beta_{ij}}{2} \right)^2\]

\[L \equiv L_1 = \frac{\tau_j A_{\text{Fuchs}}}{4\beta_{ij} N_1}\]

The kinetic theory of gases is used to evaluate \( \tau_j \) and \( \beta_{ij} \) [McMurry, 1983]. The Fuchs surface area, \( A_{\text{Fuchs}} \) [Fuchs and Sutugin, 1971] accounts for the fact that preexisting atmospheric particles have sizes that fall in the transition between free molecular and diffusional cluster transport regimes. The steady state concentration of the condensing vapor can be expressed as:

\[N_1 \approx 4R/\tau_j A_{\text{Fuchs}}\]

where \( R \) is the rate of monomer production per volume of gas. In Appendix A we show that the expression for \( L \) given by equation (4) is equal to that derived previously [McMurry and Friedlander, 1979; McMurry, 1983]. Other investigators have discussed other criteria for identifying days on which nucleation occurs, and relationships among these approaches are also discussed in Appendix A.

[8] Several assumptions or approximations were made in deriving equation (1). It is assumed that if clusters contain more than one species, only one of them (e.g., sulfuric acid) limits condensational growth rates, while others (e.g., water vapor and ammonia) rapidly achieve equilibrium when another sulfuric acid is added. Therefore the cluster size, \( j \), is equal to the number of molecules of the rate-limiting species in the cluster, while the cluster mass or volume that is used when calculating \( \tau_j \) and \( \beta_{ij} \) includes the other species as well. Also, the mean free path of clusters, \( \lambda \), depends on cluster size. As an approximation we have assumed that all clusters have the same value of \( \lambda \). We chose \( \lambda \) by comparing collision rates of clusters calculated using the above approach with values determined using Fuchs’ transition regime coagulation expression [Fuchs, 1964] and concluded that a value of \( \lambda \) = 0.1 \( \mu \text{m} \) provides reasonable estimates (±10%) for overall coagulation rates of clusters ranging in size from one molecule to about 3 nm with preexisting aerosol.

[9] The loss ratio in equation (1) decreases with increasing cluster size, indicating that larger clusters of a given size are more likely than smaller ones to grow than to be lost by coagulation with preexisting particles. A rigorous determination of the number of nucleated clusters that will ultimately grow to a detectable size for a given value of \( L \) requires a numerical solution of the coupled population balance equations. Such solutions show that for collision-controlled (barrierless) nucleation, new particle formation can occur for \( L < 1 \), but decreases rapidly as \( L \) increases beyond one [McMurry, 1983; Rao and McMurry, 1989]. This can be understood intuitively by noting that for \( L = 1 \), equal numbers of condensing vapor molecules are consumed in producing new particles \( j = 2 \) and condensing on preexisting particles, indicating that new particle formation would be dominant for \( L < 1 \) and loss of vapor and clusters to preexisting particles would be dominant for \( L > 1 \). If a significant nucleation barrier exists, then the concentration of stable nuclei that would be present for a given value of \( L \) would decrease. It follows that the likelihood of new particle formation would be even lower in this case. Therefore nucleation should always be insignificant for values of \( L \) greater than about one and might be important when \( L \) is less than about one.

[10] In this analysis we assume that \( N_1 \) is the concentration of sulfuric acid vapor molecules, which was measured. We also assume that particle growth rates are limited by sulfuric acid condensation rates, and that growing particles consist of ammonium sulfate. This assumption is consistent with Nano TDMA [Sakurai et al., 2005] and TDCIMS [Smith et al., 2005] measurements, which show that freshly nucleated particles at this site consisted primarily of ammonium sulfate. (We define particles as “freshly nucleated” if it is apparent from size distribution data that they have grown during the course of the day from the smallest detectable size (3 nm), or if they are included with a “burst” of nanoparticles that is well correlated with the impact of a sulfur dioxide plume. Both types of freshly nucleated particles are included in Figure 1, which is discussed below.) It is also consistent with the work of Stolzenburg et al. [2005], who found that growth rates of nucleated sub-15 nm particles are reasonably explained by the condensation of sulfuric acid during the periods investigated. Stolzenburg et al. [2005] also found that growth rates of larger (~40 nm) particles exceeded values that could be explained by sulfuric acid condensation during two
midday growth events, and this could contribute to some of the scatter in the results discussed below.

