REPORT MA-956

Title:

Size and structures of carbon nanoparticles and soot generated in gas-phase reactive systems: The influence of temperature and chemical composition

Proposers:

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Introduction:

The Project aims at investigating the influence of initial temperature and chemical composition on the size and structure of carbon nanoparticles and soot produced: 1) in conventional flames and 2) in prototype reacting systems, using combined in situ SAXS/WAXS measurements with high dynamic range and time resolution (down to milliseconds time scale). These experiments will provide systematic data sets not only from the gas phase, but also on the experimentally challenging transition from the gas to the condensed phase, which will give fundamental information that is hard to obtain from modelling. Such data will therefore provide valuable input for researchers working on theory and models describing condensation phenomena and the formation of nanostructured materials from gas-phase reactions. Not the least, there are many aspects which are of multidisciplinary interest that range from combustion theory to materials science and environmental as well as health science.

Scientific background:

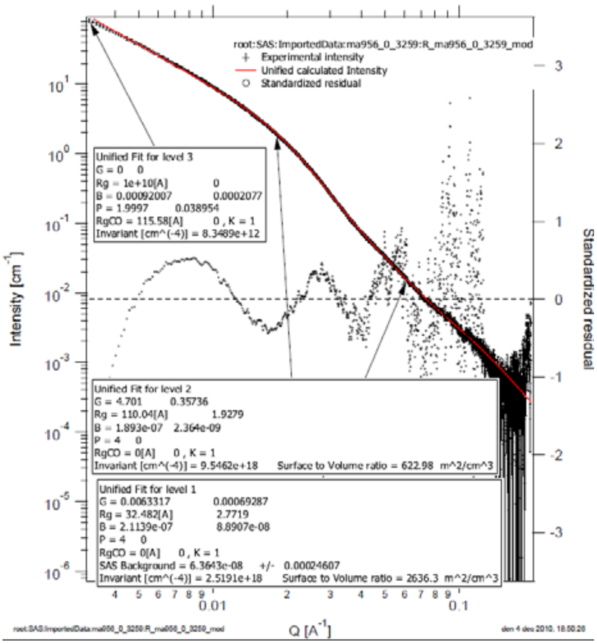
The chemical and physical properties of nanoparticles are strongly related to their size and structure, which are the main objectives of SAXS and WAXS. Understanding carbon nanoparticles formation and evolution in high temperature environment is of broad interest for basic and applied sciences. Many unknowns remain due to the complexities of the processes taking place, their fast time scale, the reactivity of the species being formed, and the added requirement of in situ diagnostic. Experimental techniques with sufficient spatial and temporal resolution to obtain information at the atomic level are needed to reveal the details of these phenomena. SAXS (size distribution) [1-3] and WAXS (structural data) [4,5] are just starting to be combined and their use in the field of Combustion Science has been realized [5].

Recently, the new detector prototype enabling SAXS/WAXS measurements with high dynamic range and time resolution has allowed our research team to study the transition from gas to condensed phase in a diffusion flame stabilized by a metal plate [5]. In the gas phase, they have evidenced the existence of processes that do not lead directly to graphitic structures. They also have revealed that the condensed soot is not static, the interlayer distance between the graphene-like sheets decreasing with temperature, stressing the importance of in situ monitoring.

Measurements performed during the campaign MA 956 June 21 – June 24, 2010 and preliminary analysis:

SAXS and WAXS intensities were measured from partially premixed diffusion flames stabilized by a metal plate. The formation and phase transitions of nanoparticles were studied close to the plate. The wide range of the momentum exchange parameter yielded observable length scales in the range 1.3 Å to 3700 Å. 2D-detectors from ID-02 were used to measure the SAXS and WAXS intensities synchronously. X-ray scattering measurements were performed at energies of 12.46 keV and 14 keV. The photon flux of the radiation was 10^{11} photons, typically, and the cross section of the beam was 100 μm ×100 μm.

We were able to measure the SAXS and WAXS signals for periods of hours and capture the scattering properties of pure gas-phase particle ensembles and those from the transition region between gas-phase and condensed phase. The condensed material was also investigated. Temperatures were continuously monitored at 3 different heights using thermocouples: Close to the burner surface; at medium height; and close to the condensation plate.



Fit of a SAXS scattering curve using the "Unified Fit" in the IRENA software package produced by Jan Ilavsky (http://usaxs.xor.aps.anl.gov/staff/ilavsky/irena.html). Fit by Stefano di Stasio.

The experiments were performed on pure diffusion and partially premixed ethylene/air flames for different fuel air-ratios. The cross section of the burner was circular with a diameter of 20 mm. All the measurements were performed 1-2 mm below a steel plate and 12-18 mm above the burner surface. The SAXS and WAXS data are currently being evaluated.

The main advantages compared to previous experiments were that much smaller q-values could be investigated. Important information regarding structure size, degree of clustering and shape of the particles were obtained. At least three typical size modes were evidenced from the SAXS: 2-4 nm; 10-30 nm and 100 nm or larger. For the largest size group the Porod region could be evaluated, but the Guinier regions were not clearly evidenced. Therefore it will be necessary expanding the investigations into further lower q-ranges that will demand USAXS in such a way that complete Guinier regions can be used to evaluate the size of the largest particles. Regarding the WAXS measurements we were able to observe structural graphitization appearing at a certain point of time close to and during the phase transition. However, it was hard to interpret the evolution of structural changes due to the limited spatial resolution when using the 2-D open WAXS detector. The combined SAXS and WAXS detectors from Lund University will improve the resolution in the up-coming experiments.

The first preliminary results show already new important insights in the dynamics compared to our previous measurements. A paper describing the results is planned to be submitted during spring of 2011.

Operation of the beamline:
The ID-02 beamline performed well. The lost experimental time due to beam loss from the ring was 5-6 hours of our effective experimental time.

Summary and prospective:
The results from the data evaluated so far are very good and confirm the importance of the project. It is important to clarify the role of temperature on the dynamics of particle formation and phase transitions. The investigations at ID-02 need to be extended into a wider q-range so that it will be possible to describe both the properties of particles in the gas phase and structures of the condensed material above the size of 200 nm and finer details approaching the atomic scale. We will continue the investigations with new experiments hopefully already during the autumn of 2011, depending on the outcome of the applications to the ESRF. Of particular importance will be adapting the WAXS techniques with improved spatial resolution and procedures optimized with respect to signal to noise and able to resolve mesoscopic molecular clusters and particles such as graphene [6]. This will be possible by complementing the detection systems with the new detectors developed in our group. These enable high-dynamic-range and fast response dynamics measurements on the order of one millisecond under continuous sampling [7]. In addition, USAXS will be important to investigate the largest particles and the structure of the condensed material

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