Dynamics of Nanoscale Soot in Diesel Exhaust via Small-Angle X-ray Scattering

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12'th ETH Conference on Combustion Generated Nanoparticles

Background: Diffusion Flame Measured at ESRF Grenoble, France

SAXS (Small-Angle X-ray Scattering) for Diesel Exhaust

Why you might be interested in SAXS:

-In situ observation of soot & inorganic nanostructure with no dilution
(calibrate/verify DMA)
-Measure from ~ 1 Å to 1 μm (direct observation of all possible nucleation modes)
-Wide sample concentration range solid powder to exhaust aerosol
-Volatile, semi-volatile, and solid particles (no dilution, charging or denuding)
-Unique details of aggregate structure including mass fractal dimension, branch content
-Volume and number density as well as primary particle size distribution
-20 ms measurement (possibility of observation within engine cycle)

Why you might *not* be interested in SAXS

-Requires a synchrotron for in situ aerosol measurements
(powders can be measured in the lab)
-Non-portable measurement
-More or less requires a specialist (involved data anaylsis)
-Composition is more difficult than structure (electron density or use anomalous SAXS)
-New method (This is the pioneering study and is still in preparation for publication)

Outline

1) SAXS Tutorial - 6 min

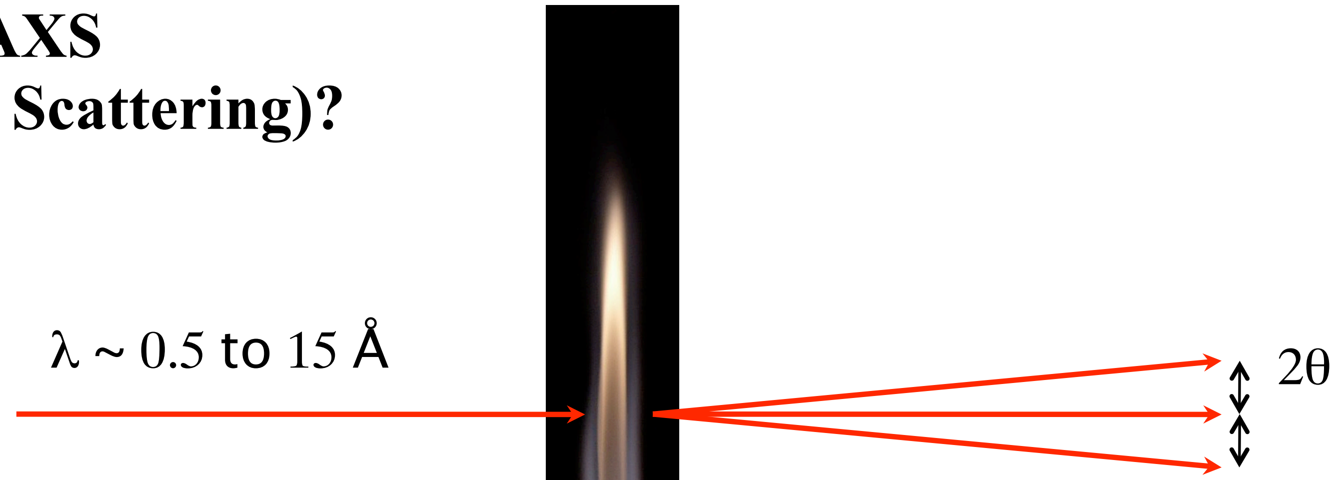
2) In situ Flame Work - 2 min

3) In Situ Diesel Exhaust Study - 5 min

4) Summary - 1 min

Background: ESRF Synchrotron Grenoble France

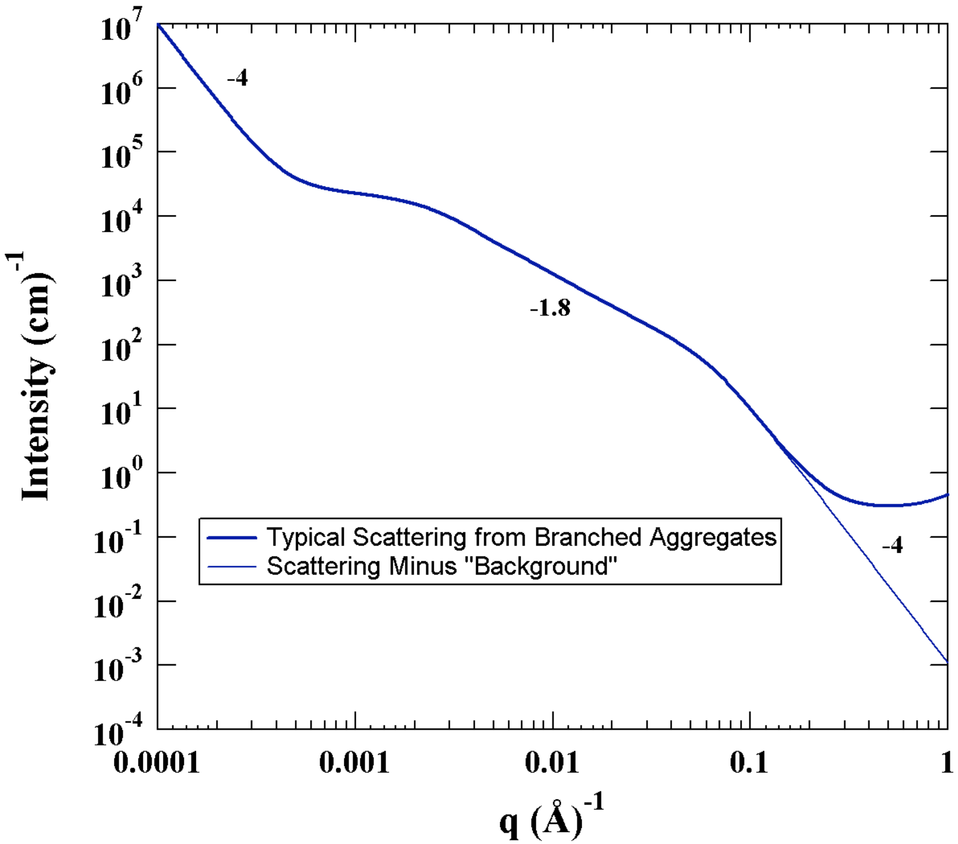
What is SAXS
(Small Angle X-ray Scattering)?



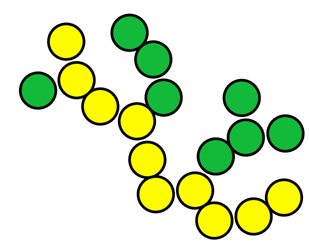
$$d = \lambda/(2 \sin \theta) = 2\pi/q$$

