

mechanisms particles: implications for nucleation Size distributions of 3−**10 nm atmospheric**

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Size distributions of 3–10 nm atmospheric Size distributions of 3–10 nm atmospheric
particles: implications for nucleation mechanisms

articles: implications for nucleation mechanisms
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The formation of new atmospheric particles by gas-to-particle conversion leads to
enhanced concentrations of nanoparticles. We have studied the formation and growth The formation of new atmospheric particles by gas-to-particle conversion leads to
enhanced concentrations of nanoparticles. We have studied the formation and growth
of new particles in urban Atlanta and in the remote atmos The formation of new atmospheric particles by gas-to-particle conversion leads to
enhanced concentrations of nanoparticles. We have studied the formation and growth
of new particles in urban Atlanta and in the remote atmos enhanced concentrations of nanoparticles. We have studied the formation and growth
of new particles in urban Atlanta and in the remote atmosphere in locations ranging
from the North Pole to Mauna Loa, Tasmania and the Sout of new particles in urban Atlanta and in the remote atmosphere in locations ranging
from the North Pole to Mauna Loa, Tasmania and the South Pole. Key to this work
was our development of new measurement techniques for fres from the North Pole to Mauna Loa, Tasmania and the South Pole. Key to this work
was our development of new measurement techniques for freshly formed nucleation
mode particles between 3 and 10 nm. In this paper we show that was our development of new measurement techniques for freshly formed nucleation mode particles between 3 and 10 nm. In this paper we show that measured aerosol size distributions in the $3{\text -}10$ nm diameter range often i mode particles between 3 and 10 nm. In this paper we show that measured aerosol
size distributions in the 3–10 nm diameter range often increase with decreasing size
down to our minimum detectable size of 3 nm, presumably size distributions in the 3–10 nm diameter range often increase with decreasing size
down to our minimum detectable size of 3 nm, presumably because nucleation was
occurring during the measurement. Furthermore, we show tha occurring during the measurement. Furthermore, we show that the Atlanta nucleation mode size distributions are consistent with a collision-controlled nucleation process in which accommodation coefficients for all collision occurring during the measurement. Furthermore, we show that the Atlanta nucle-
ation mode size distributions are consistent with a collision-controlled nucleation
process in which accommodation coefficients for all collisi ation mode size distributions are consistent with a collision-controlled nucleation
process in which accommodation coefficients for all collisions between condensing
molecules and molecular clusters are assumed to be
equal process in which accommodation coefficients for all collisions between condensing
molecules and molecular clusters and between molecular clusters are assumed to be
equal to one, and in which evaporation from molecular clus molecules and molecular clusters and between mo
equal to one, and in which evaporation from molec
be expected for a highly supersaturated vapour.

ected for a highly supersaturated vapour.
Keywords: atmospheric aerosol; ultrafine aerosol; homogeneous nucleation;
sulphuric acid: nanoparticles: nucleation mode: gas-to-particle conversion sulphuric acid; nanoparticles; nucleation mode; gas-to-particle conversion
sulphuric acid; nanoparticles; nucleation mode; gas-to-particle conversion

1. Introduction

The recent development of instrumentation for measuring particles as small as 3 nm (see, for example, Stolzenburg & McMurry 1991; Winklmayr *et al.* 1991; Saros *et*
(see, for example, Stolzenburg & McMurry 1991; Winklmayr *et al.* 1991; Saros *et*
(d) 1996; Beischl *et al.* 1997; Chen *et al.* 1998) has The recent development of instrumentation for measuring particles as small as 3 nm
(see, for example, Stolzenburg & McMurry 1991; Winklmayr *et al.* 1991; Saros *et
al.* 1996; Reischl *et al.* 1997; Chen *et al.* 1998) has (see, for example, Stolzenburg & McMurry 1991; Winklmayr *et al.* 1991; Saros *et al.* 1996; Reischl *et al.* 1997; Chen *et al.* 1998) has led to the discovery of a new mode of atmospheric particles in the nanometre size al. 1996; Reischl *et al.* 1997; Chen *et al.* 1998) has led to the discovery of a new mode of atmospheric particles in the nanometre size range (Covert *et al.* 1996a). We refer to these 3-10 nm particles as 'nucleation mode of atmospheric particles in the nanometre size range (Covert *et al.* 1996*a*). We
refer to these 3–10 nm particles as 'nucleation mode' aerosols, as they are almost
certainly produced by recent nucleation from the g refer to these $3-10$ nm particles as 'nucleation mode' aerosols, as they are almost certainly produced by recent nucleation from the gas phase. Other modes that have been previously documented include the nuclei or Aitke certainly produced by recent nucleation from the gas phase. Other modes that have
been previously documented include the nuclei or Aitken mode (typically $ca. 20-50 \text{ nm}$ mean size), the accumulation mode (between 0.1 and been previously documented include the nuclei or Aitken mode (typically $ca.20-50 \text{ nm}$ mean size), the accumulation mode (between 0.1 and 1.0 μ m) and the coarse particle mode (greater than 1 μ m) (Whitby 1978). This 50 nm mean size), the accumulation mode (between 0.1 and 1.0 μ m) and the coarse
particle mode (greater than 1 μ m) (Whitby 1978). This paper briefly describes the
instruments that we have developed and used to measur particle mode (greater than $1 \mu m$) (Whitby 1978). This paper briefly describes the instruments that we have developed and used to measure nucleation mode aerosols troposphere. and discusses some results of those measurements in urban Atlanta and in the remote troposphere.
Nucleation mode aerosols have been observed in several characteristic situations in

a wide variety of locations. The appearance of 3{10 nm particles sometimes follows

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aerosol inlet
Figure 1. Schematic of the UCPC-PHA instrument. The alcohol saturation ratio required to
initiate condensational growth increases sharply with decreasing size below 10 nm. Therefore Figure 1. Schematic of the UCPC-PHA instrument. The alcohol saturation ratio required to initiate condensational growth increases sharply with decreasing size below 10 nm. Therefore, small particles must travel further int Figure 1. Schematic of the UCPC-PHA instrument. The alcohol saturation ratio required to
initiate condensational growth increases sharply with decreasing size below 10 nm. Therefore,
small particles must travel further int initiate condensational growth increases sharply with decreasing size below 10 nm. Therefore,
small particles must travel further into the condenser before they begin to grow, and they grow
to a smaller ultimate size. The to a smaller ultimate size. The initial particle size is inferred from measurements of the final droplet size measured with the white light optical detector.

regular diurnal patterns, with peak particle production rates occurring near midday, regular diurnal patterns, with peak particle production rates occurring near midday,
when solar radiation is most intense (Bradbury & Meuron 1938; Went 1964; Hogan
1968: Koutsenovii & Jaenicke 1994). At other times, nucle regular diurnal patterns, with peak particle production rates occurring near midday,
when solar radiation is most intense (Bradbury & Meuron 1938; Went 1964; Hogan
1968; Koutsenogii & Jaenicke 1994). At other times, nuclea when solar radiation is most intense (Bradbury & Meuron 1938; Went 1964; Hogan 1968; Koutsenogii & Jaenicke 1994). At other times, nucleation occurs in response to atmospheric perturbations, such as the removal of pre-exi 1968; Koutsenogii & Jaenicke 1994). At other times, nucleation occurs in response to atmospheric perturbations, such as the removal of pre-existing aerosol by cloud to atmospheric perturbations, such as the removal of pre-existing aerosol by cloud
processing (Hegg *et al.* 1990; Radke & Hobbs 1991; Perry & Hobbs 1994; Clarke *et*
al. 1998) or the addition of gas phase reactants from processing (Hegg *et al.* 1990; Radke & Hobbs 1991; Perry & Hobbs 1994; Clarke *et al.* 1998) or the addition of gas phase reactants from a surface source. For example, measurements downwind of the coast at Mace Head, Ire al. 1998) or the addition of gas phase reactants from a surface source. For example, measurements downwind of the coast at Mace Head, Ireland, have shown the rapid production of exceedingly high concentrations of very smal measurements downwind of the coast at Mace Head, Ireland, have shown the rapid
production of exceedingly high concentrations of very small particles during on-shore
flow (McGovern *et al.* 1996; McGovern 1999). These event production of exceedingly high concentrations of very small particles during on-shore
flow (McGovern *et al.* 1996; McGovern 1999). These events occur only in sunlight
and during low tide. Nucleation was also detected in flow (McGovern *et al.* 1996; McGovern 1999). These events occur only in sunlight
and during low tide. Nucleation was also detected in the remote marine atmosphere
downwind of penguin colonies on Macquarie Island (Weber *e* and during low tide. Nucleation was also detected in the remote marine atmosphere downwind of penguin colonies on Macquarie Island (Weber *et al.* 1998*a*). Weber and co-workers hypothesized that new particles were produc co-workers hypothesized that new particles were produced when ammonia, or perhaps co-workers hypothesized that new particles were produced when ammonia, or perhaps
some other gas emitted by these colonies, reacted with sulphuric acid that was present
in the air flowing over the island to produce new pa some other gas emitted by these colonies, reacted with sulphuric acid that was present
in the air flowing over the island to produce new particles. Nucleation has been
observed on mountains (Shaw 1989; Marti 1990; Weber *e* observed on mountains (Shaw 1989; Marti 1990; Weber *et al.* 1995, 1997; Raes *et al.* 1997; Wiedensohler *et al.* 1997), in the boreal forests of Finland (Mäkelä *et al.* 1997; Kulmala *et al.* 1998) and in northern Finla 1997; Wiedensohler *et al.* 1997), in the boreal forests of Finland (Mäkelä *et al.* 1997; Kulmala *et al.* 1998) and in northern Finland (Pirjola *et al.* 1998) and in moderately polluted continental air in Germany (Birm Kulmala *et al.* 1998) and in northern Finland (Pirjola *et al.* 1998) and in moderately polluted continental air in Germany (Birmili & Wiedensohler 1998). Measurements of aerosol composition suggest that the freshly nucl polluted continental air in Germany (Birmili & Wiedensohler 1998). Measurements
of aerosol composition suggest that the freshly nucleated particles in the Finnish
boreal forest are enriched with dimethyl amine (Mäkelä *et* of aerosol composition suggest that the freshly nucleated particles in the Finnish
boreal forest are enriched with dimethyl amine (Mäkelä *et al.* 1999). Evidence of
nucleation in the marine boundary layer (MBL) has been r nucleation in the marine boundary layer (MBL) has been reported (Covert *et al.* 1992; Hoppel *et al.* 1994; Clarke *et al.* 1998). Several groups (Covert *et al.* 1996*a*, *b*; Wiedensohler *et al.* 1996) have argued that 1992; Hoppel *et al.* 1994; Clarke *et al.* 1998). Several groups (Covert *et al.* 1996*a*, *b*; Wiedensohler *et al.* 1996) have argued that nucleation mode particles detected in the MBL are probably produced aloft in fr Wiedensohler *et al.* 1996) have argued that nucleation mode particles detected in the MBL are probably produced aloft in free tropospheric cloud outflows and transported
to the surface. Evidence suggests that nucleation in the upper tropical troposphere
is a significant global source of atmospheric particle to the surface. Evide:
is a significant global
Clarke *et al.* 1998). *Phil. Trans. R. Soc. Lond.* A (2000)

