

## Scattering Theory

When an x-ray beam (or neutron or light) passes through a material with structures displaying sizes larger than half the wavelength of the radiation a small fraction of the incident radiation is scattered in directions that differ from that of the incident beam. Scattering arises since x-rays ionize the sample material (that is remove an electron from a molecule) and the free electron recombines with the material releasing radiation of the same wavelength but isotropically (at all angles, like a light bulb). Monochromatic (single wavelength) x-rays released in this way from different structural features interfere with each other (enhance or diminish the amplitude due to phase differences). The spatial (angular) pattern of scattered radiation resulting from this process bears a direct relationship to the structure (the pattern is a Fourier transform of the structure). At large scattering angles, small sizes are probed and for angles larger than about 6 degrees we observe the smallest scale seen in x-ray diffraction, near half the wavelength of typical x-rays, 0.075 nm. For angles less than 6 degrees nanomaterials and colloidal structures are observed. There is no theoretical large-scale limit and using specialized equipment angles as small as 1/10,000 degree can be measured allowing a continuous description of structure from the 0.1 to 1,000 nm scales. Such an experiment can be achieved in 30 microseconds using a modern synchrotron facility such as ID02 at ESRF in Grenoble France. Additionally, modern international user facilities enable measurements on extremely low concentrations, volume fractions less than  $10^{-6}$ , under almost any experimental conditions (for instance reacting liquid solutions, flames, samples undergoing industrial processing, living tissue). The speed of measurement and high intensity of x-rays allows in situ studies that can only be dreamed of by microscopists. The disadvantage of x-ray scattering is that the x-ray pattern does not result in a photograph, but in a Fourier pattern that must be interpreted using scattering theory. The University of Cincinnati is recognized as a world leader in the application of small-angle scattering to nanomaterials with pioneering work of Joon Roe, Dale Schaefer and more recently Greg Beaucage along with contributions from Steve Clarson and Jim Mark among others. For example the most popular text for small-angle scattering was written by Joon Roe at UC (emeritus faculty in Chemical and Materials Engineering).

Traditionally, scattering data is converted to structural information either by calculation of a "*correlation function*" from theoretical models, or by using generalized functions that consider average features such as the moment of inertia (radius of gyration) and average surface to volume ratio for particles. The flexibility of generalized functions has been limited by their applicability to narrow ranges of size since the generalized functions describe only one component of the often complex structure. For example, Guinier's law describes the radius of gyration (moment of inertia) and number density of any dispersed material but does not describe the surface scattering or clustering/aggregation of the material. Recent Cincinnati theoretical efforts by Beaucage have focused on broadening the applicability of generalized scattering functions through the derivation of the Unified Scattering Function and through deriving relationships between the parameters obtained from localized functions to obtain a description of structure over more than 4 orders of size including complex, hierarchical nanomaterials. Citations of the Unified Function number in the hundreds and the approach is rapidly

gaining popularity due to its simplicity and applicability in a general sense to most scattering problems.

For example, the Unified Function is particularly useful in describing disordered aggregated particulate nanomaterials and polymers where chain structure varies from a random walk. In polymers this structure is seen if a polymer is dissolved in a good solvent or when chain branching occurs such as in polyethylene (produced in Cincinnati at Equistar Corporation). For ceramic aggregates, there is no available global function other than the Unified Function that can routinely be used to analyze complex scattering from these hierarchical nanomaterials. Recent in situ studies of nanomaterials dispersed in aerosols have made necessary the derivation of new tools to describe nano-particle size polydispersity, aggregate branch content and aggregate polydispersity using generalized scattering parameters. Comparison has been made between commonly used laboratory techniques such as gas absorption for particle size and TEM. However, these laboratory techniques are not amenable to in situ studies of growth, among other problems.