θ ~ 0.0001 to 6°

d ~1 μm to 1 Å



Branched Aggregates

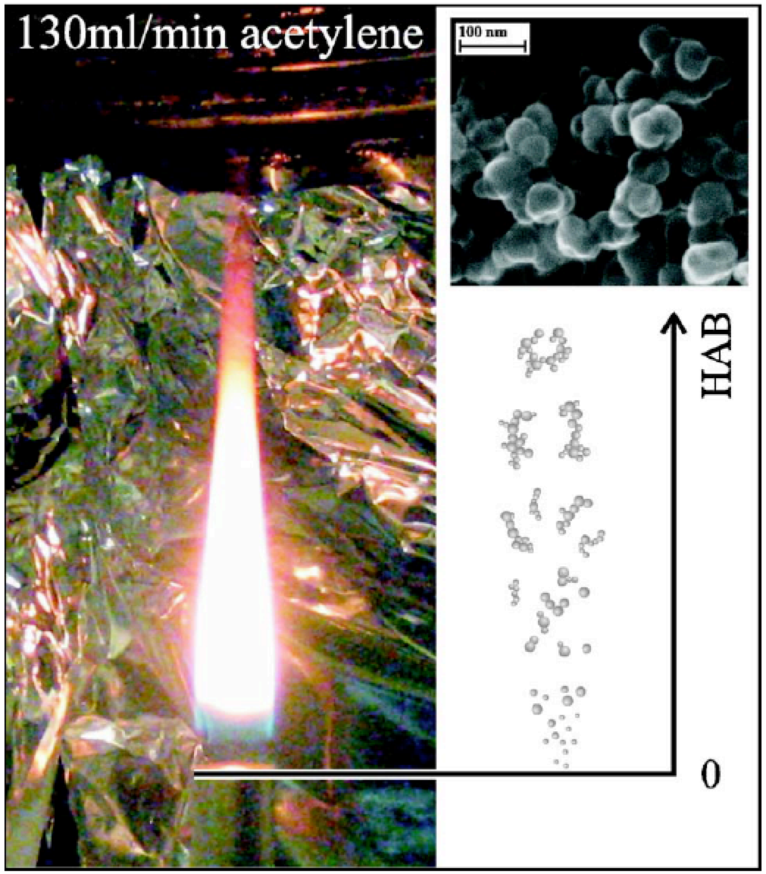


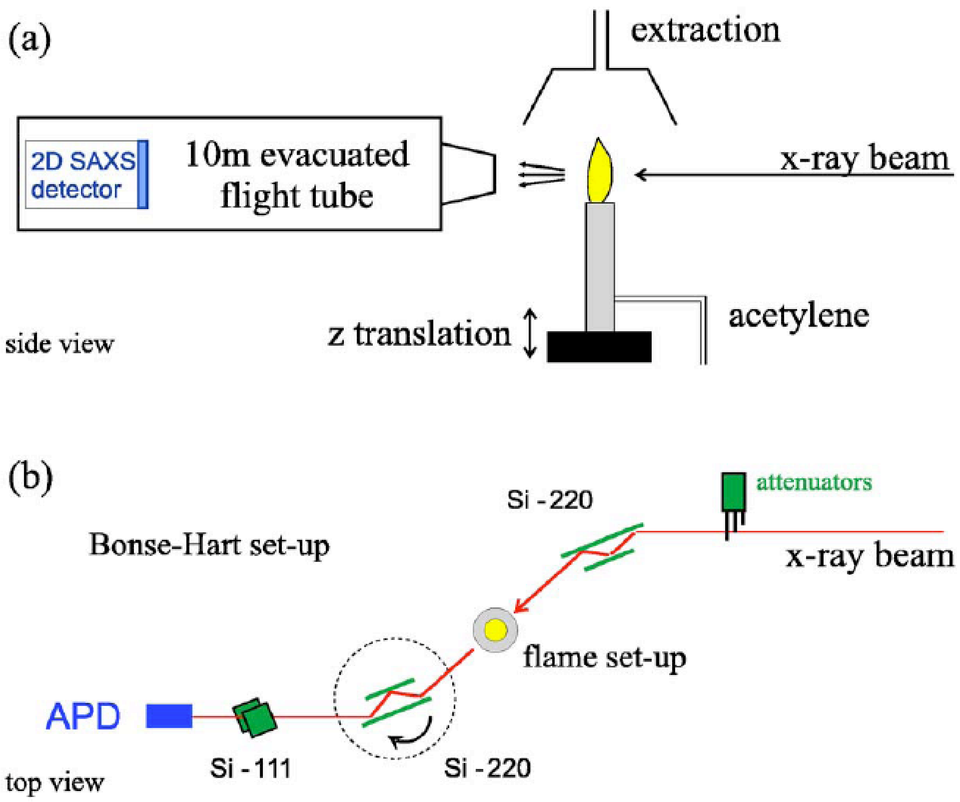
$$q = \frac{2\pi}{d} \qquad I(q) = N(d) n_e^2(d)$$

N = Number Density at Size "d"