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Size distributions of $3-10$ nm atmospheric particles 2627
While nucleation in a wide variety of circumstances is now well documented, we
not yet have validated models for predicting nucleation rates. Evidence suggests While nucleation in a wide variety of circumstances is now well documented, we
do not yet have validated models for predicting nucleation rates. Evidence suggests
that sulphuric acid vapour may often participate in nuclea While nucleation in a wide variety of circumstances is now well documented, we
do not yet have validated models for predicting nucleation rates. Evidence suggests
that sulphuric acid vapour may often participate in nuclea do not yet have validated models for predicting nucleation rates. Evidence suggests
that sulphuric acid vapour may often participate in nucleation (Eisele & McMurry
1997; Clarke *et al.* 1998). Observed nucleation rates ar that sulphuric acid vapour may often participate in nucleation (Eisele & McMurry 1997; Clarke *et al.* 1998). Observed nucleation rates are occasionally consistent with predictions of the binary theory for sulphuric acid predictions of the binary theory for sulphuric acid and water (Weber $et al.$ 1999), but predictions of the binary theory for sulphuric acid and water (Weber *et al.* 1999), but
rates of particle formation are often orders of magnitude higher than can be explained
by the binary theory. Furthermore, growth rate rates of particle formation are often orders of magnitude higher than can be explained
by the binary theory. Furthermore, growth rates of freshly nucleated particles are
typically two to ten times higher than can be expla by the binary theory. Furthermore, growth rates of freshly nucleated particles are
typically two to ten times higher than can be explained by the condensation of
sulphuric acid and its associated water and ammonia (Weber typically two t
sulphuric acid
1998a, 1999).
The present lphuric acid and its associated water and ammonia (Weber *et al.* 1996, 1997, 98*a*, 1999).
The present paper reports on measurements of freshly nucleated 3–10 nm aerosol
ce distributions. We show that in systems where nu

1998a, 1999).
The present paper reports on measurements of freshly nucleated 3–10 nm aerosol
size distributions. We show that in systems where nucleation is occurring or has
recently occurred size distributions exhibit an The present paper reports on measurements of freshly nucleated 3–10 nm aerosol
size distributions. We show that in systems where nucleation is occurring or has
recently occurred, size distributions exhibit an increasing tr size distributions. We show that in systems where nucleation is occurring or has
recently occurred, size distributions exhibit an increasing trend with decreasing par-
ticle size. Our measurements were made possible by our recently occurred, size distributions exhibit an increasing trend with decreasing particle size. Our measurements were made possible by our development of new instrumentation for measuring size distributions in the 3-10 nm ticle size. Our measurements were made possible by our development of new instrumentation for measuring size distributions in the 3–10 nm diameter range. We also show that 3–10 nm size distributions measured in Atlanta are mentation for measuring size distributions in the 3–10 nm diameter range. We also show that 3–10 nm size distributions measured in Atlanta are consistent with the theoretical predictions for collision-controlled nucleation

2. Advances in instrumentation

2. Advances in instrumentation
The measurements described in this paper use two different instruments for measur-
ing nucleation mode size distributions: the ultrafine condensation particle counter The measurements described in this paper use two different instruments for measur-
ing nucleation mode size distributions: the ultrafine condensation particle counter
pulse height analysis method (UCPC-PHA) (Saros *et al.* The measurements described in this paper use two different instruments for measuring nucleation mode size distributions: the ultrafine condensation particle counter pulse height analysis method (UCPC-PHA) (Saros *et al.* 1 ing nucleation mode size distributions: the ultrafine condensation particle counter
pulse height analysis method (UCPC-PHA) (Saros *et al.* 1996) and the nanome-
tre scanning mobility sizer (nano-SMPS). The nano-SMPS uses pulse height analysis method (UCPC-PHA) (Saros *et al.* 1996) and the nanometre scanning mobility sizer (nano-SMPS). The nano-SMPS uses the new nano-DMA (Chen *et al.* 1998) to classify particles according to electrical mo tre scanning mobility sizer (nano-SMPS). The nano-SMPS uses the new nano-DMA (Chen *et al.* 1998) to classify particles according to electrical mobility. In this section we briefly summarize the relative strengths of thes

The UCPC-PHA technique uses the instrument described by Stolzenburg & Mcwe briefly summarize the relative strengths of these techniques.
The UCPC-PHA technique uses the instrument described by Stolzenburg & Mc-
Murry (1991), the prototype of the TSI 3025 UCPC. A schematic of this instrument
is The UCPC-PHA technique uses the instrument described by Stolzenburg & Mc-
Murry (1991), the prototype of the TSI 3025 UCPC. A schematic of this instrument
is shown in figure 1. The sampled aerosol enters the condenser, wh Murry (1991), the prototype of the TSI 3025 UCPC. A schematic of this instrument
is shown in figure 1. The sampled aerosol enters the condenser, where it is sur-
rounded by an annular filtered sheath flow that has been sa is shown in figure 1. The sampled aerosol enters the condenser, where it is sur-
rounded by an annular filtered sheath flow that has been saturated with butanol at
 40° C. Because the flow in the condenser is laminar, rounded by an annular filtered sheath flow that has been saturated with butanol at 40 °C. Because the flow in the condenser is laminar, the particles remain on axis as they flow through it. The butanol rapidly diffuses in 40 °C. Because the flow in the condenser is laminar, the particles remain on axis as they flow through it. The butanol rapidly diffuses into the aerosol, where it becomes supersaturated as a result of heat transfer from t they flow through it. The butanol rapidly diffuses into the aerosol, where it becomes
supersaturated as a result of heat transfer from the 10 °C walls. Saturation ratios
along the axis increase from the inlet value of 1.0 supersaturated as a result of heat transfer from the 10° C walls. Saturation ratios along the axis increase from the inlet value of 1.0 until, due to condensation on the cool walls, they decrease after reaching a peak along the axis increase from the inlet value of 1.0 until, due to condensation on the cool walls, they decrease after reaching a peak value about two-thirds of the way through the condenser. The saturation ratio that is re the cool walls, they decrease after reaching a peak value about two-thirds of the way through the condenser. The saturation ratio that is required to initiate condensational growth increases with decreasing size due to the way through the condenser. The saturation ratio that is required to initiate con-
densational growth increases with decreasing size due to the effect of curvature on
equilibrium vapour pressure (Thomson 1871). The highest densational growth increases with decreasing size due to the effect of curvature on
equilibrium vapour pressure (Thomson 1871). The highest saturation ratio that is
achieved in the condenser is sufficient to initiate conde equilibrium vapour pressure (Thomson 1871). The highest saturation ratio that is achieved in the condenser is sufficient to initiate condensational growth on ca . 3 nm particles, but these particles have a relatively shor particles is activated at lower saturation ratios. The final droplet size at the exit from particles, but these particles have a relatively short time to grow. Growth of larger
particles is activated at lower saturation ratios. The final droplet size at the exit from
the condenser decreases with decreasing growt particles is activated at lower saturation ratios. The final droplet size at the exit from
the condenser decreases with decreasing growth time. Therefore, very small particles
grow to a smaller final droplet size and scatt the condenser decreases with decreasing growth time. Therefore, very small particles grow to a smaller final droplet size and scatter less light than do larger particles.
The PHA technique involves measuring the voltage pu grow to a smaller final droplet size and scatter less light than do larger particles.
The PHA technique involves measuring the voltage pulses produced by individual
droplets as they flow through the optical detector. The m The PHA technique involves measuring the voltage pulses produced by individual droplets as they flow through the optical detector. The measured distribution of pulse heights can be inverted to obtain information about siz droplets as they flow through the optical detector. The measured distribution of pulse heights can be inverted to obtain information about size distributions in the 3–10 nm diameter range (Weber *et al.* 1998*b*).

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Figure 2. Examples of nucleation mode size distributions measured with the UCPC-PHA in the remote marine troposphere. The symbols on the curves are shown to identify the measurements, and do not correspond to 'size bins' f Figure 2. Examples of nucleation mode size distributions m
remote marine troposphere. The symbols on the curves are
and do not correspond to 'size bins' for the PHA-UCPC.

and do not correspond to 'size bins' for the PHA-UCPC.
The advantage of the UCPC-PHA technique is that all 3-10 nm particles in the The advantage of the UCPC-PHA technique is that all 3–10 nm particles in the sampled flow are detected. This enables fast measurements at very low concentra-
tions. The lower limit on concentration is determined by countin The advantage of the UCPC-PHA technique is that all 3–10 nm particles in the sampled flow are detected. This enables fast measurements at very low concentrations. The lower limit on concentration is determined by counting sampled flow are detected. This enables fations. The lower limit on concentration is quantities. The aerosol flow rate is $0.5 \text{ cm}^3 \text{ s}^{-1}$ s^{-1} . T t measurements at very low concentra-
etermined by counting statistical uncer-
. The number of nanoparticles counted, tions. The low
tainties. The a
therefore, is C₃₋₁₀ = $0.5N_{3-10}t$, (2.1)

$$
C_{3-10} = 0.5N_{3-10}t, \t\t(2.1)
$$

 $C_{3-10} = 0.5N_{3-10}t,$ (2.1)
where N_{3-10} is the number concentration of 3-10 nm diameter particles and t is the
counting time in seconds. The Poisson counting statistical uncertainty varies as the where N_{3-10} is the number concentration of 3–10 nm diameter particles and t is the
counting time in seconds. The Poisson counting statistical uncertainty varies as the
square root of the number of counts. If we assume where N_{3-10} is the number concentration of 3–10 nm diameter particles and t is the counting time in seconds. The Poisson counting statistical uncertainty varies as the square root of the number of counts. If we assume counting time in seconds. The Poisson counting statistical uncertainty varies as the square root of the number of counts. If we assume that particle counts are equally distributed among 10 size (pulse height) bins, then th square root of the number of counts. If we assume that particle counts are equally distributed among 10 size (pulse height) bins, then the relative uncertainty in any one bin is, approximately,

$$
\left(\frac{\Delta C}{C}\right)_{\text{PHA Bin}} \approx \left(\frac{20}{N_{3-10}t}\right)^{0.5}.
$$
\n(2.2)

