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Perspective

Atmospheric Nanoparticles and Climate Change

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Introduction

For several decades, chemical engineers have been studying the atmosphere as a vast chemical reactor to understand air pollution and climate change. Predicting future climate change requires accounting not only for greenhouse gases but also atmospheric particles and their interactions with clouds. Homogeneous nucleation of nanoparticles, first detectable when they are 1–3 nm, has been frequently observed in the atmosphere, but the chemistry driving their formation is still mysterious. This process may affect the climate; if these particles can grow to ~100 nm dia., they will modify the optical properties of clouds by serving as cloud nucleation sites. In most areas, growth of nanoparticles is dominated by organic oxidation chemistry that is also not well understood. This perspective article will survey the state of knowledge on these issues, highlight recent progress including contributions from chemical engineers, and point to promising future research areas. The next section provides background information about climate change and the role of atmospheric particles in the climate system. The section Gases and Nanoparticles discusses how nanoparticles form in the atmosphere with an emphasis on recent advances in the instruments that measure these processes. The fate of these nanoparticles and their potential to grow large enough to affect clouds is the subject of the section titled Nanoparticles to Cloud Condensation Nuclei. The section A Global Picture of CCN, Clouds, and Climate, places these processes in a global context by reviewing their incorporation into global climate models.

Atmospheric Particles, Clouds, and Climate Change

Climate change is controlled by two factors (1) changes in the Earth's energy balance from changes in atmospheric composition such as greenhouse gases, and (2) the sensitivity of temperature and other climate variables to a unit change in energy flux. For small perturbations to the Earth's energy balance, the global-mean temperature response, ΔT, is proportional to a "forcing", ΔF, of the climate system

$$\Delta T = \lambda \Delta F \tag{1}$$

In Eq. 1, the forcing is the change in the Earth's energy balance (W m^{-2}) resulting from an instantaneous change in the atmosphere's composition, for example, changing the carbon dioxide concentration from preindustrial levels to the present value. The internal dynamics of the climate system are represented by the "climate sensitivity", λ, an emergent parameter of the climate system that represents the ability of a warmer (or cooler) Earth to radiate more (or less) infrared radiation to space after internal feedbacks occur and the system equilibrates. John Seinfeld has recently provided *AIChE* readers with a more in-depth review of climate forcings and feedbacks than we can provide here.[1]

The average intensity of sunlight at the top of the Earth's atmosphere is 345 W m^{-2}. If the Earth were a blackbody, a simple application of the Stefan-Boltzmann law shows that its climate sensitivity would be 0.2–0.3 K W^{-1} m^2. Since the Earth maintains energy balance by thermal radiation to space, it is not surprising that general circulation models (GCMs), physical models of the climate system, suggest similar values for the climate sensitivity: 0.6 to 1.2 K W^{-1} m^2.[2] The tendency for atmospheric water vapor, a potent greenhouse gas, to increase with temperature is largely responsible for the higher climate sensitivities estimated by climate models,[3] and the larger spread is mainly due to their difficulty in predicting the response of clouds to climate change.[4] Despite its simplicity, Eq. 1 provides a useful decomposition of climate change into two, separate problems: externally driven changes in the energy balance and internal responses. Detailed climate simulations suggest that, for the most part, these two problems are indeed largely independent of each other since unit forcings of different kinds (e.g., changes in greenhouse gases or changes in solar activity) lead to very similar climate responses.[5,6]

The fact that GCMs exhibit climate sensitivities that differ from each other by a factor of two hampers our ability to

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forecast climate change. One might ask why we do not infer the climate sensitivity of the Earth from past climate change, either prehistoric or over the 20th century. From detailed line-by-line calculations of atmospheric radiative transfer and records of atmospheric CO_2 and other long-lived greenhouse gases, we know that their collective forcing since the start of the Industrial Revolution is 2.6 W m^{-2} with an uncertainty of only $\sim$10%.[2] The corresponding temperature change from 1850–1899 to 2001–2005 was 0.76 K +/− 0.19 K,[2] suggesting a climate sensitivity of $\sim$0.3 K W^{-1} m^2. A value this low would be comforting if it were true.

The flaw in this simple calculation is that greenhouse gases are not the only drivers of climate change. Over the industrial era, there has also been a marked increase in atmospheric aerosol concentrations, where we use "aerosol" in the broad sense to denote any airborne suspension of liquid or solid particles (i.e., not just the familiar spray cans). Atmospheric aerosols have natural sources including sea spray, desert dust, and volcanoes but also anthropogenic sources from combustion processes including transportation, industrial emissions, wood burning, etc. On average, anthropogenic aerosols cool the climate by reflecting sunlight back to space and enhancing the reflectivity of clouds, so that the net anthropogenic forcing over the industrial era is lower than 2.6 W m^{-2}: 0.6 to 2.4 W m^{-2}.[2] In other words, aerosol pollution has masked somewhere between 15 and 80% of global warming to date, and the empirically inferred climate sensitivity is larger but uncertain.

While at first blush, a strong cooling effect of aerosols might seem to be a good thing, it would be profoundly disturbing for two reasons. First, many nations are making efforts to control aerosols for compelling reasons of public health, but doing so leads to faster global warming in the short term as the masking effect of aerosols is removed.[7] Second, given the 20th century temperature record, a strong aerosol cooling implies a high climate sensitivity[8,9] and greater climate change as greenhouse gases continue to accumulate in the atmosphere.

Describing the ability of aerosols to reflect sunlight is a challenge, but the bigger difficulty lies in understanding how anthropogenic aerosols have modified cloud properties over the past two centuries. This "indirect aerosol forcing" is due to the fact that, when a liquid cloud droplet forms, it is always seeded by a pre-existing atmospheric particle known as a cloud condensation nucleus (CCN). CCN behavior is well predicted by Köhler theory, which says that formation of cloud droplets from particles is limited by surface tension, and a particle must contain enough solute so that the Raoult effect can compete. For in-cloud supersaturations of a fraction of a percent, a particle should be moderately large ($\sim$100 nm dia.), and at least partly soluble to function as a CCN. The total liquid water condensed in a cloud depends primarily on thermodynamics: the humidity of an air mass and its cooling rate. The number and sizes of the resulting cloud droplets, however, depend on the CCN concentration. More polluted air masses with higher CCN number, therefore, form clouds with (approximately) the same liquid water spread across cloud droplets that are more numerous but smaller than in a clean air mass. The resulting cloud has a higher surface area, making it optically brighter and reflecting more sunlight back to space[10,11] (see Figure 1). Moreover, polluted clouds with smaller droplets may be less likely to rain, extending cloud cover and further cooling climate.[12] Since clouds reflect $\sim$45 W m^{-2} (13%) of incoming sunlight, even small changes in their properties have profound climate impacts. Clouds, a seemingly mundane feature of the atmosphere, are a twin curse for climate scientists. GCMs have a difficult time predicting them, and aerosol-cloud interactions are the biggest uncertainty in climate forcing.

Atmospheric particles arise in only one of two ways. They must either be emitted to the atmosphere or spontaneously formed therein (see Figure 2). In fact, nucleation of tiny ($\sim$1 nm dia.) particles is observed frequently in the atmosphere, approximately one out of 3 days, on average, at most continental locations where long-term observations are available.[13–15] In contrast, smoke from combustion sources and windblown sea spray and desert dust are the leading sources of emitted particles to the atmosphere. All nucleated particles, most combustion particles, and even some natural particles are initially too small to be CCN. However, in the atmosphere, both inorganic and organic gases are oxidized to form more polar and less volatile products, many of which condense onto aerosols. Model calculations[16,17] and *in situ* measurements[18] suggest that most of the mass on CCN results from condensation. Most CCN grow up from particles originally much smaller than CCN sizes. However, only a fraction of nanoparticles, those with diameters less than $\sim$100 nm, bathed in the oxidizing medium of the atmosphere, will grow by condensation into CCN. Most will die. Nanoparticles are highly diffusive and prone to coagulating with other particles. Unless they grow quickly, they are unlikely to survive long enough to become CCN.