n_e = Number of Electrons in "d" Particles

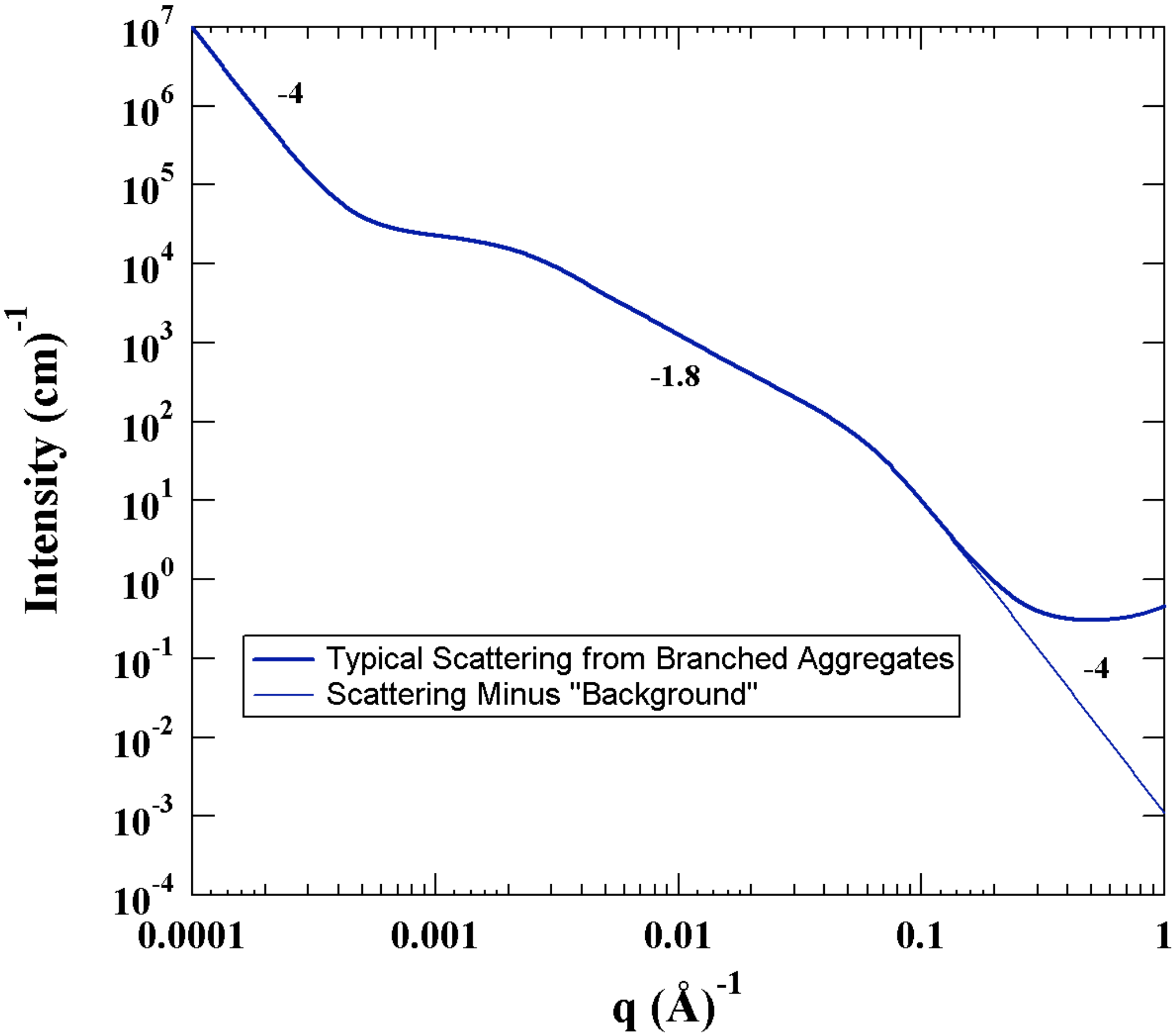
Two SAXS Camera Geometries

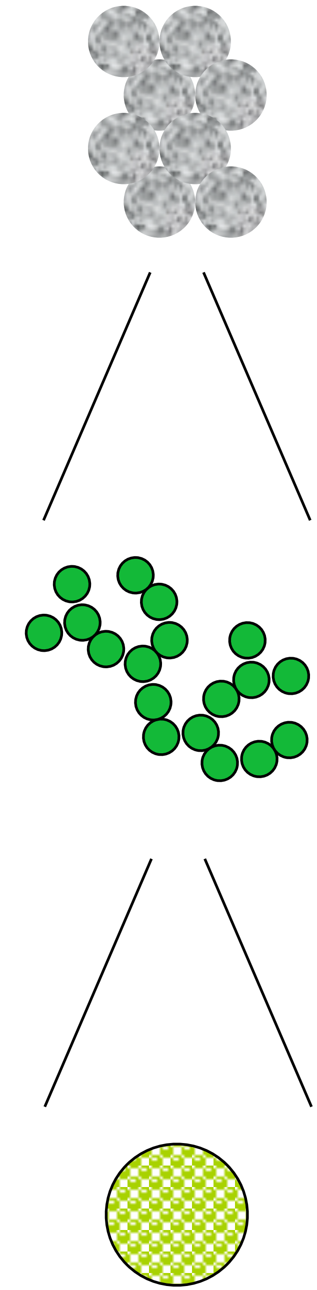




Sztucki M, Narayanan T, Beaucage G, *In situ study of aggregation of soot particles in an acetylene flame by small-angle x-ray scattering* J. Appl. Phys. **101**, 114303 (2007).