 $\left(\frac{\overline{C}}{C}\right)_{\text{PHA Bin}} \approx \left(\frac{N_{3-10}t}{N_{3-10}t}\right)$ (2.2)
Assuming that an acceptable relative uncertainty for measurements is *ca*. 10%, it
lows that Assuming the
follows that $N_{3-10}t \ge 2000 \text{ cm}^{-3} \text{ s}^1$

$$
N_{3-10}t \ge 2000 \text{ cm}^{-3} \text{ s}^1. \tag{2.3}
$$

Therefore, a typical counting time of 20 s permits measurements of 3 -10 nm size Therefore, a typical counting time of 20 s permits measurements of 3–10 nm size
distributions when N_{3-10} exceeds *ca*. 100 cm⁻³. Coincidence errors occur when more
than one particle is simultaneously present in the Therefore, a typical counting time of 20 s permits measurements of 3–10 nm size
distributions when N_{3-10} exceeds $ca.100 \text{ cm}^{-3}$. Coincidence errors occur when more
than one particle is simultaneously present in the o distributions when N_{3-10} exceeds $ca. 100 \text{ cm}^{-3}$. Coincidence errors occur when more
than one particle is simultaneously present in the optical detector, and this happens
when total concentrations of all particles ex than one particle is simultaneously present in the optical detector, and this happens
when total concentrations of all particles exceed $ca.4000 \text{ cm}^{-3}$. It is necessary to
dilute the aerosol prior to measurement when sam when total concentrations of all particles exceed $ca. 4000 \text{ cm}^{-3}$. It is necessary to dilute the aerosol prior to measurement when sampling aerosols with concentrations higher than this.

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The nano-SMPS was designed for optimal measurements of electrical mobility The nano-SMPS was designed for optimal measurements of electrical mobility
distributions of particles in the 3-50 nm diameter range. This instrument system
consists of a TSI 3080N nano-DMA with a TSI 3025 UCPC detector. Fo The nano-SMPS was designed for optimal measurements of electrical mobility
distributions of particles in the 3–50 nm diameter range. This instrument system
consists of a TSI 3080N nano-DMA with a TSI 3025 UCPC detector. Fo distributions of particles in the 3–50 nm diameter range. This instrument system
consists of a TSI 3080N nano-DMA with a TSI 3025 UCPC detector. For the mea-
surements discussed in this paper, aerosols are exposed to a bip consists of a TSI 3080N nano-DMA with a TSI 3025 UCPC detector. For the measurements discussed in this paper, aerosols are exposed to a bipolar ion cloud, where they are brought to a known charge distribution (Wiedensohle they are brought to a known charge distribution (Wiedensohler 1988). At the exit particles contain -1 elementary charges. The aerosol then is classified according to electrical mobility by the nano-DMA and counted with the UCPC, which samples particles contain -1 elementary charges. The aerosol then is classified according to
electrical mobility by the nano-DMA and counted with the UCPC, which samples
at $0.5 \text{ cm}^3 \text{ s}^{-1}$ downstream of the nano-DMA. The r electrical mobility by the nano-DMA and counted with the UCPC, which samples
at $0.5 \text{ cm}^3 \text{ s}^{-1}$ downstream of the nano-DMA. The relationship between the concen-
tration detected by the UCPC and the size distribution at $0.5 \text{ cm}^3 \text{ s}^{-1}$ downstream of the nano-DMA. The itration detected by the UCPC and the size distributhan the mean free path of air is (Knutson 1976)

$$
N_{\text{UCPC}} \approx 0.5 f_{\text{aerosol}} \varphi \frac{\text{d}N}{\text{d}\ln D_{\text{p}}} \approx 0.5 f_{\text{aerosol}} \varphi \frac{N_{3-10}}{\ln(10/3)},\tag{2.4}
$$

 $N_{\text{UCPC}} \approx 0.5 f_{\text{aerosol}} \varphi \frac{1}{d \ln D_{\text{p}}} \approx 0.5 f_{\text{aerosol}} \varphi \frac{1}{\ln(10/3)},$ (2.4)
where f_{aerosol} is the ratio of the aerosol to sheath air flow rates into and out of
the nano-DMA φ is the fraction of aerosol at a gi where f_{aerosol} is the ratio of the aerosol to sheath air flow rates into and out of
the nano-DMA, φ is the fraction of aerosol at a given size that carries an elemen-
tary charge and $dN/d \ln D_z$ is the value of the m where f_{aerosol} is the ratio of the aerosol to sheath air flow rates into and out of
the nano-DMA, φ is the fraction of aerosol at a given size that carries an elemen-
tary charge, and $dN/d \ln D_p$ is the value of the the nano-DMA, φ is the fraction of aerosol at a given size that carries an elementary charge, and $dN/d \ln D_p$ is the value of the measured aerosol size distribution function. Using arguments similar to those discus tary charge, and $dN/d \ln D_p$ is the value of the measured aerosol size distribution
function. Using arguments similar to those discussed previously for the UCPC-PHA
technique, we conclude that measurements providing 10 function. Using arguments similar to those discusse
technique, we conclude that measurements providin
DMA classifying voltage will be obtained when

$$
N_{3-10}t_{\text{nano-DMA voltage setting}} \geqslant \frac{5000}{\varphi} \text{ cm}^{-3} \text{ s},
$$

$$
\sim 3.7 \times 10^5 \text{ cm}^{-3} \text{ s} \quad \text{(for 3 nm particles)},
$$

$$
\sim 1.0 \times 10^5 \text{ cm}^{-3} \text{ s} \quad \text{(for 10 nm particles)}. \tag{2.5}
$$

The total time required to measure the size distribution between 3 and 10 nm varies in proportion to the number of DMA classifying voltages employed. Thus, The total time required to measure the size distribution between 3 and 10 nm
varies in proportion to the number of DMA classifying voltages employed. Thus,
for a given counting time the UCPC-PHA can measure size distributi varies in proportion to the number of DMA classifying voltages employed. Thus,
for a given counting time the UCPC-PHA can measure size distributions that are
about a factor of 500–1000 times lower than can be measured with for a given counting time the UCPC-PHA can measure size distributions that are
about a factor of 500–1000 times lower than can be measured with the nano-DMA.
However, the time response of the nano-DMA could be improved by about a factor of 500–1000 times lower than can be measured with the nano-DMA.
However, the time response of the nano-DMA could be improved by about a factor
of five to ten by using a higher flow-rate detector, and an add However, the time response of the nano-DMA could be improved by about a
of five to ten by using a higher flow-rate detector, and an additional factor of
using a unipolar charger in place of the bipolar charger (Chen & Pui five to ten by using a higher flow-rate detector, and an additional factor of ten by
ing a unipolar charger in place of the bipolar charger (Chen $\&$ Pui 1999).
The sizing resolution of the nano-DMA is superior to that o

using a unipolar charger in place of the bipolar charger (Chen & Pui 1999).
The sizing resolution of the nano-DMA is superior to that of the UCPC-PHA. For
example, laboratory calibrations with monodisperse calibration aer The sizing resolution of the nano-DMA is superior to that of the UCPC-PHA. For example, laboratory calibrations with monodisperse calibration aerosols show that particles that vary by $\pm 50\%$ in diameter can produce the example, laboratory calibrations with monodisperse calibration aerosols show that particles that vary by $\pm 50\%$ in diameter can produce the same pulse height with the UCPC-PHA. In contrast, particles that vary by about particles that vary by $\pm 50\%$ in diameter can produce the same pulse height with the UCPC-PHA. In contrast, particles that vary by about $\pm 4\%$ in diameter will exit
the nano-DMA at a given classifying voltage under operating conditions used in our
studies. Therefore, the nano-DMA is the instrument the nano-DMA at a given classifying voltage under operating conditions used in our studies. Therefore, the nano-DMA is the instrument of choice if concentrations are sufficiently high to permit measurements in a reasonable studies. Therefore, the nano-DMA is the instrument of choice if concentrations are sufficiently high to permit measurements in a reasonable period of time. Because the UCPC-PHA can rapidly measure size distributions at low sufficiently high to permit measurements in a reasonable period of time. Because the UCPC-PHA can rapidly measure size distributions at low concentrations, it has advantages for measurements in the clean troposphere.

3. Tropospheric measurements

We have used the PHA-UCPC to study nucleation in the remote marine and conti-We have used the PHA-UCPC to study nucleation in the remote marine and conti-
nental troposphere. The PHA-UCPC measurements were done as part of short-term
(four to six weeks) intensive field programmes at locations includ We have used the PHA-UCPC to study nucleation in the remote marine and continental troposphere. The PHA-UCPC measurements were done as part of short-term (four to six weeks) intensive field programmes at locations includin *Phil. Trans. R. Soc. Lond.* A (2000)

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Figure 3. Nucleation mode size distributions measured with the nano-DMA in urban Atlanta,
GA These measurements represent all data during a one-year period where significant concen-Figure 3. Nucleation mode size distributions measured with the nano-DMA in urban Atlanta,
GA. These measurements represent all data during a one-year period where significant concen-
trations of 3–10 nm particles were pres GA. These measurements represent all data during a one-year period where significant concentrations of 3–10 nm particles were present.

