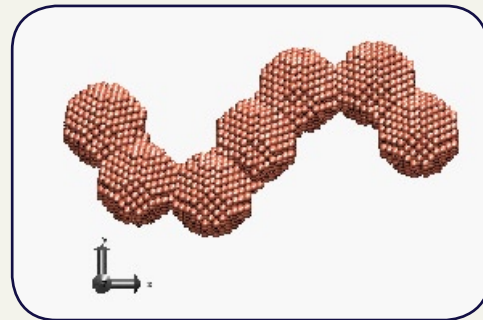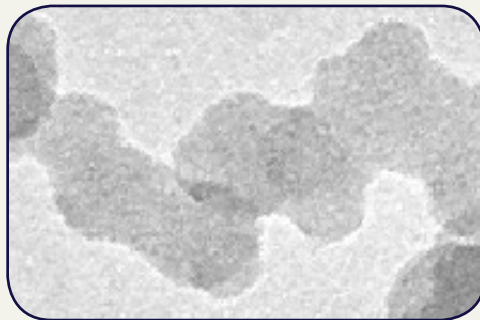NSF Workshop Report on

"Emerging Issues in Nanoparticle Aerosol Science and Technology (NAST)"

University of California, Los Angeles
June 27-28, 2003

Sponsored by NSF, Southern California Particle Center,
and UCLA Department of Chemical Engineering

Sheldon K. Friedlander, Workshop Chair
David Y. H. Pui, Workshop Co-Chair

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Right: Computer model of a copper nanoparticle aggregate for studying mechanical behavior under strain (A. Dalis, S.K.Friedlander).

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EMERGING ISSUES IN NANOPARTICLE AEROSOL SCIENCE AND TECHNOLOGY (NAST)

Results of a Workshop held at UCLA, June 27-28, 2003

Sponsored by NSF, Southern California Particle Center and

UCLA Department of Chemical Engineering

Sheldon K. Friedlander, Chair

David Y. H. Pui, Co-Chair

PREFACE

The field of aerosol science and technology covers the basic principles that underlie the formation, measurement and modeling of systems of small particles in gases. These systems play an important role in nature and industry. Many government agencies including EPA, NIOSH, DOE, NOAA and NIST have substantial aerosol research activities. The EPA is responsible for the establishment of ambient air quality standards for particulate matter, NIOSH is concerned with workplace exposure to particulate matter, the DOE has responsibility for nuclear reactor safety which includes emissions of radioactive particles in reactor accidents and NIST plays a role in providing primary calibration standards for particle size and chemical content. Aerosol technology plays an important role in inhalation therapy and in counter-terrorism, fields likely to be of interest to NIH including NIEHS. Industry uses aerosol processes for the manufacture of powdered materials of many different kinds including reinforcing fillers, pigments and catalysts and in the manufacture of optical fibers. The Particle Technology Forum sponsored by AIChE, includes substantial industry participation and has a strong interest in aerosol technology. Finally, the American Association for Aerosol Research (AAAR), the principal professional society in the field, with a membership of about one thousand, sponsors regular research meetings in the field.

Aerosols of interest to government agencies and industry cover a wide range of particle sizes, shapes and chemical compositions. The Workshop focused on Nanoparticle Aerosol Science and Technology (NAST), a new subdiscipline in which a basic understanding of the relevant science and technology is only now emerging. Nanoparticle aerosols refer to particles smaller than 100 nanometers (0.1 micrometers) which may be present as individual particles or as aggregates. Nanoparticles may have unusual mechanical, optical, biochemical and catalytic properties that make them of special interest. Novel experimental and theoretical methods are under development and/or needed to characterize their formation and behavior. In the Workshop, we limit consideration to nanoparticle aerosols and do not consider hydrosols; the gas phase processes and their particle products, regardless of their applications identified below, often involve a similar set of measurement methods and theoretical approaches which differ from condensed phase suspensions.

Advances in NAST have applications in many fields that include (but are not limited to) (1) characterization and control of ultrafine aerosols emitted by air pollution sources, (2) industrial production of nanoparticle reinforcing fillers such as carbon black and fumed silica and catalysts such as titania, (3) start-up companies that manufacture specialty nanoparticle products by aerosol processes, (4) atmospheric dynamics of fractal-like nanoparticle aerosols (e.g. diesel emissions), (5) nanoparticle emissions from aerosol control technologies including filters and electrostatic precipitators, (6) nanoparticle formation in the upper atmosphere by entry of bodies from space and by emissions from solid fuel rockets, (7) control of workplace exposure to ultrafine aerosols, (8) manufacture of optical fibers, (9) manufacture of composites composed of blends of nanoparticles and molecular polymers (e.g., rubber), (10) fabrication of nanoparticle coatings, (11) on-line measurement of nanoparticle chemical composition and (12) contamination control in the microelectronics industry as line features shrink.

These applications are undergoing rapid changes as NAST develops. There is a need for a coordinated effort by participants from university research groups, government agencies and industry sectors interested in nanoparticle aerosols. A group of this type can accelerate progress in the field and reduce duplication of effort. The goals of the

Workshop are (1) to review the current status of the field and identify research needs and (2) to set up a prototype group that can be activated as needed by industry and government to promote research and development in this field.

Planning for the workshop began with a meeting of the co-chairs with NSF and NIST representatives in Washington, in January 2003. (Before this the co-chairs had from-time-to-time discussed the concept for over a year). Following the Washington meeting , informal discussions began with potential invitees with a late spring Workshop in mind. After official NSF approval, the Workshop time was set for late June and invitations issued. Except for two people who had other commitments, everyone that we invited accepted, an indicator of the strong interest among the invitees.

The organizing principle for the Workshop was as follows: As a scientific discipline, NAST depends on: (1) Experimental and measurement methods (2) Basic principles of nanoparticle aerosol formation and (3) Computational simulation of nanoparticle aerosol behavior. Two major fields of application of these methods and principles include: (4) Aerosol reaction engineering and (5) Atmospheric nanoparticles (ultrafine aerosol). Thus the Workshop was organized into five Panels that covered the basic areas and two major fields of application. The reports prepared by the Panels constitute the main body of the Workshop document. This Preface is followed by an Executive Summary that includes all of the recommendations by the individual Panels and brief statements on their applications. A section on Terminology points out that there are differences in the terms used to describe atmospheric and air pollution aerosols on the one hand and industrial nanoparticle products on the other. This is an illustration of the importance of communications among groups working on different applications. Following the reports of the Panels is an Epilogue that puts the results in perspective.

During the editing, we have imposed what we consider a reasonable consistency in the format. There are some variations among the Panel reports because of significant differences in material covered and in styles of the Panel chairs and their members.

We wish to acknowledge the special assistance rendered by Dr. Rajdip Bandyopadhyaya and Mr. Adamos Dalis, working with the Chairs in the preparation of the Workshop report.

S. Friedlander, Chair   November 2003

D. Pui, Co-Chair.

EXECUTIVE SUMMARY

Experimental Methods and Instrumentation:

The role of nanoparticles, whether for improved materials, for semiconductor fabrication, for pharmaceuticals, for environmental assessment or for evaluation of global climatic, depends on their chemistry as well as their physical characteristics. The unique functionality of nanoparticle-based materials and devices depends directly on size- and structure-dependent properties, as do the environmental impacts and health consequences of airborne nanoparticles. Often chemistry is key to elucidating sources and formation mechanisms of nanoparticles, both in the atmosphere and in industrial applications.

Physical characterization of aerosol nanoparticles is critical to the advancement of the underlying science and development practical nanotechnologies. Nanoparticle size must be tightly controlled to take full advantage of quantum size effects in photonic applications, and agglomeration must be prevented. Agglomeration can only be prevented if the number concentrations are tightly controlled, which requires that the rate of new particle formation be quantitatively determined. Real-time measurements of particle size distributions and particle structure are, thus, enabling technologies for the advancement of nanotechnology. Key areas of research to improve our physical characterization capabilities include: (1) rapid aerosol nanoparticle measurements; (2) detection, characterization, and behavior in the low nanometer (<5nm) size regime; (3) particle standards for size, concentration, morphology and structure; (4) charging behavior and technology throughout the ultrafine and nanoparticle size regimes; (5) distributed nanoparticle aerosol measurements; (6) integral parameter measurement; (7) off-line morphological, structural, and chemical characterization of nanoparticles; (8) on-line morphological and structural characterization of nanoparticles; (9) nanoparticle size distribution measurements with high detection efficiencies.

Ultrafine particles present an exceptional challenge for chemical analyses because their mass is small, of the order of attograms. Recent years have seen many advances in on-line analyses of the chemical constituents of ultrafine particles. Most prominent are the advances in particle mass spectrometry, with systems providing data on single

particle composition, or size- and composition-resolved data for an ensemble of particles. While much has been accomplished, much is needed to improve our ability our analytical capabilities for the ultrafine particle size fraction.   Key areas of research include (1) unbiased sampling of ultrafine particles, both into particle beam systems and for sampling into a liquid stream for subsequent on-line analyses (2) identification and quantification of organic fraction at the compound or compound-class level; (3) better chemical characterization of light-absorbing particles; (4) means for quantification and calibration, especially for organic compounds; (5) morphological and surface chemistry determinations; (6) fast response systems; (7) systems that can operate under extreme conditions of temperature or pressure; and (8) better and more rapid on-line data reduction schemes.   Importantly, the systems must be more accessible, and easier to use. They need to be made smaller in size, lower in weight and cost, especially for targeted needs.

Assessment of the role of nanoparticles in global climate, in health implications of aerosol nanoparticle exposure, whether due to ambient or occupational exposures, must await entirely new chemical and physical characterization technologies that enable distributed measurements.   Full understanding of the sources of nanoparticle aerosols, whether in the environment, in industrial processes, in offices and homes.   This will require larger numbers of sensors that are simplified, robust and below the cost of the laboratory instruments in use today.   Such instruments must not require an aerosol scientist to operate them, and reliable enough to provide the continuous data records.

Fundamentals of Nanoparticle Aerosol Formation

Particles form in gases by various mechanisms.   Some of the major routes are considered in this section.   Small solid particles often appear as aggregates which are also discussed.

Physics of Nucleation

Studies at the end of the nineteenth century by C.T.R.Wilson showed that at least three types of nuclei were activated when atmospheric air was saturated by adiabatic expansion: (i) existing aerosol particles at saturation ratios near unity, (ii) ionized gas

molecules at higher values of the supersaturation and (iii) water molecules themselves at much higher supersaturations. Advances in theory and instrumentation may permit detailed characterization of atmospheric nuclei, not possible before. Applications are to reducing major uncertainties in the global radiation balance, especially the poorly understood "indirect effects" produced by nuclei that modify the global cloud cover and the hydrologic cycle. Other important applications are to aerosols produced when hot vapors from pollution sources are injected into the atmosphere.

Research Recommendations

(1) Use of modern computational methods, including quantum theory, to calculate thermodynamic properties of atmospheric nanoclusters, charged and neutral.

(2) Effects of atmospheric nanoparticles on global climate through their role as fog and cloud condensation nuclei.

(3) Theoretical and experimental studies of the effects of turbulence on nucleation rates.

Chemical Nucleation: Soot Formation

There are many examples of chemically reacting gases that generate nanoparticles through complex chemical reaction pathways. Soot formation is the case that has been studied most because of its environmental and industrial importance. Controversy remains concerning the chemical steps that lead to particle formation, and the chemical nature and structure of the soot particles that are usually present as nanoparticle chain aggregates. Although experimental and conceptual difficulties abound, the payoff in fuel efficiency and environmental protection continue to stimulate research in this field.

Research Recommendations

(4) Well-characterized soot generators (reactors), the characterization of soot primary particles and their aggegates and proven chemical mechanisms for describing soot inception are needed.

Collision-Coalescence Formation Processes: Aggregate Dynamics

Over the last few decades, we have learned much about how small solid particles of inorganic oxides form, based on collision-coalescence concepts. This is a limiting case in which the chemical reactions that result in condensable molecules are very rapid compared with particle collision and coalescence; the equations of aerosol dynamics can be generalized to incorporate the rate of coalescence of particles in contact. Solid

particles so formed then aggregate. Molecular dynamics (MD) show promise for calculating coalescence rates and characterizing the dynamic properties (e.g., elastic modulus and tensile strength) of aggregates. Measurements of *the dynamic behavior* (in addition to morphology) of chain aggregates should be possible with modern instrumentation. Applications are to (1) formation of primary solid particles and their aggregates in commercial synthesis of nanopowders and in emissions from industrial sources e.g., coal fired power plants and incinerators, (2) nanocomposite materials such as rubber that incorporate aggregates and (3) dynamics of aggregates in flowing gases and at surfaces.

Research Recommendations

(5) Computational statistical mechanics (e.g., molecular dynamic and Monte Carlo techniques) calculations of (i) coalescence rates of nanoparticles in contact and (ii) individual nanoparticle thermodynamic properties (e.g. surface tension) and transport properties (e.g., solid state diffusion coefficients)

(6) Experimental studies of individual nanoparticle chain aggregates and their networks under stress, to measure their tensile strength and elastic modulus.

(7) MD studies of the effects of tension on nanoparticles chains to determine elastic modulus, tensile strength and locus of fracture. Compare calculations with data.

Aggregate Morphology

The ability to characterize aggregate morphology quantitatively, for example through the fractal dimension, has motivated research on aggregate structure and led to the discovery of "superaggregate" structures with fractal dimensions that differ from the substructures. Also important is the measurement of the optical cross-section of soot agglomerates over a wide wavelength range for applications to radiant transport through smoke and postflame gases.

Research Recommendations

(8) Understand the growth kinetics and morphologies of superaggregate structures.

(9) Determine aggregate transport properties over the entire range of Knudsen numbers based on primary particle and aggregate sizes.

(10) Measure optical cross sections of soot agglomerates from the uv to at least 10 micrometers, for high temperature soot in the flame and under post-flame conditions as a function of agglomerate size and morphology.

Computational Simulation of Aerosol Behavior

Numerical Methods and Fundamental Modeling

Accurate and reliable models for simulating transport, deposition, coagulation, and dispersion of nanoparticles and their aggregates are needed for the development of design tools for technological nanoparticle applications, including:

o Nanoparticle instrumentation including sampling, sensing, dilution, focusing, mixing, etc

o Nanoparticle behavior in complex geometry passages including the human respiratory tract, aerosol transport/delivery systems, energy systems, etc.

o Nanoparticle behavior in chemically reactive systems including combustors, aerosol reactors, etc.

o Development of efficient numerical schemes for simulating nanoparticle transport and deposition.

Atmospheric Aerosol Simulation

Modeling of atmospheric nanoparticles together with the rest of the particulate matter (PM) is needed for:

o Simulation of the radiative effects of both the nanoparticles (indirect effect on climate) and the larger particles (direct effect).

o Design of abatement strategies for both nanoparticles and particle mass concentration (PM2.5 and PM10).

o Simulation at different spatial scales presents an especially challenging problem for:

  o Global scale (climate)

  o Near sources (effect of atmospheric conditions on nanoparticle emission rates)

  o Devices (filters)

Simulation of the compositional mixing state of atmospheric particles is important since the optical properties and the health effects of atmospheric particles may depend on how

chemical species are mixed at the individual particle level. Also, the extent of mixing of black carbon and sulfate in individual particles has a profound effect on the radiative properties of the entire aerosol population and therefore on their direct climatic effect.

Aerosol Reaction Engineering (ARE)

Many industrial applications of 'tailored' nano-particles (including nanotubes) have been identified in recent years including their use in fabricating: selective catalysts or membranes, electronic/magnetic information storage or chemical sensor (detection) devices, optical films/fibers, additives for the control of rheological or thermophysical properties, energetic chemical propulsion fuel additives, etc. Remarkable applications are being rapidly discovered, and the increased availability of low-cost nanoparticles for exploratory R&D , made possible by the ARE-research recommended here, will accelerate these advances.

To capitalize on the unique properties of nanoparticles in applications, they will have to be synthesized in large quantities under carefully controlled conditions. For this purpose, 'aerosol' (gas-to-particle) chemical reactors will be attractive because of their ability to satisfy the demands of: high product purity, scale-up potential, improved control of phase identity/composition, and small environmental 'footprint'. However, because of the stringent new demands associated with tailored nanoparticle synthesis, the science/technology base for designing/optimizing/controlling particle-producing reactors is presently inadequate. Developing this frontier area of chemical reaction engineering will pay dividends by facilitating the emergence of this new branch of 'specialty chemicals', and provide valuable guidance for the many start-up companies needed to supply the diverse and rapidly growing nanoparticle requirements of industry. Specific research recommendations are included for each of the following 16 ARE-areas:

(1) Nanoparticle Precursor Selection

(2) 'Reduced' Kinetics of Precursor Evolution to Embryonic   Particles

(3) Models of 'Chemical' Nucleation Rates

(4) Nanoparticle Growth by Heterogeneous Reactions

(5) Modeling Brownian Coagulation Rates

(6) Improved Rate-Laws for Nanoparticle Restructuring

(7) Modeling Phase Change Within Nanoparticles

(8) Improved Prediction of Nanoparticle Transport Properties

(9) Development/Implementation/Testing of Efficient EAD-Simulation Methods

(10) Testing "ARE'' Models against Well-Instrumented Laboratory Experiments

(11) Model-Based Control of Aerosol Reactors

(12) Model-Based Scale-Up

(13) Anticipating and Controlling Deposition

(14) Health/Safety Precautions for Handling Nanoparticle Products

(15) Surface Modification/Coating Opportunities

(16) Property-Resolved Nanoparticle Reactor-Separators

Atmospheric Nanoparticles (Ultrafine Particles)

Atmospheric ultrafine particles (UFP) - with diameters less than about 0.10 µm - are formed from gases by a variety of gas-to-particle conversion processes. There are at least three sources of gases, which may be converted to particles. UFP may be formed at high temperature sources and emitted directly to the atmosphere. Some processes may emit hot supersaturated vapors, which undergo nucleation and condensation while cooling to ambient temperatures. Chemical reactions in the atmosphere may lead to chemical species with very low saturation vapor pressures. These chemical species may form particles by a variety of nucleation processes. Although the UFP mass fraction is usually very small, this size range contains the highest number of ambient particles and an appreciable portion of total surface area. Because of their increased number and surface area, UFP are particularly important in atmospheric chemistry and environmental health. Toxicological and epidemiological evidence linking respiratory health effects and exposures to UFP has been increasing over the last several years. Recent epidemiological studies demonstrated a stronger association between health effects and UFP compared to accumulation mode or coarse particles. More recent toxicological studies indicate that ultrafine particles are most potent in inducing oxidative stress. UFP also localize in mitochondria where they induce major structural damage. Moreover, the concentrations

of these particles in ambient air are spatially inhomogeneous and very dependent on the proximity to their sources.   This inhomogeneity strongly affects   population exposures, with a portion of the population (depending on activity pattern, profession, lifestyle, commuting time, etc.) being exposed acutely to very high UFP concentrations.

The science of atmospheric nanoparticle aerosols is relatively new, and despite recent progress much remains to be done. There is a fundamental lack of information on how nanoparticles form and grow to sizes that can serve as cloud condensation nuclei (CCN) and affect the earth's climate and albedo. There is also lack of knowledge on the fraction of these particles that are formed by direct emission, nucleation of hot vapor upon cooling, or atmospheric formation of gases that undergo nucleation.   UFP physical, chemical and toxicological properties are poorly understood. Many of the measurements that are needed require instrumentation that currently does not exist.   Little information is also available on the concentrations or physical/chemical properties of UFP in places where people live and work: in community air, in homes, in schools, in workplaces, or in vehicles.   To determine   UFP health effects, it is essential to develop and deploy technologies that can assess the nature and extent to which people are exposed to these particles. The complexity of the sources and nature of UFP suggest that much effort will be needed to either discover and/or refine our understanding of linkages between exposures and health effects.   Studies focusing on heath effects are also needed to identify mechanisms by which UFP induce cellular damage and generate oxidative stress, how they penetrate the cellular structure, and how the above effects depend on chemical composition. This information is essential in reducing emissions of UFP that are a risk to public health. Finally, there is a need to better detect UFP that pose a biological threat. Examples include viruses, nanometer sized fragments of biological particles, and condensed chemical agents on UFP surfaces.

In summary, our panel identified the following topics for research:

(1)   Photochemically-driven nucleation in the atmosphere

(2)   Nucleation and rapid growth that occurs as hot pollutant exhaust gases mix with cooler air in the ambient environment

(3)   Growth rates of freshly nucleated atmospheric ultrafine particles

(4)   Chemical and physical transformations of atmospheric ultrafine particles

(5)   Improvements in measurement technology for ultrafine particles

(6)   Atmospheric measurement needs for ultrafine particles

(7)   Measurement and characterization of ultrafine particle emissions from sources

(8)   Source apportionment of ultrafine particles

(9)   Population exposure assessment

(10)   Dosimetry

(11)   Health effects of UFP

(12)   Control technology

(13)   UFP and homeland security

TERMINOLOGY

R. Flagan (with contributions by S. Friedlander)

Introduction

The focus of this report is on the science and technology of aerosol nanoparticles. One of the goals of the Workshop was to bring together representatives from different aerosol communities to improve communications and to identify and encourage commonalities in approaches, as appropriate. To this end, in this section we have summarized some of the terms used in describing aerosols in different contexts.

An *aerosol* is a metastable suspension of particles in a gas. In contrast to colloids, aerosols cannot generally be made long term stable. The time scale over which the aerosol can be considered stable varies from system to system. The key feature is that the aerosol is stable on times comparable to those of interest in a given situation or experiment. The particles may be solid or liquid, or a mixture of multiple solid and/or liquid phases. Aerosols may form in any gas. The gas may not be ideal and usually is a mixture of components. Some or all of the components may be condensable, or may partition to the particle phase by a variety of mechanisms (condensation, adsorption, chemical reaction).

Common usage defines *ultrafine particles* as particles smaller than 100 nm in diameter. This definition has, for example, been adopted in the EPA Criteria Document for the particulate standard.

Diameter refers to a measured size-related characteristic. Not all particles are spherical for which a particle diameter is uniquely defined. More commonly, the particle diameter is defined as that of a spherical particle that would behave the same as the measured particle in a particular measurement device or scenario. Several such equivalent diameters are used. The *classical aerodynamic diameter* of a particle is the diameter of a spherical particle of unit specific gravity that has the same settling velocity as the particle

in question in air at atmospheric pressure and ambient temperature.

Nanotechnology deals with phenomena whose physics or chemistry differs from that of bulk materials of the same composition. Extending this interpretation, **nanoparticles** are particles in which the small size influences the intrinsic properties or behavior of the particle. Properties of interest may be: surface properties (e.g., surface free energy), quantum mechanical properties (e.g., optical transitions), chemical or biological reactivity, etc.

Nanostructured particles are particles that exhibit fine structure at scales sufficiently small that the intrinsic properties differ from those of the bulk material, even though the overall size (maximum dimension) of the particle may be too large to be considered nanoscale. Most of the discussions in this Workshop have focused on nanostructured particles that from by the combination of aerosol nanoparticles and retain the nanoscale structure of those particles.