Complex Scattering Pattern
(Unified Function, Beaucage 1995 *J. Appl. Cryst.*)





$$q = \frac{2\pi}{d} \qquad I(q) = N(d)n_e^2(d)$$

N = Number Density at Size "d"
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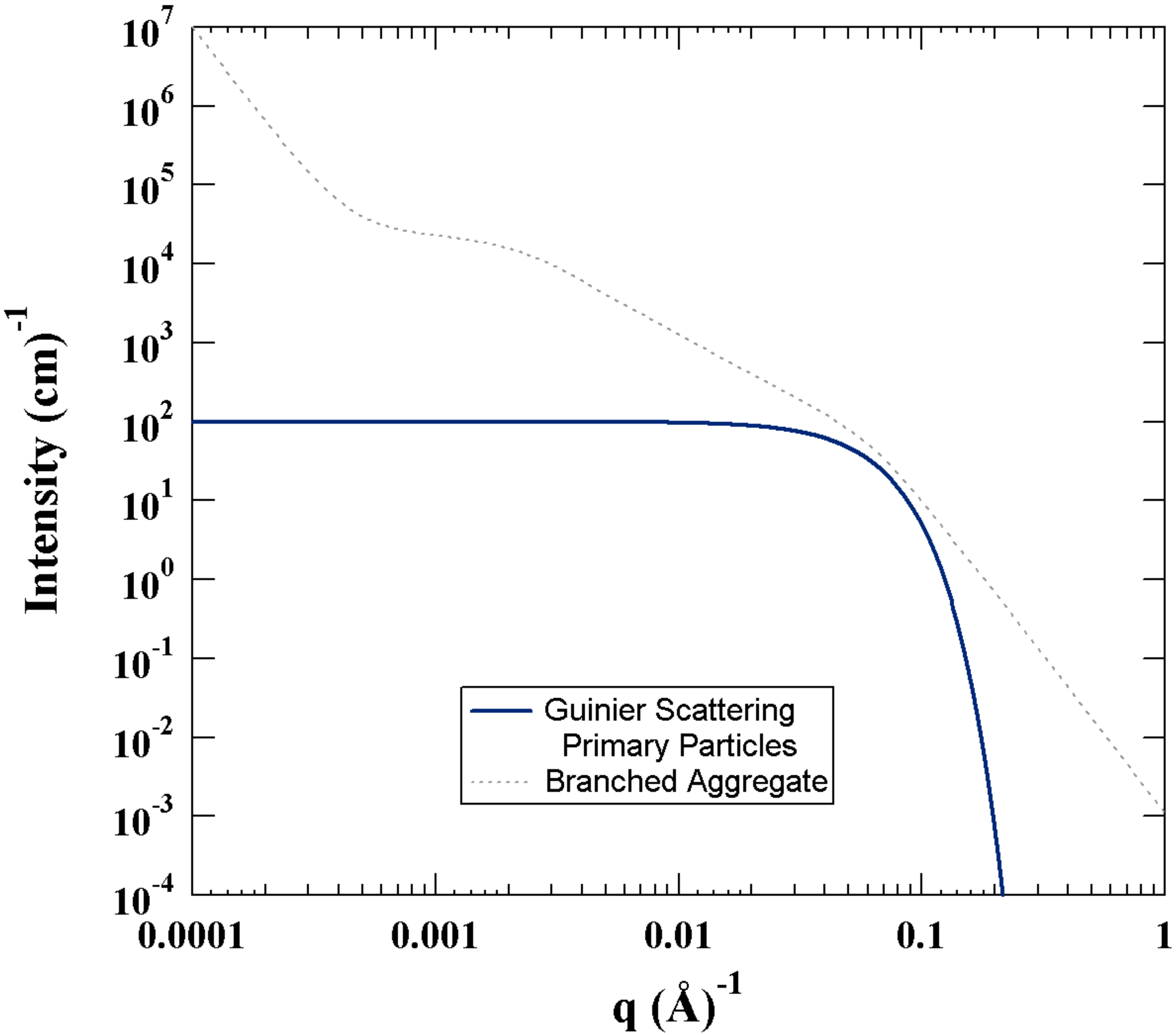
Guinier's Law