4. Results and Discussion

[11] Figure 1 shows data for 23 August 2002, when a “regional nucleation event” was superimposed upon periods of intermittent SO2 plume impacts. The contour plot in Figure 1a shows time of day on the abscissa, particle size on the ordinate, and value of the size distribution function in color. Although the “birth” of new particles was not observed at the smallest detectable sizes early in the morning, particle concentrations increased during the morning and particles were observed to grow continuously from about 9:00 until 15:00. The high concentrations of 3 to 5 nm particles observed periodically between 10:00 and 13:00 were correlated with elevated levels of SO2, suggesting that they were associated with a plume containing combustion emissions. Figure 1b shows a time series of $L$, calculated using measured values of sulfuric acid ($N_1$) and aerosol size distributions (used to calculate $A_{Fuchs}$). $J_{ternary}$ was calculated using the theory of Napari et al. [2002b].

[12] Similar data are shown in Figure 2 for 27 August, when no evidence for the production of sub-10 nm particles by nucleation was observed. Note that on this day $L$ dropped to 1.0 for a very short period just before 9:00, but subsequently remained above 1.0 for the remainder of the day. Note also that ternary theory predicts that nucleation occurred on this day, but at much lower rates than are predicted for 23 August (Figure 1b). Under such conditions, few new particles would be formed, and those that are would mostly be scavenged by preexisting particles before they grow to a detectable size.

[13] The remainder of the discussion focuses on the relationship between the concentration of particles in the 3 to 4 nm diameter range ($N_{3-4}$) and other measured variables. These are the smallest particles that could be detected with our instrumentation. By definition, if the formation of detectable particles were occurring, then particles in this size range would be detected. We began by examining data from days during which new particle formation was not observed. Data from a day of this type are shown in Figure 2. On these days we did not observe a significant increase in concentrations of sub-10 nm particle concentrations during the course of the day, nor did we see evidence of nanoparticle growth. However, low concentrations of particles in all size ranges, including 3 to 4 nm, were observed. Unlike particles produced by photochemical nucleation, which are typically observed near midday (Figure 1), these particles were observed throughout the 24 hour day. We are confident that our measurements are valid, because during the 11–30 August period there were...
4860 5-min periods when concentrations of 3 to 4 nm particles were measured using two independent instruments. One of these was the scanning Nano SMPS listed in Table 1, and the second was a Nano DMA/PHA-UCPC [Saros et al., 1996; Weber et al., 1998b] system that continuously measured the 3.5 nm size distribution function. Because the latter instrument did not scan through the Nano DMA voltages, as is done with the Nano SMPS, more 3 to 4 nm particles were counted during each 5-min measurement period, and counting statistical uncertainties were much lower than for the Nano SMPS. We found that 88% of the 3 to 4 nm counts measured using the scanning Nano SMPS were within two standard deviations of the values measured using the Nano DMA/PHA-UCPC system, compared to 95% predicted by theory. The small discrepancy between the two instruments is likely due to the fact that the measurements by two instruments are not exactly contemporaneous: the Nano DMA-UCPC sampled continuously at 3.5 nm, while the Nano SMPS scanned over a range of sizes and only measured particles in the 3 to 4 nm range during a fraction of the 5-min sampling period.

We hypothesize that the 3 to 4 nm particles that were observed on nonnucleation days are primary particles, possibly vehicular emissions. Figure 3 shows the relationship between \( N_{3\ to\ 4\ nm} \) and aethalometer measurements of black carbon (BC) concentrations [Hansen et al., 1984] which originate primarily from vehicles. The solid lines show an approximate upper bound for \( N_{3\ to\ 4\ nm} \) versus BC. The relationship between \( N_{3\ to\ 4\ nm} \) and BC was similar throughout the 24-hour day on days when photochemical nucleation was not observed. We hypothesize that the increase of \( N_{3\ to\ 4\ nm} \) with BC at low BC concentrations reflects their common source, and the variability of \( N_{3\ to\ 4\ nm} \) at a given value of BC reflects the varying lifetimes of sampled air parcels. The coagulation lifetime of 3.5 nm particles in Atlanta typically ranges from 10 to 30 min, depending upon the aerosol loading, so significant depletion could occur during transport to the sampling site. We hypothesize that the observed decrease in the upper bound for \( N_{3\ to\ 4\ nm} \) for high BC concentrations reflects the rapid depletion of \( N_{3\ to\ 4\ nm} \) that occurs when aerosol concentrations are high. In the following analysis we use the results shown in Figure 3 to distinguish between 3 to 4 nm particles that could have been due to vehicular emissions (we refer to these as “urban background” particles) from those that were probably formed by photochemical nucleation. When \( N_{3\ to\ 4\ nm} \) was above the line, we argue that these particles were due to photochemical nucleation. Note that the criterion is not perfect since several points fall above the line.