As noted above, an aerosol is an ensemble of particles. Only rarely are particles uniformly sized, i.e., monodisperse. More commonly, the aerosol includes particles with a range of sizes. The aerosol is, therefore, characterized in terms of a differential **particle size distribution**. The distribution may be presented in terms of the distribution of particle number concentration with respect to size (number distribution), particle mass concentration with respect to size (mass distribution), particle surface area per unit volume with respect to size (surface area distribution), etc. One or more peaks will be observed in these different representations of the particle size distribution.

Atmospheric Aerosol

 Several such peaks, or **modes**, are commonly observed in the atmospheric aerosol particle size distribution, and have been labeled. **Coarse particles** broadly describe particles produced by mechanical processes such as soil dust, cloud droplets, and many biological particles. These particles frequently dominate the aerosol mass loading. **Fine**

particles are primarily those formed from the vapor phase, either in emission sources or in the atmosphere. The *coarse particle* and *fine particle* size regimes cannot be separated by any precise size cut. Indeed, the particle size ranges of the two classes overlap.

Within the *fine particle* regime, a number of modes are commonly found in the atmospheric aerosol. These are labeled and defined in terms of the distinct peaks or modes that are seen in the size distribution. The **nucleation mode** includes particles formed directly by homogeneous nucleation, and includes both freshly emitted particles and particles formed by homogeneous nucleation in the atmosphere. The **Aitken mode** comprises nuclei that have aged and grown somewhat. The **accumulation mode** includes well aged particles that have grown substantially, to a size at which growth dramatically slows. Under certain conditions, the *accumulation mode* splits into a smaller **condensation mode** (hydrophobic) and a larger **droplet mode** (hydrophilic) thought to result from growth due to aqueous phase chemical reactions within the droplet during high relative humidity conditions.

These modes are clearly identified in the atmospheric aerosol. Other systems also exhibit associated different particle formation or growth mechanisms. The *nucleation mode* is common to systems in which new particle formation occurs. High concentration aerosols produce a **coagulation mode** due to rapid growth by this mechanism, while coagulation in the atmospheric aerosol contributes more to the loss of fine particles than to the growth of larger ones. Caution must, therefore, be exercised in extending the modal descriptions of atmospheric aerosols to combustion aerosols, aerosol synthesis reactors, and other aerosol systems.

Commercial Nanoparticle Products

As an example, commercial nanoparticle products such as reinforcing fillers and catalysts occur as chain aggregates of individual nanoparticles. These nanoparticle products have been characterized using the following terms based on their morphological properties:

- Primary particles, the smallest identifiable individual particles, are usually in the size range between 5 and 50 nm. These are often present as individual crystals.

- Aggregates are assemblies of primary particles held together by strong bonds, probably ionic/covalent in nature.

- Agglomerates are assemblies of aggregates held together by weak bonds which may be due to van der Waals forces or ionic/covalent bonds operating over very small contact areas. Agglomerates may break up to form aggregates, for example, when they are blended with polymers in the manufacture of rubber.

This terminology is used by manufacturers of inorganic oxide aerosol products and carbon black. It may also be helpful in some applications to describe aerosol particle emissions in the size range smaller than 100 nm from diesel engines and other sources of incomplete combustion. However, we note that the use of the terms *strong* and *weak* to characterize such systems tends to be qualitative and/or based largely on empirical methods of assessment.

Equations of Aerosol Dynamics

The dynamics of nanoparticle aerosols can often be simulated by a special form of population balance equations which take into account the change in the distribution function of the particles with respect to such independent variables as particle size, area, fractal dimension and chemical composition. The Equations of Aerosol Dynamics (EAD) include such parameters as rates of particle formation, collision and coalescence. The simplest EAD form, sometimes called the General Dynamic Equation (GDE) was in the past a simple generalization of the Smoluchowski equation of coagulation. These equations are particularly important for nanoparticle aerosols when concentrations are high. The equations are essential in analyzing problems of air pollution (at sources and in the atmosphere) and in industrial synthesis of fine particles. The EAD can, in the role that they play in aerosol science, be regarded as analogous to the role of the equations of motion in fluid dynamics.

1. EXPERIMENTAL METHODS AND INSTRUMENTATION

Physical Characterization:

D. Pui (Chair), R. Flagan, S. Kaufman, A. Maynard, Juan F. de la Mora.

Chemical Characterization:

S. Hering (Chair), Jose-Luis Jimenez, K. Prather, A. Wexler, P. Ziemann.

OVERVIEW, PRACTICAL IMPLICATIONS

Nanoparticle aerosols play an important role in the environment, in global climate, in human health, in materials processing and in nanotechnology. Knowledge of nanoparticle chemical and physical characteristics is critical to each of these fields. In the environment, data on nanoparticle chemistry is important to understanding nucleation processes, to identifying origins of cloud nuclei, and to evaluating implications for human health. Nanoparticle-based materials continue to be developed whose unique functionality depend upon the constituent particle size, composition and structural properties. In materials processing, methods are needed for on-line determination of the performance in nanoparticle reactors, and for identifying sources of particulate contaminants in clean rooms as semiconductors go to smaller line sizes.

Atmospheric aerosols are important to the global radiation balance, both directly and through their influence on clouds. The "ultrafine" (< 100 nm) fraction dominates the number concentration of these airborne particles, and thus while their mass concentration may be small, their potential to affect cloud condensation nuclei populations is important. Air quality monitoring for particles is driven by the epidemiological correlation between ambient particulate matter loading and rates of morbidity and mortality. Recent evidence has specifically implicated the ultrafine size fraction and its role in human health.

Fundamental understanding of the formation and growth of nanoparticle aerosols is essential to the development of aerosol nanotechnology. Particle size must be tightly controlled to take full advantage of quantum size effects in photonic applications. Agglomeration, which can quickly dominate once particle formation begins, must be tightly controlled, and requires that the rate of new particle formation be quantitatively determined. Real-time measurements of these nanoparticle aerosols are enabling technologies for the advancement of nanotechnology.

Chemical and physical properties are equally important to the characterization of nanoparticle aerosols. Often effects may depend upon physical properties of aerosol, while chemical composition provides the important link to particle sources and formation mechanism. Current developments in aerosol instrumentation have been driven by atmospheric aerosol research, including global climate and air quality monitoring needs. Yet there are many market sectors that can benefit from improved instrumentation for characterizing the chemical constituents and physical characteristics of nanoparticles.

- Environmental –Particles and their precursors are emitted by numerous natural and anthropogenic sources. On urban and regional scales particles correlate to health effects, carry the acidity in acid deposition and degrade visibility. On a global scale, particles provide the surfaces for heterogeneous reactions that form the ozone hole, affect the earth's radiation balance through scattering and absorption of light, and act as cloud condensation nuclei further affecting the reflection of solar radiation back to space of infrared radiation back to the Earth's surface. Aerosol particle chemical analysis is an essential research tool for understanding their environmental effects , for tracing their sources and understanding their formation mechanisms.

- Pharmaceutical – The pharmaceutical industry has at least two important uses for aerosol analytical instruments: occupational health and inhaled drug delivery. Hypodermic needles transmit disease, are difficult to dispose of safely, cause venous hardening for those patients who need many treatments, and elicit fear in

the hearts of many patients. The lungs provide a huge surface, about a tennis court worth in typical adults, for transferring drugs to the blood stream using metered dose inhalers. Yet the size, morphology, density and composition of the aerosolized drugs influence the location of deposition, which in turn influences the rate and route of entry into the blood stream. Characterization of these particles is key to their success.

With the advent of genetic engineering, the pharmaceutical industry has been able to produce drugs that are targeted to very specific diseases and have extremely high potency. Manufacture of such high potency drugs poses a terrible threat to line workers. Increasing the challenge is that these high potency drugs, the so-called incipient, are mixed with an inert carrier, the excipient. Distinguishing occupational exposure to the incipient from that to the excipient is the goal.

- Occupational Health – the pharmaceutical industry's exposure needs are one extreme example of occupational health. Workers in many industries are exposed to particle phase pollutants that cause a myriad of health effects. Many of the challenges for occupational exposure are very practical. Because occupational aerosols exhibit wide spatial variability in the workplace, personal sampling is the norm. Yet current personal samplers integrate over long periods of time and have numerous sampling artifacts. In any case, they are all subject to serious constraints on their cost, weight, and chemical specificity. Analytes of interest cover most materials that may be generated or present as aerosols in the workplace, although particular attention is paid to materials showing accute or chronic toxicity in specific size ranges, including asbestos, crystalline silica, metals and metal compounds, and biological materials.

- Military and Homeland Security – and related to Occupational Health are illegal radioactive, chemical and biological warfare agents that have been developed or are under development by governments, cults, and terrorist organizations. The current US administration is refocusing tremendous research dollars to Homeland Security issues and a significant component of this research is detecting and

analyzing airborne particles for threats.   In the next decade, security-related research on aerosol instrumentation may surpass that for environmental research.

- Semiconductor Industry – the smaller the feature size, the smaller the particles that matter.   Small particles are a continual problem for semiconductor processing. The peak in the number distribution for atmospheric particles is in the ultrafine size range.   A new source of particles can shut a production line down costing millions of dollars per day.   Although the size and number of the particles indicates the degree of damage that will be caused, the composition indicates the source of the particles so is essential for diagnosing their source and remedying the problems.

- Forensics - For many decades forensic science has utilized the identification of small particles including fibers and gun powder residue. Extension to the nanoparticle regime could open further opportunities for forensic applications.

- Nanoparticle synthesis - On-line characterization methods are needed as diagnostics during the development of new aerosol reactors or processes, and to monitor nanoparticle products, both for product control and worker protection.

The structure of nanoparticle aerosols can be quite complex, as shown in Figure 1. Important characteristics include size, morphology, single particle chemical composition and single particle surface composition.   For specific applications, physical characteristics such as the ability to act as cloud condensation nuclei, or to have the required material characteristics, are important. Thus the challenge of nanoparticle characterization has many facets.   Which characteristics are most important will depend upon the application.

It is important that measurements of nanoparticle aerosols be directed to include the smallest possible particle sizes, of the order of 1 nm or less. From the point of view of basic science, the characterization of nanoparticles is critical to understanding the rate of

inception of new particle formation. The process of creating stable nuclei by vapor condensation cannot yet be predicted quantitatively. The more complex processes involved in new particle formation in reactive systems pose even greater theoretical challenges. Measurements of incipient nuclei must, therefore, be pushed to the lowest possible sizes to enable a quantitative understanding of nucleation processes and the validation of improved theories of improved nucleation models. (See also the Panel 2 report.)

The transient nature of aerosol nanoparticles makes real-time, spatially- resolved measurements essential. To understand nucleation events and to evaluate the health effects of aerosol nanoparticles, measurements must be made near the source and with high time resolution. In nanoparticle synthesis and process technologies, occupational exposure assessments require measurements near where workers may be exposed in the plant. To understand ambient exposures, measurements must be made where the emissions and exposures occur, i.e., on roadways and in communities immediately downwind of industrial sources. Air pollution monitoring strategies that employ small numbers of monitoring stations to characterize regional exposures often miss the peaks that occur within 10's to 100's of meters from highways.
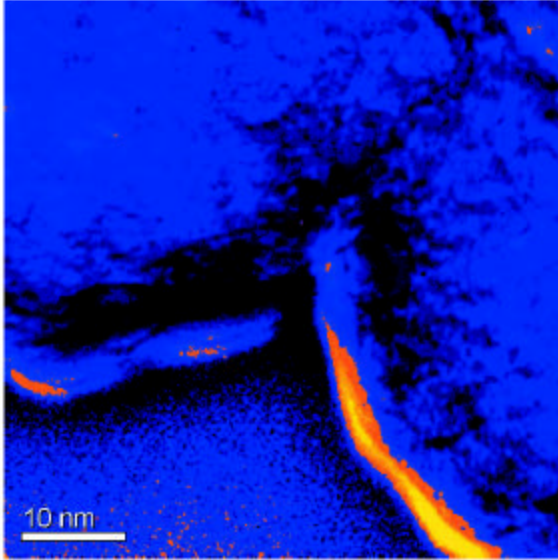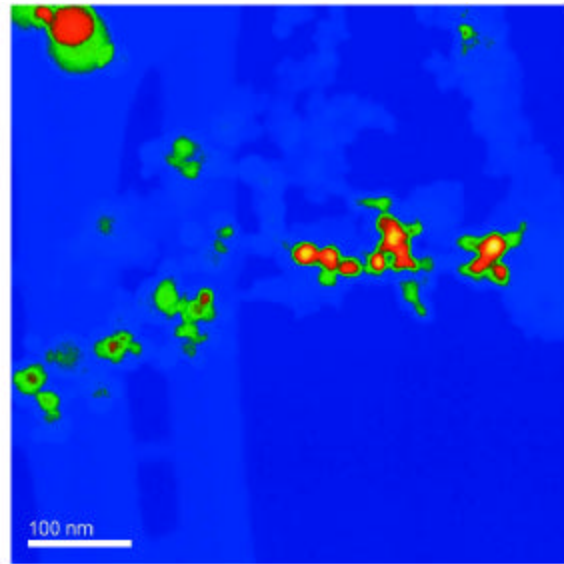
Electron energy-filtered image of nanoparticles from gas metal arc welding. Hot colors indicate a high ration of Si to Fe: Si enrichment is seen at the surface of the particles.
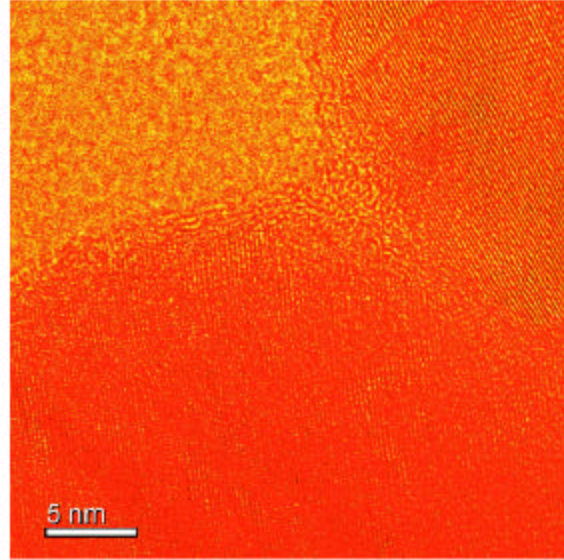
Nanoparticles from gas metal arc welding, showing the presence of an amorphous layer surrounding a crystalline core.
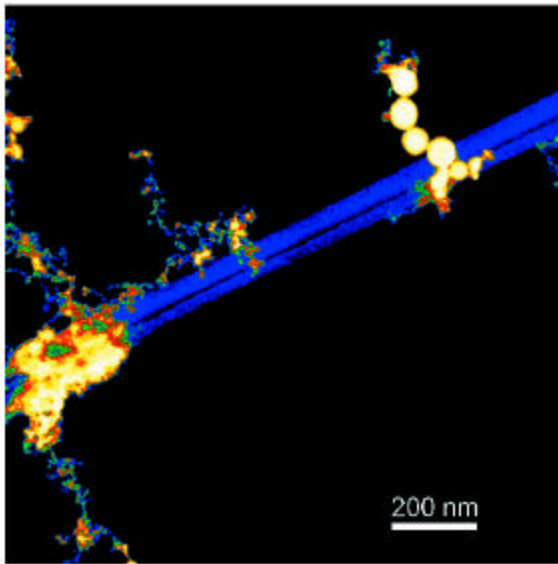
Nanoparticles from gas metal arc welding.

Z-contrast image of particles from gas metal arc welding on steel coated in lead-based paint. Hotter colors indicate a higher lead content in the particles.

Nanoparticles from gas metal arc welding, showing structural differences between the core and surface regions.
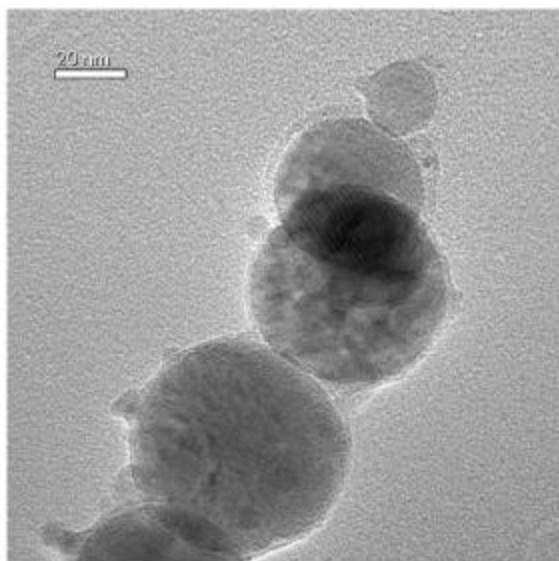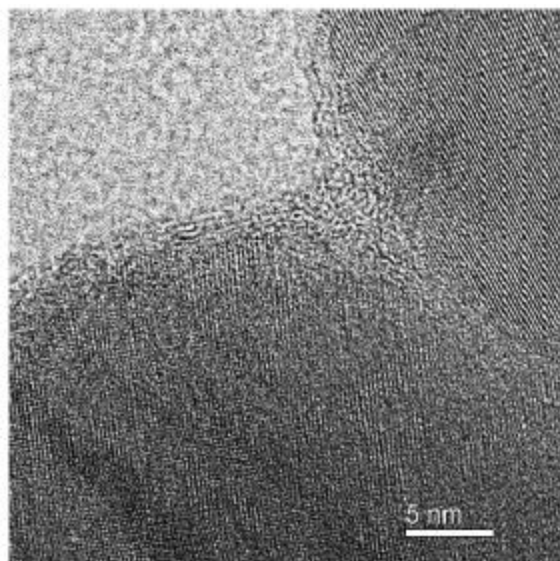
Nanoparticles from gas metal arc welding, showing the presence of an amorphous layer surrounding a crystalline core.
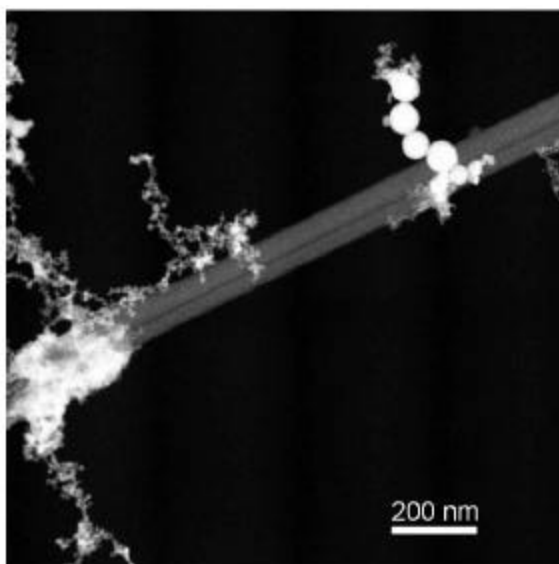
Nanoparticles from gas metal arc welding.

Z-contrast image of particles from gas metal arc welding on steel coated in lead-based paint. Brighter regions indicate a higher lead content in the particles.
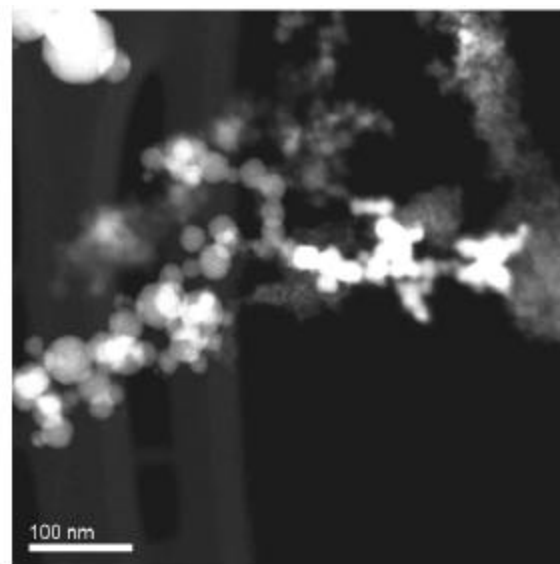
Figure 1-1. The structure of nanoparticle aerosols (Courtesy of Andrew Maynard, NIOSH and Yasuo Ito, Argonne National Lab).

Full understanding of the health implications of aerosol nanoparticle exposure, whether due to ambient or occupational exposures, must await the development of entirely new characterization technologies that enable measurements to be made at the points of exposure. This will require larger numbers of sensors than needed to monitor more stable gases and larger particles. Not only will the sensors have to be simplified to reduce the cost below that of the laboratory instruments in use today, they will have to be sufficiently robust that they do not require an aerosol scientist to operate them, and reliable enough to provide the continuous data records required for epidemiological studies.

SPECIFIC RESEARCH NEEDS FOR NANOPARTICLE PHYSICAL CHARACTERIZATION

Background

The simplest characterizations of aerosols and individual aerosol particles are invariably physical, providing such information as size, morphology, mass, density, and particle concentration. It is especially important to be able to make these measurements for nanoparticles because of the expectation that many of the particles' other properties will be significantly different from those of the bulk material, and that these differences will depend in first order on these simple physical characteristics. Their extremely small size (a 1-nanometer diameter spherical particle may contain as few as 25 atoms) and their transient behavior, due to high diffusion rates and high typical concentrations, present unique challenges to making these measurements.

Among single-particle measurement methods in the nanometer range, the measurement of size via electrical mobility and the measurement of concentration using condensation nuclei counters have perhaps received the most development effort. Nevertheless, these methods are still in need of extension to smaller sizes and higher and lower concentrations, and there are still unanswered questions concerning the relationship between size and electrical mobility, as well as effects of other physical parameters such as particle shape and flexibility on these measurements.

Morphology information is available through transmission electron microscopy and scanning microscopies. Because of the small size of the particles, perturbations of the particles by the microscope are often significant and need to be better understood.

Conventional aerosol mass determinations use filters and impactors, techniques often inaccurate in the nanoparticle range due to the negligible particle mass. Indirect mass determinations inferred from size distributions measured by electrical mobility are often used, though this requires assuming an effective density, which would depend in turn on particle morphology. Combining results of aerodynamic size from low-pressure impactors and of electrical mobility size from a DMA can in principle be used to infer mass, again indirectly. Direct mass determination of individual whole particles (as contrasted with mass spectroscopic chemical characterization of particle constituents) is a desirable objective. Centrifugal methods are being developed and should be extended, while other methods should be sought as well.

None of the methods discussed above has sufficient time resolution to meet the present needs of nanoparticle emission studies, control of aerosol reactors, or fundamental studies of particle inception and interactions. Nanoparticle aerosols can form, aggregate and react rapidly, and studying these processes will require far better real-time performance than what is now available. Specific needs for physical characterization of nanoparticle aerosols are enumerated below.

1. Rapid aerosol nanoparticle measurements (Physical Characterization)

Recommendation: The time scale on which aerosol particle concentrations change decreases with decreasing particle size. To understand the dynamics of such particles, and exposures of people or objects to them requires that measurements be made rapidly.