The figures below show some examples of the use of scattering theory developed at Cincinnati in application to disordered ceramic materials. Figure 1 compares a tedious TEM counting measurement with the 30 micro-second SAXS measurement in terms of nano-particle size distribution as discussed in the 2004 *Journal of Applied Crystallography* paper by Beaucage. Figure 2 shows a comparison of Unified fits to non-aggregated and aggregated nano-particles. Figure 3 shows 2D maps of nano-particle size and particle polydispersity from insitu measurements as reported in *Nature Materials*. Figure 4 shows an axial plot from the same fit parameters as shown in fig. 3, fit to a diffusion limited growth model.

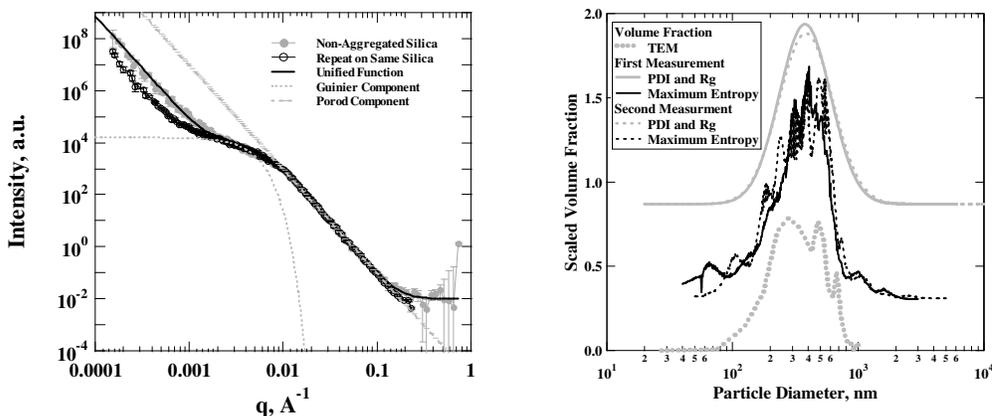
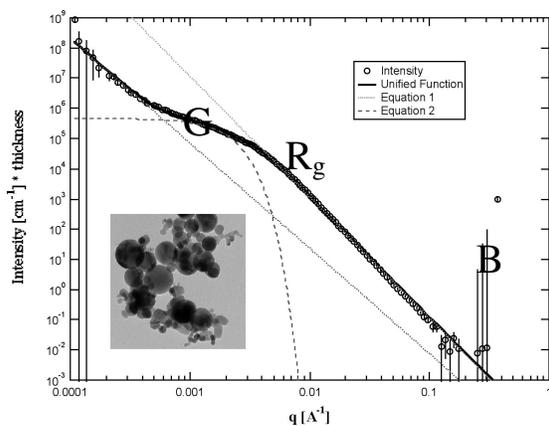


Figure 1. 3.1 g/hr Silica. a) Repeat runs on a non-aggregated silica powder.  $PDI = 23.1$  and  $Rg = 442.2 \text{ \AA}$ . b) Particle size distributions from TEM, Equations (1, 2, 17 and 18) PDI and Rg, and using the maximum entropy program of Jemian ([www.uni.aps.anl.gov](http://www.uni.aps.anl.gov)).

### Non-Aggregated Polydisperse



### Aggregated and Polydisperse

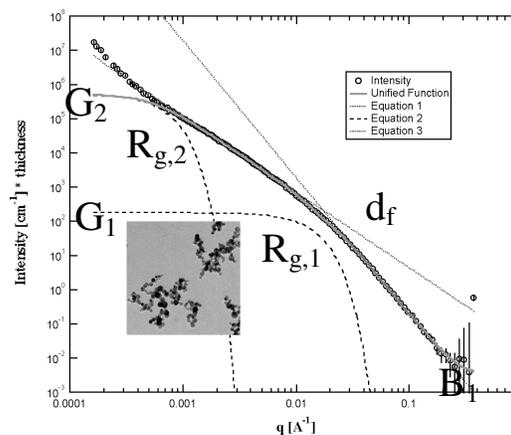


Figure 2. Unified fits for non-aggregated and aggregated nanomaterials.