Gases to Nanoparticles

How do nanoparticles form?

Observations of the formation and growth of nanoparticles in the atmosphere of the sort shown in Figure 3 are now well-known. The figure shows the number concentration of particles (color contours) as a function of particle size and time of day. The distinctive feature of such events is the sudden detection of a "nucleation burst", a high concentration of particles with diameters of $\sim$3 nm, frequently observed in the morning. In Figure 3, some of the nucleated particles are able to grow quite quickly, resulting in a high concentration of particles with diameters of $\sim$80 nm by the end of the day. Not all events show such fast growth, and the growth rate of the nucleated particles plays a critical role in whether they will form CCN or simply coagulate with pre-existing particles.

The precise chemistry by which atmospheric vapors form thermodynamically stable nanoparticles has been the subject of much investigation. In recent years, improved measurements provide a window onto the behavior of the molecular clusters and smallest particles bridging the gap between vapor and particle. Except for unique coastal nucleation events that seem to be driven by iodine oxides,[19–21] there is consensus that sulfuric acid plays a central role in atmospheric new-particle formation events. In 1992, measurements

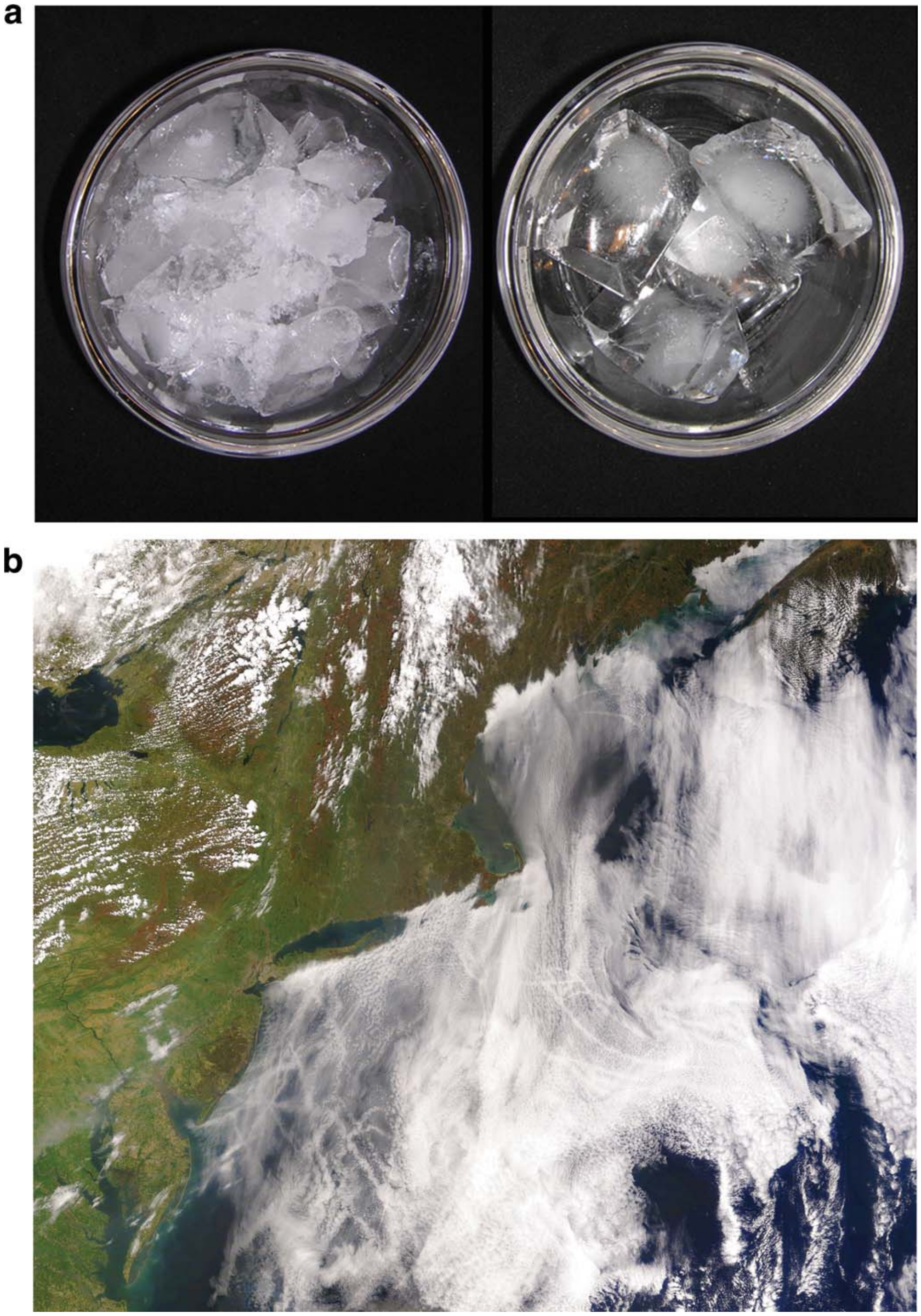

Figure 1. The distribution of water across cloud droplets depends on the number of atmospheric particles known as cloud condensation nuclei (CCN).

Pollution enhances CCN concentrations, resulting in clouds with more numerous, but smaller, cloud drops on average. Since cloud reflectivity depends on surface area, clouds with high CCN concentrations tend to reflect more sunlight to space, cooling the climate. The upper photos (courtesy Dr. Amy Sage) demonstrate the effect of surface area on reflection with ice particles, but the topic of interest here is the analogous effect on liquid cloud droplets. The lower image (courtesy NASA Earth Observatory) from the MODIS satellite instrument shows this effect in the western Atlantic Ocean, where clouds influenced by pollution particles from ships form distinct and brighter tracks. Although ship tracks are the most easily visible manifestation of the link between aerosols and clouds, widespread enhancements in CCN concentrations from a range of pollution sources are more important for climate.