Figure 4 shows \( L_{3\ to\ 4\ nm} \) versus average values of \( L \) measured during the same 5-min period for all data obtained between 9 a.m. and 3 p.m. during the ANARChE study. The open circles apply to the 229 5-min measurement periods during which \( N_{3\ to\ 4\ nm} \) was above the urban background criterion discussed above, and the crosses apply to the 1344 data points that fell below this criterion. The solid curve shows the expected relationship between steady state \( N_{3\ to\ 4\ nm} \) and \( L \) if nucleation were collision controlled [McMurry, 1983]. Solutions of the time-dependent population balance equations show that these steady state values of 3 to 4 nm concentrations are achieved after 15 to 200 min under conditions pertinent to these measurements (sulfuric acid production rates of \( 4 \times 10^4 \) cm\(^{-3}\) s\(^{-1}\) to \( 7 \times 10^6 \) cm\(^{-3}\) s\(^{-1}\), calculated from equation (5) assuming a...
plotted on Figure 4 (i.e., the true cluster growth rates would have exceeded the growth rate due to condensation of sulfuric acid alone, which was used in evaluating the denominator of equation (1)). All other measurements at high values of $L$ fall below the “urban background criterion,” suggesting that they originated from primary emissions and not photochemical nucleation.

The results in Figure 4 also show that at a given value of $L$, values of $N_{3\text{ to }4\text{ nm}}$ vary over several orders of magnitude. Figure 5 shows the dependence of $N_{3\text{ to }4\text{ nm}}$ on ammonia mixing ratios for a relatively narrow range of $L$ values ($0.18 < L < 0.4$). Although there is considerable scatter, the data suggest that $N_{3\text{ to }4\text{ nm}}$ tends to increase with increasing ammonia mixing ratios. This dependence may help to explain the variability in the dependence of $N_{3\text{ to }4\text{ nm}}$ on $L$ that is observed in Figure 4. Table 2 summarizes observed relationships between $N_{3\text{ to }4\text{ nm}}$ and ammonia for all 9 a.m. to 3 p.m. ANARChE data above the “urban background criterion.” The last column is the probability of finding the calculated slope if there were no correlation between $N_{3\text{ to }4\text{ nm}}$ and $[\text{NH}_3]$, on the basis of the two-tailed $t$-test. According to this statistic, the first (0.18 $< L < 0.4$) and last (1 $< L < 2$) slopes are positive at the 95% confidence level. No association was found between $N_{3\text{ to }4\text{ nm}}$ and $[\text{NH}_3]$ for 0.4 $< L < 0.8$. For the other ranges of $L$, there is a weak but suggestive dependence. These observations support the hypothesis that both ammonia and sulfuric acid participate in new particle formation, but the association is not sufficiently strong to show this definitively. The current theory for ternary nucleation [Napari et al., 2002b] suggests that nucleation rates should be independent of ammonia mixing ratios above 0.1 ppbv. During ANARChE, ammonia mixing ratios typically fell in the 1 to 10 ppbv range. If the observed sensitivity is borne out in future studies, the ternary theory would need to be revisited. In any event it appears that the sensitivity of nucleation rates to ammonia does not explain much of the variability of $N_{3\text{ to }4\text{ nm}}(L)$ in Figure 4. This suggests that some other species may have participated in nucleation.