Background: Nanoparticles form by homogeneous nucleation, and then grow by coagulation and condensation, or vapor deposition. Due to their high diffusivities, nanoparticles are also lost rapidly by coagulation with larger particles. As a result,

nanoparticles emitted from vehicles decay rapidly with distance from the roadway. When particles are formed by homogeneous nucleation in the atmosphere, they rapidly pass through the low nanometer size range. The nanoparticle burst may extend over large areas in this case, but the time duration is sufficiently short that instruments that are commonly available cannot capture the transient size distributions. Measurements of nanoparticle fluxes by eddy-flux-correlation methods require measurements at least at 1 Hz for stationary measurements, or at 10Hz or greater for airborne measurements. This can now be done with total (>3nm) nanoparticle measurements using condensation nucleus counters, but instrumentation capable of such rapid measurements of size distributions have only been demonstrated in the laboratory. In nanoparticle synthesis reactors, once agglomeration begins, nanoparticle concentrations diminish rapidly due to scavenging of the nanoparticles as they coagulate with the larger aggregates. Understanding the dynamics of aerosol reactors requires measurements that have sufficient time response to capture transients between different modes of reactor operation. Particle size is a critical parameter for many engineered nanoparticles, so rapid response size distribution measurements are needed for process control applications. (See also the Panel 4 report.)

Most of the commercial aerosol instrumentation was originally developed for steady state measurements and lacks the time resolution necessary for measurement of these dynamic processes and exposures. Typical condensation nucleus counters exhibit inherent time constants at 1-3 seconds, even if they report counts in smaller intervals. The ultrafine condensation nucleus counter marketed by TSI (Model 3025 CPC) has a time constant of about 0.1s, but samples at such a small flow rate that it is impractical as a detector for differential mobility analysis under many conditions. Only when concentrations are very high or the aerosol is steady enough to allow significant time averaging can size distributions be obtained in a single scan. A higher throughput mixing-type condensation nucleus counter that is better suited to rapid DMA measurements has been demonstrated, but that instrument has seen little use to date. Other investigators have demonstrated that rapid scanning mobility measurements can be made using electrometer detectors, at least at relatively high particle concentrations. A DMA has been produced with a segmented

collection electrode that is connected to a number of electrometers of remarkable sensitivity. This approach has recently been applied to produce an analyzer for source-level measurements with high time response. A commercial version of this instrument has recently been offered by Cambustion.

Still, no instrument is generally available for high time response measurements of nanoparticle size distributions at ambient concentrations. DMA measurements suffer a number of problems in nanoparticle measurements, especially the low probability with which nanoparticles are charged. Improved aerosol charging technology with quantified charging probabilities would greatly enhance these measurements. For rapid DMA size distribution measurements, the residence time in a DMA must be shorter than the desired measurement time or uncertainties become excessive. Alternate ways of making the measurements may facilitate faster measurements. Time of flight mobility analysis is routinely used for molecular characterization in the so-called ion mobility spectrometer. Extensions to the lower mobilities of aerosol nanoparticles might prove fruitful, but alternate methods for aerosol nanoparticle size distribution measurements should also be explored.

Practical Implications:
- Enable the detection of nanoparticle burst formed by homogeneous nucleation in the atmosphere.
- Understand the dynamics of aerosol reactors during different modes of reactor operations.
- Fast response instrument is needed for process control of reactors.
- Measure transient behavior of diesel engines and jet engines.

2. Detection, characterization, and behavior in the low nanometer (<5nm) size regime (Physical Characterization).

Recommendation: The development of improved methods for detection and characterization of particles below 5 nm would open to observation a number of

important phenomena. Among others, the possibility to directly observe the formation of new particles (nucleation) in the atmosphere or other settings, as well as following their time evolution.

Background: At present, state of the art single particle detectors (CNCs) are limited to particle diameters above 3 nm. On-line sizing techniques (mobility or mass analysis) depend on charging, which is particularly problematic and inefficient in the low nanometer range. Extending the size range of CNCs below 3 nm may be possible with neutral particles with suitable selection of vapor, but a lower detection limit (LDL) is almost unavoidable, at diameters that have been estimated at about 1.5 nm. Many ambiguities remain regarding the optimal materials for minimizing this LDL and its dependence on particle properties. The possibility to detect single particles with 100% efficiency at ~ 1nm diameters has been demonstrated in the laboratory, provided they are charged. But much remains to be done (both in terms of charging as well as from the ion nucleation viewpoint) before this leads to practical instrumentation sensitive at 1 nm or below. Mobility analysis can be extended to subnanometer sizes, but the accurate interpretation of this information is limited at diameters below 2-3 nm by ambiguities in the gas-particle interaction (accommodation coefficient, gas or water adsorption, etc.), as well as by the increasing importance of the charge in the particle and the polarizable gas molecule (polarization). The polarization effect remains to be analyzed in the case of inelastic collisions, which is the one relevant in air. Further information on particle shape or density can be inferred by combining the DMA output with existing MS systems with atmospheric pressure sources, though their limited mass range confines this possibility to relatively small diameters.

Practical implications:
- Direct observation of new particle formation/nucleation
- Variation of particle drag due to gas molecule/particle interactions
- Probability that particles stick upon collision
- Transition between molecular and particulate behavior in filtration, i.e., at what size do particles pass through a filter like vapor molecules?

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- Tools for biomolecule and macromolecule characterization: Electrospray has enabled the production of aerosols of individual biomolecules, whereby developments in aerosol technology are directly applicable to biotechnology. Mobility measurement in tandem with mass spectrometry is rapidly developing as a promising tool in proteomics. The mobility separation could arguably be carried out advantageously in atmospheric air in the DMA. Aerosol classification and detection techniques are similarly applicable to the sensitive detection of ambient species existing in the vapor phase (provided that they can be cleanly and efficiently charged). Important applications include explosives detection and food and medical diagnostics. No single-molecule detector exists at present under atmospheric pressure conditions, so that CNC based detectors would represent large sensitivity improvements over existing alternatives.

- Characterization of nanoparticles synthesized for materials applications, e.g., quantum dots, luminescent silicon

- Atmospheric nanoparticles - climate and health effects

3. Particle standards for size, concentration, morphology and structure (Physical Characterization)

Recommendation: There is a need to develop sources of stable and well-characterized monodisperse particles having a series of diameters in the nanometer range. Likewise, there is a need to develop well-defined, reproducible protocols for dispersing these particles to generate test aerosols whose particle size is known. Beyond this, protocols are needed for generating and validating known concentrations of aerosols of the size-standard test aerosols to produce concentration standards.

Background: Test aerosols must be available having well-defined properties such as particle size, concentration, and other parameters. Such aerosol standards will make possible the comparison of different instrumental methods and the calibration and assessment of the reproducibility of the measurements. To be suitable as size standards, test particles must be accurately characterized and be stable under storage. Concentration

standards require in addition a well-defined and reproducible protocol for dispersion and dilution to the concentration desired. The means of dispersion must not introduce changes in the particle size. In the size range below 5 nanometers, unanswered fundamental questions such as those discussed in the Panel 2 report pose significant challenges to the problem of standards.

Particle shape and structure are rarely amenable to standardization, but in the nanometer size range there is a possibility that macromolecules of well-defined structure could be utilized.

Practical implications:

- *Calibration of instruments.* To ensure that data on nanoparticle aerosols is reliable, instruments need initial and periodic calibration. Without calibration standards, , the data may be of limited utility; with good standards, confidence in the data is improved. Manufactured instruments must be calibrated, and well-defined standards make it possible to specify manufacturing processes and final instrument accuracy unambiguously as well as to define required routine maintenance protocols.

- *Comparisons among alternative methods.* When more than one measurement method is available, it is important to compare results of the different methods using the same or equivalent aerosols. This is greatly facilitated when well-defined standards and standard protocols are available for the test aerosol generation.

- *Communication of results between working groups.* When good standards have been developed, groups working at different locations are able to check their work by comparing the results of measurements on the standard aerosols. This gives a degree of confidence and allows researchers to fulfill the obligation to publish results in a form which permits their replication by others working in the field.

4. Charging behavior and technology throughout the ultrafine and nanoparticle size regimes (Physical Characterization).

Recommendation: Fundamental study on nanoparticle aerosol charging is needed to better quantify the charging probability. High efficiency charger is needed to increase the detection sensitivity of sub-3 nm nanoparticles.

Background: Methods for size-analysis, such as mobility and mass spectrometry methods. Because the original charge state of suspended nanoparticles is often unknown, charging to a well defined level is the first stage for such analyses. In addition, charging may also be a helpful (probably essential below 1.5 nm) step for nanoparticle detection with the highest possible sensitivity. The reason is that charging enables individual counting of objects even at molecular dimensions, either in condensation nucleus counters (CNCs) via ion –induced nucleation, in cryogenic balometers now being developed as detectors for large biomolecules in mass spectrometry, or electron multipliers. Because nanoparticle charging occurs generally with low and not sufficiently well understood probabilities, it is essential to understand and control particle charging much better. Quantifying this probability is vital for concentration measurement in mobility approaches. Increasing its value would impact the sensitivity of such measurements.

Practical implications:
- Essential for quantitative measurements of nanoparticle size distributions by mobility techniques.
- Improve throughput for DMA classification
- Facilitate single particle counting below 3nm (ion-induced nucleation)
- Humidity effects of DMA measurements.
- Improved sensitivity of nanoparticle measurements
- Chemical effects on particle charging may bias measurements due to composition sensitivity
- Neutralization

- Eliminate radioactive source in particle charging

5. Distributed nanoparticle aerosol measurements (Physical Characterization).

Recommendation: There is a basic need to develop instruments that are sufficiently simple, robust, and inexpensive to be deployed in large numbers to quantify nanoparticles in the environment. The time scale on which aerosol particle concentrations change decreases with decreasing particle size, leading to substantial variations in the concentrations of such particles over relatively small scales. Present nanoparticle measurements are too complex and expensive to permit measurements with sufficient density in regions of concern to quantify exposures and risks.

Background: Instruments presently available for aerosol measurements in general, and nanoparticle measurements in particular are expensive and complex, limiting their application to small numbers of research sites. Since nanoparticle concentrations may decay rapidly by coagulation with larger particles, measurements must be made near the primary sources to understand exposures to such particles. Epidemiological studies require large, and complete data sets. The labor intensive methods for measuring aerosol nanoparticles that are presently available are impractical for the generation of such data sets. The high variations in particle concentrations in occupational settings mean that occupational exposures or process contamination by nanoparticles can only be quantified if large numbers of sensors can be deployed.

Mobile laboratories may take present measurements to a variety of locations, but there is a basic need for instrumentation that is sufficiently simple, robust, and inexpensive to be deployed in large numbers to quantify nanoparticles in the environment.

The development of such instrumentation requires research into new methods of aerosol and nanoparticle measurement. There have been some recent developments along this line, e.g., simplified condensation nucleus counters for rapid nanoparticle measurements,

and a MEMS-based mobility analyzer. None has yet produced an instrument suitable for wide deployment of nanoparticle measurement systems.

The possibility of developing micro-electro-mechanical systems (MEMS) based aerosol instrumentation is particularly intriguing. A MEMS condenser mobility analyzer has already been demonstrated, although few details are presently available.

Practical Implications:

- Large array of inexpensive instruments can be set up to quantify spatial variations of nanoparticles in the environment.
- Compact, perhaps MEMS-based monitors, can become valuable tools for epidemiological studies.

6. Integral parameter measurement (Physical Characterization).

Recommendation: Instrument is needed to measure the integral parameters of size distributions. The simplified instrument is a cost effective way to conduct epidemiological studies of human health effects.

Background: Traditional analysis on particle size distributions involves the use of volume (3rd moment of size distribution), surface area (2nd moment) and number (0th moment). For example, the current inhalation standards are based on mass (volume*density) dosage. Recent toxicological studies of the effects of the particles on health have suggested that effects may correlate better with particle surface area than with particle number or mass. It is therefore desirable to develop integral parameter measurement methods that measure a moment of the particle size distributions most closely related to health effect. Recent studies indicate that by integrating the particle size distributions measured at the St. Louis Supersite with the appropriate lung deposition curves, the total particle surface area deposited in the tracheal bronchial (TB) region and the alveolar region (AL) correlate well with the moment of particle size distributions in

the range of 1.1-1.6. An instrument that provides continuous measurement of this moment may provide a good indication of the quantity of surface area deposited in the lung. It may therefore be a useful indicator for use in epidemiologic studies of human health effects of atmospheric and industrial aerosols.

Practical Implications:

- Integral parameter measurement instruments are cost effective way to conduct epidemiological studies of human health effects. It is more likely that these instruments can be developed into a form suitable for personal sampling. For example, a personal sampler that measures the moment of 1.1-1.6 of size distributions can be correlated to the total surface areas deposited in human lungs. They can be worn by school children and commuters to study the nanoparticle inhalation on health effects. These low cost samplers can also be effective detectors for distributed measurements of particle fluxes from a source or sink. It is also possible that an integral parameter can be found that correlate well with biologically relevant sampling and may be introduced as hazard alarms.

7. Off-line morphological, structural, and chemical characterization of nanoparticles (Physical and Chemical Characterization)

Recommendation: Development and implementation of techniques for the Off-line morphological, structural, and chemical characterization of nanoparticles

- Adaptation and application of emerging analytical techniques in the Transmission Electron Microscope (TEM), Scanning Transmission Electron Microscope (TEM) and Environmental Scanning Electron Microscope (ESEM). Specific techniques include Z-contrast imaging, Electron Energy Loss Spectroscopy (EELS), imaging and analysis using aberration-corrected STEM, use of novel imaging and reaction techniques in the ESEM.
- Exploration of the use of scanning probe microscopy to ultrafine particle characterization.
- Use of advanced light sources

- Development of appropriate ultrafine aerosol sampling and preparation techniques for off-line analysis, particularly in the case of low number concentrations and particles sensitive to conventional sample preparation methods.

Background: The behavior of nanoparticles in a range of environments is strongly influenced by their size, morphology, composition and structure. The unique nature of nanometer particles, and those with nanometer-scale structural attributes is widely used in the engineering of nanomaterials, and in many cases, the properties of these materials is closely coupled to the precise nature of the precursor aerosol. Ultrafine particle size, structure, morphology and shape are also associated with their toxicity. It has been speculated that quantum effects within nanoparticles may lead to unique modes of biological activity, and thus toxicity. The toxicity of larger ultrafine particles has been associated with their surface characteristics, which may be dominated by atomic and molecular layers less than 1 nm thick.

An understanding of the behavior of ultrafine particles requires precise characterization of these aspects, and in particular associations between different characteristics within the same particle, requires the application of high resolution off-line analytical techniques. A number of research tools are available that have the potential to characterize nanoparticles at sub-nm spatial resolution, including neutron scattering, scanning probe microscopy and electron microscopy. None of these methods has been applied to ultrafine aerosol analysis on more than an occasional basis, and each technique has the potential to provide significantly more information than is currently realized. Neutron scattering enables the size and shape of nanoparticles to be probed, as well as internal structures at an atomic level. Advanced Light Sources also provide an interesting means of probing particles down to the nm level. These techniques have the potential to provide unique information on ensembles of particles. Microscopy techniques on the other hand have the potential to provide very detailed information on individual particles. Scanning Probe Microscopy (SPM) has the potential to characterize particle size and morphology to sub-nm resolution under atmospheric and liquid conditions with relative ease. Various forms of SPM may have the potential to provide chemical information on individual

particles. Electron microscopy provides a more challenging environment for particle analysis, but offers the potential to characterize the physical and chemical nature of individual particles to a very high degree. Z-contrast imaging and Electron Energy Loss Spectroscopy in the Scanning Transmission Electron Microscope (STEM) provide the means to characterize particle structure, composition and surface activity down to nanometer resolution, and the recent advent of aberration-corrected STEM pushes the analytical spatial resolution down to the sub-Å level.

While advances have been made in the development and utilization of nm-resolution off-line analysis techniques to relatively large particles, their application to ultrafine aerosol characterization brings with it a unique set of challenges. These include collecting and preparing samples for the high vacuum environment within the TEM and STEM, preventing beam-damage within sensitive samples, isolating particle characteristics from those of particle support substrates and understanding the three-dimensional structure of particles using a two-dimensional projection. Further research into the development and application of these and similar off-line techniques will make a major impact on our understanding of the ultrafine particle behavior.

Practical Implications:
- Understand the relationship between particle characteristics (size, morphology, chemistry, structure, activity) and their behavior in a wide range of systems.
- Off-line nm-resolution analytical techniques offer the potential for unprecedented detail in structural, morphological and chemical characterization.
- Off-line techniques such as electron microscopy provide the means to validate particle standards, in terms of particle size, morphology and structure. Additional information is also available on particle chemistry.
- The sub-nm spatial resolution analytical capabilities of off-line techniques such as Scanning Transmission Electron Microscopy provide the only means currently available for refining the properties of engineered nanoparticles.
- Detailed characterization of individual particles and particle ensembles in terms of multiple attributes can potentially enable precise fingerprinting of aerosol sources,

and contribute to source apportionment

- Forensic investigations can benefit from characterizing individual particles in terms of their physical and chemical characteristics.

8 On-line morphological and structural characterization of nanoparticles (Physical Characterization).

Recommendation: On-line methods are needed to characterize the morphology of ultrafine aerosols, including fractal dimension and deviations from a spherical geometry.

Background: The morphology of nanoparticles and ultrafine aerosol particles can be associated with generation/growth processes, the physicochemical nature of nanoparticles, and relationships between measurements of particle diameter, surface-area and mass. At the nanoparticle scale, morphology may be associated with atomic structure within the particle, which may have a profound influence on physicochemical characteristics. At a larger length scale, particle morphology provides a key link between measures of particle diameter using a range of techniques, and is associated with transformations between metrics of number, mass and surface area concentration. There are indications that the fractal dimension of atmospheric agglomerates are dependent on time of day, suggesting that this may be used as an indicator of aerosol sources, or the history of agglomerates prior to sampling. On-line methods for measuring particle morphology in the ultrafine region would contribute to an understanding of the nature and significance of shape in engineered nanoparticles; would further advance the ability to characterize aerosol exposure and flux measurements in terms of particle number, surface area and mass; and would contribute to reconciling disparate measures of aerosol properties that are dependent on particle morphology.

Practical Implications:

- Research into the significance of particle morphology on the properties of nanoparticles.
- Use of rapid feedback on particle morphology and structure to monitor and

control processes generation processes

- Reconciling measurements of particle diameter using different technologies, and refining calculations of particle mass and surface area flux, based on size and number concentration measurements.

- Use of particle morphology, including fractal dimension, in fingerprinting sources.

- Relating morphology to particle generation/growth/transport history

9. Nanoparticle size distribution measurements with high detection efficiencies (Physical Characterization).

Recommendation: Alternative high efficiency techniques are needed to detect sub-3 nm nanoparticles.

Background: The most widely used on-line size distribution measurement techniques for nanoparticles rely on charging, and are subject to ambiguities in the charging level as well as low efficiency counting. Alternative high efficiency techniques are therefore most desirable. Two approaches have been used in an exploratory fashion. The one based on inertial effects is limited by the need to operate at low pressures, which complicates (but does not preclude) the use of high efficiency detectors (CNCs). Inertial separation down to at least 2 nm diameters has been demonstrated in the laboratory, but there is a need to improve its resolution and speed. CNC's have also been used as sizing instruments. For neutral particles, this approach might conceivably be extended down to 1.5-2 nm. At least two approaches have been demonstrated, one based on scanning over the supersaturation variable, the other based on the dependence of the size of the grown drop on that of the original seed nucleus.

Practical Implications:
- Measurements of nanoparticle formation in the clean atmosphere
- Reduced measurement time
- Non-mobility measurements of nanoparticle distributions

- Clean room

- High altitude measurements

- Measurements at reduced pressure (high altitude or vacuum systems)

SPECIFIC RESEARCH NEEDS FOR NANOPARTICLE CHEMICAL CHARACTERIZATION

Background

The last decade has witnessed an explosion in our ability to analyze the chemical composition of aerosol particles. Nanoparticles present an exceptional challenge for chemical analyses because their mass is small. Presently, there is a range of particle mass spectrometer instruments that provide compositional data at the attogram (10^{-18}) level. Those that discriminate by size offer an advantage to selectively analyzing the nanoparticle size fraction. Some particle mass spectrometers provide analysis at the single particle level, while others measure size- and composition-resolved or compound-resolved data for an ensemble of particles. Additionally, recent years have seen a growth in the development of thermal desorption and liquid chromatography techniques for on-line, quantitative monitoring of particulate species concentrations. These automated monitors provide greatly improved time resolution by comparison to traditional sampling methods, but as yet do not target the nanoparticle fraction.

There is a wide range of chemical properties of aerosol particles that can be analyzed with current instruments, but much remains to be done. There is a need for improved quantitation with size resolution. The instruments themselves could be made to be more accessible and easier to use. With analytical capabilities, generally, more is better – greater size range, greater size resolution, better temporal resolution, more compositions or composition classes, and greater morphological characterization. Regarding instrument characteristics, generally less is better – lower cost, less size and weight, lower power requirements, and the ability to operate at lower inlet pressures for novel applications. Specific research needs are enumerated below.

10. On-line, chemical characterization methods for nanoparticle aerosols (Chemical Characterization)

Recommendation: The last few years have shown tremendous advances in on-line chemical characteristics of aerosols, but further efforts are needed to bring these into the realm of nanoparticles. In addition, research is needed to develop completely new techniques specifically designed for nanoparticles.

Background: Over the last decade a number of particle beam mass spectrometers (PBMS) have been developed to provide on-line mass spectrometry analysis of aerosol particles. These instruments are sensitive, but further research is needed to achieve quantitative chemical analysis of nanoparticles. Advances are required in several areas, including particle focusing techniques for the sub-20 nm size range, more efficient particle detection or higher "hit" rates, faster data capture, improved quantitation, and reduction of matrix effects.

The two most common approaches for analyzing particles in mass spectrometers involves 1) using a heated surface to desorb species from the particles and then ionize the evaporated molecules by electron or chemical ionization; and 2) use one or two lasers to desorb and ionize species from the particle ("Laser Desorption-Ionization" or LDI). Both approaches offer certain advantages. Decoupling vaporization and ionization provides higher quantification potential, and a quantitative analysis of the species present in an ensemble of particles over a certain size range. However the heated surface approach is generally limited to analyzing non-refractory species, and thus cannot be used to detect dust or elemental carbon particles. The LDI approach allows for the analysis of elemental carbon, dust, inorganics (including metals), and organics but typically does not provide information that is as quantitative due to shot-to-shot variability in the ion signal due to laser "hot spots". Matrix effects also make quantitation difficult although ensembles of particles of different compositions can be averaged to account for these variations to some extent. For both approaches, one can obtain ion peaks at virtually every m/z making identification of species, in particular organics difficult to impossible.

There are many ways to improve in this area including using chemical ionization to selectively ionize particular classes of organics, selective LDI using various wavelengths, and implementing higher resolution mass spectrometers which provide exact mass information. This area is wide open for investigation.

While PBMS instruments have the analytical sensitivity to capture signals from individual nanoparticles, the "hit rate" (number of individual particles detected per unit time) is low. Those instruments that rely on optical signal from the target particle to trigger the desorption laser are limited by the smallest particle whose light scattering can be effectively detected. These methods critically need a means to detect the presence of particles smaller than 100 nm. Those instruments that rely on random laser firing for preselected particles would benefit from lasers with faster repetition rates and sufficient power for vaporization and ionization. If the speeds of the overall data acquisition system and the associated electronics can be increased, then faster rep rate lasers would allow single particle MS systems to analyze particles at rates above 1000 Hz, opening new doors in probing particle dynamics.

