Title: Nanoparticle Aerosols Determining the Structural basis for the Hydrodynamic Radius.
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Time Span: Two years
Number of Graduate Students: 1

Abstract: Aerosols are dispersions of nano- to micron-scale particles in a gas such as air. Aerosols are encountered in atmospheric science, combustion science, and in drug and particulate delivery. Often, aerosols are composed of complex hierarchical particles such as fractal aggregates. A number of methods to characterize aerosols exist. These techniques are most challenged by nanoscale particulates with fractal structure such as silica fume and carbon black or combustion soot such as in diesel engine exhaust. Techniques to characterize aerosols involve fractionation of the polydisperse streams of aggregates. This fractionation can be carried out based on mobility by charging the aerosols particles and separating the particles in a field in a differential mobility analyzer (DMA). Alternatively, the fractionation is carried out by mass using centrifugal force in a centrifugal particle mass analyzer (CPMA). For complex fractal morphologies, the relationship between mobility or mass and structure is not straightforward. Over the past four decades this complication has been addressed through theory and simulation such as discussed in Friedlander's classic text "Smoke, Dust, and Haze". Verification of these theoretical and simulation results linking particle mobility and particle mass to mass-fractal structure is lacking in the literature. The primary technique that can directly quantify fractal structure is small-angle x-ray scattering (SAXS). SAXS can be carried out in situ on aerosol streams as was done with the USAXS instrument at APS on combustion aerosols as well as on diesel engine exhaust several years ago. Verification of theory and simulations for mass fractal aerosols would require linking expertise in modeling and simulation of aerosols, instrumentation for aerosol fractionation, expertise in small angle scattering (SAXS) theory, and SAXS experimental methods, an extremely high flux source with previous experience with aerosol studies and a wide q-range to cover nano primary particles to micron scale aggregates and agglomerates (USAXS). It is proposed to assemble a team with workers at NIOSH in Cincinnati and industrial partners to develop an understanding of the structural basis for transport coefficients obtained from particle nebulizer, DMA and CPMA instruments. The work will involve setting up the instruments with helium carrier gas to reduce the air background at the synchrotron either in Chicago, at NSLS II, or at CHESS at Cornell. The result of this study will serve as a basis for understanding aerosols in a range of fields from occupational exposure to dust and exhaust streams containing nanoparticles such as in industrial manufacturing environments.

Purpose and Importance of the Research:

Aerosols are nano to micron scale dispersions of solids or liquids in a gas. Aerosols are commonly encountered as combustion byproducts, clouds and plumes in the atmosphere, air pollution, medical inhalation therapy, and consumer products such as insecticides and hair spray. Characterization of aerosols is a challenge since manipulation of aerosol streams tends to modify the particulate or droplet structure. For example, it is usually necessary to cool and dilute combustion aerosols in order to study the particle mobility distribution in a differential mobility analyzer (DMA). The available tools to study aerosols allow for characterization in terms of the particle mass distribution or in terms of the particulate mobility. However, aerosol particulates and droplets can be complex fractal structures such as flame made silica and titania powders/molten aggregates in flame synthesis or carbon aggregates in combustion streams. For these complex morphologies the relationship between mobility diameter, mass, and fractal structure is based on theory and simulation. USAXS can directly observe details of the fractal structure such as branch content, branch length, aggregate mass and primary particle size. The calibration of standard aerosol techniques (DMA and CPMA) using USAXS will allow a detailed understanding of the structure of these aerosol streams based on experimental observation rather than theory. This will result in a direct correlation with properties and health impact.

In order to understand the validity of theoretical predictions of fractal structure based on mobility and mass we seek to study model nanoscale aerosols produced in a nebulizer. The polydisperse parent aerosol will be measured using USAXS. This aerosol stream will then be passed through a DMA to produce narrow distribution streams of particles based on mobility for study by USAXS. The same parent aerosol stream will be passed through a centrifugal particle mass analyzer (CPMA) to produce a narrow distribution aerosol based on mass. These fractionated streams, by mass and by mobility, will be studied using in situ USAXS. By comparing the structure for a number of mass and mobility streams we hope to map the particle mobility/mass/structure spectrum in order to understand the selectivity criterion for these methods for fractal aerosols and to verify theoretical predictions of structure based on mobility and mass distributions. The experiment will effectively calibrate the DMA and CPMA instruments with the actual structure determined using in situ USAXS. DMA and CPMA can be used in the field, for example at industrial sites where workers are exposed to nanoparticulate aerosols or on diesel trucks during highway operation to measure nanoparticles in the tailpipe emission. Calibration of these measurements will be made with the actual fractal structure of materials like nanoscale carbon soot using USAXS.

Description of Experiments

The project will study silica and carbon aerosols produced from commercial samples of HiSil 200 from PPG and CB330 from Continental Carbon. The particles will be suspended in water and a liquid aerosol will be generated. This aerosol will be dried in-stream and passed through the USAXS/SAXS instrument in a sealed tube made of Kapton sheet or aluminum foil. The effluent nanoparticles will be collected in a filter before being fed into the existing vent system. Helium will be used as a carrier gas to enhance contrast. A similar experiment was performed in Italy in 2019 [1]. The experiment will involve collaboration with the National Institute of Occupational Safety and Health (NIOSH) research lab in Cincinnati who is an expert at aerosol characterization using DMA, CPMA, and particle nebulizers. Dr. Kulkarni has built similar instruments as part of his research. A successful experiment relies on stable aerosol generation, proper functioning of the DMA and CPMA, successful operation of the USAXS scan and capture of the aerosol stream at the end of the process. Other silica, titania and carbon black samples will be measured. (We have a library of 100 commercial nanoscale silicas, titanias and carbons.) The proposed experimental program will consist of two stages, proof of concept and verification of theoretical and simulation predictions on model aerosols.

1. P. S. Bauer, H. Amenitsch, B. Baumgartner, G. Köberl, C. Rentenberger, P. M. Winkler, In-situ aerosol nanoparticle characterization by small angle X-ray scattering at ultra-low volume fraction. Nat Commun 10, 1122 (2019). https://doi.org/10.1038/s41467-019-09066-4