Figure 6 shows the relationship between $N_{3\text{ to }4\text{ nm}}$ and sulfuric acid concentrations for all daytime data collected during ANARChE. Figure 6 presents an alternative approach to interpreting our data, along the lines of the arguments made by Clement et al. [2001]. They argue that one might expect to find evidence for nucleation when concentrations of the nucleating vapor (believed to be sulfuric acid in our case) exceed a critical value, but not below that value. As can be seen in Figure 6, we often observed nucleation when sulfuric acid concentrations exceeded $5 \times 10^6$ cm$^{-3}$, but not for lower levels, so this might be interpreted as the minimum vapor concentration required for nucleation. Indeed, ternary nucleation theory

### Table 2. Sensitivity of $N_{3\text{ to }4\text{ nm}}$ on Ammonia Mixing Ratios

<table>
<thead>
<tr>
<th>Range of $L$ Values</th>
<th>Count</th>
<th>Average $[\text{H}_2\text{SO}_4]$</th>
<th>$N_{3\text{ to }4\text{ nm}}$ Least Squares Fit:</th>
<th>$R^2$</th>
<th>Probability That $N_{3\text{ to }4\text{ nm}}$ Is Not Dependent on $\text{NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.18 &lt; L &lt; 0.4$</td>
<td>27</td>
<td>$15.0 \pm 6.6$</td>
<td>$\text{Exp}(8.28 \pm 0.64)*[\text{NH}_3]^{1.17 \pm 0.48}$</td>
<td>0.178</td>
<td>0.023</td>
</tr>
<tr>
<td>$0.4 &lt; L &lt; 0.6$</td>
<td>41</td>
<td>$8.2 \pm 3.7$</td>
<td>$\text{Exp}(8.49 \pm 0.48)*[\text{NH}_3]^{0.19 \pm 0.40}$</td>
<td>0.006</td>
<td>0.636</td>
</tr>
<tr>
<td>$0.6 &lt; L &lt; 0.8$</td>
<td>20</td>
<td>$5.6 \pm 2.2$</td>
<td>$\text{Exp}(8.89 \pm 0.48)*[\text{NH}_3]^{0.09 \pm 0.41}$</td>
<td>0.002</td>
<td>0.832</td>
</tr>
<tr>
<td>$0.8 &lt; L &lt; 1.0$</td>
<td>5</td>
<td>$4.2 \pm 1.4$</td>
<td>$\text{Exp}(6.24 \pm 1.56)*[\text{NH}_3]^{1.32 \pm 0.78}$</td>
<td>0.299</td>
<td>0.205</td>
</tr>
<tr>
<td>$1.0 &lt; L &lt; 2.0$</td>
<td>7</td>
<td>$3.2 \pm 1.8$</td>
<td>$\text{Exp}(5.85 \pm 1.09)*[\text{NH}_3]^{1.32 \pm 0.78}$</td>
<td>0.560</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Figure 5. Number concentration of particles with mobility diameters between 3 and 4 nm versus ammonia mixing ratios for all ANARChE data measured from 9 a.m. to 3 p.m. that fell above the “urban background criterion” for data having values of $L$ between 0.18 and 0.4. Standard errors in the best fit parameters and statistical information are provided in Table 2.
Napari et al., 2002a) predicts that at 298 K and with ammonia concentrations of 0.1 ppb, nucleation rates should decrease rapidly as sulfuric acid concentrations drop below $5 \times 10^6$ cm$^{-3}$. Figures 4 and 6 provide complementary information regarding factors that influence whether or not new particle formation is observed.

In a previous paper we argued that sub-10 nm size distributions measured in Atlanta during nucleation events are consistent with expectations for collision-controlled nucleation [McMurry et al., 2000]. That paper was based on the observed functional dependence of nanoparticle size distributions measured during nucleation events on particle size. Sulfuric acid concentrations were not measured in that study, so it was necessary to make assumptions when calculating $L$ and $R$. Figure 7 compares a nanoparticle size distribution measured during an ANARChE nucleation event, when sulfuric acid was measured, with predictions of collision-controlled theory [McMurry, 1983]. In this case measurements and theory can be compared assuming only that sulfuric acid is the rate-limiting species for nucleation.