Aerodynamic lenses are used in many particle beam mass spectrometers because they provide enhanced sampling efficiencies for nanoparticles down to ~20 nm. However they are not very effective below this size because of beam broadening from Brownian motion. Potential improvements are the use of electrostatic or electrodynamic focusing, or particle concentrators. Focusing and concentration methods could aid the adaption of existing on-line methods such as thermal desorption, chromatography, photoelectric analyzers, ICPMS could be extended into the nanoparticle size range through advances in nanoparticle sampling. Coupling particle collection and flash evaporation also offers sensitivity enhancements, although the analysis is then semi-continuous rather than real-time.

Research efforts should include development of methods that specifically target nanoparticles. One example is the Thermal Desorption Chemical Ionization Mass Spectrometer (TD-CIMS), which can provide semicontinuous chemical analysis of size-

classified aerosol in the 4-25 nm range, while not attempting to analyze larger particles. Further development of targeted nanoparticles chemical analysis techniques should be pursued.

11.   Sampling of nanoparticles for chemical analyses (Chemical Characterization)

Recommendation: Methods are needed for concentrating and sampling nanoparticles in a manner that is compatible with existing and emerging analytical technologies.

Background: A major challenge of measuring the chemical composition of nanoparticles is their small analyte mass (~ 1 attogram) relative to larger particle sizes.   Sampling in a manner that effectively excludes larger particles and interfering vapors, yet is compatible with the target analysis technique is needed.   Many analytical methods use some sort of separation technique in a liquid, such as HPLC, ion chromatography or capillary electrophoresis.   Bioscience assay methods are evolving rapidly and offer an opportunity for identifying biologically active particle constituents.   Most often these require that the sample be in aqueous or some sort of liquid suspension.   A means of sampling or introducing nanoparticles into the liquid with minimal interference from vapors or larger particles is needed. This is important for both on-line and off-line analysis techniques.

12.   Organic characterization of nanoparticles, including analysis at the molecular level (Chemical Characterization)

Recommendation: Improved methods are needed for identification and quantitation of organic compounds at the compound level and for compound classes.   Methodology needs to be developed for the on-line analysis of single particles, particle ensembles, and small aerosol samples.

Background: Organic matter is an important component of primary and secondary atmospheric aerosols and has the potential for affecting human health and the environment (e.g., visibility and global climate). Marker compounds are needed for

source identification and apportionment. They may be important to pharmaceuticals and nanoparticle manufacture, both for monitoring product quality and assessing worker exposures.

There are currently no methods available for analysis of speciated organic compounds in nanoparticle aerosols on a reasonable time scale. Currently, particle beam mass spectrometers can identify classes of compounds (PAH, oxygenated, soot-like, hydrocarbons). FTIR methods provide data on functional group, but quantification is difficult. Size classified, time integrated samples are difficult to quantify at the compound level because of sampling artifacts and the requirement for larger samples than are readily collected for the atmosphere. There are a few laser-based instruments that employ multiple lasers (one for desorption [IR] and the other for ionization [VUV] to decrease molecule fragmentation) that have shown promise for analysis of organic compounds, but for single-particle analysis these generally require particles larger than nanoparticles. There are other mass spectrometric methods for real-time particle analysis that employ thermal vaporization instead of laser vaporization. The lower evaporation temperatures lead to less decomposition/fragmentation and so provide molecular information on organics that can be quantitative. However single particle information is not obtained, and the chemical resolution of these methods is still insufficient. Another approach is the operation in a semi-continuous mode involving particle collection/vaporization and subsequent analysis. This approach has been demonstrated to analyze a few individual compounds and particles 20 nm and smaller. Another possibility is coupling collection/vaporization with GC/MS for full speciated organic analysis. However this approach does not have the sensitivity for speciated organic analysis of nanoparticles on reasonable time scales, and it cannot analyze most polar organic compounds.

Research needs include methods to quantify target compounds, either needed for a specific application or as markers for a broader range compounds. Generally it is sufficient to acquire this type of data for ensembles of particles. Possible approaches

include selective ionization methods, and MS/MS techniques. The analysis of small amounts of complex mixtures remains a significant challenge.

13. Characterization of ultrafine, light-absorbing carbonaceous particles (Chemical Characterization).

Recommendation: Techniques are needed for the quantification of the mass concentration and the state of mixing of strongly light-absorbing carbonaceous particles, commonly called "black carbon" (BC). These techniques need to be able to analyze BC as found in the atmosphere and as emitted from combustion sources, including characterization of particle size, mixing state, hygroscopicity and capability to act as CCN.

Background: BC particles play an important role in global climate. Diesel nanoparticles, many of which are partly or totally composed of black carbon, may be more toxic to humans than other nanoparticles. The characteristics of these particles that are important for health may not be the same as those that are important to the atmospheric radiation balance. The extent to which BC may be used as a tracer for various combustion sources may depend on how well it can be characterized.

The measurement of black carbon mass concentrations has steadily progressed in the last few years. However current capabilities are poor for the rapid measurement of black carbon size-resolved concentration and state of mixing (external vs. internal, and in the later case, with how much of which species). Although black carbon is an important fraction of the ultrafine aerosol in the atmosphere, its measurement is functionally defined. Correspondences between particle beam MS measurements and filter thermal-optical analyses, incandescence and filter absorbance methods are not known. Advances in measurement of black carbon may permit us to identify mixing state, capability to act as CCN, and light absorption characteristics.

14.   Nanoparticle standards (Chemical Characterization).

Recommendation: Quantitative chemical assay of nanoparticle aerosols will require the development of a nanoparticle standard.   Such a standard will consist of a means to generate particles of known composition in the nanometer size range, coupled to a means to independently verify particle size, concentration and composition.   Research efforts should include designing systems on a scale that can be transportable to allow calibration of instruments in the field.

Background: While the quantitative measurement of particles size is well established, further progress needs to be made in the quantification of chemical composition at the single-particle or small particle ensemble level.   For particle beam systems, quantification is not as straight forward, as it requires an aerosol standard.   For semi-continuous systems, the analytical step may be calibrated through readily available, non-aerosol standards.   Nonetheless, testing of the complete system needs an aerosol standard that generates an appropriate airborne concentration of the target analyte at the required sampling rate and with the appropriate particle size spectrum.

Needed is a nanoparticle generation standard which is accurate, reproducible and representative.   The aerosol standard must have known size and chemical composition, and should cover the size-composition-morphology domain for the application of interest. For ambient aerosol measurements, the standard must also be portable, to allow field calibration checks of instrument performance. Laboratory and field studies are necessary to evaluate interferences and specific analytical difficulties. In particular, standards for photochemically produced organic compounds need to be produced, since these compounds are generally not available from commercial sources.

15.   Reduced size and increased usability (Chemical Characterization)

Recommendation: Research efforts should include the development of specific aerosol instruments with reduced size, weight and power consumption, with lower costs and

increased usability. While such instruments are not expected to provide the wide range of detailed particle characterization possible with larger systems, they can enable measurements for specific applications such as aircraft, balloon packages, and wide-ranging monitoring networks.

Background: Size, weight and power consumption are important instrument characteristics for a number of applications. Airborne environmental measurements and measurements at remote locations place serious limits on these parameters. For the semiconductor industry, space in clean rooms and tools is very limited and very expensive. For both measurements aloft and in the semiconductor industry, measurements must often be performed at pressures substantially below one atmosphere, which may change instrument performance. Robustness under pressure change is rarely taken into consideration in instrument design. Finally, cost is the overarching impediment to more widespread use of real time aerosol instruments. Yet the spatial and temporal variation of ultrafine atmospheric particles is much larger than for accumulation mode aerosols, suggesting that more intensive monitoring is appropriate. Smaller, more cost-effective instrumentation will enable more extensive monitoring, improving knowledge of spatial and temporal variations in global aerosols, and in human exposures. Process monitoring, clean rooms, pharmaceutical manufacturing all need small instruments.

Plasma techniques (laser induced breakdown or laser induced plasma methods) can provide elemental composition in a small package. For particle mass spectrometers, needed improvements include small pumps, and zero-emission system for clean rooms. There is room for developing simplified versions of current mass spectrometer systems in which some performance specifications are reduced (e.g. lower mass resolution, lower size resolution, more limited chemical analysis) to allow for size, weight, power, and cost gains . . There is potential to take advantage of developments in other subfields, such as miniaturized methods for specific target compounds, offered through microchip technology or miniaturized mass spectrometers.

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Relative to particle beam mass spectrometers, semi-continuous instruments (not MS-based) are inexpensive to buy and operate, and the results are straightforward to interpret. There is a need for instruments that do not require high technical skill for operation, that measure one class of compounds in the nanoparticle fraction.

16. Morphologically independent sampling into mass spectrometer systems (Chemical Characterization).

Recommendation: Evaluation of the influence of particle morphology on the quantitative measurement of ultrafine particles is needed. This issue is known to be important for particle beam mass spectrometers, but has not yet been effectively addressed.

Background: Aerosol mass spectrometers of various types dominate the research landscape for performing these measurements. Almost all aerosol mass spectrometers require the introduction of particles into a high-vacuum region and their focusing into a narrow beam. Particle shape is known to affect this focusing, with irregular particles being focused less well than spherical particles. However the data from most instruments is presented "as recorded" since no reliable corrections exist to account for the effect of particle shape. This could lead to large biases in the measured parameters if a fraction of the particles being sampled are irregular, or if the non-sphericity is correlated with size and/or composition. *These biases are probably much worse than those in the previous generation of instruments such as MOUDIs, because the old instruments did not require the tight aerosol beams that most aerosol mass spectrometers require.* Very little is known about the relationship between particle shape and aerodynamic focusing properties and detection efficiency; or about the focusing properties of most emitted and ambient particles. A research program in this area may require computational fluid dynamics studies to relate particle shape and particle focusing properties at a fundamental level. (See Panel 3 report.) It will certainly require laboratory studies, emission source sampling field studies, and ambient sampling field studies combining aerosol mass spectrometry with other detection techniques such as electron microscopy, atomic force microscopy, and mobility classification.

17   Measurements under extreme conditions (Chemical Characterization).

Recommendation: Research efforts are needed specifically to develop methods for the assay of the chemical composition of nanoparticles under the extreme conditions encountered for industrial processing.

Background: Industrial processing for nanoparticles often involve extremes in temperature, pressure or particle concentration (e.g. number concentrations of 10^{12}-10^{15} particles/cm^3 with mass fractions of 10%-20%). The environment can often be corrosive. On-line methods that can accurately measure in this realm, and can tolerate these extreme environments are needed for monitoring processes, and to ensure worker safety.   For process control, response times of milliseconds to seconds are desired.   Desired chemical characteristics of the particles depend on the application, but include mixing state, particle morphology and surface composition.

18.   Improved and rapid data analysis tools (Chemical Characterization)

Recommendation: As analytical capabilities and the speed of data acquisition increases, research efforts must include the development of sophisticated data analysis tools for processing large data sets in real time, and in providing meaningful analysis. The type of categorization of data required, whether by particle classes, compound and size categorization, or individual chemical species concentrations, will depend upon the application.

Background: Real-time single particle mass spectrometers are capable of acquiring the size and chemical composition of thousands of particles in one hour.   The instruments can run 24 hours a day for as long as desired (months, years). However, instruments are often run continuously for months.   There are limited methods available for analyzing the data and acquiring an overview of single particle size and composition relationships. It is important that the data analysis approaches provide a bridge to modeling. Techniques

such as CART, ART2a, other neural network programs, and categorization schemes have been used for this purpose. However, to date, few of these techniques have been applied to the single particle mass spectral data as they are acquired. For the instruments to be truly "real-time", they will need to be able to process the data as fast as it is acquired, ideally providing a rapid picture of the species present in the air immediately. Ideally, as new particle types appear (or certain particle types disappear), one should be able to observe these changes. This type of information would make these instruments ideal for allowing operators of off-line sampling systems to use a "trigger" for when to start sampling, based on the goals of the particular experiment. This multi-tiered (tandem) analysis approach could provide valuable insight into aerosols. Also, being able to trigger particle sampling and acquire an early "warning" of what is present in a given air mass would be extremely important in toxic air plumes such as instances of biological and chemical warfare episodes.

Source apportionment techniques that use the wealth of data from newer aerosol instruments need to be developed and applied. Atmospheric aerosols have important effects on human health, regional visibility, acid and nutrient deposition, and climate. Source apportionment techniques attempt to separate the contributions of various primary and secondary aerosol sources to the observed particle concentrations, with the goal of developing cost-effective control strategies. This research is still fraught with uncertainties, e.g. there are large disagreements between the results of very similar studies. Until recently these techniques have only been performed with long (e.g. 24 hr) averages of aerosol data. However, aerosol concentrations and properties can change in time scales of minutes for an urban area and of hours for the free troposphere. New measurement techniques can record a much larger record of multiple aerosol properties (such as size, composition, concentration, and light-scattering properties) with a time resolution of minutes. There is an opportunity for a quantum leap on the quality of source apportionment results using the information from new aerosol measurements.

19. **Fast (up to 10Hz) temporal resolution for fluxes and aircraft measurements (Chemical Characterization)**

Recommendation: For specific measurements, instruments are needed to provide quantitative measurements with a time response of the order of 10 Hz.

Background: Both aircraft measurements and eddy covariance flux measurements require fast temporal resolution, of the order of 10 Hz. Aircraft measurements are key to understanding the source and processes that contribute to ambient aerosol levels, thanks to their wide spatial coverage. With typical speeds of 100 m/s for research aircraft, measurements need to be fast (~ 1 second) in order not to smear the features and gradients in ambient aerosol concentrations.

In addition, techniques for the direct measurement of nanoparticle aerosol fluxes need to be developed and validated. A large fraction of atmospheric nanoparticles are either emitted from the Earth's surface (e.g. in urban areas) or removed from the atmosphere via dry deposition to the surface. The direct quantification of these processes and their parameterization is of critical importance for our understanding of many aerosol sources and effects, as well as for the development of improved aerosol air quality models; our understanding of many trace gases in the Earth's atmosphere has been greatly improved by flux measurements. While there has been much progress in the measurement of aerosol concentrations and properties in field settings, the measurement of these exchange fluxes is in its infancy. Size- and chemically-resolved fluxes are especially lacking. Existing and new aerosol measurement techniques with fast time resolution (> 1 Hz) need to be adapted to the measurement of aerosol fluxes.

20. Direct measures of targeted physico-chemical properties (Chemical Characterization)

Recommendation: For many applications it would be sufficient to measure an integral property of the aerosol, such as the hydrogen to carbon ratio in newly emitted soot particles, or the concentration of organic acids or inorganic ion in nanoparticles, or the difference in the bulk composition of particles that form cloud droplets and those that are

not activated. In particular, the quantitative measurement of the water content of aerosols has lagged behind that of most other components. Some new techniques for performing this measurement have recently emerged. These techniques need to be validated, and new techniques may need to be developed. Instruments that target specific physico-chemical properties may offer advantages in ease of quantitation, size, power and cost.

21. Methods of on-line analysis of nanoparticle surface composition (Chemical Characterization)

Recommendation: There is a need for methods of on-line analysis of nanoparticle surface composition, including elemental and molecular information on inorganic and organic particles.

Background: Many of the important properties of particles depend on their surface structure and chemical composition. Currently, surface analysis requires that samples be collected, transported, and analyzed by microscopy, which only works for particles with highly stable surfaces. There are currently no on-line methods for surface composition analysis, either for nanoparticles or larger particles. Some information can be obtained by LDI analysis using low laser powers, but this method is not reliable and has not been thoroughly developed. There have been few attempts to develop optical or electron spectroscopies commonly used in the surface science community for on-line analysis of particle surface composition.

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2. FUNDAMENTALS OF NANOPARTICLE AEROSOL FORMATION

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INTRODUCTION AND OVERVIEW

Particle formation in gases takes place through various routes (Fig. 2-1): In cloud chamber experiments, C.T.R. Wilson showed that the *nucleation* process depended on the saturation ratio. The air in a chamber was first saturated with water vapor. Small particles initially present were cleared by repeatedly expanding the chamber contents and allowing the drops that formed to settle. With the clean system, there were two types of nuclei. The first acted at smaller values of the supersaturation; these were ionized air molecules that were continuously regenerated. At much higher supersaturations, dense clouds of very small particles formed; uncharged water molecules served as the nuclei. Advances in computational quantum chemistry and instrumentation may permit elucidation of the nature of the atmospheric chemical components-charged and uncharged-that serve as condensation and cloud condensation nuclei. This in turn will permit better estimates of aerosol effects on climate and the sources of the aerosol, major uncertainties in current climate models.

There are many examples of chemically reacting gases that generate nanoparticles through complex *chemical reaction pathways*. Soot formation is the example that has been studied most because of its environmental and industrial importance. Despite the attention it has received, controversy remains concerning the basic chemical steps that lead to particle formation, and the chemical nature and structure of the soot particles that are usually present as nanoparticle chain aggregates. Experimental and conceptual difficulties abound, but the payoff in fuel efficiency and environmental protection continue to stimulate research in this field.

Over the last few decades, much has been learned about the formation of small solid particles of inorganic oxides, based on the *collision-coalescence mechanism*. This is a limiting case in which the chemical reactions that lead to particle formation are very

rapid, and all particles stick when they collide (zero activation energy for nucleation). Based on this idea, the Smoluchowski theory of coagulation can be generalized to incorporate the rate of coalescence in the equations of aerosol dynamics (EAD). In the past, coalescence rates have been calculated from methods based on ceramic sintering theory developed for coarse particles. However, for nanoparticle coalescence, continuum models may not apply, and molecular dynamics (MD) methods show promise. MD calculations also have application to the characterization of chain aggregates of nanoparticles, including their tensile strength and elastic modulus; measurements of the dynamic behavior (in addition to morphology) of individual chain aggregates have applications to new materials development and the monitoring..

Advances in our ability to characterize the morphology of nanoparticle chain aggregates, for example, through the fractal dimension, has motivated more research on aggregate structure. This has led to the discovery of "superaggregates", larger scale structures than the usual agglomerates that have been studied before. Both experimental and theoretical research is underway in this emerging field. Finally, characterization of the optical cross-section of soot agglomerates over wider wavelength ranges is needed in applications to radiant transport through smoke and postflame gases.

NUCLEATION

Properties and Effects of Nanoclusters

(1) Research recommendation: Modern computational studies of nanoclusters

Employ modern computational techniques (including methods based on quantum theory) to calculate the basic structures and thermodynamic properties of nanoclusters—charged and neutral—that are likely to serve as nuclei for atmospheric aerosol formation.
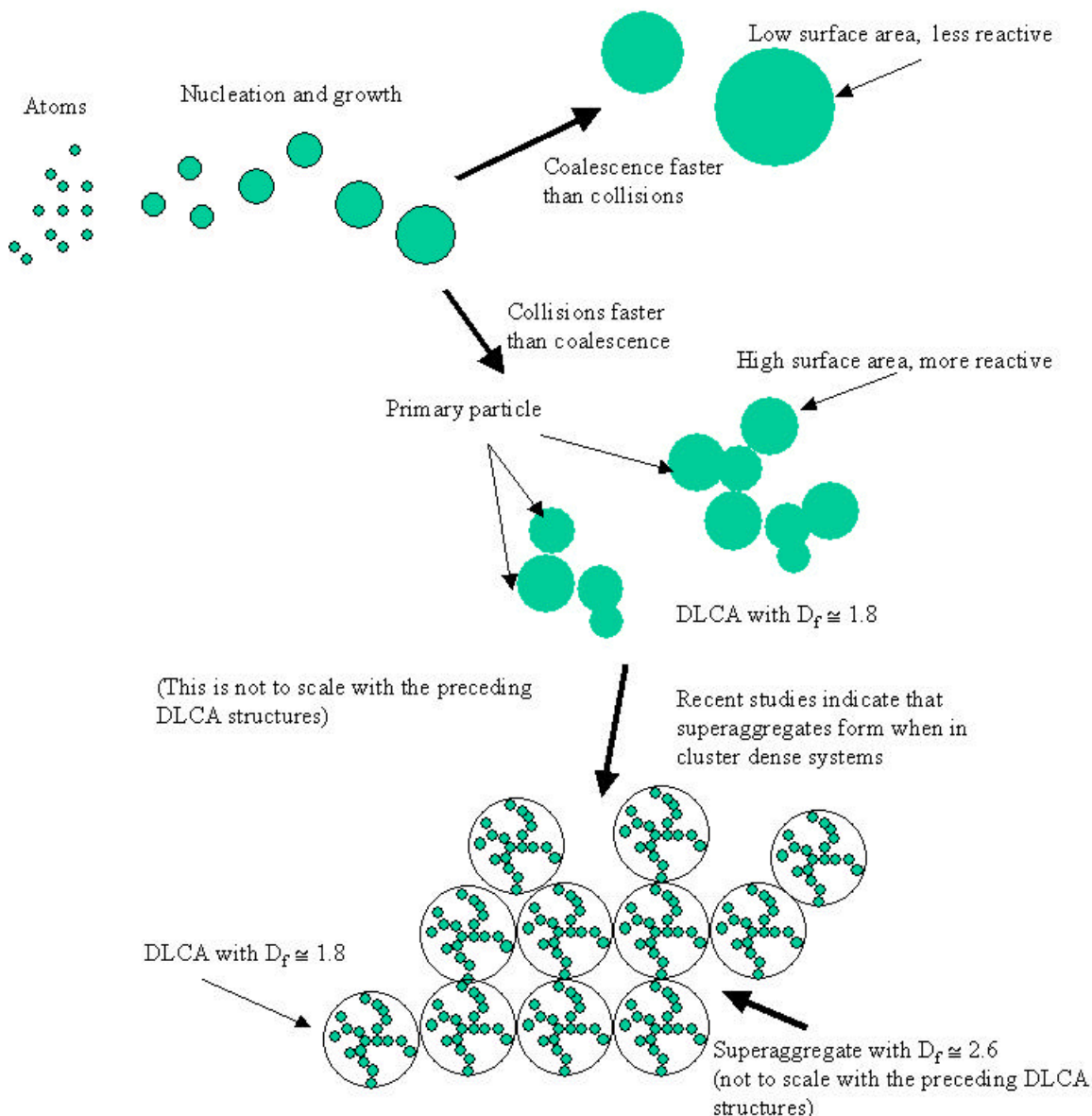
Figure 2-1. Nucleation and coagulative growth of aerosols – Large range of length scales is involved from 0.2 nm to 10,000 nm. DLCA stands for diffusion limited cluster aggregate.

Background

The formation of ultrafine or nano-particles involves nucleation processes, most of which are poorly understood. The phase changes involved in nucleation, and in other processes such as freezing and deliquescence, pass through a stage of molecular aggregation involving embryonic nano-clusters. The critical sizes of typical nucleation embryos under

atmospheric conditions are predicted to be in the range of two to ten molecules. This ephemeral aerosol is difficult to study experimentally. However, a variety of new computational-based techniques are becoming available, in conjunction with advanced computer processors that allow such clusters to be simulated numerically. The theoretical approaches that are usually applied to small clusters of environmental importance, or particle formation in combustion systems, need to be refined and tested. For this purpose, well-designed laboratory and atmospheric measurements are needed that are capable of characterizing matter in its smallest aggregate states. Both neutral and charged nano-clusters should be considered.