(Covert *et al*. 1996a), Mauna Loa, HI (Weber *et al*. 1995), the Rocky Mountains of Covert *et al.* 1996a), Mauna Loa, HI (Weber *et al.* 1995), the Rocky Mountains of Colorado (Weber *et al.* 1997), the South Pole and over the Southern Ocean during ACF-1 (Weber *et al.* 1998a, 1999). Examples of nucleati (Covert *et al.* 1996*a*), Mauna Loa, HI (Weber *et al.* 1995), the Rocky Mountains of Colorado (Weber *et al.* 1997), the South Pole and over the Southern Ocean during ACE-1 (Weber *et al.* 1998*a*, 1999). Examples of nu Colorado (Weber *et al.* 1997), the South Pole and over the Southern Ocean during ACE-1 (Weber *et al.* 1998*a*, 1999). Examples of nucleation mode size distributions measured over the Southern Ocean are shown in figure 2 ACE-1 (Weber *et al.* 1998*a*, 1999). Examples of nucleation mode size distributions measured over the Southern Ocean are shown in figure 2. The data labelled 'MI' were measured downwind of Macquarie Island, the site of a measured over the Southern Ocean are shown in figure 2. The data labelled 'MI'
were measured downwind of Macquarie Island, the site of a large penguin colony.
Distributions 233 and 242 were measured *ca*. 1 km downwind of were measured downwind of Macquarie Island, the site of a large penguin colony.
Distributions 233 and 242 were measured ca . 1 km downwind of the island, and dis-
tributions 227 and 226 were measured 21 and 32 km downwind Distributions 233 and 242 were measured ca . 1 km downwind of the island, and distributions 227 and 226 were measured 21 and 32 km downwind respectively. We believe nucleation occurred during these measurements when marin tributions 227 and 226 were measured 21 and 32 km downwind respectively. We
believe nucleation occurred during these measurements when marine air entrained
emissions (possibly ammonia or amines) from the island. Distributi believe nucleation occurred during these measurements whe
emissions (possibly ammonia or amines) from the island. Dis
were measured in the outflow regions of convective clouds.
Several interesting features can be observed issions (possibly ammonia or amines) from the island. Distributions 102 and 103
Several interesting features can be observed in the size distribution functions shown
figure 2. Most significantly, observed distributions oft

were measured in the outflow regions of convective clouds.
Several interesting features can be observed in the size distribution functions shown
in figure 2. Most significantly, observed distributions often increase with d Several interesting features can be observed in the size distribution functions shown
in figure 2. Most significantly, observed distributions often increase with decreasing
diameter at the bottom end of our measurement ran in figure 2. Most significantly, observed distributions often increase with decreasing
diameter at the bottom end of our measurement range, especially shortly after nucle-
ation is first observed. For example, distribution diameter at the bottom end of our measurement range, especially shortly after nucle-
ation is first observed. For example, distributions 233 and 242, which were measured
immediately downwind of Macquarie Island, show a pro ation is first observed. For example, distributions 233 and 242, which were measured
immediately downwind of Macquarie Island, show a pronounced increasing trend
with decreasing size. We believe this is because nucleation immediately downwind of Macquarie Island, show a pronounced increasing trend
with decreasing size. We believe this is because nucleation was occurring during
our measurements, and there was a continual flux of particles in with decreasing size. We believe this is because nucleation was occurring during
our measurements, and there was a continual flux of particles into the measured
size range at these times. This rising trend often disappeare our measurements, and there was a continual flux of particles into the measured size range at these times. This rising trend often disappeared after nucleation had proceeded for some time (see, for example, distribution 22 size range at these times. This rising trend often disappeared after nucleation had
proceeded for some time (see, for example, distribution 226). The sharp minima in
several of the distributions are also intriguing. Due to proceeded for some time (see, for example, distribution 226). The sharp minima in
several of the distributions are also intriguing. Due to inherent limits in size resolu-
tion of the UCPC-PHA technique, we are not absolute several of the distributions are also intriguing. Due to inherent limits in size resolution of the UCPC-PHA technique, we are not absolutely certain these minima are real. However, our analyses suggest that it should be po real. However, our analyses suggest that it should be possible to recover such minima
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when inverting UCPC-PHA data (Weber *et al*. 1998b). Furthermore, it will be shown when inverting UCPC-PHA data (Weber *et al.* 1998*b*). Furthermore, it will be shown
in the following section that theory shows such minima can occur during nucleation.
The nano-DMA was used to measure size distributions The nano-DMA was used to measure size distributions of 3-50 nm particles in
The nano-DMA was used to measure size distributions of 3-50 nm particles in
clanta (Woo *et al.* 2000). In this study we also used a conventional

in the following section that theory shows such minima can occur during nucleation.
The nano-DMA was used to measure size distributions of 3–50 nm particles in
Atlanta (Woo *et al.* 2000). In this study we also used a conv The nano-DMA was used to measure size distributions of 3–50 nm particles in Atlanta (Woo *et al.* 2000). In this study we also used a conventional SMPS for particles between 20 and 250 nm, and a PMS LASAIR optical particl Atlanta (Woo *et al.* 2000). In this study we also used a conventional SMPS for particles between 20 and 250 nm, and a PMS LASAIR optical particle counter for particles between 0.1 and 2 μ m. These measurements are bein cles between 20 and 250 nm, and a PMS LASAIR optical particle counter for particles between 0.1 and 2 μ m. These measurements are being carried out as part of the ARIES aerosol health-effects experiment. Measurements be ARIES aerosol health-effects experiment. Measurements began in August 1998, and size distributions have been measured every 12 min all year round. During the first ARIES aerosol health-effects experiment. Measurements began in August 1998, and
size distributions have been measured every 12 min all year round. During the first
year of this study we measured 85 hourly-average size dist size distributions have been measured every 12 min all year round. During the first
year of this study we measured 85 hourly-average size distributions that increased
with decreasing size in the 3-10 nm diameter range. The year of this study v
with decreasing siz
shown in figure 3.
The data in figur with decreasing size in the $3-10$ nm diameter range. These size distributions are shown in figure 3.
The data in figure 3 exhibit several interesting features. Size distributions again

increase with decreasing size down to our minimum detectable size, suggesting that The data in figure 3 exhibit several interesting features. Size distributions again
increase with decreasing size down to our minimum detectable size, suggesting that
nucleation was occurring. Also, while the magnitudes of increase with decreasing size down to our minimum detectable size, suggesting that nucleation was occurring. Also, while the magnitudes of the distributions vary by about a factor of 10 at any given size, the slopes are q nucleation was occurring. Also, wh
about a factor of 10 at any given si
of -3.5 and fall within the range,

$$
-1.19 > \frac{d}{d \log D_p} \log \left(\frac{dN}{d \log D_p}\right) > -5.64. \tag{3.1}
$$

 $-1.19 > \frac{1}{d \log D_p} \log \left(\frac{1}{d \log D_p} \right) > -5.64.$ (3.1)
The magnitudes of the nucleation mode distribution functions measured in Atlanta
exceed those measured in the remote tronosphere by typically one to two orders The magnitudes of the nucleation mode distribution functions measured in Atlanta
exceed those measured in the remote troposphere by typically one to two orders
of magnitude. As with the distributions measured in the remot The magnitudes of the nucleation mode distribution functions measured in Atlanta exceed those measured in the remote troposphere by typically one to two orders of magnitude. As with the distributions measured in the remote exceed those measured in the remote troposphere by typically one to two orders
of magnitude. As with the distributions measured in the remote troposphere, min-
ima are occasionally observed, although the minima for Atlanta of magnitude. As with the distributions measured is
ima are occasionally observed, although the minin
somewhat larger sizes and are not as pronounced. somewhat larger sizes and are not as pronounced.
4. Discussion

4. Discussion
In previous work we calculated numerically time-dependent size distributions of
nucleation mode aerosols in systems where a condensable species (the 'monomer') is In previous work we calculated numerically time-dependent size distributions of
nucleation mode aerosols in systems where a condensable species (the 'monomer') is
produced at a constant rate R . The calculations take acc In previous work we calculated numerically time-dependent size distributions of nucleation mode aerosols in systems where a condensable species (the 'monomer') is produced at a constant rate, R . The calculations take ac nucleation mode aerosols in systems where a condensable species (the 'monomer') is
produced at a constant rate, R . The calculations take account of monomer production
by gas phase chemical reactions, condensation of mon produced at a constant rate, R. The calculations take account of monomer production
by gas phase chemical reactions, condensation of monomer on newly formed molecular
clusters and on pre-existing aerosol, coagulation betwe by gas phase chemical reactions, condensation of monomer on newly formed molecular clusters and on pre-existing aerosol, coagulation between molecular clusters, evaporation of monomer from molecular clusters, and coagulati ular clusters and on pre-existing aerosol, coagulation between molecular clusters, evaporation of monomer from molecular clusters, and coagulation between molecular clusters and pre-existing aerosol. Following the approach evaporation of monomer from molecular clusters, and coagulation between molecular clusters and pre-existing aerosol. Following the approach typically used with nucleation theory, we assumed that evaporation rates can be ca clusters and pre-existing aerosol. Following the approach typically used with nucleation theory, we assumed that evaporation rates can be calculated using the capillarity approximation. We assumed that the size distributio ation theory, we assumed that evaporation rates can be calculated using the capillarity approximation. We assumed that the size distribution of the pre-existing aerosol is not significantly altered by condensation during t is not significantly altered by condensation during the nucleation event, and that is not significantly altered by condensation during the nucleation event, and that
the mass accommodation coefficient of monomer on pre-existing aerosol or molecu-
lar clusters equals one, which is justified by both theor the mass accommodation coefficient of monomer on pre-existing aerosol or molecular clusters equals one, which is justified by both theory and measurement (Clement *et al.* 1996; Jefferson *et al.* 1997). These analyses sh lar clusters equals one, which is justified by both theory and measurement (Clement *et al.* 1996; Jefferson *et al.* 1997). These analyses showed that the time-dependent nucleation mode size distributions depend on three *et al.* 1996; Jefferson
nucleation mode siz
and L , defined as

$$
E = N_s \left(\frac{\beta_{11}}{R}\right)^{1/2},\tag{4.1}
$$

$$
A = 4\left(\frac{\pi}{6}\right)^{1/3} \frac{v_1^{2/3}\sigma}{k_B T},
$$
\n(4.2)

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²⁶³² *P.H.McMurryandothers* Downloaded from rsta.royalsocietypublishing.org

$$
\sqrt{L} = \left(\frac{k_{\rm B}T}{2\pi m_1}\right)^{1/2} \frac{I}{\sqrt{\beta_{11}R}}.\tag{4.3}
$$