Note that theory and experiment show similar functional dependencies on size, but the measurements are a factor of $\approx 40$ below the theory. In other cases measurements ranged from a factor of 10 to 100 below theory. These results support the conclusion drawn from the results in Figure 4: Collision-controlled theory provides an upper limit to the number of particles produced, but often significantly overpredicts particle production.

In a previous study at the coastal site of Mace Head, Ireland, in which both sulfuric acid and ammonia were measured during nucleation events, it was concluded that ternary nucleation may have been responsible for the formation of stable molecular embryos, but that other species were required to account for the high subsequent growth rates that were observed [Kulmala et al., 2002]. Our analyses suggest that in Atlanta, nanoparticle growth can often be explained by the condensation of sulfuric acid and its associated ammonia [Stolzenburg et al., 2005], a result that is consistent with our independent observations that freshly nucleated nanoparticles were composed mostly of ammonium sulfate [Sakurai et al., 2005; Smith et al., 2005].

There were times, however, when observed growth rates were too high to be explained by sulfuric acid condensation, and during those times organics may have participated in growth. Unfortunately, we did not obtain measurements of nanoparticle composition during such episodes.

5. Conclusions

The growth of nucleated particles to a detectable size involves a competition between the coagulation loss of nucleated clusters to preexisting particles and their growth to larger sizes. Measurements carried out during the ANARChE intensive study of nucleation in Atlanta confirm that new particle formation was observed when the dimensionless parameter, $L$ (equation (4)), was smaller than about one but did not occur when $L$ was greater than about one. $L$ is the rate at which the nucleating vapor molecules condense on preexisting particles divided by the rate at which they collide to produce molecular clusters. The observation that $L \approx 1$ separates days on which new particle formation can occur from those on which it cannot is consistent with theoretical predictions published about 20 years ago. We
also found that new particle formation was not observed during periods when sulfuric acid concentrations were below $5 \times 10^6$ cm$^{-3}$.

[21] Our ANARChE measurements also suggest that when new particle formation was observed, the number concentration of particles with mobility diameters between 3 and 4 nm was sensitive to ammonia mixing ratios, which fell in the 1 and 10 ppbv range during most of our study. If valid, this would be a surprising result, since existing theories predict that ternary nucleation rates of sulfuric acid, ammonia and water are independent of ammonia above 0.1 ppbv. Our measurements, however, exhibit considerable scatter and do not show definitively that particle production was sensitive to ammonia.

Appendix A: Relationships Among Published Criteria for Occurrence of New Particle Formation

[22] Several approaches have been discussed in the literature for determining whether or not new particle formation will occur on a given day. In Appendix A, relationships among these criteria are summarized using common notation.

[23] McMurry and Friedlander [1979] derived the parameter, $L$, that determines whether nucleated particles will grow to a detectable size when condensable vapor is produced by chemical reaction in the presence of an aerosol and when nucleation is occurring at the collision-limited rate. This parameter is:

$$L = \frac{\gamma^2 A_{\text{Fuchs}}^2}{R^2 s_1} \quad \text{(A1)}$$

where $\gamma = \pi s_1/4$ and $R$ is the rate at which the condensable vapor is produced by chemical reactions. Assuming that vapor condensation on preexisting particles is the dominant removal mechanism for the condensing vapor, the steady state balance between vapor (monomer) production and loss is:

$$R = \tau_{\text{Fuchs}} A_{\text{Fuchs}} N_1 / 4. \quad \text{(A2)}$$

It follows that equation (A1) can be expressed as:

$$L = \frac{\tau_{\text{Fuchs}} A_{\text{Fuchs}}}{4N_1 s_1} \quad \text{(A3)}$$

which is identical to equation (4). McMurry [1983] reported numerical calculations which showed that new particle production is suppressed when $L > 1$. This model assumes that the concentration of the nucleating vapor is greatly in excess of its saturation value, and that nucleation occurs at the collision-limited rate. Whether or not new particle production is observed depends upon the probability that growing clusters reach a detectable size before they are scavenged by preexisting particles.