An extensive literature—both experimental and computational—exists for charged ionic species ranging from simple ions to large molecular clusters with multiple inorganic and organic ligands. This methodology should be applied to the massive ionic clusters known to exist throughout the atmosphere. The nucleation of vapors onto these clusters represents a source of particles that can have environmental implications. The thermodynamic properties and size distributions—and corresponding nucleation rates—of such clusters are accessible through molecular structure and dynamics simulations, owing to the relative stability of charged species relative to their neutral equivalents. ionic clusters that lie within the nucleation size range are quite amenable to computational analysis using several techniques, from *ab initio* to density functional approaches.

Practical Application

There is evidence that ionization—both natural ions in air, and chemiions generated by combustion processes—are involved in the formation of nanoclusters and embryonic aerosols in the atmosphere. For example, measurements in the exhaust streams of jet engines indicate that chemiionization plays an important role in controlling the number of particles emitted. Widespread nucleation "events" that are observed in Earth's boundary layer, and in upper air layers as well, have been linked to ambient charged nanoclusters. This points to the need for experimental characterization and microphysical modeling of localized nanoparticle formation processes. A major uncertainty concerning the effect of

human activities on global climate has been the *indirect* effects associated with aerosols. Indirect effects include modification of cloud cover and changes in the hydrologic cycle. In this respect, the formation of condensation nuclei from NOx, SO2, NH3 and other gases emitted by man-made sources, may play a major role. Better data on atmospheric nucleation will enable us to put tighter limits on the uncertainties and thereby permit better policy decisions. The same analytical approaches would be relevant to a wide range of nanocluster systems, including applications in engineering and manufacturing processes.

(2) Research recommendation: Effects on global climate

Study the connections between aerosol formation on charged ionic clusters and global climate change, related to the growth of nanoclusters into condensation nuclei (CN) and cloud condensation nuclei (CCN). Likewise, investigate the influences of human activities on the production of nanoclusters, and their effects on atmospheric radiation, clouds, and regional climate.

Background

Recently, the modulation of galactic cosmic ray fluxes by solar variations has been linked to climate change through ion/aerosol/cloud processes. Recent statistical studies have identified an apparent correlation between satellite measurements of global cloud coverage and the solar 11-year cycle in galactic cosmic radiation (GCR) intensities. The GCRs are modulated by the solar cycle through the mechanism of the solar wind interaction with Earth's magnetosphere. While still uncertain, several climate-related effects have been noted in the literature, including synchronous changes in the properties of stratospheric aerosols. At least two mechanisms have been identified that might explain such a correlation, and both mechanisms are based on the formation of charged clusters by cosmic rays.

Cosmic rays continuously create ions throughout the atmosphere, resulting in a ubiquitous population of large molecular clusters formed about these ions. The clusters are composed of the common environmental substances such as water, nitrates and

sulfates, ammonium, and various organic compounds. By absorbing abundant background gases, the clusters can form larger particles and affect the microphysical and radiative properties of clouds.

Practical Application

The links between galactic cosmic radiation, solar variability and climate change are controversial and require more study in light of proposed regulations to mitigate climate change associated with human activities. The issue could be studied through modeling and data analysis, to identify and quantify potential climate-change mechanisms in a systematic manner. Anthropogenic processes that affect atmospheric ionization and aerosol formation (e.g., combustion emissions from aircraft) should also be assessed as a competing cause of environmental change.

B. Effects of Turbulence on Nucleation Rates

(3) Research recommendation: Theoretical and experimental studies of nucleation in turbulent gases

Theoretical and experimental studies are needed of the effects of turbulent fluctuations in concentration and temperature on nucleation rates in supersaturated gases. Geometric configurations and regimes applicable to technological and atmospheric systems such as jets should be investigated.

Background

Calculations indicate that turbulent fluctuations can significantly affect nucleation rates when a warm vapor is mixed with a cool gas. The calculations were made for water vapor nucleation in the shear layer of a free turbulent jet, 5 to10 nozzle diameters from the nozzle exit. This geometry is of interest in applications to fugitive emissions of hot vapors to the atmosphere, emissions from mobile sources (vehicles and aircraft) and for industrial systems such as aerosol reactors in which gas streams are mixed and particles form. Nucleation rates were calculated using measured probability distribution functions for the temperature fluctuations; these rates were compared with rates based on the mean

temperature and concentration profiles in the same region of the shear layer. The calculations were made using the classical Becker-Doring theory which captures the strong non-linear dependence of the nucleation rate on gas temperature and supersaturation. Both the concentration and temperature appear in the activation energy of the expression for the rate of nucleation.

Turbulent fluctuations markedly affected the nucleation rate profile across the shear layer. The presence of turbulence led to a very strong peak in a narrow region inside the

layer compared with calculations based on the mean concentration and temperature profiles. Although there were large effects on *local* nucleation rates, turbulence had a much smaller effect on the *overall* rate of particle formation across the layer. Further calculations are needed over a wider range of parameter space for different substances and aerodynamic regimes including the atmospheric boundary layer. Measurements of local particle nucleation rates in turbulent gases have not been reported and would represent an important contribution to the field.

SOOT FORMATION: CHEMICAL NUCLEATION

(4) Research recommendation: Soot reactors, measurement methods, chemical pathways
Improved reactors, methods of aerosol measurement and testable hypotheses are needed for investigating soot inception which remains one of the outstanding problems in combustion. Its solution would have important practical applications in the design of combustors and of fuel additives to reduce soot emission.

Background
There is a major gap in our understanding of soot inception or soot nucleation. One suggested pathway to the formation of soot is through the growth of ever increasing PAH structures. Early "soot" sampled from a diffusion flame and analyzed by laser microprobe mass spectroscopy appear to be consistent with this model. One puzzling

aspect is the dominance of 5 ring, 6 ring, and 7 ring species that would be expected to be in the gas phase at temperatures above $800^{o}C$.

Another proposed pathway proposed involves the growth of structures involving 2 and 3 ring PAHs held together by carbon-carbon bonds. The predicted molecular weight distribution is in qualitative agreement with experimental data. More recent developments of this approach utilizing Monte Carlo methods has allowed an estimation of the three dimensional structure of this intermediate structure and how it changes depending on the nature of the fuel.

While there is a limited effort in modeling the soot inception, more study is needed both in understanding the basic chemical pathways in the flame controlling the concentration of the smaller species as well as understanding routes to large structures that are quasi-stable at the high temperatures and ultimately become soot..

There are a number of promising experimental developments that might help bridge the gap between the largest molecules in the flame and the smallest particles. One of these is the nano-particle sizers including a commercial nano-DMA capable of measuring particles as small as 2 – 3 nm and a high flow research nano-DMA capable of measuring sizes as small as 1 nm. A recently developed in situ electrical mobility measurement utilizes a pulse laser to ionize the nm size incipient soot particle and a tungsten electrode/oscilloscope to measure the current versus time. An abrupt increase in the electrical observed by this technique appears to be the best optical diagnostic for the inception of the smallest soot particles. One challenge of using the nano-DMAs is the need to rapidly dilute the smoke to avoid vapor nucleation, condensation, and particle coagulation. Progress has been made in developing a rapid quench diluter that minimizes the coagulation of the incipient particles and this advance promises to promote more use of nano-DMAs for soot studies.

Another promising approach is the use of well-stirred reactors for studying the kinetics of soot formation. The reactor has the advantage of having a mixing time that is fast

compared the soot formation time. The plug flow section allows for the study of the species concentration versus time. It is also possible to insert additives in the transition between the two reactor sections for help in characterizing the kinetics of key species.

The analysis of PAHs with up to seven rings has become quantitative with development of Standard Reference Samples and the use of selective ion mass spectroscopy. For larger PAH structures as well as combination aliphatic-PAH structures, the analysis is much more challenging because of the large number of isomers and the lack of standards. However, less detailed information on the molecular weight distribution obtained by liquid chromatography could be of great use.

There are also a number of other simpler measurements that could provide insight into the nature of the soot inception chemistry. These include the measurement of the carbon-hydrogen ratio, the thermogravimetric characteristics of the particulate, and the organic-graphitic fraction. A major challenge in chemical analysis is to minimize sampling artifacts such as vapor condensation on the particles being collected.

INORGANIC OXIDE AND METAL NANOPARTICLE FORMATION: COLLISION-COALESCENCE PROCESSES

(5) Research recommendation: Application of computational statistical mechanics to nanoparticle behavior

There is a need for the application of computational statistical mechanical tools (e.g., molecular dynamics and Monte Carlo techniques) to the estimation of properties of nanoparticles, both thermodynamic (e.g. surface tension and melting point) and transport (e.g. diffusion coefficient and viscosity) that depend on particle size.

Background

As particle size is reduced to the nanoscale, a substantial fraction of the molecules in the particles are present near the surface; thermodynamic and transport properties of the

particle phase material begin to vary from the bulk values. The effects of particle size on these properties can be estimated using several approaches. In the most common, the capillarity approximation, it is assumed that a thermodynamic property of a nanoparticle can be written as the sum of the property of the bulk material and the property of the interface. In this approximation, the free energy per mole of the material inside a nanoparticle is assumed to be independent of particle size and equal to that of the bulk material. Similarly, the free energy per unit surface area is assumed to be independent of particle size. Both of these approximations break down as particle size decreases, and there is controversy over the size at which the approximations fail. Depending on the material and the temperature, the critical size may vary from 2 to 50 nm.

A molecular approach to calculating particle size effects on properties may be able to overcome the shortcomings of the capillarity approximation. This might include *ab initio* and density functional methods to compute free energies, and or, as a training set to develop accurate interatomic potentials. Once the interatomic potential is available, molecular dynamics (MD) and/or Monte Carlo (MC) simulations can be used for the estimation of properties of interest as a function of particle size, structure, temperature and other parameters. Accurate potentials for more materials, valid over wide ranges of temperatures and densities, are needed to explore the full potential of these simulation techniques. There are important applications of such simulations to nanoparticle aerosols: For example, current models for the rate of coalescence of nanoparticles in contact were developed for micron-sized ceramic powders. They almost certainly begin to break down in the nano range. *Molecular dynamics simulations may provide fundamental parameters needed to employ the equations of aerosol dynamics in the prediction of primary particle sizes for particles smaller than 5 to 10 nm.* The computational methods are also well-suited to the study of nanoparticles with structured coatings for sizes smaller than 10 nm. Simulations for larger particles, of the order of ten's of nanometers, will require the use of massively parallel computers and fast algorithms. Materials of interest include metal oxide nanoparticles which have applications to advanced ceramic materials, catalysts and sensor coatings.

(6) Research recommendation: Experimental studies of dynamics of individual chain aggregates

There is a need to measure the dynamic behavior of individual nanoparticle chain aggregates (NCA) and their networks. Applications are to the behavior of nanocomposite materials, break-up of aggregates by impaction and shear and monitoring the properties of nanoparticle powdered materials produced in aerosol reactors.

Background

There have been many morphological studies of chain aggregates. Almost all involved the static characterization of aggregate structures based on fractal dimension and light scattering. Studies have shown that NCA have unusual *dynamic* properties when stressed. The original studies were made by depositing NCA on an electron microscope grid coated with a carbon/Formvar film. As a result of holes that developed in the film while in the electron microscope, the NCA came under tension and stretched until they became taut. At some point they broke and rapidly contracted, displaying unexpected elastic properties. More quantitative studies of this phenomenon are needed. Several methods are possible: (1) Some researchers have used a nanostructure manipulation device that consists of a 3 mm ductile alloy disc with a slit a few microns wide. Aggregates are deposited across the slit which is mounted in a commercial electron microscope specimen holder; aggregate stretching is observed as the slit is widened in the electron microscope. (2) Atomic force microscopy and similar instruments may be applicable. The results have applications to understanding and improving the properties of nanocomposite materials including elastomers composed of blends of polymers and reinforcing fillers such as carbon black and fumed silica. Other possible applications are to the behavior of flexible coatings of nanoparticles on substrates and possibly, chemical and mechanical polishing using nanoparticles such as silica. It may prove useful to characterize reinforcing fillers by monitoring their dynamic properties both in manufacture and use.

(7) Research recommendation: Molecular dynamics of effects of stress on chain aggregates

Use molecular dynamics calculations to study the effects of applying stress on individual chains of nanoparticles to determine their elastic modulus, tensile strength and locus of fracture.

Background

Much work has been done on the mechanisms of formation and morphology of nanoparticle chain aggregates (NCA); nevertheless little is known about their dynamic properties such as their behavior under stress cycles or the energy input necessary for their breakage. Such information would be valuable in the emerging fields of nanocomposite materials, NCA interaction with cells, nanoparticle sampling by impaction from flowing gases.

Computational studies at the atomistic level can be employed for the estimation of interparticle bond energies as a function of particle size, structure and composition. Such studies have the potential to reveal the detailed mechanism of individual NCA breakage when tensile or shear stress is applied to them. Of particular interest are studies of aggregates made of carbon, silica and metal oxides (such as titania and alumina) and metals because of their commercial applications. Interatomic potentials are available for these materials and a number of studies simulating the bulk properties have been made. There is a need for computational studies of the energetics of nanoparticle bonding in aggregates and also their behavior under mechanical and/or thermal stress. In these studies, parameters such as particle sintering temperature and time need to be considered. The influence of thin oxide layers and other impurities on interactions between the primary particles composing the aggregates would be of importance in commercial applications.

AGGREGATE FORMATION

A. Superaggregate Formation

(8) Research recommendation: Studies of superaggregates overall fractal dimension different from the fractal dimension of the smaller aggregates that compose it. In the

limit of cluster volume fraction near unity, gelation can occur. There is a need to understand the growth kinetics and resulting morphologies of such systems.

Background

A number of recent experiments have indicated the presence of anomalously large aggregates in a number of combustion situations. Microsecond flash photography has been used to detect the formation of very large aggregates and a cylindrical gel-like soot structure in the plume of a diffusion flames. Small angle light scattering measurements established that the large aggregates are produced within the flame. This occurs generally for fuels with a high sooting tendency. Supersoot balls on the order of mms in diameter have been produced by turbulent diffusion flames with a heat release rate of about 1 Megawatt. Both fiber-like and hollow cylinder structures up to a cm in length have been observed in silane flames. Burning under microgravity conditions results in a "crown" structure of soot bursting out of an acetylene flame. The transition from 1-g to micro-g combustion for a 30 % silane/N_2 fuel resulted in a 10 fold broadening of the plume and an increase in size of the aggregates from several micrometers to a low density structure as wide as the 8 mm plume.

Current research suggests that large aggregates form when the aggregate volume function becomes large, i.e., the system becomes "cluster dense." This can occur in any solid particle system because these aggregates have fractal dimensionalities less than the spatial dimensionality, hence the effective aggregate volume fraction increases as the system aggregates.

Current theories for aggregation kinetics involving the Smoluchowski equation are not adequate to describe dense systems. Hence both experimental and theoretical research are needed for this cluster dense regime. While there has been some success in modeling the growth dynamics of the agglomerates, quantitative results are lacking. Brownian dynamics even allowing for gelation does not appear to account for the rapid growth from a 30 nm structure to a 1 cm structure in a few tenths of a second. Other particle growth processes are probably involved. For the silane flame, flame temperature plays a key role

in determining whether the primary spheres fuse to form a fiber like particle or grow as a low density structure. Quantitative studies will require more rigorous flame modeling including the flow and gradients likely to affect the trajectory of the growing agglomerates.

Potential impacts of better understanding of these phenomena are to radiative transport in sooty flames with superaggregates, the use of aerosol gelation to make low density, high purity materials akin to aerogels, and the development of more sensitive smoke detectors for microgravity application.

B. Aggregate Transport and Aggregation Kinetics

(9) Research recommendation: Aggregate transport properties

Aggregate morphology can be described by at least three parameters: primary particle size, aggregate size and effective fractal dimension. There is a need to better understand both random diffusive and directed phoretic transport of these aggregates over the entire range of Knudsen numbers based on primary particle and aggregate sizes. These results should be applied to improved calculations of aggregation kinetics.

Background

Aggregates have at least two length scales, the primary particle size and the aggregate size. Thus an aggregate suspended in a gas has two Knudsen numbers, the ratio of the gas mean free path to either length scale. Transport of aggregates, Brownian diffusion, thermophoretic and photophoretic, depends on these Knudsen numbers and is poorly understood across the range of Knudsen number regimes. Some progress has been made for aggregates in the continuum regime but there is a great need for more work for aggregates in the crossover and free molecular regimes, especially for large aggregates. It is also important to study transport as a function aggregate fractal dimension since the properties appear to have a distinct difference above and below fractal dimension 2. Both experiments and theoretical efforts, most likely simulations, are needed to elucidate these phenomena. Brownian transport has direct input to the description of aggregation

kinetics. Thus studies that consider both and correlate them should prove to be especially useful.

AGGREGATE SCATTERING AND ABSORPTION

(10) Research recommendation: Optical cross-section of aggregates

There is a need to characterize the optical cross section of soot agglomerates from the uv to at least 10 micrometers, for both soot in the flame and post-flame soot and to develop quantitative models for computing these properties. The data and models are needed for modeling radiant heat transport within a flame or to a target, radiant transport within the atmosphere, visibility through smoke, and for estimating soot concentration from optical measurements including remote sensing. Other potential impacts include new optical diagnostics for measuring the primary sphere size in agglomerate, a more accurate determination of the refractive index of soot, and a quantitative calculation method for validating experimental data and for predicting optical properties where data are not available.

Background

Since soot (often called "black carbon" or "elemental carbon") dominates light absorption by the atmospheric aerosol, knowledge of its optical properties is essential to studies of the global energy budget, the interpretation of remote sensing observations, and visibility degradation by the atmospheric aerosol. The link between the properties observed in flames and in the atmosphere needs to be established to quantify the relationship between emission characteristics and environmental impacts. There have been several measurements of the mass specific extinction coefficient of post flame soot at visible wavelengths, a few data sets in the near IR, and a single set in the mid IR. All of these measurements are limited to post-flame soot at near ambient conditions. A few measurements have been made on the specific extinction of smoke produced by an underventilated diffusion flame. The data for the single scattering albedo are mostly at

visible wavelengths with one set in the near IR. The data are primarily for polydisperse smoke coming from laminar diffusion flames.

There is an urgent need for data on the specific extinction coefficient at elevated temperature. The measurements mentioned above are more than 50 % larger than other values widely used. There is reluctance to use the newer value because it is based on post-flame soot and there is concern that the properties are affected by the condensation of low vapor pressure species including PAH on the soot. This optical property is a key quantity for modeling radiative transport in the flame. Ultimately there needs to be a closure experiment involving the measurement of the temperature field, soot volume fraction distribution, and the radiative flux coupled with the predicted radiant flux based on the measured temperature and soot volume fraction together with the soot optical properties.

There is a need for scattering data in the mid IR. For agglomerates with a fractal dimension of about 1.8, the single scattering albedo is predicted to vary roughly as $1/\lambda$. One recent study found the single scattering albedo to be constant from 633 nm to 856 nm. There is a need to repeat these experiments and obtain data in the mid-IR.

There is also a need for improved methods of calculating optical properties of agglomerates. The Rayleigh-Debye scattering approximation has been a useful first order approximation for computing agglomerate light scattering. In this approximation, each primary sphere acts as a dipole source of scattered radiation excited solely by the incident field. This approach has been useful for determining the fractal dimension and radius of gyration of agglomerates based on light scattering. However, the agreement between theory and experiment is not good for the total scattering and the absorption cross sections (difference in the range of 30 % to 70 %). This theory is not able to provide even a first order estimate of the polarization ratio or the depolarization characteristics of the soot. Coupled dipole methods have been developed which include the effect of the local field emitted by each particle in the agglomerate. For relatively small agglomerates, an exact solution of the scattering equation has even been developed. There has been

little effort to compare predictions with experiment; the implications of the few comparisons that have been made are tentative because the calculations are typically carried out for individual clusters and the experiments are performed on polydisperse agglomerates. There are confounding factors including the uncertainty of the refractive index of the soot particle, the effect of the asphericity and overlap of the primary particles, and the condensation of organics or moisture on the soot particle. There is a need for measurements and computations of nearly monodisperse soot agglomerates. It would be helpful to include agglomerate particles made of a better defined material such as silica or silver so that the refractive index uncertainty is not an issue. Metal agglomerates would also provide a test of the coupled dipole methods, since in this case the large imaginary part of the refractive index is predicted to lead to a singular behavior for which only the exact coupled dipole solution method would provide quantitative results.

The discussion above has focused on light in the visible or IR ranges. There is also potential for small angle x-ray and neutron scattering, which will provide detailed information on the primary particle because of the small wavelength. A second advantage of the x-ray sources is that Rayleigh-Debye theory should be valid because the refractive index for the x-rays is close to unity.

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3. COMPUTATIONAL SIMULATION OF AEROSOL BEHAVIOR

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Introduction

Computational simulation is essential in the predictive modeling of aerosol behavior in natural and technological processes and in analyzing experimental data for such systems. This Panel report reviews research needs for (1) numerical methods and fundamental modeling including computational fluid dynamics (CFD) and (2) atmospheric nanoparticle aerosol simulation.

Existing methods and codes may have to be modified to deal with nanoparticle aerosols: (i) In the nanoparticle size range, collision and coagulation processes usually determine the particle size distribution and chemical composition as a function of particle size. Significant uncertainties remain in expressions for aerosol collision rates in the transition and free molecule ranges which determine nanoparticle collision dynamics. (ii) Problems that directly involve molecular phenomena play a key role in the nanoparticle size range. For example, the formation of solid nanoparticles may require molecular dynamic methods to analyze coalescence rates which determine primary particle size. (iii) Nucleation processes also involve the introduction of molecular phenomena in the aerosol dynamic equations. (See also the Panel 2 and 4 reports for discussions of nucleation and coagulation processes).

Suitable modifications of the aerosol General Dynamic Equation (GDE) that take into account these phenomena must be followed by the development of accurate and efficient numerical methods for its solution. Improved aerosol dynamic simulation codes need to be interfaced with suitable CFD codes for applications to such problems as aerosol reactor design (see also Panel 4 report) and atmospheric ultrafine aerosol behavior (see also Panel 5 report). Finally, a major effort is needed to develop a better understanding of the dynamics of aerosol collision processes in turbulent gases.

Numerical Methods and Fundamental Modeling including CFD

Recommendations:

Fundamental Models

Research is needed to better understand the variation of hydrodynamic forces (drag, lift, Basset, etc.) as well as surface, Brownian, electrical, and thermophoretic forces, and capillary effects with nanoparticle size, shape and the flow conditions. This includes: (1) slip correction for drag, lift for nonspherical nanoparticles and aggregates of nanoparticles; and (2) Brownian, electrical and thermophoretic forces for nonspherical nanoparticles and aggregates of nanoparticles.

Also needed are improved models for nanoparticle population dynamics that include nucleation rate in nanoparticle synthesis reactors, particle growth due to humidity, nanoparticle transport properties, nanoparticle growth by Brownian and turbulent coagulation, particle growth with heterogeneous reaction, and improved rate laws for nanoparticle restructuring and sintering. (See also the Panel 2 and 4 reports).

Develop a fundamental understanding of nanoparticle interaction with turbulence for application to nanoparticle dispersion, transport and deposition in turbulent flows.