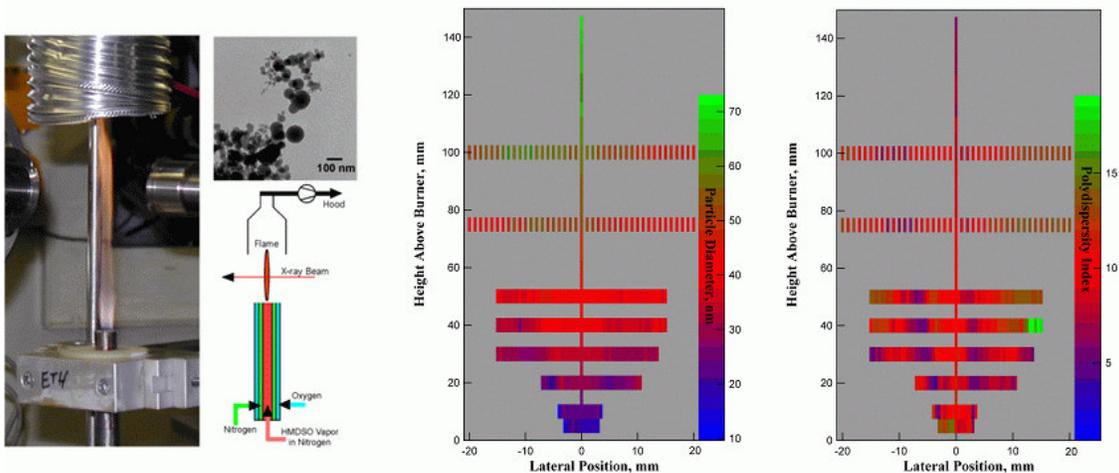


Figure 3. In situ results of Unified fits for a silica diffusion flame published in *Nature Materials*.

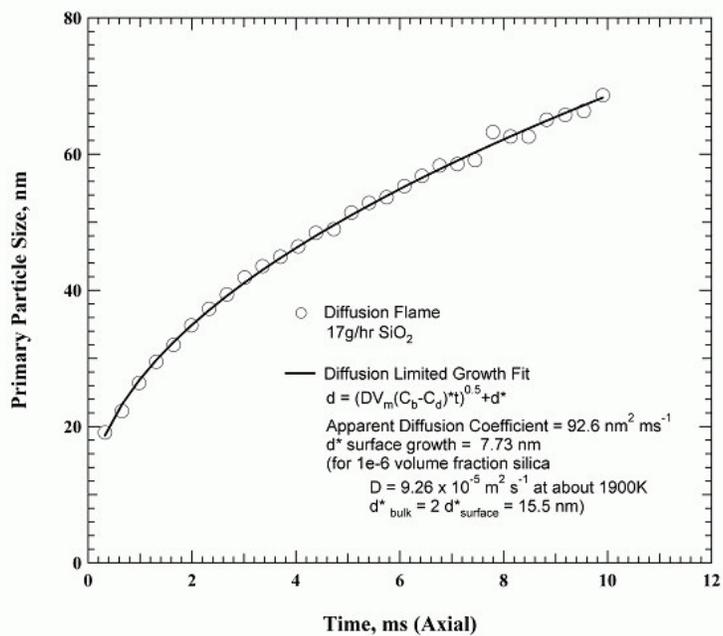
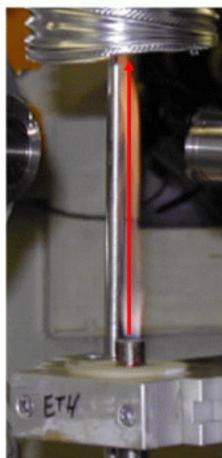


Figure 4. In situ axial data from Unified fit, fit to diffusion limited growth model.