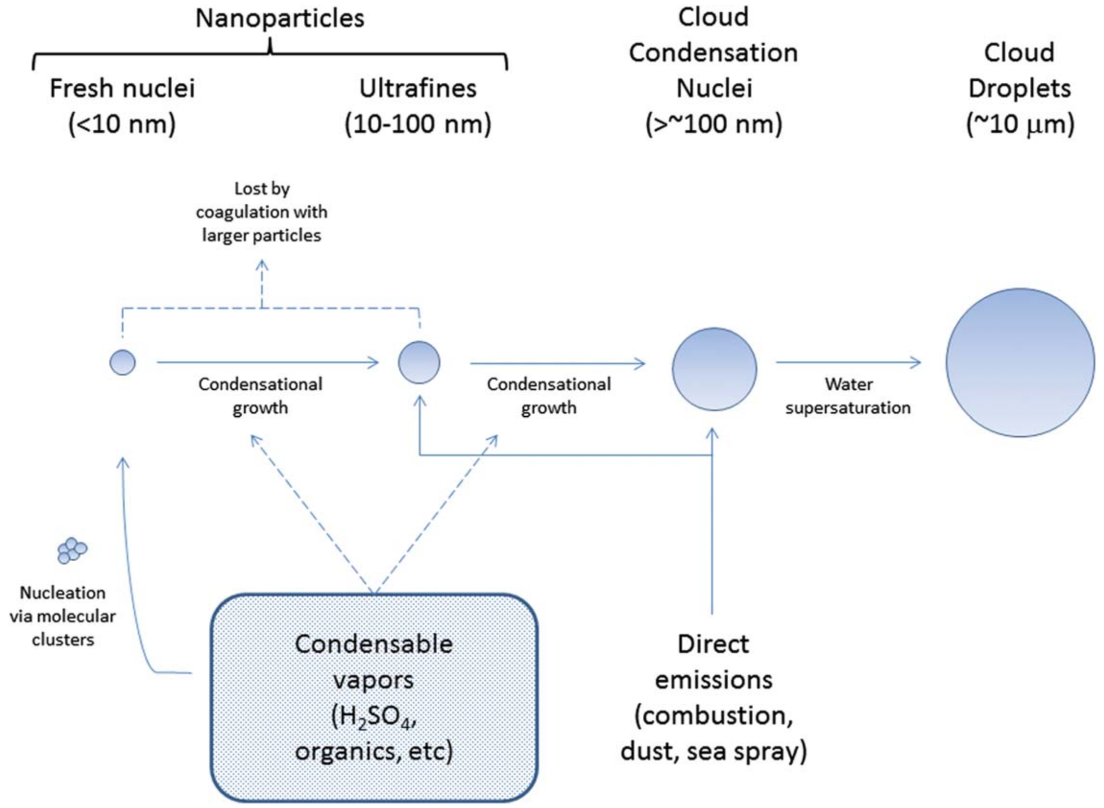

Figure 2. A schematic of processes that form cloud condensation nuclei (CCN).

Particles may either be directly emitted (primary) or nucleated in the atmosphere itself (secondary). Nucleated particles (1–2 nm dia.) must grow substantially via condensation of sulfuric acid and organics to approximately ~100 nm dia. before they can nucleate cloud droplets. Along the way, many of the nucleated particles are lost by coagulating with pre-existing, larger particles.

at the Mauna Loa Observatory showed a close correlation between the concentrations of 3–4 nm dia. nanoparticles and sulfuric acid vapor.[22] This association has been observed elsewhere, including the boreal forest site of Hyytiälä, Finland.[23] Sulfuric acid is a prime candidate because it is readily produced in the gas phase via the oxidation of sulfur dioxide by the hydroxyl radical, a photochemically driven process consistent with the frequent observation of nucleation bursts a few hours after sunrise (as in Figure 3). Sulfuric acid has a vapor pressure vastly lower than its precursor. This single-step reduction in vapor pressure is essential to achieve a supersaturation that allows the product to nucleate rather than simply condense onto pre-existing particles, and sulfur oxidation appears to be unique in atmospheric chemistry in this regard.

An early hypothesis was that particles were formed by binary nucleation, in which both sulfuric acid and water vapor participated. Water vapor is a plausible accomplice because sulfuric acid is hygroscopic, and water vapor is orders of magnitude more plentiful in the atmosphere than other candidates. Unfortunately, although a long series of nucleation theories for the H_2SO_4-H_2O system have been developed,[24–29] it has been shown repeatedly that the nucleation rate inferred from ambient data is orders of magnitude faster than the predictions of any of these theories.[22,30,31] It has also been shown that sulfuric acid vapor concentration

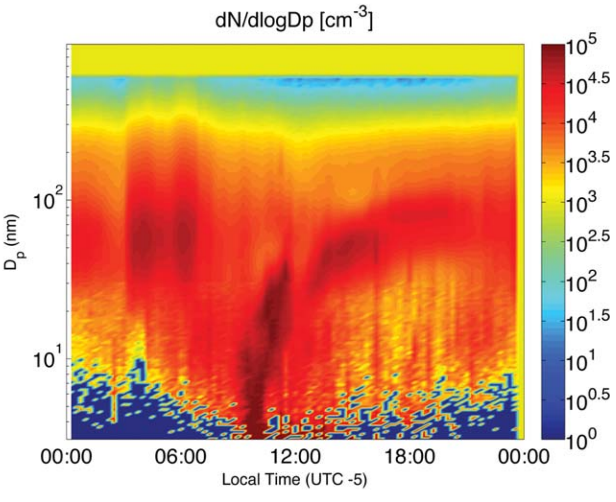

Figure 3. Sample nucleation and growth event observed in Pittsburgh, April 16, 2002.

The *x*-axis shows time of day and the *y*-axis shows particle size (nm). Color contours represent the number size distribution function, which is essentially the number concentration of particles of a given size observed at the corresponding time. Late morning, a high concentration of 3 nm particles is observed, indicating a nucleation event in process. Over the course of the day, the mode of particles is observed to grow nearly to 100 nm (as indicated by the dark red curved feature).

alone appears to be a poor predictor of whether nucleation will be observed or not on any given day.[13]

As a result of these observations, an avid search is on to determine what other species combine with sulfuric acid to form atmospheric nanoparticles. Ammonia is one candidate to participate in a "ternary" H_2SO_4-NH_3-H_2O nucleation mechanism via acid–base salt formation[32] and, more recently, it has been proposed that amines may participate for similar reasons.[33] In an assessment of six competing nucleation theories applied to 10 days in Pittsburgh, we showed that ammonia-driven ternary nucleation theory was the only theory to discriminate successfully between nucleation and nonnucleation days.[34] Although the ternary nucleation theory showed skill in recognizing circumstances conducive to nucleation, it badly over-predicted nucleation rates, suggesting that ammonia may be important but that the theory used may have over-estimated its effect on nucleation rates. Recent theoretical work has shown that the over-prediction of early theory, based on bulk thermodynamics, arises because the ammonia sulfuric-acid pairs do not dissociate into ammonium bisulfate until formation of the (3:1) cluster.[35]

Alternatively, it may be that amines are the key agents to help sulfuric acid nucleate and that the ternary ammonia theory performs well because ammonia and amine concentrations are correlated in the atmosphere. While amine levels are well below ammonia levels, as stronger bases, they may undergo salt formation even for the (1:1) heterodimer and thus form new particles far more efficiently than ammonia. Another hypothesis says that organic acids in the atmosphere cluster with sulfuric acid via hydrogen bonding,[36] stabilizing them until they grow to become stable nanoparticles. A third broad set of nucleation theories are the ion-induced theories that argue that electrostatic attraction between ions of the species already listed enhances nucleation rates over what would be predicted for neutral species alone.[37–39] It is entirely possible that all of these mechanisms contribute significantly in the atmosphere, in different places and at different times.

The debate over the nucleation mechanism matters. Some have argued that 20th century climate change is driven in part by slower nucleation due to changes in the solar wind, leading to fewer CCN and less reflective clouds.[40] However, quantitative global modeling suggests this effect is negligibly weak (see below). More generally, it appears that anthropogenic emissions of sulfur and nitrogen-containing compounds may have profound climate impacts through nucleation mechanisms we do not fully understand. These emissions include sulfur dioxide from coal-fired power plants, ammonia from livestock husbandry and use of synthetic fertilizers and, potentially, use of amine scrubbing to capture carbon dioxide from flue gas streams.