Particle with No Interface

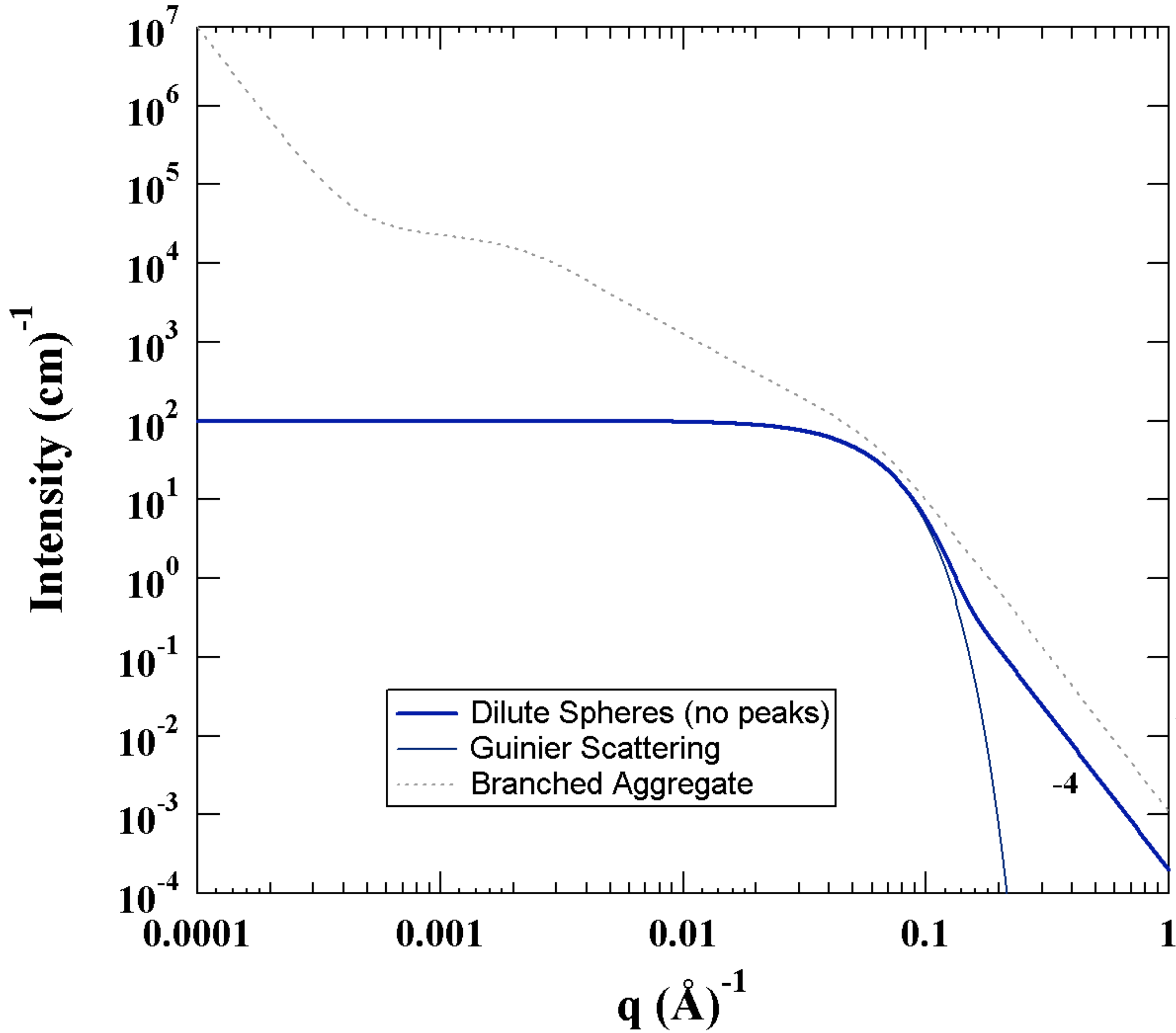
$$I(q) = N(d)n_e^2(d)$$

$$I(q) = G_1 \exp\left(\frac{-q^2\left\langle R_{g,1}^2\right\rangle}{3}\right)$$

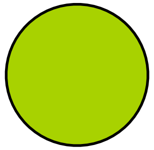
$$G = N\rho_e^2\left\langle V^2\right\rangle \sim \left\langle \mathrm{R}^6\right\rangle$$

$$\left\langle R_g^2\right\rangle \sim \frac{\left\langle \mathrm{R}^8\right\rangle}{\left\langle \mathrm{R}^6\right\rangle}$$