 $\sqrt{L} = \left(\frac{2\pi m_1}{2\pi m_1}\right) \frac{\sqrt{\beta_{11}R}}{\sqrt{\beta_{11}R}}$. (4.3)
Variables are defined in the nomenclature. The parameters E and A determine the
significance of monomer evaporation (Rao & McMurry 1989); calculated distribution Variables are defined in the nomenclature. The parameters E and A determine the significance of monomer evaporation (Rao & McMurry 1989); calculated distribution functions are highly sensitive to these parameters. The Variables are defined in the nomenclature. The parameters E and A determine the significance of monomer evaporation (Rao $\&$ McMurry 1989); calculated distribution functions are highly sensitive to these parameters. significance of monomer evaporation (Rao & McMurry 1989); calculated distribution functions are highly sensitive to these parameters. The surface tension parameter A depends only on temperature and properties of the con functions are highly sensitive to these parameters. The surface tension parameter A depends only on temperature and properties of the condensing species. For systems in which the vapour is produced at a very high rate (depends only on temperature and properties of the condensing species. For systems
in which the vapour is produced at a very high rate (i.e. R is large) or for which
the monomer saturation vapour pressure is small $(N_s$ i in which the vapour is produced at a very high rate (i.e. R is large) or for which
the monomer saturation vapour pressure is small $(N_s$ is very small), E approaches
zero and the monomer evaporation terms become neglig the monomer saturation vapour pressure is small $(N_s$ is very small), E approaches zero and the monomer evaporation terms become negligible. We refer to this as the 'collision-controlled regime'. McMurry (1980) found tha zero and the monomer evaporation terms become negligible. We refer to this as the 'collision-controlled regime'. McMurry (1980) found that total number concentrations
and size distributions of aerosols larger than 10 nm p "collision-controlled regime". McMurry (1980) found that total number concentra
and size distributions of aerosols larger than 10 nm produced by the photo-oxid
of SO_2 in smog chambers at reaction rates exceeding *ca*. s^{-1} are and size distributions of aerosols larger than 10 nm produced by the photo-oxidation
of SO_2 in smog chambers at reaction rates exceeding ca . 10^6 molecules cm^{-3} s⁻¹ are
in good agreement with predictions of the c in good agreement with predictions of the collision-controlled theory. L determines the significance of monomer condensation and the coagulation of freshly formed parin good agreement with predictions of the collision-controlled theory. L determines
the significance of monomer condensation and the coagulation of freshly formed par-
ticles onto pre-existing aerosol (McMurry 1983). Note the significance of monomer condensation and the coagulation of freshly formed particles onto pre-existing aerosol (McMurry 1983). Note that \sqrt{L} varies in proportion to the Fuchs integral, I, which equals the aerosol ticles onto pre-existing aerosol (McMurry 1983). Note that \sqrt{L} varies in proportion
to the Fuchs integral, I, which equals the aerosol surface area for particles that are
much smaller than the gas mean free path. For to the Fuchs integral, I, which equals the aerosol surface area for particles that are
much smaller than the gas mean free path. For typical transition regime atmospheric
aerosols, the Fuchs integral is a bit smaller than much smaller than the gas mean free path. For typical transition regime atmospheric aerosols, the Fuchs integral is a bit smaller than the surface area. Although atmospheric nucleation is undoubtedly heteromolecular, this aerosols, the Fuchs integral is a bit smaller than the surface area. Although atmo-
spheric nucleation is undoubtedly heteromolecular, this theory treats the process as
a quasi-single-component process, with the growth or clusters rate limited by a single, low-vapour-pressure species. quasi-single-component process, with the growth or evaporation of the molecular
usters rate limited by a single, low-vapour-pressure species.
Figure 4 shows calculated size distributions as a function of the heterogeneous

clusters rate limited by a single, low-vapour-pressure species.
Figure 4 shows calculated size distributions as a function of the heterogeneous
loss parameter, L, for collision-controlled nucleation ($E = 0$). The results Figure 4 shows calculated size distributions as a function of the heterogeneous loss parameter, L , for collision-controlled nucleation ($E = 0$). The results shown are dimensionless. The relationship between the dimensio loss parameter, L, for collision-controlled nucleation ($E = 0$). The results shown
are dimensionless. The relationship between the dimensional and dimensionless size
variables is

$$
\frac{dN}{d \log D_p}\Big|_{\text{dimensional}} = \left(\frac{R}{\beta_{11}}\right)^{1/2} \frac{d\tilde{N}}{d \log \tilde{D}_p}\Big|_{\text{dimensionless}},\tag{4.4}
$$

$$
D_{\rm p}|_{\rm dimensional} \quad \langle P_{11} \rangle \quad \text{d log } D_{\rm p}|_{\rm dimensionless}
$$
\n
$$
D_{\rm p}|_{\rm dimensional} = v_1^{1/3} \tilde{D}_{\rm p}|_{\rm dimensionless}. \tag{4.5}
$$

 $D_{\rm p}|_{\rm dimensional} = v_1^{1/3} \tilde{D}_{\rm p}|_{\rm dimensionless}$. (4.5)
The analysis shows that size distributions rapidly achieve a steady state that depends
on L and it is these steady state results that are shown in figure 4. The vertical lines The analysis shows that size distributions rapidly achieve a steady state that depends
on L, and it is these steady state results that are shown in figure 4. The vertical lines
in figure 4 show the 3–10 nm window correspo The analysis shows that size distributions rapidly achieve a steady state that depends
on L , and it is these steady state results that are shown in figure 4. The vertical lines
in figure 4 show the 3-10 nm window corres on L , and it is these steady state results that are shown in figure 4. The vertical lines
in figure 4 show the 3–10 nm window corresponding to the range of data shown in
figures 2 and 3. These dimensional sizes were obt in figure 4 show the 3–10 nm window corresponding to the range of data shown in
figures 2 and 3. These dimensional sizes were obtained from equation (4.5) assuming
a monomer volume of $v_1 \approx 3 \times 10^{-22} \text{ cm}^3$. This corre figures 2 and 3. These dimensional sizes were obtained from equation (4.5) assuming
a monomer volume of $v_1 \approx 3 \times 10^{-22} \text{ cm}^3$. This corresponds approximately to the
molecular volume of sulphuric acid and its associate a monomer volume of $v_1 \approx 3 \times 10^{-22} \text{ cm}^3$. This corresponds approximately to the molecular volume of sulphuric acid and its associated water at 50% relative humidity, and is slightly smaller than the volume of a molec molecular volume of sulphu
and is slightly smaller than
sionless size varies as $v_1^{1/3}$,
slopes of the distribution phuric acid and its associated water at 50% relative humidity,
han the volume of a molecule of $(NH_4)_2SO_4$. Because dimen-
 $1/3$, it is not necessary to know v_1 precisely. Note that the
on functions become steeper as L and is slightly smaller than the volume of a molecule of $(NH_4)_2SO_4$. Because dimensionless size varies as $v_1^{1/3}$, it is not necessary to know v_1 precisely. Note that the slopes of the distribution functions become sionless size varies as $v_1^{1/3}$, it is not necessary to know v_1 precisely. Note that the slopes of the distribution functions become steeper as L increases. The calculated distribution functions have slopes of -2.3 slopes of the distribution functions become steeper as L increases. The calculated distribution functions have slopes of -2.38 for $L = 0.56$, and -6.56 for $L = 2.0$. These slopes are in the range of the values measure

Figure 5 shows calculated steady-state size distributions as a function of the evap-These slopes are in the range of the values measured in Atlanta (figure 3).
Figure 5 shows calculated steady-state size distributions as a function of the evaporation parameter E for $L = 0.58$ and $A = 8$. This value of A Figure 5 shows calculated steady-state size distributions as a function of the evaporation parameter E for $L = 0.58$ and $A = 8$. This value of A is typical of values that would be expected for organics but is smaller than oration parameter E for $L = 0.58$ and $A = 8$. This value of A is typical of values
that would be expected for organics but is smaller than the characteristic value for
sulphuric acid $(A \sim 16)$. Calculations were done usin that would be expected for organics but is smaller than the characteristic value for sulphuric acid $(A \sim 16)$. Calculations were done using $A = 8$ because the equations became exceedingly stiff and difficult to solve for sulphuric acid ($A \sim 16$). Calculations were done using $A = 8$ because the equa-

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Figure 4. Calculated steady-state aerosol size distributions when condensable vapour is produced
at a constant rate in a collision-controlled system. The parameter L increases with increasing
aerosol surface area of par at a constant rate in a collision-controlled system. The parameter L increases with increasing aerosol surface area of particles larger than ca . 10 nm.

% aerosol surface area of particles larger than ca . 10 nm.

that is produced for a system initially free of particles, and reflects loss of monomer

and clusters to particles larger than ca 10 nm that were produced by n that is produced for a system initially free of particles, and reflects loss of monomer
and clusters to particles larger than ca . 10 nm that were produced by nucleation.
Note that size distributions are highly sensitive that is produced for a system initially free of particles, and reflects loss of monomer
and clusters to particles larger than ca . 10 nm that were produced by nucleation.
Note that size distributions are highly sensitive and clusters to particles larger than ca . 10 nm that were produced by nucleation.
Note that size distributions are highly sensitive to E for $E > 0.02$. Also, for large values of E , minima are predicted for particles values of E , minima are predicted for particles in the $3-10$ nm diameter range. These values of E , minima are predicted for particles in the 3-10 nm diameter range. These
trends would be even more pronounced for larger values of A . The size distributions
for values of E up to 0.02 are qualitatively c trends would be even more pronounced for larger values of A . The size distributions
for values of E up to 0.02 are qualitatively consistent with observed size distributions
in Atlanta. The measured size distributions for values of E up to 0.02 are qualitatively consistent with observed size distributions
in Atlanta. The measured size distributions are quite different from size distributions
calculated for larger values of E , howev in Atlanta. The measured size distributions are quite different from size distributions calculated for larger values of E , however. The size distributions observed for larger values of E might be consistent with the P calculated for larger values of E might be comproped to the controposphere (figure 2).
If we assume that nuclear It we assume that nucleation is collision-controlled, two approaches can be used to id the monomer production rate. R , for the Atlanta data (figure 3). The slope of

If we assume that nucleation is collision-controlled, two approaches can be used to find the monomer production rate, R , for the Atlanta data (figure 3). The slope of If we assume that nucleation is collision-controlled, two approaches can be used to find the monomer production rate, R , for the Atlanta data (figure 3). The slope of the measured distribution function provides a value find the monomer production rate, R , for the Atlanta data (figure 3). The slope of the measured distribution function provides a value for the dimensionless scavenging rate parameter, L (see figure 4). R is then eva the measured distribution function provides a value for the dimensionless scavenging
rate parameter, L (see figure 4). R is then evaluated from equation (4.3), where the
Fuchs integral, I, is calculated from measured size rate parameter, L (see figure 4). R is then evaluated from equation (4.3), where the Fuchs integral, I, is calculated from measured size distributions. We refer to this value of R as R_L . Alternatively, the slope of the Fuchs integral, I, is calculated from measured size distributions. We refer to this value of R as R_L . Alternatively, the slope of the measured size distribution is used to find the value of the dimensionless size distri value of R as R_L . Alternatively, the slope of the measured size distribution is used to find the value of the dimensionless size distribution at the minimum detectable size (see figure 4), and the value of R that scales (see figure 4), and the value of R that scales the dimensionless to the dimensional (see figure 4), and the value of R that scales the dimensionless to the dimensional
size distribution is evaluated from equation (4.4). We refer to this value of R as
 R_{scale} . R_L and R_{scale} are compared in figure 6 size distribution is evaluated from equation (4.4). We refer to this value of R as R_{scale} . R_L and R_{scale} are compared in figure 6. As was shown in figure 3, most of the size distributions measured in Atlanta had linea *Phil. Trans. R. Soc. Lond.* A (2000)

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lated steady-state aerosol size distributions for several values of th
parameter E. Calculations were done using $A = 8$ and $L = 0.58$.