[24] McGrow and Marlow [1983] showed that the classical Becker-Döring theory of homogeneous nucleation can be extended to cluster removal by preexisting particles, and that this loss term becomes significant when the ratio $A / N_1 s_1$ is greater than 1, where $A$ is the surface area concentration of preexisting particles and $s_1$ is the surface area of a condensing vapor molecule. Noting that $s_1 \equiv 431 \mu m^2$, it follows that $A / N_1 s_1 \equiv L$. Therefore, in addition to determining whether or not nucleated particles can grow to a detectable size, as is argued in this paper, $L = 1$ determines whether or not cluster scavenging can be neglected in the population balance equations used in nucleation theory.

[25] Another approach for identifying days on which nucleation occurs was introduced by Clement et al. [2001] and recently used by Birmili et al. [2003]. This approach assumes that the rate at which condensable vapor is produced varies in proportion to the solar radiation intensity, $R \sim I_{\text{rad}}$. Furthermore, the vapor removal rate, $R_A$, defined by Clement et al. [2001] can also be expressed as $R_A \equiv \tau_{\text{Fuchs}} A_{\text{Fuchs}}/4$. It follows from equation (A2) that the steady state concentration of the nucleating vapor is

$$N_1 = \frac{4R}{\tau_{\text{Fuchs}} A_{\text{Fuchs}}} \sim \frac{I_{\text{rad}}}{R_A}. \quad \text{(A4)}$$

Clement and coworkers showed that when $I_{\text{rad}} / R_A$ was plotted versus $I_{\text{rad}}$ for data collected in the Finnish boreal forests, days on which nucleation events were observed were cleanly separated from days on which they did not occur. Birmili and coworkers found a similar result for their measurements in Hohenpeissenberg. The conceptual argument behind Clement’s model is somewhat different from arguments that led McMurry to the parameter $L$. Clement assumes that nucleation only occurs when $N_1$ exceeds the critical value required to overcome the energy barrier and does not explicitly account for the probability that nucleated particles will grow to a detectable size. In contrast, McMurry’s approach assumes that nucleation always occurs but that nucleation will lead to “new particle formation” only if growth is sufficiently fast relative to coagulation loss to the preexisting aerosol.

[26] It should also be pointed out here that the “condensation sink (CS)” introduced by Kulmala et al. [2001] and used by others is related to the other parameters cited above as follows:

$$CS = R_A = \tau_{\text{Fuchs}} A_{\text{Fuchs}}/4. \quad \text{(A5)}$$

Kerminen and Kulmala [2002] showed that the probability that a critical nucleus formed at rate $J(D^*, t)$ will grow to size $D_p$ before it is scavenged by preexisting particles occurs is:

$$P = \frac{J(D^*, t) - J_{\text{mix}}(D^*, t)}{J_{\text{mix}}(D^*, t)} = \exp \left[ -\frac{\gamma \cdot CS'}{GR} \left( \frac{1}{D_p} - \frac{1}{D_p^*} \right) \right]. \quad \text{(A6)}$$

where $GR$ is the diameter growth rate of nucleated particles, $CS' = CS/4\pi D$, and $D$ is vapor diffusivity. We refer the reader to their paper for the definition of $\gamma$, which was obtained by fitting a function to numerical simulations. Using similar conceptual ideas but starting with the free molecule transport approximation, Weber et al. [1997] showed that the probability that nucleated particles will
grow from size $D_{p1}$ to $D_{p2}$ before they are scavenged by preexisting particles is:

$$P \approx \exp \left\{ \frac{-1 \cdot A_{\text{fuchs}}}{2 \cdot GR} \cdot \frac{48kT}{\pi \cdot \rho} \cdot \frac{1}{D_{p2}^{1/2}} \cdot \frac{1}{D_{p1}^{1/2}} \right\}$$

Using equations (A5) and (4), and assuming that growth rates are determined by rates of sulfuric acid condensation it can be shown that:

$$CS \approx \frac{4 \cdot 2^{1/6} \cdot 3^{2/3}}{\pi^{1/4} \cdot v_{\text{i}}^{1/3}} \cdot L$$

where $K$ is a constant and where $L$ is defined by equation (4) of this paper and previously by McMurry and Friedlander [1979].

This relationship could be generalized to account for contributions of species other than sulfuric acid to growth, as was recently done by Kerminen et al. [2004]. With this result, equations (A7) and (A8) can both be expressed in the form:

$$P \approx \exp \left\{ -K \cdot f(D_{p1}, D_{p2}) \cdot L \right\}$$

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