Observing the nucleation process

The leading challenge in understanding nucleation has been making measurements of the number and composition of freshly nucleated particles with sizes of ~1 nm as well as the concentration of the suite of trace gases likely to cluster to form them. Not so long ago, the lower size limits for counting particles was ~3 nm, for reliably sizing particles was ~10 nm, and composition measurements were only available for particles larger than ~30 nm. Measurements of difficult precursor gases, such as sulfuric acid and ammonia, were not always available. Contamination has likely been a severe problem in past laboratory measurements of the nucleation rate, which is now known to be sensitive in some degree to ionization rates, background levels of difficult-to-control gases like ammonia and perhaps other species that are not yet identified.

In the past decade, our ability to observe the nucleation process has been greatly enhanced, and this has yielded some important insights. The basic instrument for counting atmospheric nanoparticles is the condensation particle counter (CPC). The traditional CPC mixes a particle-laden sample air flow with butanol vapor, cools the sample to generate a strong butanol supersaturation, which rapidly condenses onto the particles.[41] In this way, particles as small as 3 nm can grow to ~10 μm in a fraction of a second, after which they can be easily counted by scattering laser light. Detection of particles smaller than 3 nm was impossible since it required even higher supersaturations of butanol, which would cause homogeneous nucleation of the butanol itself, introducing unwanted particles into the sample.[41] With butanol CPCs, it was impossible to detect the nucleating particles themselves, and the 3 nm limitation was especially problematic for ambient studies where nucleating particles often grow at ~2 nm h^{-1}, so the nucleation event was not detected until an hour or more later. Recently, practical instruments have been developed for counting particles as small as ~1.5 nm in a two-step process.[42] In the first step, a compound with a surface tension higher than butanol, typically diethylene glycol (DEG), is used as the condensing vapor. The high-surface tension of DEG suppresses its homogeneous nucleation. However, particles in this first stage do not grow efficiently due to DEG's low vapor pressure. Therefore, the second stage involves sending them to a traditional butanol CPC to finish growing to sizes that can be detected optically. A powerful variation of the DEG CPC known as the particle size magnifier (PSM)[43] varies the proportions of DEG and air sample to vary every 2 min the lower detection limit of particles between 1–2 nm dia.[44] By differencing the signals, particles in this range can be sized as well as counted. Another variation of the CPC methodology involves simultaneous deployment of CPCs based on water as well as butanol. The ability of a particle to grow in either system depends on its hygroscopicity, so that comparison of the two measurements provides clues about the composition of recently nucleated (still smaller than 10 nm) particles. Application of this system to the atmosphere suggests that organics are present in recently nucleated particles and become increasingly important as these particles grow.[45]

A second workhorse instrument for aerosol measurements is the differential mobility analyzer (DMA), which goes beyond the simple counting of CPCs to measure the actual size distribution of the particles. DMAs size select particles according to their electrical mobility. An aerosol sample is first passed through a radioactive ion source to achieve a Boltzmann charge distribution, in which a fraction of the particles carry a single charge and an even smaller fraction (negligible for very small, recently nucleated particles) carries multiple charges. Particles are then passed between two concentric cylinders carrying a voltage to generate an electrical field. The (mostly singly) charged particles migrate in the electrical field according to their size with larger particles migrating more slowly. Particles with the desired size reach a narrow outlet on the opposite side of the channel and are passed to a CPC to be counted. The voltage across the plates can be varied to select and then count different particle sizes, thereby measuring the particle size distribution. The most common configuration today is the scanning mobility particle sizer (SMPS) that rapidly scans through the full range of voltages in a few minutes and then uses a sophisticated deconvolution procedure that accounts for multiply charged particles and time lags in the system to infer the size distribution of particles.[46]

Before the mid-90s, 10 nm was the effective lower limit for SMPS systems for several reasons. Losses of the smallest particles by diffusion to the instrument walls reduced counting statistics, a problem aggravated by the fact that only ~1% of 3 nm particles carry a charge at Boltzmann equilibrium.[41] Also, diffusion allows nanoparticles that do not have the size corresponding to the applied voltage to reach the DMA outlet, effectively smearing the measured size distribution at the smallest sizes. Improvements to operating conditions and better characterization of this "diffusional broadening" of the measurements means that modern SMPS systems can achieve lower size limits of 3 nm.[41] Although nucleation events of the sort shown in Figure 3 were certainly visible in the earlier 10 nm measurements in clean areas, routine measurement of the size distribution down to 3 nm has greatly improved the quantitative information available for nucleation studies. Nucleated particles are detected sooner after the nucleation event, and tracking the mode of the nucleated particles (e.g., Figure 3) allows one to infer their growth rates. More importantly, nucleation rates can be inferred from these measurements and related to the concentrations of precursor vapors.[14,23] For this purpose, it is important to have the 3 nm measurements since the tiniest particles are rapidly lost by coagulation, requiring a nontrivial correction that is more difficult for measurements starting at 10 nm.[47]

Recent improvements in mass spectrometry of atmospheric gases and molecular clusters have also transformed the field. Chemical ionization mass spectrometry (CIMS) can now reliably measure concentrations of known or suspected nucleation precursors, including H_2SO_4, NH_3, and amines, at very low levels with high time resolution. On the particle side, whereas more traditional mass spectrometry would measure the composition of particles as small as 30 nm, recent improvements have allowed measurement of the composition of nanoparticles with diameters between 6 and 15 nm.[48] Although quite small, these particles are still substantially larger than the 1–2 nm nucleating clusters, so these measurements are more useful for determining what species contribute to the growth of the newly formed nanoparticles. Depending on the environment, strong contributions of organic species and aminium salts have been found.[49,50]

Perhaps the most exciting advances are in the ability to identify directly some of the key molecular clusters participating in the nucleation process. Much of this stems from improvements in time-of-flight mass spectrometry. Nucleating clusters have concentrations as low as $\sim 10^4$ molecules cm^{-3} (parts per quadrillion in air), and nucleation events are highly dynamic, so high transmission/detection efficiency and fast data processing are important to achieve reliable signal at averaging times of a few minutes. Much of this work has been done with high mass resolution as well in order to identify unambiguously the elemental composition of larger clusters (up to approximately ~1000 amu).

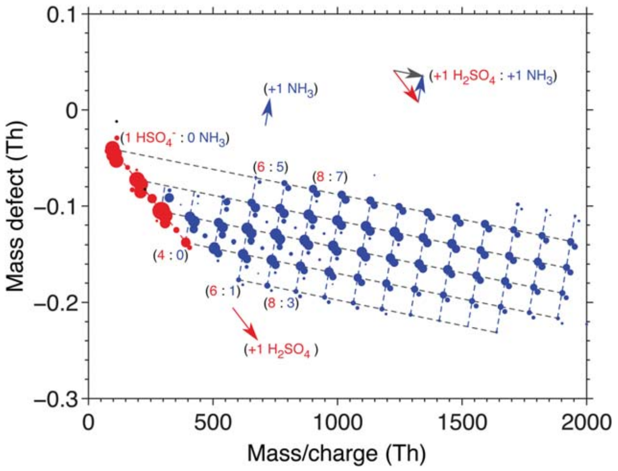

Figure 4. Mass defect plot from an experiment at the CERN CLOUD chamber showing the growth of clusters by addition of H_2SO4 and NH_3.

Cluster mass is shown on the x-axis. The y-axis shows the mass defect (a measure of the nuclear binding energy that allows an unambiguous determination of the constituents) measured by the high-resolution MS. The composition of selected clusters is shown in parentheses as (X:Y), where X is the number of H_2SO_4 molecules and Y is the number of NH_3 molecules in the cluster. Gridlines are to guide the eye to the stepwise addition of H_2SO_4 and NH_3. The appearance of multiple circles around a single grid point results from smaller differences in composition (e.g., when one or more H_2SO_4 molecules is in the form of HSO_4^- or HSO_5^-). On such a mass defect plot, addition of H_2SO_4 results in a strong shift downward and rightward (red arrow) whereas addition of NH_3 results in a smaller upward shift indicated by the blue arrow. Initially (red circles), the clusters grow by simple addition of H_2SO_4. Soon, however, H_2SO_4 and NH_3 add nearly simultaneously (blue circles) to allow the cluster to nucleate into a particle.