 R_{scale} (molecules cm⁻³ s⁻¹)
Figure 6. Comparison of monomer production rates for Atlanta calculated in two different
ways. Calculations assume that nucleation is collision-controlled mparison of monomer production rates for Atlanta calculated in tways. Calculations assume that nucleation is collision-controlled.

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 $D_{\rm p}$ (μ m)
Figure 7. Comparison of measured and theoretical size distributions for 3-10 nm aerosols for
one typical Atlanta measurement. The theory assumes collision-controlled nucleation ($E = 0$) Figure 7. Comparison of measured and theoretical size distributions for 3–10 nm aerosols for
one typical Atlanta measurement. The theory assumes collision-controlled nucleation $(E = 0)$.
Theoretical results are shown for t one typical Atlanta measurement. The theory assumes collision-controlled nucleation $(E = 0)$.
Theoretical results are shown for the monomer production rate, R, calculated in two different ways.

ways.
circles in figure 6 apply to data with nonlinear slopes. Note that for *ca*.90% of our
measurements, the values of *R* calculated in these ways agreed to within a factor of circles in figure 6 apply to data with nonlinear slopes. Note that for $ca.90\%$ of our measurements, the values of R calculated in these ways agreed to within a factor of 10 . Several of the outliers apply to measureme measurements, the values of R calculated in these ways agreed to within a factor of 10. Several of the outliers apply to measurements with nonlinear slopes. Several of measurements, the values of R calculated in these ways agreed to within a factor of 10. Several of the outliers apply to measurements with nonlinear slopes. Several of these measurements were made early in the morning or l 10. Several of the outliers apply to measurements with nonlinear slopes. Several of these measurements were made early in the morning or late in the evening, when the assumption that nucleation mode aerosol size distribut these measurements were made early in the morning or late in the evening, when the assumption that nucleation mode aerosol size distributions are at steady state would be invalid. The values of R determined by these two ap assumption that nucleation mode aerosol size distributions are at steady state would
be invalid. The values of R determined by these two approaches are not systematically
different, although there is significant scatter. be invalid. The values of R determined by these two approaches are not systematically different, although there is significant scatter. Measured and theoretical collision-controlled (i.e. $E = 0$) size distributions are sh different, although there is significant scatter. Measured and theoretical collision-
controlled (i.e. $E = 0$) size distributions are shown for one typical measurement in
figure 7. Theoretical size distributions correspon controlled (i.e. $E = 0$) size distributions are shown for one typical measurement in
figure 7. Theoretical size distributions corresponding to the values of R_L and R_{scale}
obtained for this measurement $(2.5 \times 10^5$ mole $\rm cm^{-3} \ s^{-1}, \ r$ Theoretical size distribution
for this measurement $(2.5 \times$, respectively) are shown.
sults shown in figures 6 and tained for this measurement $(2.5 \times 10^5$ molecules cm⁻³ s⁻¹ and 5.7×10^5 molecules
 n^{-3} s⁻¹, respectively) are shown.

The results shown in figures 6 and 7 are based on the assumption that nucleation

Atlant

 $\text{cm}^{-3} \text{ s}^{-1}$, respectively) are shown.
The results shown in figures 6 and 7 are based on the assumption that nucleation
in Atlanta was collision-controlled. A more rigorous testing of this hypothesis would
require s The results shown in figures 6 and 7 are based on the assumption that nucleation
in Atlanta was collision-controlled. A more rigorous testing of this hypothesis would
require solutions of the cluster balance equations for in Atlanta was collision-controlled. A more rigorous testing of this hypothesis would
require solutions of the cluster balance equations for $E > 0$ over a wider range of
L and for values of A applicable to the nucleating require solutions of the cluster balance equations for $E > 0$ over a wider range of L and for values of A applicable to the nucleating aerosols; the results shown in figure 5 were done for $L=0.58$, and we have not ca L and for values of A applicable to the nucleating aerosols; the results shown in figure 5 were done for $L=0.58$, and we have not carried out calculations for other values of L. However, if the results in figure 5 are ch figure 5 were done for $L=0.58$, and we have not carried out calculations for other values of L. However, if the results in figure 5 are characteristic of those for other values of L, it would appear unlikely R_L and $R_{$ values of L. However, if the results in figure 5 are characteristic of those for other values of L, it would appear unlikely R_L and R_{scale} would have been comparable in magnitude (figure 6) if evaporation from clusters values of *L*, it would appear unlikely R_L and R_{scale} would have been comparable in magnitude (figure 6) if evaporation from clusters had played a significant role. The results of figure 5 show that slopes of the distri magnitude (figure 6) if evaporation from clusters had played a significant role. The results of figure 5 show that slopes of the distribution are comparable for $E = 0$, $E = 0.01$ and $E = 0.02$, but the 3.5 nm intercepts v results of figure 5 show that slopes of the distribution are comparable for $E = 0$, $E = 0.01$ and $E = 0.02$, but the 3.5 nm intercepts vary by more than a factor of ten.
If the true value of E had been 0.02 (rather than 0 $E = 0.01$ and $E = 0.02$, but the 3.5 nm intercepts vary by more than a factor of ten.
If the true value of E had been 0.02 (rather than 0 as was assumed above), then R_{scale} would have been more than a factor of 100 hig R_{scale} would have been more than a factor of 100 higher than was found for collision-

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mas of any
Hydroxyl radical concentrations required to produce calculated m
production rates for measured concentrations of sulphur dioxide.

production rates for measured concentrations of sulphur dioxide.

if calculations had been done for larger values of A and L , as might be appropriate for

these atmospheric aerosols. Because the slopes of these curves if calculations had been done for larger values of A and L, as might be appropriate for
these atmospheric aerosols. Because the slopes of these curves are similar, however,
 R_L would be changed by only a small amount. Th if calculations had been done for larger values of A and L, as might be appropriate for
these atmospheric aerosols. Because the slopes of these curves are similar, however,
 R_L would be changed by only a small amount. Th these atmospheric aerosols. Because the slopes of these curves are similar, however, R_L would be changed by only a small amount. Therefore, values of E as small as 0.01 or 0.02 would have led to $R_{scale} \gg R_L$. The results R_L would be changed by only a small amount. Therefore, values of E as small as 0.01 or 0.02 would have led to $R_{scale} \gg R_L$. The results shown in figure 6 show that this is not the case. Furthermore, for values of $E > 0.02$ 0.01 or 0.02 would have led to $R_{\text{scale}} \gg R_L$. The results shown in figure 6 show that this is not the case. Furthermore, for values of $E > 0.02$, theory shows that the slope of the distribution function would not have bee that this is not the case. Furthermore, for values of $E > 0.02$, theory shows that the slope of the distribution function would not have been linear as was experimentally observed in Atlanta, further supporting our argume slope of the distribution function would not have been linear as was experimentally
observed in Atlanta, further supporting our argument that nucleation was collision-
controlled. The remote tropospheric distribution funct controlled. The remote tropospheric distribution functions (figure 3), however, do not have linear slopes. This could reflect the importance of cluster evaporation during controlled. The remote tropospheric distribution functions (figure 3), however, do not
have linear slopes. This could reflect the importance of cluster evaporation during
these measurements. In order to explain such size d have linear slopes. This could reflect the importance of cluster evaporation during
these measurements. In order to explain such size distributions with theory, it will
be necessary to fit the measured distribution functio these measurements. In order to explain such size distribut
be necessary to fit the measured distribution function to a t
is similar in shape. We have not yet attempted to do this.
It is instructive to speculate on species be necessary to fit the measured distribution function to a theoretical function that is similar in shape. We have not yet attempted to do this.
It is instructive to speculate on species that might be responsible for the o

nucleation. For collision-controlled nucleation, the dimensionless monomer concen-It is instructive to speculate on species that might be responsible for the observed
nucleation. For collision-controlled nucleation, the dimensionless monomer concentration is insensitive to L, ranging from 0.58 for $L =$ nucleation. For collision-controlled nucleation, the dimensionless monomer concentration is insensitive to L, ranging from 0.58 for $L = 0.6$ to 0.49 for $L = 2$ (McMurry 1983). As an approximation we assume a typical value tration is insensitive to L , ranging from
1983). As an approximation we assume
tration is therefore (McMurry 1983) tration is therefore (McMurry 1983)

$$
N1 = 0.5 \left(\frac{R}{\beta_{11}}\right)^{0.5}
$$
 ≈ 2.24 × 10⁴√R molecules cm⁻³. (4.6)

Based on the values of R shown in figure 6 (similar results are obtained with either Based on the values of R shown in figure 6 (similar results are obtained with either R_L or R_{scale}), we find that N_1 falls below 1.2×10^7 molecules cm⁻³ for 50% of our measurements and below 2.2×10^7 molecul Based on the values of R shown in figure 6 (similar results are obtained with either R_L or R_{scale}), we find that N_1 falls below 1.2×10^7 molecules cm⁻³ for 50% of our measurements and below 2.2×10^7 mole R_L or R_{scale}), we find that N_1 falls below 1.2×10^7 molecules cm⁻³ for 50% of our measurements. Based on our previous studies (see, for example, Eisele & McMurry 1997), we believe that sulphuric acid may par our measurements and below 2.2×10^7 molecules cm⁻³ for 90% of our measure-
ments. Based on our previous studies (see, for example, Eisele & McMurry 1997),
we believe that sulphuric acid may participate in nucleation ments. Based on our previous studies (see, for example, Eisele & McMurry 1997), we believe that sulphuric acid may participate in nucleation. Sulphuric acid vapour was not measured during the Atlanta study. In our previou