Guinier and Porod Scattering



Spherical, Monodisperse Particle With Interface (Porod)



$$I(q) = B_P q^{-4}$$

$$B_P = 2\pi N \rho_e^2 \langle S \rangle$$

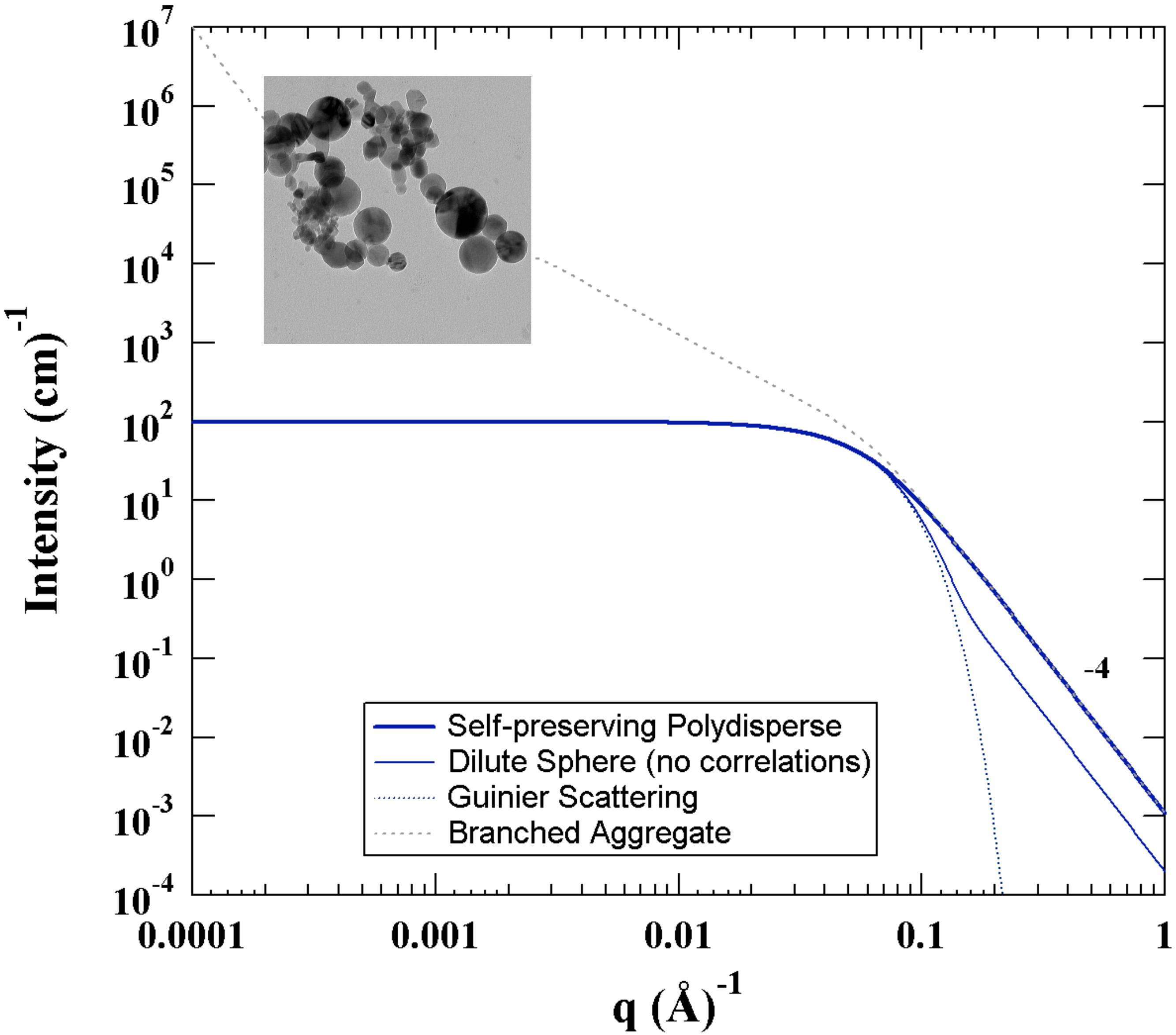
$$\langle S \rangle \sim \langle R^2 \rangle$$