A sample result from the Atmospheric Pressure Interface Time-of-Flight (APi-TOF) mass spectrometer[51,52] is shown in Figure 4, showing data from the CLOUD experiment at CERN for sulfuric acid—ammonia ternary nucleation.[53,54] This instrument does not employ any ionization source but rather directly samples naturally charged clusters into the MS. Each circle in Figure 4 represents the signal related to a specific cluster composition observed by the MS, and one observes clusters with up to ~17 H_2SO_4 molecules ($>$ 2 nm particles). The high-resolution MS allows an unambiguous determination of the composition since the mass defects of the constituent atoms are uniquely related to their nuclear binding energies (sulfur and oxygen are relatively light, and hydrogen is very heavy, per nucleon, compared to carbon). As visualized in Figure 4, addition of H_2SO_4 to a cluster strongly increases the cluster weight and reduces the mass defect while addition of NH_3 increases the mass defect with a small increase in the overall cluster weight. The growth of the clusters initially proceeds by simple addition of H_2SO_4 molecules to a bisulfate anion but then switches to a neutral growth in which each H_2SO_4 addition is quickly matched by a NH_3 molecule. The major limitation of these observations is that only naturally charged clusters are detected, which are thought to make only a minor contribution ($<10\%$) to most nucleation events. The composition of the natural ions may be representative of the neutral clusters that nucleate most of the particles, but this has not yet been confirmed experimentally.

There is strong interest in measuring the neutral clusters directly using mass spectrometry, but this is challenging. Nucleating clusters are, by definition, thermodynamically fragile, and the ionization processes required to detect them in an MS instrument can be harsh and strip away the ternary species that investigators are trying to find. Ionization times need to be long enough to ensure adequate signal, but if they are too long, the ions formed will combine into larger clusters, leading to spurious results. Peter McMurry and collaborators have reported a successful measurement of the spectrum of neutral clusters (sulfuric acid monomers, dimers, trimers, etc.), resulting in an observationally based kinetic model for nucleation.[54] By measuring only selected masses, they are able to maximize signal from the instrument. However, their ionization process strips basic species out of the sulfuric acid cluster, so they infer the effects of ammonia and amines by observing an increase in the proportion of sulfuric acid dimers when the concentrations of basic gases increase.

New insights

Deployment of these instruments in the laboratory and the field has led to a number of insights. We have just mentioned a new kinetic model of sulfuric-acid nucleation, stabilized by basic gases, constrained by observations of the cluster distribution. Another exciting development is experiments from the CLOUD chamber at CERN, where the pion beam source is being used to study systematically the effects of ionization on nucleation rates. That chamber can operate at natural background levels of ionization, enhanced levels from the pion beam, and also under neutral conditions by applying an electric field to sweep ions out of the chamber. Because the nucleation rate is known to be sensitive to trace levels of species besides sulfuric acid, considerable effort has been expended to maintain a clean chamber and use the purest ingredients. Even without deliberate addition of ammonia or amines to the chamber, these species were initially observed in the charged nucleating clusters, a testament to the power of basic species to enhance nucleation and the importance of varying and measuring their concentrations through the full atmospheric range. Overall, the CLOUD experiments have thus far shown that ions and ammonia can both enhance nucleation rates, at least under some atmospheric conditions, but neither of them are able to explain the high nucleation rates observed in the atmosphere.[53] Recent experiments have shown that amines and oxidized organic species may play an important role in stabilizing the nucleating clusters.[54,56]

Measurements at a boreal-forest site in Finland with the PSM and other instruments have provided a picture of the behavior of charged and neutral 1–2 nm clusters during ambient nucleation events.[44] Ion-induced nucleation made only a minor contribution to particle formation there, which proceeded predominantly by neutral channels. PSM measurements suggested that cluster stabilization occurred preferentially at a size of around 1.5 nm with smaller clusters not playing a discernible role during nucleation events. Analysis of PSM and other measurements showed that cluster diameter growth rates accelerated as the particles grew from $\sim$1.5 nm to 4.5 nm, suggesting an important role for organic species in early stages of the growth of these particles.

In summary, advances in instrumentation have provided a picture of the atmospheric new particle formation process in far greater detail than was possible even a few years ago. Number concentrations of precursor gases, nucleating clusters, and particles of all sizes can now be reliably measured at high-time resolution providing a reasonably complete picture of nucleation and growth processes. New mass spectroscopic instruments have provided tantalizing glimpses of the composition of nucleating clusters, and work is underway to perfect composition measurements of the neutral clusters. This will be one major focus of research in the near future along with understanding how the complex suite of amines and organics stabilize nucleating clusters.

Nanoparticles to Cloud Condensation Nuclei

Growing pains

Although the nucleation step itself is chemically complex, the fresh particle still has quite a bit of work to do before it can affect clouds and climate. It needs to grow, adding enough solute and increasing its mass by a factor of $\sim 10^5-10^6$ before it can function as a CCN. Left alone, atmospheric nanoparticles are likely to collide and coagulate with larger, pre-existing “accumulation mode” particles with diameters larger than 100 nm. These pre-existing particles may be combustion emissions, dust, sea spray, or particles that nucleated earlier and managed to grow to larger sizes. The lifetime of nanoparticles against coagulation is quite short. Even under clean conditions, most particles smaller than $\sim$5 nm will coagulate in an hour or so. Early growth is important; because larger particles undergo less Brownian motion, the lifetime of a particle in the 10 to 100 nm size range will be many hours or perhaps one or 2 days. Clearly, nanoparticle growth must be relatively fast for nucleation to create many CCN. Particle growth rates in excess of 20 nm h^{-1} have been measured, but 2–3 nm h^{-1} is more typical of days with nucleation events.[15] Measurements of several, relatively strong, nucleation and growth events suggest that $>80\%$ of nucleated particles are lost by coagulation before reaching a CCN-relevant size of 100 nm,[56] and a recent analysis of longer-term measurements at several sites worldwide shows that, typically, only a few percent of nucleated particles survive to become CCN.[15]

During nanoparticle growth, sulfuric acid loses the central role it occupied during nucleation. Condensable gases that are responsible for the growth of nanoparticles include a multitude of oxidized organic species in addition to sulfuric acid, ammonia, and nitric acid. Compared to the organics, the gas-phase chemistry of the inorganic acids is relatively well understood as are the emissions of their precursors, sulfur dioxide and nitrogen oxides. Condensation of nitric acid is important only in limited environments and is not thought to contribute much to nanoparticle growth in general. At least in Pittsburgh, with a large number of coal-fired power plants upwind, sulfuric acid levels are high enough to explain most of the growth of nanoparticles on nucleation days.[34] More typically, sulfuric acid accounts for only a minor fraction of nanoparticle growth,[31,58] which is dominated by condensable organics.