Computational Models

Continue development of reliable aerosol dynamic models for simulating transport, deposition, coagulation, and dispersion of nanoparticles of different shapes, including aggregates, for applications that include: (1) nanoparticle instrumentation for sampling, sensing, dilution, focusing, mixing, etc.; (2) nanoparticle behavior in passages with complex geometry such as the human respiratory tract, aerosol transport/delivery systems, energy systems; and (3) nanoparticle behavior in chemically reacting gases with applications to combustors and aerosol reactors.

Develop efficient numerical schemes for simulating nanoparticle transport and deposition, including schemes with controlled numerical diffusion for Eulerian

simulation of nanoparticle aerosol dynamics as well as Lagrangian nanoparticle simulation procedures.

Develop aerosol dynamic codes that include processes such as nucleation, condensation, coagulation, capable of integration with CFD codes. This includes computational models for nanoparticles in reactive and non-reactive laminar and turbulent flows, comparison with experimental data and code validation and effective visualization user interface.

Background:

The conservation equation that governs aerosol dynamics is termed the General Dynamic Equation (GDE) (See also the *Terminology* section). Expressed in its most basic form as a balance on particle number concentration (and particle composition for multicomponent particles) as a function of particle size, the GDE includes all processes that affect the aerosol size and composition distribution function, such as coagulation and growth/evaporation and source and removal processes. For most systems of practical interest, the GDE must be solved numerically. The challenges in numerical solution are significant because particle diameters and particle number concentrations in typical applications can range over several orders of magnitude. When multicomponent particles undergo coagulation, keeping track of the evolving composition distribution of the aerosol population is especially demanding.

There are essentially three approaches that have been used for solving the GDE numerically: (1) assuming a size distribution *a priori* such as log-normal, and determining the evolution of the parameters of the distribution; (2) writing equations for the moments of the size distribution and solving the dynamic equations for these moments; and (3) the *sectional approach*, which is the most general but also the most computationally demanding, in which the size distribution is segmented into a number of sections, or bins, and the conservation equation is transformed into a set of coupled equations for the concentrations in the sections. The most advanced application couples the sectional and moment methods to generate equations for the evolving moments within each of the sections. The global number distribution of tropospheric aerosols shown in Figure 3 was computed with this combined approach. Most current work in modeling aerosol evolution in the atmosphere and in chemical reactors follows approaches (2) or

(3). Yet, significant challenges remain in devising accurate and efficient numerical techniques for solving the GDE. Because solving the GDE underpins modeling aerosol processes ranging from aerosol reactors to the atmosphere, developing such techniques represents a high priority research need.

Areas that require special attention to improve simulation include the following:

There has been some success in applications of numerical modeling of nanoparticle behavior to aerosol instrumentation. Examples are to low pressure virtual impactors (Figure 1) and differential mobility analyzers (DMAs), making it possible to explain experimental observations and improve instrument performance. However, interactions of nanoparticles/agglomerates with flows (especially turbulent) and external force fields are poorly understood and appropriate computer simulation procedures are lacking.

In addition, nanoparticle aggregate transport in external force fields is not well understood. Some researchers have used commercial codes for the external field computation and developed their own codes for particle trajectory calculation (either Monte Carlo simulation or convective-diffusion modeling). In these analyses, however, effects of external fields are essentially decoupled from particle dynamics. For nanoparticles/aggregates at high concentrations (often encountered in practical applications), the interaction of nanoparticle aggregates with external fields is poorly understood. Decoupling risks the omission of potentially important effects. The situation worsens when nanoparticles/aggregates, especially multicomponent, are exposed to chemically reactive environments.

Current CFD codes provide reasonable results for the flow and thermal behavior of carrier gases in complex passages. However, there is no commercial CFD code capable of handling nanoparticle aerosol dynamics. In particular, comparison with experimental data for code validation is generally lacking, and a convenient interface to account for the coupling effect is not available.

Summarizing, examples of applications that would benefit from improvements in aerosol dynamic simulation methods are: (1) aircraft aerosol sampling probe design, including temperature rise, compressibility effects, sudden changes in flow direction, etc.; (2)

modeling emissions from combustion sources such as aircraft engines, diesel engines, incinerators, power stations; (3) design of nanoparticle aerosol reactors for material synthesis; (4) design of nanoparticle instrumentation including supersonic impactors, DMAs, condensation particle counters, focused nanoparticle beam generators; (5) modeling of personal exposure including lung deposition; and (6) simulation of multi-scale dispersion in buildings, street canyons, and cities.

Atmospheric Aerosol Simulation

1. Modeling of nanoparticles together with the rest of the particulate matter (PM)

Recommendations: Extension of currently available 3D atmospheric aerosol models to the nanoparticle range. These tools need to be able to simulate efficiently the size/composition distribution not only of the particles dominating the aerosol mass (larger than 100 nm) but also that of the nanoparticles (smaller than 100 nm).

Practical Implications: This will allow the simulation of the radiative impacts of both the nanoparticles (indirect effect on climate) and the larger particles (direct effect). These tools will also be used for the design of control strategies for both the nanoparticles and the particle mass concentration (PM2.5 and PM10).

Background: Simulation of the atmospheric aerosol is especially challenging because atmospheric particles range over several orders of magnitude in size and consist of a wide variety of chemical components (Figure 2). The particles themselves may consist of more than one phase, and the chemical components may be moving continuously back and forth between the gas and particle phases depending on ambient conditions. Most of the model development work for atmospheric aerosols has focused on the aerosol mass distribution which is dominated by particles larger than 100 nm. Relatively little work has been performed for the simulation of nanoparticles which is especially challenging. The nanoparticle concentration in the atmosphere is dominated by nucleation and coagulation processes that are highly nonlinear and usually neglected (or treated inadequately) in current models. Treatment of both the nanoparticles together with the rest of the fine particles increases the simulated PM size range by 2 orders of magnitude and makes an

already numerically challenging problem even tougher. Most of the model development and application in urban and regional scales during the last 20 years has focused on the PM mass size/composition distribution, which is what is needed for visibility, PM10, and PM2.5 regulations, as well as direct radiative climatic effects. The climatic effect of aerosols on clouds depends on global particle number concentrations, since it is particle number that determines cloud droplet number. Global particle number distributions are computed with three-dimensional chemical transport or general circulation models that have intrinsic computational cell sizes of order hundreds of kilometers (Figure 3). Yet, the microphysical processes that determine atmospheric particle number concentrations, such as nucleation of gas-phase species or coagulation of primary exhaust particles, occur on spatial scales as small as a few meters. In fact, the question of the spatial scale of atmospheric nucleation, whether it be the order of meters or the order of many kilometers, is not well understood. The development of techniques to handle multiscale atmospheric particle phenomena will be essential to simulating the climatic effects of aerosols on clouds. In the same vein, the ability to scale particle simulations downward from the urban scale of a few kilometers to the "person scale" will allow estimation of the particle number concentrations and sizes breathed by individuals.

2. Simulation at different spatial scales

Recommendations: The effect of spatial scale (e.g., coagulation or nucleation near sources) is not represented adequately in models that compute average concentrations over computational cells that are at least several km^3.

Practical Implications: The link between these two different length-scales is not well understood and this limits the study of nanoparticles in urban, regional, and global scales. Similar challenges exist in the simulation of aerosols on global scale (computational cells are 100s of kilometers), filtration, estimation exposure of humans to nanoaerosols, etc.

Background: The atmospheric nanoparticle size/composition distribution changes rapidly in the vicinity of particle sources. For example, nanoparticles are formed within a few meters from the exhaust of a diesel vehicle and they rapidly grow by condensation

while they are coagulating with the preexisting aerosol. These changes take place in length-scales of meters (or timescales of seconds). Atmospheric chemical transport models cannot directly describe processes that have length-scales smaller than the computational cell size (usually a few km by a few km).

3. Evaluation of nanoparticle simulation tools

Recommendations: Evaluation of atmospheric Chemical Transport Models against comprehensive nanoparticle datasets. Design and performance of the appropriate field studies.

Practical Implications: Evaluation of the fidelity of numerical models is essential in establishing their validity.

Background: The few existing numerical models for atmospheric nanoparticles have not been thoroughly evaluated against sets of comprehensive measurements. This evaluation and the subsequent feedback to fundamental research are limited by the availability of suitable measurements. For most atmospheric field studies (especially at the urban and regional scales) the study of nanoparticles has not been a major objective.

4. Simulation of the Compositional Mixing State of Atmospheric Particles

Recommendations: There is a need to develop techniques that are computationally feasible to simulate the manner in which particles of different species interact and to simulate the aging of particles originally emitted in one form that evolve in size and composition as different species condense on them.

Practical Implications: This will help quantify the uncertainty inherent in assessments of the climatic effects of aerosols. It will also allow model predictions to be compared directly with data from single particle aerosol mass spectrometers.

Background: Both the optical properties and the health effects of atmospheric particles depend significantly on the extent to which atmospheric species are mixed at the individual particle level. For example, the extent of mixing of black carbon and sulfate in individual particles has a profound effect on the radiative properties of the entire aerosol population and therefore on their direct climatic effect.

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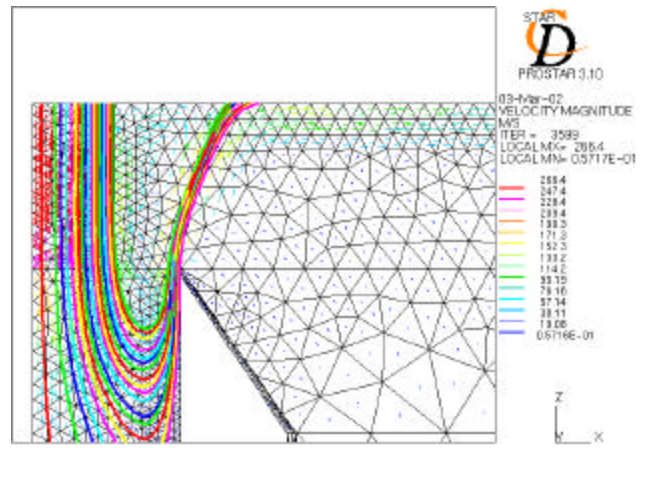Jacobson, M.J., *Fundamentals of Atmospheric Modeling,* Cambridge University Press, Cambridge, UK, 1999.

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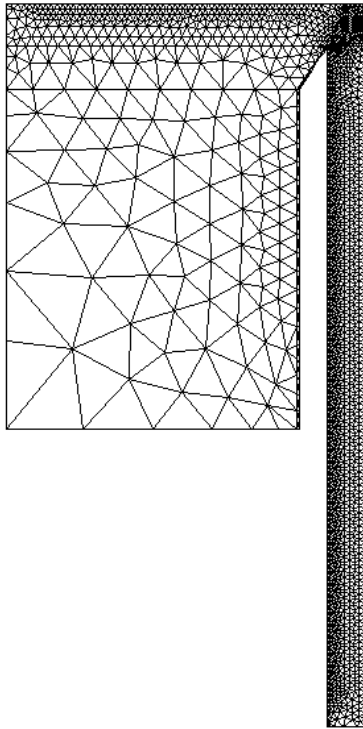
D_2/D_1=1.8, L/D_1=1.0

Mass flow rate: 8.99×10^{-5} kg/m^3

Figure 3-1. Numerical modeling of the nanoparticle virtual impactor (Da-Ren Chen, personal communication).
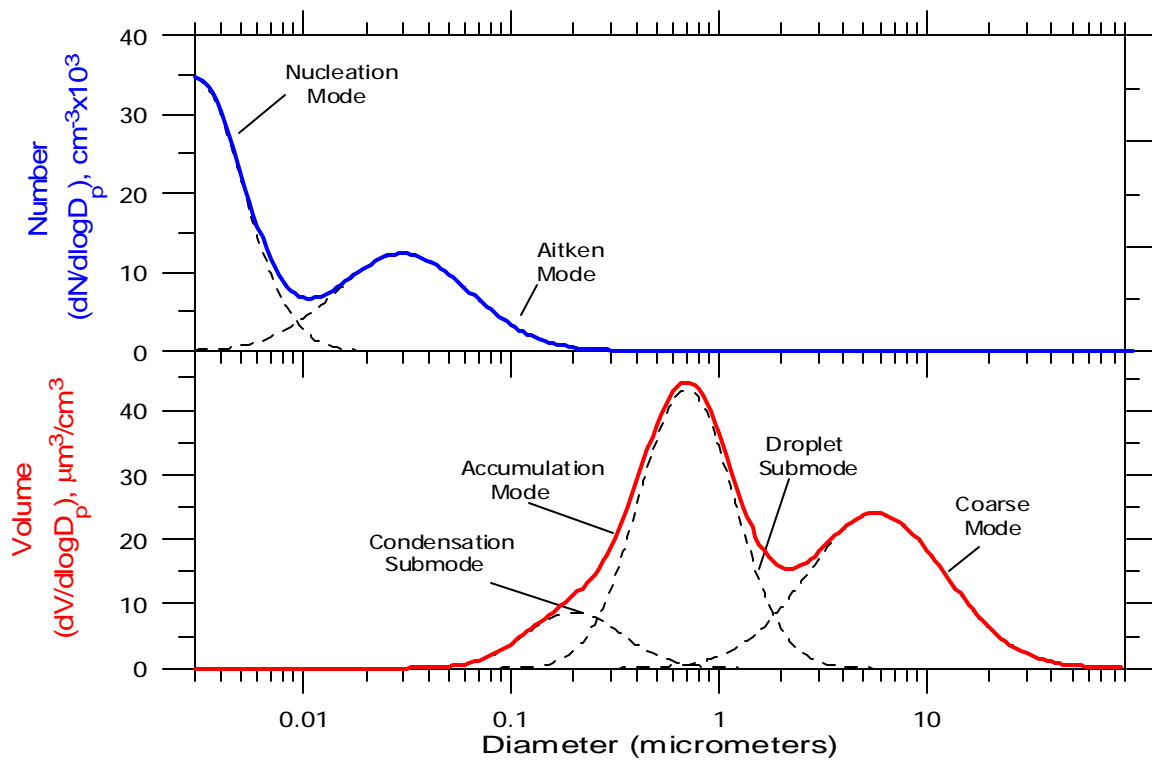
Figure 3-2. Schematic of typical atmospheric number and volume distributions (NARSTO Particulate Matter Assessment Report, 2003).
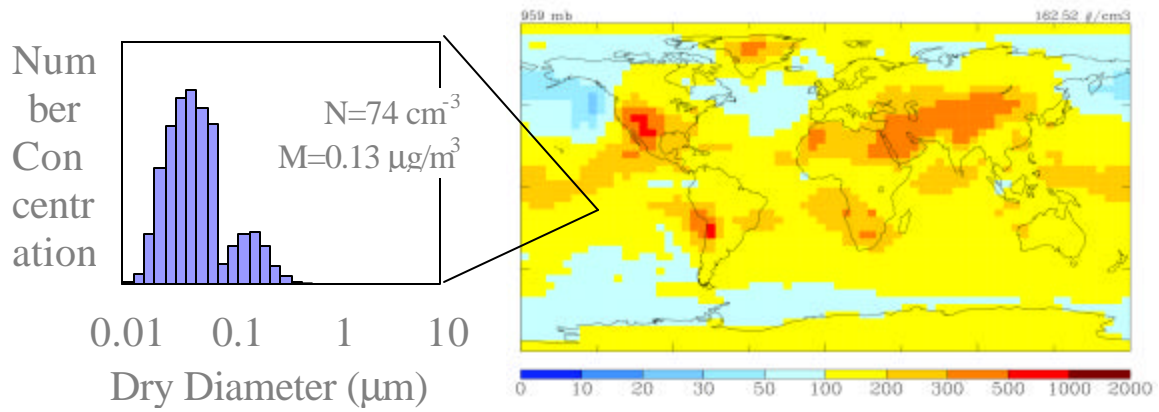
Figure 3-3. Prediction of Global Number Concentration of Particles in the Goddard Institute for Space Studies (GISS) General Circulation Model II-prime (Adams and Seinfeld, 2003)

4. AEROSOL REACTION ENGINEERING (ARE)

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Background and Current Status: Aerosol Reaction Engineering

Many industrial applications of 'tailored' nanoparticles have already been identified -e.g., their use in fabricating: selective catalysts or membranes, electronic information   storage or chemical sensor devices, optical films/fibers, additives for the control of   rheological or thermophysical properties, energetic fuel additives, etc. Further applications continue to be discovered. In many cases, 'aerosol' (gas-to-particle) synthesis routes will be attractive in order to satisfy demands for high product purity, scale-up potential, improved control of stoichiometry and phase selection, and small environmental 'footprint'. These factors have already led to the dominance of specially designed particle-synthesizing *combustors* that can produce many tons of nanoparticle products per day. However, we will not limit our discussion to such sources. Regardless of the reactor type chosen (combustion, thermal, plasma, laser, etc.), future cost-effective large-scale nanoparticle production will inevitably require an ability to 'engineer' reactors to selectively produce particles with characteristics that go beyond 'size' (mono-dispersity) and overall chemical composition. Additional particle attributes of current industrial interest include: external morphology, surface composition, internal distribution of (nano-crystalline) phases; this list will probably grow as the properties of these particles are studied further, and the impetus for their large scale industrial synthesis increases. If large quantities of inexpensive nanoparticles could be made readily available for exploratory research, new industrial applications would probably stimulate this entire field.

Most laboratory studies of flame-synthesized nanoparticles reported in the last decade or so have been carried out in one of the three basic types of burners shown in Fig. 4-1 (a,b,c) below. In some sense these are 'locally containerless' flow reactors in that heated sidewalls are not physically present in the particle inception regions of these flames. The burners shown accept *vapor* precursors, although *liquid* precursors sprayed directly into

flames have also been used. Figure 4-1a depicts a 'premixed' type of burner that has been used for sub-atmospheric pressure studies of nanoparticle synthesis, whereas the gaseous fuel and oxidizer are not pre-mixed in the so-called "diffusion-flame" burners shown in Figures 4-1b and 4-1c. Figure 4-1b shows an 'opposed jet' configuration, whereas Figure 4-1c shows a 'co-flow' configuration. Frequently these are axisymmetric, and, depending on pressure and flow rate, the flows can be laminar or turbulent. While 'flame' reactors have their advantages, reactors that use other types of energy sources (furnaces, lasers, electrical discharges, etc.) have also been used to synthesize nanoparticles from the vapor phase (*ie. via* an aerosol route).

Existing methods to predict/control the performance of vapor-to-particle synthesis reactors, which have emphasized only particle size in highly idealized reactor configurations, must now be generalized to make this possible. Indeed, the design of particle producing reactors is already considered a frontier problem in the more general field of chemical reaction engineering (e. g., see Engineering. Foundation Conf.: *CFD in CRE*, May 2003, Davos, Switzerland)). Economically synthesizing high-value nanoparticles for large-scale industrial applications, will require a research program that addresses the key ARE-oriented research needs identified below. Several of these fundamental issues are common to the other Panels (eg.., Panel 2); for the purposes of ARE, understanding based on fundamental computer simulations or real experiments must be cast in the form of quantitative, verifiable correlation formulae for subsequent use in CFD-based design, optimization and control. Similarly, experimental techniques capable of measuring these additional particle attributes will have to function in the 'harsh' environments which often characterize these reactors. Research recommendations follow:

Research Need 1. Nanoparticle Precursor Selection Criteria
Any particular type of nanoparticle can generally be synthesized from a wide variety of precursor chemicals, each of which has its own cost, impurity, volatilty, stability,... 'profile'. Rationally- based guidelines are needed to economically converge on a subset of truly viable candidates, using versatile reactors well-suited to this task.
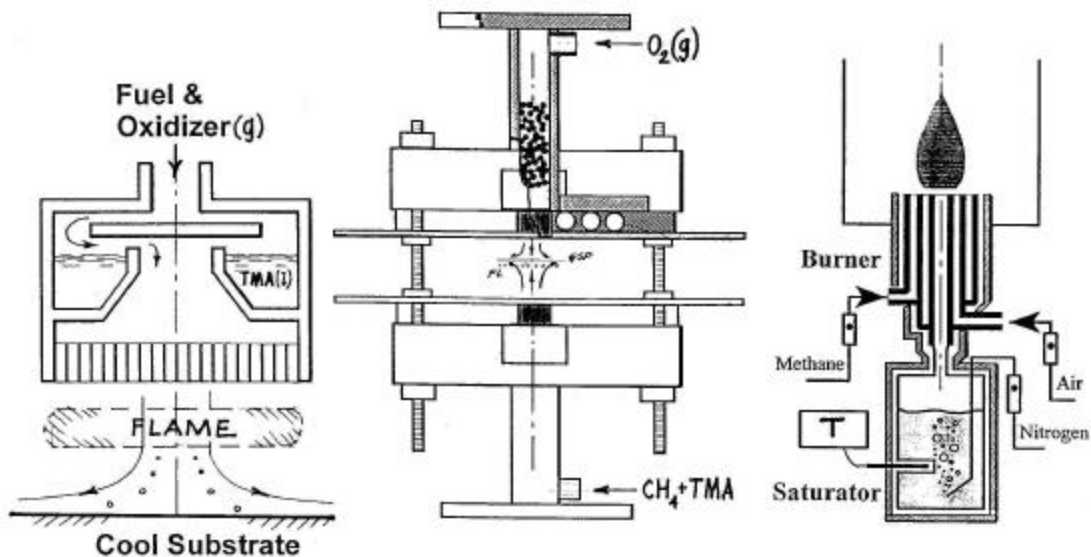
Figure 4-1. Types of gaseous fuel combustors used for nano-particle synthesis: a) pre-mixed flat flame burner (inverted), b) counterflow diffusion flame burner (slot type), c) multi-annulus co-flow diffusion flame burner (after Rosner(2003))

Background: In practice, there may be many alternative 'feed' chemicals, hopefully already commercially available, that could be processed to yield a particularly valuable nanoparticle product. Of course, each is expected to have its own cost and operational problems and some (if not most), after lengthy laboratory trials, may prove unworkable after-all. For these reasons it will be essential to develop useful quantitative guidelines (based on both physico-chemical properties and cost) to screen/select promising vapor, liquid, or solid precursors. These leading candidate materials will then have to be experimentally tested using versatile, small-scale reactors, initiating an iterative process to improve the abovementioned precursor screening guidelines.

It should be mentioned that in special cases it may actually be possible to exploit recent advances to suggest new processes for producing high-value nanoparticle-based products from less valuable particulate effluents from, say, smelters, power plants,… (these might provide attractive alternatives to the 'cinderblocks-from-flyash' paradigm) (cf. Panel #5)

Practical Implications: Rational and 'battle-tested' precursor screening guidelines would dramatically reduce the R&D costs of bringing a particular nano-particle product to the marketplace.

Research Need 2. 'Reduced' Kinetic Description of Precursor Evolution Under Reactor Conditions

Tractable representations of the actual network of physical and chemical steps leading from precursor introduction to nanoparticle-embryos are needed to develop rate quantitative laws for synthesis reactor design, optimization and control.

Background: Whether the particle precursor is the 'fuel' itself, a combination of the 'fuel' and oxidizer, or an additive ("seed"), it will be necessary to understand and summarize the physics and chemistry of precursor vaporization, decomposition and chemical reactions (hydrolysis, oxidation,…) which produce the embryos that ultimately nucleate/grow. To be readily interfaced with aerosol dynamic simulations for rational aerosol reactor design/control and eventual scale-up, this research must be systematically 'reduced' to lead to rational mesoscopic rate laws that can be used/verified in efficient reactor simulation codes.