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troposphere, however, sulphuric acid vapour concentrations measured during ation events occasionally reached levels as high as 2×10^7 molecules cm⁻³ (V et al. 1996) but covered the range 1×10^4 < [H_aSO₄] < 2 **MATHEMATICAL,
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SCIENCES troposphere, however, sulphuric acid vapour concentrations measured during nucle-
ation events occasionally reached levels as high as 2×10^7 molecules cm⁻³ (Weber
et al. 1996), but covered the range $1 \times 10^4 < [H_2$ troposphere, however, sulphuric acid vapour concentrations measured during nucleation events occasionally reached levels as high as 2×10^7 molecules cm⁻³ (Weber
et al. 1996), but covered the range $1 \times 10^4 < [H_2SO_4] < 2 \times 10^7$ molecules cm⁻³
with an average value of $ca. 1 \times 10^6$ molecules with an average value of $ca. 1 \times 10^6$ molecules cm^{-3} . Thus, the calculated monomer concentrations for collision-controlled nucleation in Atlanta are somewhat higher (up with an average value of $ca.1 \times 10^6$ molecules cm⁻³. Thus, the calculated monomer
concentrations for collision-controlled nucleation in Atlanta are somewhat higher (up
to a factor of 10) than the sulphuric acid concent concentrations for collision-controlled nucleation in Atlanta are somewhat higher (up
to a factor of 10) than the sulphuric acid concentrations that have been measured in
the remote troposphere when nucleation is occurring to a factor of 10) than the sulphuric acid concentrations that have been measured in
the remote troposphere when nucleation is occurring. If similar species were involved
with nucleation in both locations, then the evapora the remote troposphere when nucleation is occurring. If similar species were involved with nucleation in both locations, then the evaporation terms in the cluster balance equations would certainly be less significant in Atlanta since the supersaturation of
the nucleating species was approximately a factor of ten higher. It is likely that other
species that participate in nucleation (ammonia the nucleating species was approximately a factor of ten higher. It is likely that other the nucleating species was approximately a factor of ten higher. It is likely that other
species that participate in nucleation (ammonia, amines, etc.) are more abundant in
Atlanta than in the urban troposphere. This could species that participate in nucleation (ammonia, amines, etc.) are more abundant in
Atlanta than in the urban troposphere. This could also lead to reduced sulphuric
acid vapour pressures and lead to nucleation that is more

acid vapour pressures and lead to nucleation that is more nearly collision-controlled.
An upper limit for the saturation vapour concentration of the condensing species, acid vapour pressures and lead to nucleation that is more nearly collision-controlled.
An upper limit for the saturation vapour concentration of the condensing species,
 N_s , can be estimated from equation (4.1). Based on An upper limit for the saturation vapour concentration of the condensing species, N_s , can be estimated from equation (4.1). Based on the above arguments, we assume that during nucleation in Atlanta, the E was less than N_s , can be estimated from equation (4.1). Based on the above arguments, we as that during nucleation in Atlanta, the E was less than 0.01. Because 90% of the clated monomer production rates, R_{scale} , were below $1.3 \times$ s^{-1} , w ume
, we
, 10⁵ that during nucleation in Atlanta, the E was less than 0.01. Because 90% of the calculated monomer production rates, R_{scale} , were below 1.3×10^6 molecules cm⁻³ s⁻¹, we conservatively conclude that the saturatio lated monomer production rates, R_{scale} , were below 1.3×10^6 molecules cm⁻³ s⁻¹, we
conservatively conclude that the saturation vapour concentration was below 5×10^5
molecules cm⁻³. It would be equally jus conservatively conclude that the saturation vapour concentration was below 5×10^5
molecules cm⁻³. It would be equally justifiable to use a low value of R_{scale} to esti-
mate the upper limit for N_s , since measured d molecules cm⁻³. It would be equally justifiable to use a low value of R_{scale} to estimate the upper limit for N_s , since measured distribution functions were also found to be linear for small values of R_{scale} . We mate the upper limit for N_s , since measured distribution functions were also found
to be linear for small values of R_{scale} . We found that R_{scale} was below $ca. 1.4 \times 10^4$
molecules cm⁻³ s⁻¹ for $ca. 10\%$ of our obse molecules $\text{cm}^{-3} \text{ s}^{-1}$ for ca. 10% of our observations. The corresponding upper limit to be linear for small values of R_{scale} . We found that R_{scale} was below $ca. 1.4 \times 10^4$ molecules cm⁻³ s⁻¹ for $ca. 10\%$ of our observations. The corresponding upper limit for N_s is 5×10^4 molecules cm⁻³ molecules cm⁻³ s⁻¹ for *ca*. 10% of our observations. The corresponding upper limit
for N_s is 5×10^4 molecules cm⁻³. Saturation vapour concentrations of sulphuric acid
vapour above solid ammonium sulphate aero for N_s is 5×10^4 molecules cm⁻³. Saturation vapour concentrations of sulphuric acid vapour above solid ammonium sulphate aerosol particles of $ca. 2.5 \times 10^4$ molecules cm⁻³ were reported by Marti *et al.* (1997) vapour above solid ammoni

cm⁻³ were reported by Mai

are in a reasonable range.

Another argument in sur- A^{-3} were reported by Marti *et al.* (1997). It follows that our calculated N_s values
e in a reasonable range.
Another argument in support of the hypothesis that sulphuric acid participated
nucleation in Atlanta is ou

are in a reasonable range.
Another argument in support of the hypothesis that sulphuric acid participated
in nucleation in Atlanta is our observation that sulphur dioxide concentrations were
typically elevated during the Another argument in support of the hypothesis that sulphuric acid participated
in nucleation in Atlanta is our observation that sulphur dioxide concentrations were
typically elevated during the nucleation events (Woo *et a* in nucleation in Atlanta is our observation that sulphur dioxide concentrations were
typically elevated during the nucleation events (Woo *et al.* 2000). To test the plau-
sibility of the monomer production rates shown in typically elevated during the nucleation events (Woo *et al.* 2000). To test the plausibility of the monomer production rates shown in figure 6, we have calculated the hydroxyl radical concentrations that would have been sibility of the monomer production rates shown in figure 6, we have calculated the hydroxyl radical concentrations that would have been required to produce the calculated monomer production rates. The calculated hydroxyl r hydroxyl radical concentrations that would have been required to produce the cal-
culated monomer production rates. The calculated hydroxyl radical concentrations were obtained from the following equation:

the following equation:
\n
$$
[OH] = \frac{R_{\text{scale}}}{8.5 \times 10^{-13} [\text{SO}_2]} \text{ molecules cm}^{-3}, \qquad (4.7)
$$

 $[OII] = \frac{8.5 \times 10^{-13} [SO_2]}{8.5 \times 10^{-13} [SO_2]}$
where $[SO_2]$ is the measured concentration of sulphur dioxide in molecules per cm³
and the second-order rate constant for the SO₂-OH reaction is 8.5×10^{-13} cm³ where $[SO_2]$ is the measured concentration of sulphur dioxide in molecules per cm³
and the second-order rate constant for the SO_2 -OH reaction is 8.5×10^{-13} cm³
molecule⁻¹ s⁻¹ (DeMore *et al.* 1992). Values molecule⁻¹ s⁻¹ (I he measured concentration of sulphur dioxide in molecules per cm³
order rate constant for the SO_2 -OH reaction is 8.5×10^{-13} cm³
(DeMore *et al.* 1992). Values of [OH] calculated in this way are
me of day in figu and the second-order rate constant for the SO_2 -OH reaction is 8.5×10^{-13} cm³
molecule⁻¹ s⁻¹ (DeMore *et al.* 1992). Values of [OH] calculated in this way are
plotted versus time of day in figure 8. The calcula molecule⁻¹ s⁻¹ (DeMore *et al.* 1992). Values of [OH] calculated in this way are plotted versus time of day in figure 8. The calculated hydroxyl radical concentration follows a reasonable diurnal variation, with peak plotted versus time of day in figure 8. The calculated hydroxyl radical concentration
follows a reasonable diurnal variation, with peak values occurring near noon. Half
of the calculated hydroxyl concentrations are below follows a reasonable diurnal variation, with peak values occurring near noon. Half
of the calculated hydroxyl concentrations are below $ca. 8 \times 10^5$ molecules cm⁻³ and
90% are below $ca. 8 \times 10^6$ molecules cm⁻³. These of the calculated hydroxyl concentrations are below $ca.8 \times 10^5$ molecules cm⁻³ and 90% are below $ca.8 \times 10^6$ molecules cm⁻³. These values are in a reasonable range for an urban area (W. Chamiedes, personal communica 90% are below $ca.8 \times 10^6$ molecules cm^{-3} . These values are in a reasonable range
for an urban area (W. Chamiedes, personal communication), but hydroxyl radical
concentrations have not been measured in the Atlanta at concentrations have not been measured in the Atlanta atmosphere, and we have not attempted to compare our results with models applicable to our measurement periods.

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P. H. McMurry and others
5. Conclusions

Two instruments were used to measure size distributions of 3–10 nm diameter aero-Two instruments were used to measure size distributions of 3–10 nm diameter aerosols when nucleation was occurring. One of these systems (the UCPC-PHA), which measures the amount of light scattered by individual particles Two instruments were used to measure size distributions of 3–10 nm diameter aerosols when nucleation was occurring. One of these systems (the UCPC-PHA), which measures the amount of light scattered by individual particles sols when nucleation was occurring. One of these systems (the UCPC-PHA), which
measures the amount of light scattered by individual particles downstream of the con-
denser of an ultrafine condensation particle counter, is measures the amount of light scattered by individual particles downstream of the con-
denser of an ultrafine condensation particle counter, is best suited for measurements
where concentrations are low and measurements must denser of an ultrafine condensation particle counter, is best suited for measurements
where concentrations are low and measurements must be made quickly. For example,
this instrument is well suited for aircraft measurement where concentrations are low and measurements must be made quickly. For example,
this instrument is well suited for aircraft measurements in the remote troposphere.
The other system (the nano-SMPS) determines size with a n this instrument is well suited for aircraft measurements in the remote troposphere.
The other system (the nano-SMPS) determines size with a new electrostatic classifier
that was specially designed for particles as small as The other system (the nano-SMPS) determines size with a new electrostatic classifier
that was specially designed for particles as small as 3 nm and concentration with an
ultrafine condensation particle counter. The nano-SM that was specially designed for particles as small as 3 nm and concentration with an ultrafine condensation particle counter. The nano-SMPS provides better sizing resolution than the UCPC-PHA but requires more time to comp ultrafine condensation particle counter. The nano-SMPS provides better sizing resolution than the UCPC-PHA but requires more time to complete a measurement. We used the nano-SMPS for measurements in Atlanta where concentra lution than the UCPC-PHA but requires more time to complete a measured the nano-SMPS for measurements in Atlanta where concentrate and accurate measurements could be carried out in a few minutes.
Both instrument systems sh ed the nano-SMPS for measurements in Atlanta where concentrations were high
d accurate measurements could be carried out in a few minutes.
Both instrument systems showed that aerosol size distribution functions increase
t

and accurate measurements could be carried out in a few minutes.
Both instrument systems showed that aerosol size distribution functions increase
with decreasing size at the minimum detectable particle size particle size Both instrument systems showed that aerosol size distribution functions increase
with decreasing size at the minimum detectable particle size particle size $(ca.3 \text{ nm})$
when nucleation was occurring. We are not aware that t with decreasing size at the minimum detectable part
when nucleation was occurring. We are not aware the
previously. Theory predicts that this should occur.
About 70 of the 85 observed hourly-averaged 3-10 hen nucleation was occurring. We are not aware that this trend has been observed
eviously. Theory predicts that this should occur.
About 70 of the 85 observed hourly-averaged 3–10 nm diameter size distributions
easured dur

previously. Theory predicts that this should occur.
About 70 of the 85 observed hourly-averaged 3–10 nm diameter size distributions
measured during nucleation in Atlanta over a period of one year can be expressed as

red during nucleation in Atlanta over a period of one year can be expressed as
\n
$$
\frac{dN}{d \log D_p} = A(D_p)^B; \qquad -5.64 < B < -1.19; \qquad B_{\text{average}} = -3.5. \tag{5.1}
$$