Growth processes for fresh nuclei smaller than ∼5 nm, when they are most vulnerable to loss by coagulation, may be different than for larger particles. Nucleation rates are typically "measured" by counting the formation of particles at some minimum detectable size (e.g., 3 nm or 10 nm). Then estimates of the rate of growth and of coagulation losses are used to infer what formation rate of fresh clusters (e.g., 1 nm or 1.5 nm) must have been. Corrections for coagulation losses before particles reach detectable sizes are substantial and although the ability of modern instruments such as the PSM to detect smaller particles has alleviated the problem, the challenge remains. According to the kinetic theory of gases, the growth rate of the smallest nanoparticles, measured in nm h^{-1}, will be constant with size so long as concentrations of condensable gases remain stable as does its vapor pressure.

However, the Kelvin effect, the increased vapor pressure due to surface free energy, appears to reduce the ability of organics to condense onto freshly nucleated particles.[59] Whereas sulfuric acid's vapor pressure in the presence of water is so low compared to ambient vapor pressures that the Kelvin effect is negligible, it appears to be unique in this regard. Atmospheric organics are expected to have vapor pressures comparable to their partial pressures, closer to equilibrium and, therefore, are more sensitive to the Kelvin effect. For reasonable estimates of surface tension, the Kelvin effect will be very important for particles smaller than 5–10 nm and will continue to be significant beyond that. Recent measurements confirm these expectations. Careful measurements of particle size distributions down to 1 nm with a DEG SMPS during two nucleation events showed that 3 nm particles were growing up to five times as quickly as their 1 nm counterparts under the same conditions,[58] results that have been independently verified elsewhere.[44] These findings are consistent with the hypothesis that individual organic compounds condense more easily as the Kelvin effect is relaxed for larger particles. It also suggests that particles begin growing due to condensation of sulfuric acid and a limited suite of the lowest volatility organics, but as they grow, they are able to tap into a wider spectrum of condensable organics. It is important to account for these complex growth dynamics at the smallest sizes. Not only are the smallest particles most prone to coagulation, they are also the slowest growing, and this has a profound impact on their survival to CCN-relevant sizes.[58]

Much current work focuses on the subset of organic compounds that are able to condense onto these smallest nanoparticles. There are essentially two possibilities. In the first, gas-phase oxidation of organics creates products with sufficiently low saturation vapor pressures, 10^{-7} to 10^{-8} Pa, to overcome the Kelvin barrier affecting nanoparticles between 1 and 3 nm. The difficulty is that organic compounds with saturation vapor pressures of 10^{-5} to 10^{-4} Pa are already semi-volatile under typical atmospheric conditions, so one might expect a very limited supply of low-vapor pressure compounds to grow nuclei. However, it is known that atmospheric oxidation mechanisms of alkanes and other organics frequently undergo several radical reaction steps, each one adding a functional group, so that the final stable product is often 3–6 orders of magnitude lower in vapor pressure.[60] Neil Donahue and co-authors have argued, based on a consideration of these reaction pathways, phase partitioning, and mass transfer limitations, that gas-phase oxidation can indeed take the semi-volatile precursors and oxidize them with just enough efficiency to low-volatility products to explain the nanoparticle growth rates of ∼2 nm h^{-1} typically observed in nucleation and growth events.[61] However, these semivolatile precursors are likely already to be oxidation products of some original higher volatility vapor, and understanding the multiple generations of oxidation chemistry that can occur over the multiday time scales that organics are in the atmosphere continues to challenge our laboratory capabilities for measuring these reaction pathways.

Alternatively, growth of fresh nuclei may proceed by heterogeneous reactions with potentially higher volatility organics with the right molecular structures to bind to the growing cluster. Once again, multifunctional organic compounds are likely candidates. In this scenario, one functional group undergoes hydrogen bonding with a sulfuric acid molecule already in the cluster, leaving other functional groups open and ready to take up other polar molecules. One of many potential candidate pathways is the emission of alpha-pinene by vegetation, its oxidation to cis-pinonic acid, a gas under atmospheric conditions, and then subsequent oxidation to the triacid, 3-methyl-1,2,3-butanetricarboxylic acid. Although theoretical considerations have suggested possible mechanisms and species, confirming these hypotheses will require improved instrumentation and experimental methods, and mapping out all the organic species and reaction pathways is a daunting prospect.

Growth and the secondary organic aerosol budget

Whether fresh nuclei grow by heterogeneous reactive uptake or via condensation of a subclass of very low-volatility organics, once they exceed ∼10 nm dia., the Kelvin barrier weakens, and nanoparticle growth can now proceed by condensation of a wide range of semivolatile organic compounds. At this point, the more recent challenge of understanding the fate of atmospheric nanoparticles merges with the more long-standing problem of understanding the composition and formation pathways of atmospheric organic particulate matter in general. Throughout the globe, organic compounds constitute 20–70% of the mass of fine particles (those with diameters less than 1 μm), so it is no surprise that understanding organic chemistry remains the key challenge as nanoparticles take the final steps toward becoming CCN. The various sources of particulate organics in the atmosphere are in the range of 60–240 Tg C yr^{-1}. Some of this is directly emitted "primary" organic aerosol (POA), but it is now believed that the overwhelming majority is chemically produced "secondary" organic aerosol

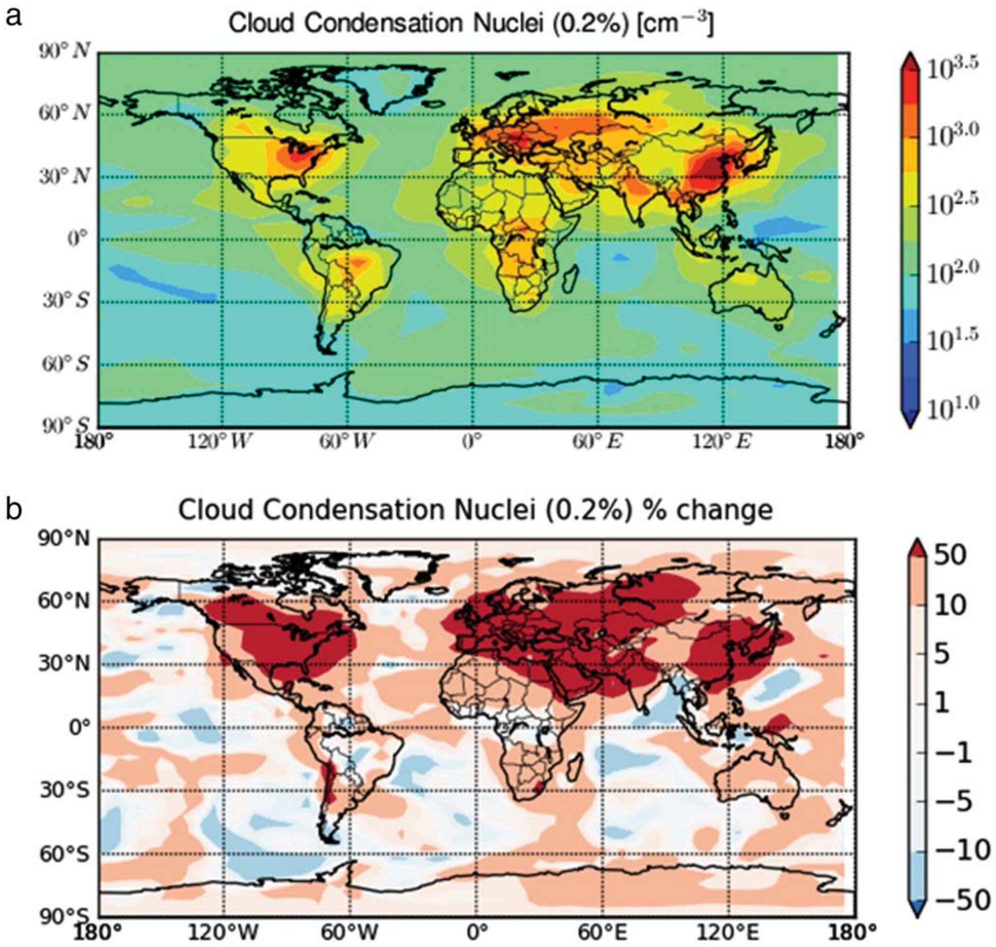

Figure 5. **(a) the number concentrations of CCN (cm^{-3}) active when the atmospheric supersaturation is 0.2% predicted in a simulation based on ternary nucleation theory, and (b) the percent difference in CCN concentrations between the same simulation and one without any nucleation at all.**