From an industrial perspective, the usually complex chemistry of precursor transformation to primary particles is perhaps the least understood of the particle synthesis processes in aerosol reactors. Particularly for combustion synthesis using turbulent flame jets it is rarely clear how the precursor chemistry is connected to primary particle evolution. Normally, a large number of intermediate species, including radicals, complicates predicting the dominant reaction pathways. But the precursor chemistry, when understood and put in a form useful to the reaction engineer, would enable greater control over the characteristics of nanoparticle aerosols.

Practical Implications: Without this information it will be impossible to predict the location of nanoparticle inception, the subsequent nucleation/growth rates of the desired particulate phases in nanoparticle synthesis reactors

Research Need 3. Tractable Mathematical Models of 'Chemical' Nucleation Rates

New methods, which account for the role of homogeneous and heterogeneous chemical reactions in the formation of nanoparticle embryos, as well as the unusual properties of multicomponent embryos in the nanometer size range, are needed to predict local nanoparticle 'birth rates' in nanoparticle synthesis reactors.

Background: It is already clear that particle nucleation in most aerosol chemical reactors occurs under conditions of supersaturation for which classical nucleation theory fails. Unfortunately, simple limiting case predictions based on calculating the rate of formation and subsequent coagulation of a hypothetical 'monomer', often overpredict the nucleation rate and ultimately overpredict the dispersity of the particles formed by 'coagulation-coalescence'. For these reasons the mechanism and rate of 'chemical nucleation' at very high supersaturations must be better understood (cf. Panel 2), again with results that can be cast in a form compatible with the requirements of an aerosol dynamic equation-based reactor simulation scheme (see RN 9, below)

Practical Implications: A reliable quantitative description of 'Chemical' Nucleation Rates will enable the prediction/control of nanoparticle size, specific surface area and number density under optimal chemical reactor condition.

Research Need 4: Rate Laws for Nanoparticle Growth By Heterogeneous Reactions

Having formed stable embryos of the nano-phase of interest, how rapidly will they grow when interacting with the non-equilibrium 'mix' of vapors in their immediate environment? What role will heterogeneous chemistry (*ie*. chemistry in the *ad*sorbed state) play in determining net rates of growth? Research is needed to address/answer these fundamental questions.

Background: Nanoparticle growth in chemical reactors is often the result of the *heterogeneous reaction* rather than 'physical condensation'. For example, although its kinetics have never been measured on nanoparticle surfaces, the overall CVD reaction:

$TiCl_4$ (g) + O_2 (g) $\rightarrow$ (on TiO_2 surface) TiO_2 (s) + $2Cl_2$ (g)
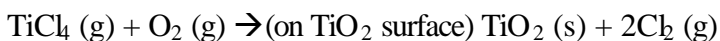
evidently influences the performance of titania pigment reactors. Usable kinetic descriptions relevant to such particle growth by CVD will be needed for a wide variety of chemical systems leading to 'precipitate' (particulate) products.

Practical Implications: By controlling rates of mixing and particle growth in nano-particle synthesis reactors it will be possible to control the size, morphology and surface characteristics of the nanoparticles produced.

Research Need 5. Rate Laws for Brownian Coagulation of Non-spherical, Non-uniform Particles

Embryonic nanoparticles will interact among themselves as a result of their Brownian motion and high local concentrations. Their complex state and effective shapes will generally alter their successful coagulation rate in ways that need to be clarified based on improved measurements and computations

Background: Nanoparticles produced by chemical nucleation rapidly coagulate due to their Brownian motion, especially in high temperature systems. Moreover, sluggish coalescence rates often lead to complex particle morphologies, making accurate coagulation predictions more difficult for two reasons: a) an uncertainty in the effective collision diameter of each participant, and b) tenuous aggregates may approach 'gelation' (span the available space) at surprisingly low particle volume fractions. Even if collision frequencies accounting for these two effects (morphology and 'excluded volume') become predictable there remains the unsolved problem of what fraction of these collisions lead to a 'successful' union of the two participants. Experimental and theoretical research leading to reliable predictions of the net coagulation rate under such conditions is needed to predict the performance of aerosol synthesis reactors, especially those operating at 'high particle mass loadings'.

Practical Implications: Whether coagulation must be avoided or encouraged to meet the desired particle property specifications, the laws governing the net rate of coagulation under aerosol reactor conditions will be necessary for reactor design/optimization/control.

Research Need 6. Improved Rate-Laws For Nanoparticle Restructuring

Nanoparticle restructuring will occur in the intervals between encounters with other nanoparticles. Rate laws governing several of the possible restructuring mechanisms have been proposed and exploited , but rational modifications seem to be needed even when these mechanisms do not operate simultaneously. More general rate laws, which have been tested against the results of well-defined experiments on nanoparticles, are needed

Background: While the 'restructuring' of aggregates is known to occur by a variety of mechanisms (viscous flow, bulk diffusion, surface diffusion, Brownian gas molecule impacts, capillary condensation) improved rate laws for nano-aggregate 'sintering' are now needed for nanoparticle synthesis reactor design purposes (this rate law appears as a coefficient function in the EAD when particle surface area is chosen as one of the independent particle 'state' variables; see RN # 9). Apart from the fact that more than one 'restructuring mechanism may be operating at the same time, presently available information has not been based on observations on nano-particle surfaces or for aggregates involving composite primary particles. Moreover, it will be valuable to gain an understanding of how the rate of nanoparticle restructuring can be manipulated, perhaps by exploiting the sensitivity of some of these mechanisms to surface energy, and hence adsorbed species. (*cf*. Panel 2)

Practical Implications: Understanding/manipulating aerosol reactor conditions that control the rate of nano-particle restructuring will enable the selective production of desired morphologies, with a minimum of off-design (unusable, or simply less valuable) product

Research Need 7. Ability to Model Phase Selection/Change Within Nanoparticles

Each nanoparticle can be viewed as a microreactor within which both chemical reactions and phase changes occur under conditions of unusual confinement, supersaturation and under rather dynamic conditions. New methods to predict competitive rates of phase change under such conditions are needed in order to control the yield of desired stoichiometries, crystal microstructures and morphologies.

Background: Aerosol routes to tailored nano-particles have intrinsic advantages when it comes to the control of *intra*particle phase behavior. However, exploitation of this situation will require a much-improved understanding of the mechanism, sequence and rates of phase-change (e. g., crystallization) within metastable nano-particles (*cf.* Panel 2)

Presently, large-scale aerosol reactors are fairly limited in their ability to control the composition and size distribution of the various crystalline phases independently of primary or aggregate particle size. But there are many applications (especially in the areas of optics, catalysis, and sensors) that would benefit from research that would provide strategies for nanophase composition/microstructure control within aggregates. As examples: the anatase (not rutile) phase of titania is known to be an effective photocatalyst in the degradation of organics in wastewaters and gases. Ceria-zirconia solid solutions are excellent oxygen storage components and are used in catalysts to suppress automobile emissions. High-surface area alpha alumina would be a promising candidate for catalyst supports that demand high temperature operation.

Practical Implications: Research which leads to a better understanding of the dynamics of phase selection/change within nano-particles will enable the design/operation of nanoparticle synthesis reactors in which intraparticle phases can be controlled nearly independently of other particle attributes.

Research Need 8. Improved prediction of nanoparticle transport properties

Each nanoparticle will experience a transient, asymmetric local vapor environment and respond according to its momentum-, energy, and mass-transport properties. But these properties are in doubt for many combinations of particle morphology and gas mean-free-path, and are also sensitive to the uncertain nature of the molecular interactions with the nanoparticle surface.

Clarification of these issues will improve the predictability and control of synthesis reactors.

Background: Both for reactor design/control purposes, and for the interpretation of certain *in-situ* nano-particle measurements (e. g., time-resolved LII, dynamic light-scattering,...) it is necessary to introduce more accurate formulae describing the transport properties of (ensembles of) non-spherical nano-particles---including 'fractal-like' aggregates. These properties embrace momentum transfer (drag), energy transfer (particle/gas), and species (mass-) transport. Since the reactor environment is generally spatially non-uniform, and may also exploit electrical or magnetic fields, additional forces, leading to 'phoresis' must also be included, at least locally. A major source of uncertainty in previous calculations is the appropriate effective accommodation coefficients, especially when the vapor mixture is complex chemically (polyatomic, containing radicals) and/or the surface is heterogeneous. For larger aggregates comprised of nanometer scale 'primary particles', especially those formed in reactors operating at super-atmospheric pressures, an additional uncertainty is the nature of the Knudsen-transition behavior when the gas molecule mean-free-path is not large compared to, say, the mobility diameter of such aggregates.

Practical Implications: Theoretical and experimental research which eliminates (or dramatically reduces) the abovementioned uncertainties will improve many aspects of aerosol reactor design/control, including nano-particle deposition (RN 13)

Research Need 9. Development/Implementation/Testing Of Efficient EAD-Simulation Methods

An evolving population of nanoparticles will interact with the local populations of vapors and turbulent eddies in ways that must be mathematically modeled using a formulation which lends itself to CFD-based reactor simulation methods. Versatile yet computationally efficient methods to deal with the resulting equations of aerosol dynamics (EAD) will be needed, based on calibrations against experiment as well as more cumbersome but accurate numerical methods.

Background: An approach based on the *Equations of Aerosol Dynamics* (EAD) will underlie the computer-aided design of future nanoparticle reactors, irrespective of the choice of reactor type, feedstocks, etc. For this purpose we now need practical EAD-

simulation methods which can: a) deal with the need for a multiple state variable description of particle 'state', b) make no presumptions about jpdf shape or the degree of correlation of these state variables, c) accept more complex/accurate rate laws (see RNs # 4-8), and d) are compatible with both evolving CFD techniques and the need for model-based controller design. This will also enable the development and iterative testing of promising reactor simulation methods capable of dealing with the generally two-way coupling between a multi-variable aerosol population and the non-uniform turbulent "carrier" vapor (cf. Panel 3)

It should be noted that, in the last 10-15 years, 'Computational Fluid Dynamics (CFD)' has been introduced in conjunction with aerosol dynamics models in preliminary attempts to describe particle formation in non-uniform turbulent reacting flows.   While the underlying assumptions have been extreme and now need to be relaxed, from an industrial perspective this approach has already provided useful insights into the effects of flow- and temperature- fields on the physicochemical processes that govern primary particle formation and coagulation.

Another foreseeable research need will be validation of the abovementioned reactor-compatible EAD-simulation schemes. Apart from ultimate comparisons with well-characterized experiments (cf. RN 10, below), this will also require the development/implementation of less-efficient but more accurate multivariable EAD-simulation techniques needed to 'calibrate' the abovementioned (RN 9) methods (which, by invoking defensible approximations, are better suited for 'ARE' design/control. design/simulation methods (cf. Panel 3)

Practical Implications: Dramatic developments in the area of computer-aided aerosol reactor design, exploiting novel approaches motivated by the increased needs of tailored nanoparticle synthesis, will pay significant dividends in reducing the R&D costs of design/scale-up of industrial aerosol reactors.

Research Need 10. Testing "ARE" Models Against Well-Instrumented Laboratory Experiments

ARE models based on the research needs discussed above must be tested against data sets obtained on well-defined and instrumented nanoparticle synthesis reactors, over a broad range of operating conditions. The scarcity of such examples in the literature has been a serious impediment to the rapid development of this field

Background: Well-defined data sets will be needed to test/calibrate/extend state-of-the-art reactor simulation techniques in more realistic environments, but yet ones which are deliberately simplified (e.g., reduced dimensionality, laminar, optically accessible). However, extending this approach will require the introduction of new, real-time aerosol instruments capable of obtaining additional information on important particle properties under more realistic reactor operating conditions including high volume fraction (e.g., above 10 ppm), high pressure and temperature and turbulence. (cf. Panel 1)

Practical Implications: Developing a credible aerosol reactor simulation/design methodology will require iterative comparisons with the results of well-instrumented/designed laboratory scale experiments

Research Need 11. Model-Based Control Of Aerosol Reactors

Nanoparticle synthesis reactors will require a high level of control to avoid producing off-design and perhaps even hazardous materials at great expense. As discussed below, this will require the introduction of real time nanoparticle sensing, and the implementation of model-based control schemes. The opportunities here are particularly great, since this strategy has been under-utilized even in the more mature industries producing ultrafine powders.

Background: To optimize the operation/ performance of aerosol processes to allow the consistent production of aerosols with desired properties/functionality, and minimal 'off-quality' product, it will also be necessary to:

1. Incorporate new real-time measurement systems in nanoparticle synthesis reactors

2. Design model-based feedback systems for the control of size, morphology and composition distribution using EAD.

3. Integrate models, measurements and controllers to synthesize real-time feedback control systems.

4. Analyze practical implementation issues and provide fundamental insights into the limitations imposed by the available monitoring techniques on our ability to achieve real-time control of aerosol size distributions, and other essential np-attributes.

5. Implement real-time measurement/model-based feedback control on experimental aerosol systems using computer-based control technology.

Practical Implications: Based on precedents from other branches of chemical industry, we expect that the operation of nanoparticle synthesis processes under advanced real-time feedback control (i. e., compensating for the detrimental effects of unpredictable variations in the operating environment) would reduce operating costs, environmental impact and product variability.

Research Need 12. Model-Based Scale-Up

Not every nanoparticle synthesis scheme lends itself to economical scale-up. A better understanding of those that do, along with methods to make reliable predictions of productivity, unit costs and product quality will be necessary.

Background: To fully exploit aerosol routes to economical nano-particle production it will be necessary to propose and test rational scale-up strategies. For example, economies of scale cannot be realized if a scaled up reactor-combustor becomes unstable---a problem which at one time plagued the development of large chemical rocket thrustors. Scale-up procedures based on rational computer simulation would eliminate the conventional need for maintaining strict constancy of certain dimensionless groups (e. g., length-ratios, Re, Sc, Dam,...), there by broadening the domain of operability.

Practical Implications: Scale-up based on an adequate understanding/mathematical models could enable the commercial exploitation of many 'bench-scale' nano-particle synthesis discoveries.

Research Need 13.   Ability to Anticipate and Control Nanoparticle Deposition

Can the laws of nanoparticle deposition/collection be developed and exploited to design reactors which perform at a high level over long periods of time with minimal wastage? Further research will be   needed to demonstrate this under conditions of industrial interest.

Background: Unwanted aerosol deposition within reactors is often the cause of costly shutdowns. Therefore methods to design/operate complex reactors which prevent such localized deposition are required. Conversely, a valuable aerosol product must be 'harvested' (collected) or the nanoparticles may be exploited in the form of thin particle layers (e. g., membranes for separation or films for heterogeneous catalysts, or chemical sensors (detectors), or optical components).   For all the above reasons the laws of nanoparticle deposition and re-entrainment must be extended, in part based on relevant new experiments, and cast in a form useful for: (a) reactor design (b) particle collection for 'packaging' and (c) synthesis of granular coatings with desired effective thermophysical/optical properties. It should be clear that an understanding of the transport coefficients for such particles (RN 8) is necessary, but certainly not sufficient, to make accurate predictions of net deposition rates/deposit microstructure/properties.

Practical Implications: Understanding the laws of nanoparticle deposition will enable the design/control of reliable synthesis reactors as well as efficient particle collection schemes

Research Need 14. Health/Safety Precautions For Handling Nanoparticle Products

Will the increased industrial availability of nano-particle products create legitimate toxicity concerns among industrial users and ultimate consumers? What precautions will be warranted by the available evidence, and how should these factors influence the reactor economics?

Background: To ensure that the demand for high-performance nanoparticles continues to increase, it will be necessary to gain an understanding of the health-effects and safety precautions necessary in their large-scale production, harvesting, shipment and ultimate use. Knowledge based on such studies would also head-off 'precautionary delays' that would inevitably be recommended in their absence. Because of the uniqueness of the industrial environment, parallel studies of the health-consequences of nanoparticles in the atmospheric environment (including near-automobile sources) will be useful but certainly not sufficient for present ARE purposes.

Practical Implications: Research which clarifies the health-effects and safety precautions necessary for the large-scale production, harvesting, shipment and ultimate use of tailored nanoparticles will remove a possible impediment to healthy expansion of this evolving industry.

Research Need 15.   Surface Modification/Coating Opportunities

The strategy of surface modification can be exploited further by ARE practitioners to economically mitigate toxicity problems and/or improve the performance of nanoparticle products.   Configurations   which   efficiently   accomplish   this   need   to   be developed/demonstrated.

Background: Closely related to the above-mentioned safety and health issues are opportunities to modify the properties of nano-particles by altering their surfaces – e. g., using some form of atomic layer deposition or CVD to form 'compound (core-shell) nanoparticles. Apart from the possibility of rendering pyrophoric particles safe to handle, ultra-thin but dense, adherent coatings could also be used to upgrade/passivate size-selected nanoparticles for special high-performance (e. g., photoluminescence) or high-volume applications or to suppress their aggregation (or facilitate their dis-aggregation). This strategy also includes adjusting refractive index (color/translucency) and providing hard/ wear resistant or hydrophobic surfaces. In some cases such 'tailored-surface' particles could be made in "one overall step" (i. e., in a single reactor envelope), but in others, multi-'stage' reactors may be necessary/desirable. In any case, research that would

identify the requirements for such coatings, and reactors to successfully deposit them, are needed.

Practical Implications: Suitably applied coatings on nano-particles will often add considerable value, and may enable entirely new applications at acceptable processing costs.

Research Need 16. Property-Resolved Nanoparticle Reactor-Separators

Novel nanoparticle synthesis reactor-separator combinations are likely to be necessary to satisfy future selectivity demands. Exploration of attractive theoretical possibilities and their experimental realization will be necessary.

Background: Precise control of particle properties is required for many potential nanoparticle applications, particularly those involving resonant quantized transitions. Even with the advances in 'ARE' recommended by this Panel, direct selective synthesis will probably not approach the precision/control required for many such applications. Therefore, efficient separation devices will have to be developed and articulated with such aerosol synthesis reactors themselves.

For many such "integrated reactor-separator" applications the ideal separation method would not be to select particles based on, say, their size, but, rather, based on the property of interest itself (e. g., a particular optical transition). In any case, alternative reactor-compatible methods which can meet the stringent nanoparticle separation requirements at hand will have to be systematically explored before one is selected/optimized. This is a novel ARE-area whose importance is likely to grow as the number of remarkable applications for nps grows.

Practical Implications: The requirements for acceptable tailored nanoparticles are becoming so stringent as to often be unattainable without the use of well-integrated reactor-separators. Research on efficient schemes of this type will dramatically reduce the final cost of such products.

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5. ATMOSPHERIC NANOPARTICLES (ULTRAFINE PARTICLES)

C. Sioutas(Chair), P. McMurry(Co-Chair), P. Biswas,W. Hinds,W. Wilson

Introduction

Atmospheric ultrafine particles (UFP), defined as particles with physical diameters less than about 100 nm, originate from combustion sources and from gas-to-particle formation processes in the atmosphere. Figure 5-1 shows the flow of these nanoparticles from their sources through the atmosphere, including atmospheric formation and loss. The diagram also illustrates pathways of human exposure and effects on climate through clouds and light scattering.

An emerging literature indicates that these particles are more toxic than other sizes of ambient particulate matter. Recent epidemiological studies have found an association between exposure to ultrafine particles and mortality due to respiratory or cardiovascular disease. These particles have also been shown to grow to sizes that act as condensation cloud nuclei (CCN), thereby affecting global climate.

Our Panel identified 13 areas within the topic of atmospheric ultrafine particles that serve as the basis for future research. These are described in subsequent paragraphs:

Research Need 1.   Photochemically-driven nucleation in the atmosphere

Background:

Photochemically driven atmospheric reactions lead to the formation of chemical species with very low, ambient temperature, saturation vapor pressures. These chemical species may form particles by a variety of nucleation processes. Nucleation may sometimes occur on ions and probably involves more than one species (i.e., is a
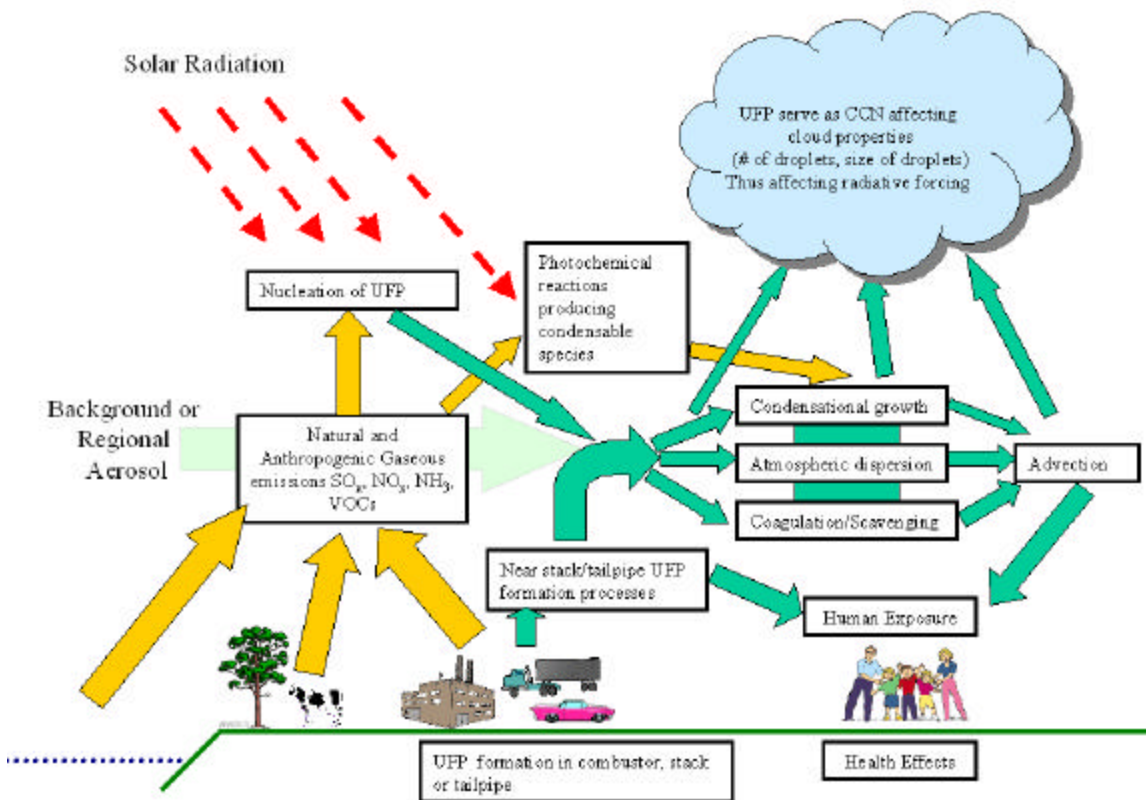
multicomponent

Figure 5-1. A diagram of the flow of ultrafine particles (UFP) from their sources through the atmosphere. Pathways of human exposure and effects on climate through clouds and light scattering are also illustrated.

process). There is good evidence that sulfuric acid vapor sometimes participates in nucleation, and there is a growing consensus that ammonia and water vapor are also involved. However, the atmosphere probably also contains other trace gases, including organic compounds, that either participate in nucleation process or react in the atmosphere to form compounds that nucleate. Because they may be present at extremely low concentrations, the identity and concentrations of those gases is not yet known.