The magnitude of the distribution function at $D_p = 3.5$ nm (the midpoint of the The magnitude of the distribution function at $D_p = 3.5$ nm (the midpoint of the smallest size range) ranged from *ca*. 10^5 to 2×10^6 cm⁻³, which was one to two orders of magnitude higher than distribution functio The magnitude of the distribution function at $D_p = 3.5$ nm (the midpoint of the smallest size range) ranged from $ca.10^5$ to 2×10^6 cm⁻³, which was one to two orders of magnitude higher than distribution functions m smallest size range) ranged from $ca. 10^5$ to 2×10^6 cm⁻³, which was one to two orders of magnitude higher than distribution functions measured in the remote troposphere. Also, the remote tropospheric distribution f orders of magnitude higher than
posphere. Also, the remote trop
simple functional relationship.
The Atlanta data are consister sphere. Also, the remote tropospheric distribution functions did not obey this
nple functional relationship.
The Atlanta data are consistent with theoretical predictions for collision-controlled
cleation. The key assumptio

simple functional relationship.
The Atlanta data are consistent with theoretical predictions for collision-controlled
nucleation. The key assumptions of collision-controlled nucleation theory are that
all condensing molecu The Atlanta data are consistent with theoretical predictions for collision-controlled
nucleation. The key assumptions of collision-controlled nucleation theory are that
all condensing molecules stick together when they col nucleation. The key assumptions of collision-controlled nucleation theory are that all condensing molecules stick together when they collide, and that evaporation from molecular clusters does not occur. We find that the mo from molecular clusters does not occur. We find that the monomer (i.e. condensing from molecular clusters does not occur. We find that the monomer (i.e. condensing
molecule) production rates that are required to produce the observed size distribu-
tions are in reasonable expectations with values that wo molecule) production rates that are required to produce the observed size distribu-
tions are in reasonable expectations with values that would be expected for the gas
phase oxidation of sulphur dioxide by the hydroxyl rad tions are in reasonable expectations with values that would be expected for the gas
phase oxidation of sulphur dioxide by the hydroxyl radical. The collision-controlled
analysis suggests that the vapour pressure of the co phase oxidation of sulphu
analysis suggests that th
 $50\,000$ molecules cm^{-3} .
Clearly more work is re alysis suggests that the vapour pressure of the condensing species is less than 000 molecules cm^{-3} .
Clearly, more work is required to verify the above hypotheses. It will be necessary definitively identify the conde

 $50\,000$ molecules cm⁻³.
Clearly, more work is required to verify the above hypotheses. It will be necessary
to definitively identify the condensing species and to show experimentally that its
concentration is equal to Clearly, more work is required to verify the above hypotheses. It will be necessary
to definitively identify the condensing species and to show experimentally that its
concentration is equal to the value predicted theoreti to definitively identify the condensing species and to show experimentally that its
concentration is equal to the value predicted theoretically. Furthermore, because the
calculated monomer concentrations and equilibrium va concentration is equal to the value predicted theoretically. Furthermore, because the calculated monomer concentrations and equilibrium vapour concentrations are far below values that would be expected for sulphuric acid a calculated monomer concentrations and equilibrium vapour concentrations are far
below values that would be expected for sulphuric acid according to the classical
binary theory, the process must involve species in addition below values that would be expected for sulphuric acidionary theory, the process must involve species in add water. It is important that these species be identified.

Nomenclature

^A surface tension parameter (see equation (4.2))

Size distributionsof3{10nmatmospheric particles ²⁶³⁹

 $D_{\rm p}$ particle diameter
 E evaporation rate particle

 $D_{\rm p}$ particle diameter
 E evaporation rate parameter (see equation (4.1))

E evaporation rate parameter (see equation (4.1))
\n
$$
I = \frac{4\pi}{3} \int_{\text{pre-existing}} D_p^2 \left(\frac{Kn + Kn^2}{1 + 1.71Kn + 1.33Kn^2} \right) \frac{dN}{d \log D_p} d \log D_p
$$
\n
$$
k_B = \text{Boltzmann's constant}
$$
\nL, dimensionless scavenging rate parameter (see equation (4.3))

-
- $k_{\rm B}$ Boltzmann's constant
 L dimensionless scavenging rate parameter (see equation (4.3))

m. monomer mass k_B Boltzmann's cons
 L dimensionless sca
 m_1 monomer mass
 N aerosol number co
-
- L dimensionless scavenging rate par
 m_1 monomer mass
 N aerosol number concentration
 N saturation concentration of nuclear
- m_1 monomer mass
 N aerosol number concentration
 N_s saturation concentration of nucleating vapour
 R monomer production rate (molecules volume⁻
- N_s acrosol number concentration
 N_s saturation concentration of nucleating vapour
 R monomer production rate (molecules volume⁻¹ tin
 T temperature $time^{-1}$)
- T temperature
- v_1 monomer volume
 Kn $2\lambda/D_p$ $\begin{array}{ccc} T & \text{tempo} \ v_1 & \text{mono} \ Kn & 2\lambda/D \ \lambda & \text{mean} \end{array}$

- λ mean free path
 β_{11} monomer collis
- $Kn = 2\lambda/D_p$

mean free path
 β_{11} monomer collision frequency function

monomer collision frequency function
=
$$
4\sqrt{2}\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6k_BT}{\rho_P}\right)^{1/2}v_1^{1/6}
$$

 σ surface tension

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Distributions in Atlanta' and by DOE grant no. DE-FG02-98ER62556, 'Composition of Freshly
Nucleated Aerosols', We gratefully acknowle This research was supported by EPRI Agreement WO9181-01
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Discussion

R. M. HARRISON (*Division of Environmental Health and Risk Management, Univer-Biscussion*
R. M. HARRISON (*Division of Environmental Health and Risk Management, Univer-*
sity of Birmingham, UK). As some of the molecules forming sulphuric acid clusters
in the atmosphere could be small ions, what w R. M. HARRISON (*Division of Environmental Health and Risk Management*, *University of Birmingham*, *UK*). As some of the molecules forming sulphuric acid clusters in the atmosphere could be small ions, what will be the ef stability?

m the atmosphere could be small lons, what will be the effect of charge on cluster
stability?
P. H. MCMURRY. Charged clusters are more stable than neutral ones. Therefore,
ion-induced nucleation occurs at a higher rate tha stability:
P. H. MCMURRY. Charged clusters are more stable than neutral ones. Therefore,
ion-induced nucleation occurs at a higher rate than homogeneous nucleation of neu-
tral species. However I do not believe the concent P. H. MCMURRY. Charged clusters are more stable than neutral ones. Therefore,
ion-induced nucleation occurs at a higher rate than homogeneous nucleation of neu-
tral species. However, I do not believe the concentration of ion-induced nucleation occurs at a higher rate than homogeneous nucleation of neu-
tral species. However, I do not believe the concentration of ions would be high enough
to explain the high rates of particle production we atmosphere.

C. F. Clement (*Oxon, UK*). What has been used for the evaporation rate in the C. F. CLEMENT (*Oxon, UK*). What has been used for the evaporation rate in the model described? Particularly with the smaller clusters, it is not obvious that only one molecule could be evaporated C. F. CLEMENT $(Oxon, UK)$. Wha
model described? Particularly with
one molecule could be evaporated.

model described: Particularly with the smaller clusters, it is not obvious that only
one molecule could be evaporated.
P. H. MCMURRY. As you point out, a primary difficulty in nucleation theory is
calculating rates at whic P. H. MCMURRY. As you point out, a primary difficulty in nucleation theory is
calculating rates at which evaporation occurs from molecular clusters. If nucleation
is collision controlled $(E = 0)$ then evaporation is neglig P. H. MCMURRY. As you point out, a primary difficulty in nucleation theory is calculating rates at which evaporation occurs from molecular clusters. If nucleation is collision controlled $(E = 0)$, then evaporation is negli calculating rates at which evaporation occurs from molecular clusters. If nucleation
is collision controlled $(E = 0)$, then evaporation is negligible relative to condensation
and can be neglected. The data for the Atlanta is collision controlled ($E = 0$), then evaporation is negligible relative to condensation
and can be neglected. The data for the Atlanta atmosphere appear to be consistent
with this hypothesis (i.e. that nucleation is col and can be neglected. The data for the Atlanta atmosphere appear to be consistent
with this hypothesis (i.e. that nucleation is collision controlled). For the theoretical
results where evaporation was included $(E > 0)$, ev with this hypothesis (i.e. that nucleation is collision controlled). For the theoretical
results where evaporation was included $(E > 0)$, evaporation rates were calculated
by invoking the usual assumptions of classical nuc results where evaporation was included $(E > 0)$, evaporation rates were calculated
by invoking the usual assumptions of classical nucleation theory: molecular clusters
are assumed to have the same properties as the bulk li by invoking the usual assumptions of classical nucleation theory: molecular clusters
are assumed to have the same properties as the bulk liquid, the effect of curvature on
vapour pressure is described by the Kelvin equatio are assumed to have the same properties as the bulk liquid, the effect of curvature on