(SOA) of various types.[62] Global modeling of CCN concentrations has shown that the SOA production rate plays a key role in determining how many nanoparticles survive to CCN sizes.[17]

Traditionally, estimates of SOA formation have derived from laboratory "smog chamber" studies, batch experiments in teflon chambers that mimic atmospheric chemistry. Organic gases are introduced to the chamber and oxidized, and the amount of particulate matter formed is measured along with its phase partitioning behavior. These experiments take place over a period of several hours during which the particles formed are gradually lost to the walls, so that the experiments are only able to measure the early steps of atmospheric oxidation.

Among early leaders in this area were Richard Flagan and John Seinfeld at Caltech, who with Jay Odum, succeeded in showing that SOA formed from gasoline vapor could be explained by the sum of a relatively small number of aromatic species in the fuel.[63] Taking a cue from Jay Odum's success, much early SOA work probed the chemistry of specific molecules with an implicit assumption that most SOA derived from a relatively short list of precursor species. After an initial focus on anthropogenic SOA in urban areas, Rob Griffin, working in the same group, performed experiments on biogenic SOA that led to the accepted estimate of global biogenic SOA formation.[64,65] A little more than a decade ago, the prevailing view was that there was a global biogenic source of $\sim$20 Tg yr^{-1}[65] produced from the oxidation of mono- and sesqui-terpenes. In comparison, anthropogenic SOA was considered to be small on the global scale (less than $\sim$3 Tg yr^{-1})[66] albeit important in polluted regions. However, even biogenic SOA was considered to be a minor contributor alongside direct (primary) emissions of $\sim$70 Tg yr^{-1} from biomass burning and fossil fuel combustion.[67] Models treated primary organic aerosol as nonvolatile and inert.

In recent years, the view that the organic aerosol budget was dominated by POA has been challenged and revised. An early wakeup call came when aerosol mass spectrometry began to be deployed in field campaigns around the Northern Hemisphere and showed that, even in urban areas, organic aerosol was considerably more oxidized than fresh vehicle exhaust; in rural and remote regions, moderately to heavily oxidized OA dominated.[18] The highly oxidized state of the OA indicated that chemical processing was much more important than previously recognized.

Around the same time, work by Allen Robinson showed that biases in sampling and modeling primary OA might lead to emissions estimates being too high by a factor of 2–3.[68] While it had been standard practice to cool combustion emissions to ambient temperatures, allowing some semivolatile components to condense, the sampling conditions had high OA concentrations. Allen Robinson showed that, similar to SOA, much of the primary combustion emissions followed a Raoult-type absorptive partitioning model and that, as these emissions were further diluted to ambient conditions, much of the organics were stripped out of the particulate phase.[68] Treatment of POA by models as nonvolatile ignored this process and over-estimated the contribution of POA.

While POA estimates were being revised downward, a proliferation of hypotheses emerged to suggest why there may be more SOA than previously realized. The evaporation of primary emissions was one potential source since only a little oxidation was required to lower their vapor pressures enough to return them to the particle phase. Similarly, more attention was paid to intermediate volatility organic compounds (IVOCs), a pool of potential SOA precursors that required little oxidation to form SOA. These had been neglected partly because of the analytical challenge of separating and identifying them and partly because their complexity did not fit the prevailing reductionist model that tried to explain SOA one precursor at a time. This has led to renewed emphasis on doing smog chamber experiments of complex combustion sources such as diesel and biomass burning emissions that has shown that, in general, it is often not possible to explain SOA formation as the sum of a small number of identifiable precursors.[67]

Other work has sought to elucidate the complex reaction pathways available to organic peroxy radicals that are typical intermediates to SOA formation; their fate depends, in part, on the amount of nitrogen oxides (NO_x) in the smog chamber, and the tendency to run experiments under high NO_x conditions may have biased SOA formation low in many cases as Sally Ng and Lea Hildebrandt showed for several aromatic compounds.[69,70] The tendency of smog chambers to probe oxidation chemistry over relatively short time scales (6–12 h when organic vapors probably have atmospheric lifetimes of several days) has led many to argue that oxidation products that remain in the gas-phase may undergo further "multigenerational" oxidation to form SOA that is not readily measured in smog chambers. Other processes that have been proposed as potential SOA sources include heterogeneous chemistry, including oligomerization reactions and in-cloud SOA formation. The details of many of these processes are still murky, and no consensus exists as to which of these processes are likely to account for most of the SOA found in the atmosphere. However, oxidation of evaporated primary OA plus IVOCs has the potential to close the gap in predicting ambient SOA levels in Mexico City[71] and can plausibly produce much of the $\sim$100 Tg yr^{-1} of oxygenated organic aerosol that seems to be missing from global models.[72,73]

Beyond understanding the amount of SOA formed, work is being done to understand the properties of these organics. Spyros Pandis, Celia Cruz, and Tim Raymond made early measurements of the CCN activity of organic compounds.[74–77] The hygroscopicity of OA is needed by Köhler theory to predict how much the organics in a particle facilitate its growth into a cloud droplet. Sonia Kreidenweis has successfully separated SOA components with HPLC and then performed CCN measurements on each showing that atmospheric chemistry produces a broad spectrum of organics with varying water uptake properties.[78] The CCN behavior of organics can be further complicated if they are surfactants, are incompletely soluble, limit uptake of water, or absorb from the gas phase into a growing cloud droplet.[79] Work in Faye McNeill's laboratory has shown that methylglyoxal and acetaldehyde, lightweight organic vapors, can absorb into growing droplets, enhancing their CCN potential. The magnitude of the effect suggests that they are acting as surfactants.[80] Led by Athanasios Nenes and Greg Roberts, improvements in CCN instruments that simulate cloud formation by imposing carefully controlled supersaturations of a fraction of a percent have provided much better experimental constraints on these behaviors.

For the foreseeable future, models of atmospheric organic chemistry will continue to rely on a healthy dose of engineering approximation. It has long been realized that the mix of oxidation products of even a single, well-studied organic precursor are usually too complex to speciate, but the emergence of IVOCs indicates that the precursor molecules also need to be treated in broad, lumped categories if we are to be able to build models that can claim to be comprehensive. A suite of new (or underutilized) measurements can provide clues about sources and processing of atmospheric organics to test the approximations of models. Lynn Russell's group has made FTIR measurements of organic aerosols in the laboratory and in the field to quantify the magnitudes of combustion, oceanic, and vegetation sources.[81] Also of interest are HNMR measurements of organic composition,[82] thermal measurements of OA volatility, and radiocarbon constraints on fossil versus modern sources of atmospheric carbon. Experimentalists are actively trying to understand the later steps of multigenerational oxidation chemistry not easily studied in smog chambers either with flow reactors at extremely high-oxidant levels[83] or by studying first-generation oxidation products as model systems. Although we have a basic understanding of the functional groups produced by atmospheric oxidation, as organic molecules become highly oxidized, they have an increasing tendency to fragment, leading to more volatile products and reduced levels of OA. This phenomenon has been successfully observed in reactors such as the Potential Aerosol Mass flow reactor, but there are nontrivial issues in interpreting these measurements. At the current time, there is no experimentally tested chemical mechanism that accounts for fragmentation of organics.