Research Recommendations:

There is a need to identify gases that react to produce new particles, to measure their atmospheric concentrations and to understand the chemical processes by which they are formed. There is also a need to understand the forward and reverse rates at which such compounds react with neutral or charged molecular clusters of known composition, since

such reactions lead to new particle formation. There is a need for atmospheric studies, controlled-laboratory studies, and model development, with the eventual goal of establishing models that are supported by observation. Ultimately, such microphysical models need to be incorporated into global climate models so that the effect of atmospheric nucleation on global climate can be taken into account. (See also the Panel 2 report.)

Research Need 2. Nucleation and rapid growth that occurs as hot pollutant exhaust gases mix with cooler air in the ambient environment

Background:

Recent laboratory and field measurements have shown that high concentrations of sub-20 nm particles can be produced when hot diesel exhaust gases mix with cooler ambient air. The number of such particles that are formed is known to increase as ambient temperatures decrease and with increases in fuel sulfur content, and has also increased as emissions controls have reduced mass concentrations of emitted particles.

Research Recommendations:

This work will require an identification of the species that participate in nucleation, including the possibility that ions play a role, and mechanisms by which those species react to produce particles. Such work will require studies of pollutant sources, as well as laboratory and modeling studies. The goal should be to understand the relationship between the pollutant source and the physical and chemical nature of the ultrafine particles that appear in ambient air. A means should be established to incorporate the output of such "emissions models" into chemical transport models for atmospheric aerosols. It is likely that nucleation also occurs when emissions from other types of sources mix into the atmosphere. Neither chemical transport models nor conventional emissions data account for such near-source processes. Such particles can account for a significant fraction of the ultrafine particles to which populations are exposed. Understanding source-receptor relationships and processes that affect human exposures will require an understanding of such processes.

Research Need 3. Growth rates of freshly nucleated atmospheric ultrafine particles

Background:

Growth rates of freshly nucleated particles determine the time required for them to grow to a size where they can serve as cloud condensation nuclei (CCN). For a given preexisting aerosol, the competition between growth (by coagulation with other nucleation mode particles) and loss (by coagulation with accumulation mode particles) determines the probability that such particles will grow into the Aitken mode where they can serve as a CCN. The CCN concentration determines the extent of cloud cover and therefore plays an important role in governing the indirect effects of aerosols on radiative forcing.

Research Recommendations:

Observations indicate that growth rates of UFP range from 1 to 20 nm/hour (increase in diameter), depending on season and locale. There is also evidence that in some locations, the species that dominate growth are different from the species that are responsible for particle formation. There is a need to carry out atmospheric observations that will determine which species contribute to growth, and to understand how atmospheric chemical transformations regulate the gas phase concentrations of those species. For a given growth rate, the likelihood that a nucleated particle will survive and grow to a CCN particle increases as fine particle mass concentrations decrease. Therefore, the interplay between PM control and ultrafine particle concentrations needs to be understood.

Research Need 4. Chemical and physical transformations of atmospheric ultrafine particles

Background:

Chemical transformations due to heterogeneous reactions between particles and gas phase oxidants may be important. For example, evidence suggests that such reactions lead to

the production of oxygenated organic compounds that are more hygroscopic than the original precursors. Atmospheric processing may also lead to changes in the fractal dimensions of agglomerate particles, as they undergo cloud processing and/or grow by condensation. This is also important in control of $PM_{2.5}$ for health effects.

Research Recommendations:

  Recent measurements have shown that optical absorption by black carbon soot plays an important role in direct radiative effects of aerosols. In polluted atmospheres, the forcing effects of aerosol absorption can be equal in magnitude (but opposite in direction) to scattering. Therefore, the optical properties of coated and uncoated agglomerate soot particles need to be well understood. Also, hygroscopicity influences the tendency of particles to form cloud droplets, and may influence deposition in the lung or elsewhere. Also, it is possible that the fractal properties of coated hygroscopic particles would change during cloud processing, and such changes would lead to changes in optical and transport properties. Transport properties determine how particles deposit, and how they are size-classified by aerosol instrumentation.

Research Need 5: Improvements in measurement technology for ultrafine particles

Background:

It is not clear to-date what metric of ultrafine particles is most closely related to health effects (mobility or aerodynamic size, number, surface area, volume, mass, chemistry). Measurements of these properties are needed, ideally in conjunction with health studies. Improved techniques for determination of fractal dimension and other particle shape classifications are also needed to determine relationships of shape to health effects and to understand other properties such as transport and deposition that are also influenced by shape.   Techniques for detection of ultrafine bioaerosols, e.g. pollen fragments,

endotoxins, viruses, and other biologically active UFP would also be useful in this context

Research Recommendations: To address many of the research items listed above, there is a need to develop instrumentation for measurement of particle number distributions for particles below 3 nm in diameter, the current lower size limit. This is essential for studying nucleation processes as discussed in Research Needs 1, 2 and 3.

Moreover, there is great need for developing techniques for determination of size-resolved chemical composition at small sizes including molecular clusters, especially for studying nucleation and growth, for source apportionment both for source category identification and exposure to source categories for epidemiology (Research Need 9), and for identifying biologically active chemical components.

Simple, reliable, cost-effective techniques for measurement of health relevant metrics for ultrafine particles are also needed for use in panel and cohort, and especially for population epidemiological studies in which measurements at many sites are needed for long time periods (years). Along these lines, the development of personal exposure monitors for health relevant UFP metrics would be very helpful in addressing the needs of epidemiological and panel studies that focus on UFP.

Research Need 6: Atmospheric measurement needs for ultrafine particles

Background:

In addition to the development of instrumentation for ultrafine particle measurement, there is a great need for larger scale measurements of the concentration and chemical and physical properties of these particles in urban and rural environments. Part of this effort has already been under way through the U.S. EPA Supersites program, but it is important that these measurements are conducted in a broader spatial (and temporal) scale than the present studies. Funding for the Supersites has ended and only a few Supersites will be

able to continue measurements of UFP. Ultrafine particle measurements need to be added to the U.S. Speciation sites for measurements of community levels of UFP. Additional sites are needed to measure UFP in or near busy roadways and other places where high concentrations of UFP are anticipated.

Research Recommendations:

There is a need for targeted measurements of UFP size and composition to assess the impacts of control strategies on ultrafine PM levels (for example, the effect of fuel de-sulfurization, or the effect of soot reduction in diesel emissions on ultrafine particle numbers). Given the high spatial and temporal variability of UFP concentrations, measurements of a higher spatial and temporal resolution are needed, especially in terms of linking these particles to health studies. Measurements of the solid vs. semi-volatile components of ultrafines are also needed. These data are useful in assessing the degree to which UFP penetrate indoors (the semi-volatile component may evaporate in indoor environments during the winter time). Furthermore, separate assessment of the toxicity of these two fractions may be important in designing effective control technologies, given that conventional control technologies remove efficiently particles that were formed during the combustion process but not vapors which condense to form the semi-volatile component of UFP.

Finally, there is a need for the identification of secondary organic components of UFP, the elucidation of chemical pathways and processes that drive the formation of these compounds, and the assessment of their toxicological properties relative to primary emissions of UFP.

Research Need 7. Measurement and characterization of ultrafine particle emissions from sources

Background:

Previous source testing experiments have characterized gaseous and PM$_{2.5}$ emissions from a variety of pollution sources. Emissions rates of major pollutants from motor vehicles, natural gas boilers, coal combustors, smelters, incinerators, food cooking, wood burning, and other point sources have been determined and are essential to atmospheric modeling studies as well as regulatory decisions. Similar source testing efforts are needed to characterize the emissions of ultrafine particles from these sources. Data on primary emissions of ultrafine particles will prove valuable in a variety of research areas. Atmospheric modelers need accurate emissions profiles as input for their models, and the more particle characteristics are known, the better they can predict particle behavior in the atmosphere. Regulators considering the control of ultrafine particle emissions will use the data to focus their efforts on the most important sources with the most severe health effects. The effectiveness of new control technologies can be assessed.

Research Recommendations:

Important properties of the emitted aerosol to be measured include ultrafine mass, number size distributions, size resolved chemistry including individual organic compounds, morphology, density, hygroscopicity, and volatility. Particle solubility in lung fluids is also important for dosimetry and health-related studies. Precursor gases to ultrafine particle formation in the atmosphere should also be measured. Due to the rapidly changing nature of ultrafine particles, great care must be taken in defining the operating parameters of the sources tested and determining their effects on the properties of the ultrafine particle emissions. Similarly, the sampling protocol must be carefully considered since different sampling dilution rates, residence times, and temperatures can significantly change particle characteristics.

In addition to measurements, there is a need for models describing particle formation and growth within these combustion systems as a function of operating conditions. Laboratory studies to develop a mechanistic understanding of the processes occurring in such systems need to be conducted and compared to model results. The impact of control technology used in the removal (or unintended enhancement) of nanoparticle emissions needs to be established.

Research Need 8. Source apportionment of ultrafine particles

Background:

Source apportionment methods such as chemical mass balance (CMB) and positive matrix factorization (PMF) have been successfully employed to apportion ambient PM levels to primary particle sources. Emitted species such as metals, organic carbon, elemental carbon, and individual organic compounds have all been used in apportionment studies. Results of receptor-oriented source apportionment models provide an important alternative to emissions inventory approaches for regulators to assess the impact of particle sources on ambient concentrations. These tools may prove particularly useful for ultrafine particles.

Research Recommendations:

Once ambient concentrations and source profiles of these species are determined for ultrafine particles, the same methods can be applied to calculate the contributions of different sources to ambient ultrafine particle levels. In addition to primary emissions, secondary organic compounds should be identified in ambient samples that may serve as indicators of photochemical atmospheric reactions and help to determine the contributions of secondary organic aerosol (SOA) to ultrafine particle mass. Due to the high degree of spatial and temporal variability of ultrafine particles in the atmosphere, source-oriented transport and process models will be challenged to predict ultrafine particle characteristics at a particular time and location. Additionally, epidemiological

and particle toxicity studies, which now try to associate health outcomes with particle characteristics including numerous chemical components, can use the results of source apportionment calculations to find associations with a smaller set of particle sources.

Research Need 9. Population exposure assessment

Background:

The health impacts of ultrafine particles are of great concern. However very little information is available on the concentrations or physical/chemical properties of ultrafine particles in places where people live and work: in community air, in homes, in schools, in workplaces, in restaurants, or in vehicles. To determine the possible health impacts of UFP, it is essential to develop and deploy technologies that can assess the nature and extent to which people are exposed to these particles.

Research Recommendations:

The complexity of the sources and nature of UFP suggest that considerable characterization efforts will be needed to either discover and/or refine our understanding of linkages between exposures and various types of health outcomes. At one extreme is the need to determine how large, spatially dispersed populations experience ultrafine exposures over prolonged periods of study. At the other extreme is the need to know how individual people experience the hour-to-hour or minute-to- minute dynamics of ambient UFP as they move within their homes, communities and across communities. The analytic technologies required to characterize the physical/chemical nature of ultrafine particles in these various microenvironments are largely unavailable or untested outside the controlled environment of the laboratory. It is essential in research approaches for determining human exposures to ultrafine particles that other known harmful components of air pollution are considered. It is of limited value to characterize a detailed ultrafine exposure with the intention of determining how it may be linked to health outcomes while ignoring gaseous and larger size fraction PM.

The nature of the information needs of health and exposure assessors suggests that various approaches should be considered to meet these needs. Air monitoring needed in support of long-term population studies typically must be expected to operate with very little operator intervention for periods of up to several years. Siting of such monitoring operations should be made with care to best represent the overall community exposures. In panel studies where small groups of individuals are followed for days or weeks it may prove practical to perform enhanced monitoring of UFP. Enhancement might include technologies that report particle size distributions, the chemical nature of UFP as well as information on physical parameters such as shape and density. Panel studies offer the opportunity for individuals under study to carry instruments and record their locations and activities. Data from these sources have been shown to be essential when modeling overall exposures as well as to identify the microenvironments of most concern. As with large-scale studies, care should be taken to consider the siting of monitoring in order to provide robust data that may be related to observed effects. While these studies offer the opportunity to determine or model exposures to individuals in the study population, it is important to develop and employ monitoring instrumentation that is suited to placement in homes, in classrooms, in cars, and that can be carried by children and adults. Data collected in these studies should be augmented with assessments of the activities of participants and descriptions of the microenvironments monitored.

When exposure models are developed and employed to estimate UFP exposures, it is important to consider both indoor and outdoor sources. For the purpose of estimating exposures related to time spent indoors, it is useful to gather data on infiltration of UFP from outside sources.

Research Need 10: Dosimetry

Background:

Further research is needed to evaluate the dosimetry of ultrafine particles. This includes experimental validation of regional lung deposition models in the ultrafine particle size

range. Dose calculations are needed to translate exposure to dose in the health effects risk assessment process.

Research Recommendations:

This effort should include determining areal density of deposition in the different regions of the respiratory system and areas such bifurcations, which experience higher deposition. Also, transport to the lymphatic system, other organs, and intracellular regions needs to be assessed. Information is needed on what characteristics of particles – size, composition, solubility, shape – control the transport of a particle across cell membranes and into a cell. More information is need on the hygroscopicity (growth with increase in relative humidity) of UFP and effect of shape on transport and deposition in the respiratory system.

Research Need 11. Health Effects of Ultrafine PM

Background:

An emerging literature indicates that ultrafine particles are more toxic than the rest of ambient particulate matter. Recent epidemiological studies have found an association between exposure to ultrafine particles and mortality due to respiratory or cardiovascular disease. This association was strongest for UFP concentrations expressed as number concentrations. Toxicological studies also indicate that these particles, unlike larger particles, are capable of penetrating the cellular membrane, where they create an inflammatory response by means of generating oxidative stress and causing damage to the mitochondria.

Research Recommendations:

Based on the above, there is a need to study the health effects of these particles more extensively, both in panel and epidemiological studies as well as toxicological

evaluations.   The recent development of aerosol concentrator technologies enables scientists in the fields of toxicology to expose humans, animals species, and cell cultures to real world UFP. A few studies of this nature have been made recently, but there is a great need for more studies in urban (and rural) areas in which ultrafine aerosol formation mechanisms and thus chemical composition will vary significantly.   Of particular interest will be to identify mechanisms by which these particles induce cellular damage and generate oxidative stress, how they penetrate the cellular structure, and how the above are modulated by their chemical composition.

Epidemiological and toxicological studies should investigate what aspects of UFP are relevant for health effects (mass, number, surface, composition, morphology) by making atmospheric measurements of these particle properties   concurrently with the health studies.   Extensive measurements of many ultrafine particle properties can be made for use in epidemiological studies that require monitoring at a few sites for time periods of a few months. Examples are panel studies i.e., a small group of people with a wide range of exposures such as comparing commuters and non-commuters, and studies of subjects living with a range of high to low exposures due to their places of residence, i.e., comparison of health status as a function of distance to busy roads. For long term acute or chronic epidemiologic studies, simple, reliable, cost-effective measurement techniques are needed that can provide daily data at many sites for three or more years.

Ultrafine PM is currently not regulated directly, other than by being part of the overwhelmingly larger mass of $PM_{2.5}$, for which the US EPA has set air quality standards.   There is increasing evidence that these particles are toxicologically more potent than the rest of the ambient aerosol. These particles are also more heterogeneous spatially because their concentrations become higher in the proximity of their sources, such as industrial sources, refineries, freeways and busy thoroughfares.   This spatial variability poses a great challenge to the research and regulatory community in terms of developing effective methods for conducting population exposure assessment to ultrafine particles. Little is known about the degree of penetration into indoor environments and how this is dependent on housing characteristics as well as proximity to particle sources

such as busy streets and freeways. Moreover, population exposure during commute may be 10-fold higher than a typical urban background, which implies that the majority of the exposure occurs acutely at high doses of these particles. The degree to which these particles pose a public health hazard, and whether this hazard is acute or chronic in nature, are major issues that need to be addressed by the scientific and ultimately the regulatory community in order to protect public health.

Research Need 12.   Control Technology

Background:

At some level, the preceding research needs are vital for the implementation of effective control strategies. For example most ultrafine particles from motor vehicles are produced after the exhaust gases leave the tailpipe; an understanding of the mechanisms of nucleation, growth, and transport is needed to control such emissions by causing formation to occur in a control device or by controlling precursor vapors prior to exiting the vehicle. Insights and understanding developed above can be used directly in the design of source control equipment and will guide the development of pollutant control strategies.

Research Recommendations:

Research is needed to better define what aspects of ultrafine particles should be controlled. Is it ultrafine particle mass, number, surface area, specific chemical compounds, or a specific particle size range within ultrafine particles? This research needs to follow advances in understanding the health effects of ultrafine particles outlined in Research Needs 10 and 11.

There are two main aspects of the research needs for control technology of atmosphericnanoparticles (1) research needs to guide the development of source control

technology and (2) research needs to assess the effect of control of other air pollutants, such as accumulation mode particles or precursor vapors, on the concentration of ultrafine particles. Both require an understanding of the formation and growth of ultrafine particles and the nature of human exposure. As an example of a research need for (2), it is likely that as the concentration of larger particles (accumulation mode) are removed from vehicle exhaust streams as a result of emission controls that the concentration of ultrafine particles will increase because there is less available surface on which these particles can coagulate.

Most particle control devices have a minimum in the collection efficiency in the sub-micrometer size ranges, and many toxic constituents are enriched in these sizes. Also, observations have now established that there is a lowering of the collection efficiency in the ultrafine (nanometer) size ranges due to partial charging. This has also been observed in coal combustion exhausts equipped with ESPs with reduced collection efficiencies below 60 nanometers. There is a need to develop a more detailed understanding and develop ESPs and other particle control technologies that are effective in capturing ultrafine particles in industrial process exhaust streams.

Research Need 13. Ultrafine particles and homeland security

Research Recommendations:

There is a need to better detect certain types of ultrafine particles, which could potentially pose a biological threat to large segments of the population. Examples of such particles could include viruses, nanometer sized fragments of biological particles, and condensed chemical agents on ultrafine particle surfaces. From a protection standpoint, there is a need to capture and inactivate such types of particles, and a host of technologies need to be developed to address these issues. Such research will lead to the protection of indoor environments, clean and safe building programs, and the protection of public health.

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EPILOGUE

This Workshop brought together individuals working in various branches of nanoparticle aerosol science and technology to identify research needs. We sought to identify commonalities of interests among the participants who came from different fields of science and engineering. The basic areas covered included the topics of the first three Panels, namely *Experimental Methods and Instrumentation*, *Fundamentals of Nanoparticle Aerosol Formation* and *Computational Simulation of Aerosol Behavior* . We next considered two important applied fields, *Aerosol Reaction Engineering* and *Atmospheric Nanoparticles (Ultrafine Particles)*. Over thirty scientists and engineers from various fields and age groups worked together effectively and enthusiastically to produce the Workshop report.

In this Epilogue, we discuss issues broader than the individual Panel reports, that relate to the future of the nanoparticle aerosol field and to future workshops. The Workshop disclosed certain gaps in the structure and procedures that we originally established. For example, although we made time available for the rotation of Panel members to Panels other than their primary assignments to promote cross fertilization, more interaction of this type would be desirable in future Workshops. A case in point: *Fundamentals of Nanoparticle Aerosol Formation* (Panel 2) focused on certain idealized or limiting particle formation processes. *Aerosol Reaction Engineering* (Panel 4) and *Ultrafine Atmospheric Aerosols* (Panel 5) often deal with problems that are too complex for idealized aerosol formation theories to provide more than qualitative guidelines or to explain and/or predict trends. Multicomponent systems that include many short-lived chemical species are present in both cases. In the future we should bring together these three groups for a few hours to discuss how to face these complex problems.

Future Workshops should cover fledgling aerosol based technologies in more detail. Examples of such technologies include optical and electronic devices, gas sensors, catalysts, nanoparticles of biological interest, nanoparticle/polymer composites, electrospray aerosols and coated nanoparticles. A challenge will be to group such topics in a coherent way and to avoid presenting a set of unconnected subjects. This may be difficult to do. Perhaps grouping the technologies according to transport mechanisms for

getting the aerosol particles to desired sites and deposition patterns would be a helpful unifying theme for some of the topics.

Future Workshops may wish to address fundamental mathematical issues in greater detail than we did. An example is the (Smoluchowski type) partial integrodifferential equation on which the mean field equations of aerosol dynamics are based. This equation plays a prominent role in the reports of Panels 2, 3 and 4. It may be desirable to invite mathematicians and/or statistical mechanicians with experience in this field and aerosol applications to the next workshop.

Morphological issues appear in the reports of Panels 1, 2, 4, and 5, usually associated with nanoparticle aggregate structures. Mathematical developments in image processing may advance the speed with which morphological structures (such as chain aggregates) can be characterized. Recent developments in this field should be reviewed in future workshops.

Much of aerosol science and technology is based on the work of scientists who probably did not consider themselves aerosol specialists or experts when they did their work. This is changing. For example, important aspects of modern aerosol instrumentation such as single particle chemical analyzers are based to a great extent on the work of individuals who may come from different backgrounds but consider themselves *aerosol scientists*. We can expect trained aerosol scientists to play a larger role in advancing the field in the future.

The two applied areas discussed in the Panels on *Aerosol Reaction Engineering* and *Atmospheric Nanoparticles (Ultrafine Particles)* have different histories. Aerosol reactor design developed in its early stages without substantial contributions from individuals who considered themselves aerosol scientists. Nevertheless engineers and scientists who worked in the field were able to design successful and economically viable technologies. In recent years, trained aerosol scientists recruited by industry appear to be making significant contributions to this vital technology.

The field of ultrafine atmospheric aerosols, on the other hand, has developed and is dominated by individuals who consider themselves aerosol specialists. Their continuing effectiveness will depend on their ability to invent and apply instruments capable of advanced measurements, and interpret their results in a way that will help

solve important problems. They should be encouraged to conduct cutting edge aerosol research, and to work with toxicologists and atmospheric scientists to help explain aerosol effects on public health and the atmospheric environment. As appropriate, aerosol scientists will be capable of playing a leading role in collaborative efforts.

The success of the Workshop supports the idea that aerosol science and technology can be viewed as a coherent discipline with its own experimental methods, basic theory and computational methods. Moreover it is a discipline with wide practical applications both in industry and natural phenomena, that is, an *enabling discipline* on which many other fields depend.

The rapid changes in technology and environment that drive research on nanoparticle aerosols are likely to justify another workshop in this field sometime in the next two or three years. Our Workshop was organized with financial support from two NSF programs and from the Southern California Particle Center (sponsored by EPA). Logistic support was provided by the UCLA Chemical Engineering Department. We thank those organizations for their support. Each Panel was composed of academics and a smaller group from industry and government agencies. In planning future workshops, we should continue to seek support and participation from the many government agencies that depend on advances in nanoparticle aerosol science and technology. Some of these were identified in the Preface. Future workshops would also benefit by increased participation from industry (including start-up companies).

Finally, we wish to express our appreciation to the Workshop participants. As noted by one of the NSF representatives at the final plenary session, participants came unusually well prepared and pitched in with great enthusiasm. We were fortunate in having many young investigators present; their enthusiasm and commitment bode well for the future of our field.

Sheldon Friedlander, Workshop Chair

David Pui, Workshop Co-Chair