A Global Picture of CCN, Clouds, and Climate

To inform our understanding of climate change, these molecular and particle scale processes need to be integrated into a global model of the Earth system. Today, most standard versions of climate models are comprehensive in the types of aerosols included, including sea spray, windblown dust, combustion smoke, and chemically produced inorganic and organic species. However, treatments of specific processes are limited not only by our scientific understanding but also computational demands since climate model simulations usually span several centuries and aerosols are but one of many aspects of the climate system represented. The usual approach is to include "bulk" aerosol models that track only the total mass concentration of each aerosol type. Such models parameterize the effects of aerosols on clouds, but cannot explicitly represent the nucleation and growth processes discussed here nor can they predict from first principles the number, size and composition of particles required to calculate CCN concentrations.

Over the past decade, several groups have developed aerosol models that represent the nucleation, growth, and coagulation processes necessary to predict CCN concentrations. Figure 5 shows the global CCN concentrations predicted using ternary nucleation theory by a global model developed in Peter Adams's group as well as the percent change between simulations with and without nucleation. These global models of aerosol microphysical processes have yielded a nuanced picture of the links between nucleation and CCN. On the one hand, perhaps half of the CCN in marine areas are the result of nucleation and growth processes with sea spray being the other major contributor.[84] On the other hand, CCN concentrations show limited sensitivity to changes in nucleation rates; while different nucleation theories yield globally averaged nucleation rates that differ by six orders of magnitude, the impact on CCN concentrations is a modest $\sim$15%.[17] This points to the fact that CCN formation is frequently limited more by condensational growth; therefore, it is as important to understand the SOA budget as the nucleation rate per se. With limited condensable vapors, higher nucleation rates translate into slower growth and greater losses by coagulational scavenging. Nevertheless, a better understanding of the nucleation mechanism has global implications and should improve predictions of where and when nucleation matters most.

One important application of these global models has been the first quantitative modeling of the relationship between solar variability, cosmic rays, clouds and climate, which has sometimes been proposed as a significant contributor to 20th century warming. Solar output has increased during the last century, but its direct impact on the Earth's energy balance is thought to be significantly less than $\sim$0.3 W m^{-2}, at least one order of magnitude smaller than changes in greenhouse gases.[2] The "clear air" cosmic ray hypothesis[40] suggests that changes in the solar wind over the past one hundred years have reduced the number of cosmic rays penetrating into the atmosphere and, therefore, the atmosphere's ionization rates. If ion-induced nucleation is a significant source of particles, it would imply a reduction in the number of nucleated particles over that period. Finally, if CCN derive primarily from nucleated particles, this would also imply a reduction in the number of CCN. The implication is that modern clouds could be optically thinner than early 20th century clouds, allowing more sunlight to penetrate to the surface, thus explaining the observed warming. Through an ion-induced nucleation-CCN link, the increase in solar intensity would be more important than it would appear at first glance based on the direct but modest effect on solar output.

Much controversy has surrounded the cosmic ray-climate hypothesis as some have seen it as an alternative to accepting the result of climate and other energy balance models that point to anthropogenic greenhouse gases as the strongest driver of recent climate change. There has been a vigorous debate about whether low-level cloud properties are observed to correlate with the solar cycle, and the hypothesis provided some of the original motivation for the CLOUD nucleation experiments at CERN. The hypothesis is plausible at least insofar as most of the processes were known or suspected to be important to some degree. Before the development of aerosol microphysical models, it was impossible to quantify the potential magnitude of these effects. In 2009, Jeff Pierce and Peter Adams published the first rigorous global aerosol model estimate of this effect and concluded it was on the order of 0.01 W m^{-2} or less, more than two-orders of magnitude smaller than greenhouse gas forcing.[85] Although they lacked definitive measurement of how nucleation rates depend on atmospheric ions, they used an upper bound estimate in which every atmospheric ion was assumed to nucleate a particle. Quite simply, the changes in atmospheric ionization rates are modest, and efficient coagulational scavenging of fresh nuclei plus limited condensable vapors means that only much larger changes in nucleation rates would have a significant climate impact. The CLOUD experiment has now provided high quality measurements of the dependence of nucleation rates on atmospheric ions as a function of temperature and atmospheric chemical regime, and the calculations of Pierce and Adams are sure to be repeated, but it appears unlikely that the results will be overturned.[86]

Another conclusion of the new global models is a reminder of the importance of direct combustion emissions that are major contributors to enhanced CCN concentrations in polluted areas.[17,87] The median size of most combustion sources is $\sim$30 nm, so these nanoparticles still need to grow substantially. However, they start their atmospheric life beyond the worst limitations that the Kelvin effect places on organic condensation, and they are large enough that their coagulational loss rates are an order of magnitude slower than 3 nm nuclei. Due to regulatory pressures, much attention has been paid to aerosol mass emissions rates from vehicles, but climate questions require much better information on the number and sizes of ultrafine particles emitted. Vehicle-to-vehicle variability makes reliable estimates of size-resolved nanoparticle emissions difficult to achieve, but Charlie Stanier has used SMPS measurements in Mexico City to infer the average emissions of the vehicle fleet there.[88] Regulations planned to protect human health will change these emissions, and we are not well situated to assess the climate impacts. Greg Carmichael has considered the air quality and climate impacts of aerosols from increasing Asian emissions[89,90] as well as heating by black carbon ("soot") particles.[91]

A weakness of the global models is the very limited set of global observations available to test them. Developed countries tend to have well-organized networks measuring aerosol mass concentrations, but the number and sizes of nanoparticles are usually not measured. The EUSAAR-ACTRIS network in Europe is the only serious regional network measuring the size distributions of nanoparticles. Outside Europe, there are a small number of research sites measuring size distributions, and a somewhat larger number of stations measure total aerosol number with CPCs. In many ways, advances in satellite-based remote sensing have provided an exciting global picture of aerosols, but nanoparticles do not reflect enough light of visible and near-infrared wavelengths to be detected. Experience has shown that global model predictions of aerosol sulfate, for which emissions and chemistry are relatively well understood, suffer because of model errors in transport and removal of particles from the atmosphere. Systematic global observations are required to keep the models on track. There is a desperate need, therefore, to collect more *in situ* measurements of nanoparticles on the global scale. These need to be integrated with models and remote sensing measurements of spatial distributions to optimally estimate nanoparticle and CCN concentrations globally. Little work has been done along these lines, and there is an opportunity here to tap into the strong expertise of chemical engineers in process control, optimization, and inverse modeling.

Conclusion

Although climate change science can be approached from a wide variety of disciplinary perspectives, the emphasis that chemical engineers place on mass, energy, and population balances; reacting flow, kinetics, and thermodynamics, puts them in an excellent position to contribute. Early on, chemical engineers made fundamental contributions to understanding and modeling of air pollution, and this same community (along with former students) has naturally moved toward addressing issues of atmospheric chemistry and global change. Understanding the formation and growth of nanoparticles and then their effect on clouds and climate is an outstanding example of how these problems are amenable to chemical engineering approaches. Chemical engineering principles ground our approach to these problems, and global models are useful to synthesize our understanding and interpret observations. However, as is often the case in science, it seems that most of the exciting advances in this area have been stimulated by the surprises that emerge when new measurement techniques come along to upset old ideas.

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