$$Q = \int q^2 I(q) dq = N \rho_e^2 \langle R^3 \rangle$$

$$d_p = \frac{Q}{2\pi B_P} = \frac{\langle R^3 \rangle}{\langle R^2 \rangle}$$

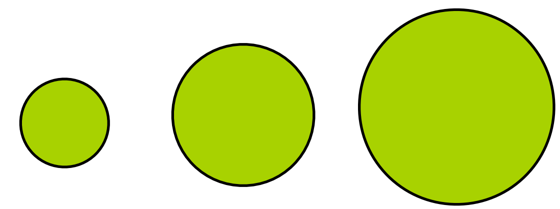
Structure of Flame Made Silica Nanoparticles
By Ultra-Small-Angle X-ray Scattering
Kammler/Beaucage Langmuir 2004 20 1915-1921

Polydispersity Index, PDI



Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. ***<u>37</u> 523-535 (2004).***

Polydisperse Particles



$$PDI = \frac{B_P R_g^4}{1.62G}$$

$$\sigma = \ln(\sigma_g) = \left[\frac{\ln(PDI)}{12}\right]^{1/2}$$

$$m = \left[\frac{5R_g^2}{3e^{14\sigma^2}}\right]^{1/2}$$

Particle Size Distribution Curves from SAXS

PDI/Maximum Entropy/TEM Counting

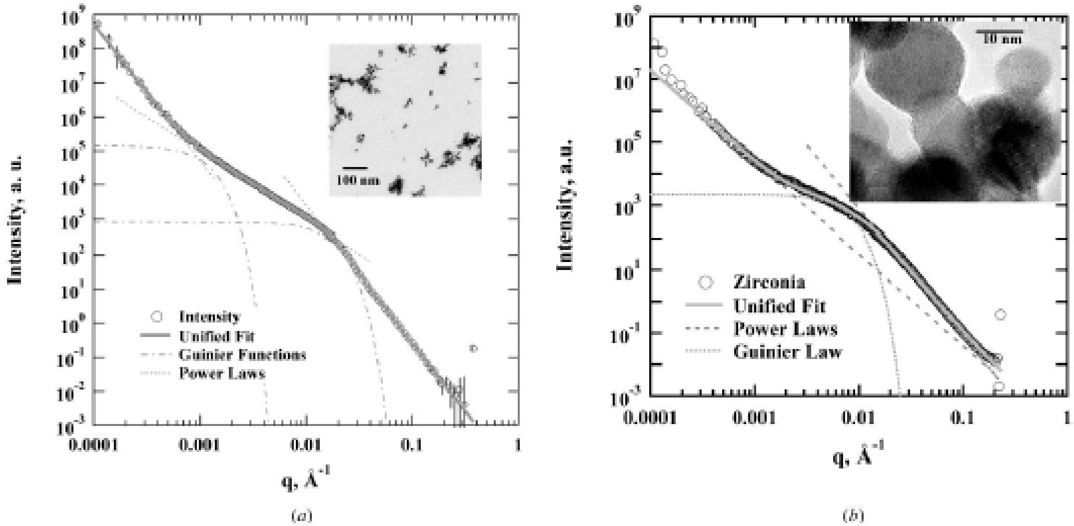


Figure 2
USAXS data from aggregated nanoparticles (circles) showing unified fits (bold grey lines), primary particle Guinier and Porod functions at high q, the intermediate mass fractal scaling regime and the aggregate Guinier regime (dashed lines). (a) Fumed titania sample with multi-grain particles and low-q excess scattering due to soft agglomerates. d_{VIS} = 16.7 nm (corrected to 18.0 nm), PDI = 3.01 (σ_g = 1.35), R_g = 11.2 nm, d_f = 1.99, $z_{2:1}$ = 175, z_{R_g} = 226, R_{g2} = 171 nm. From gas adsorption, d_p = 16.2 nm. (b) Fumed zirconia sample (Mueller *et al.*, 2004) with single-grain particles, as shown in the inset. The primary particles for this sample have high polydispersity leading to the observed hump near the primary particle scattering regime. d_{VIS} = 20.3 nm, PDI = 10.8 (σ_g = 1.56), R_g = 26.5 nm, d_f = 2.90. From gas adsorption, d_p = 19.7 nm.

Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

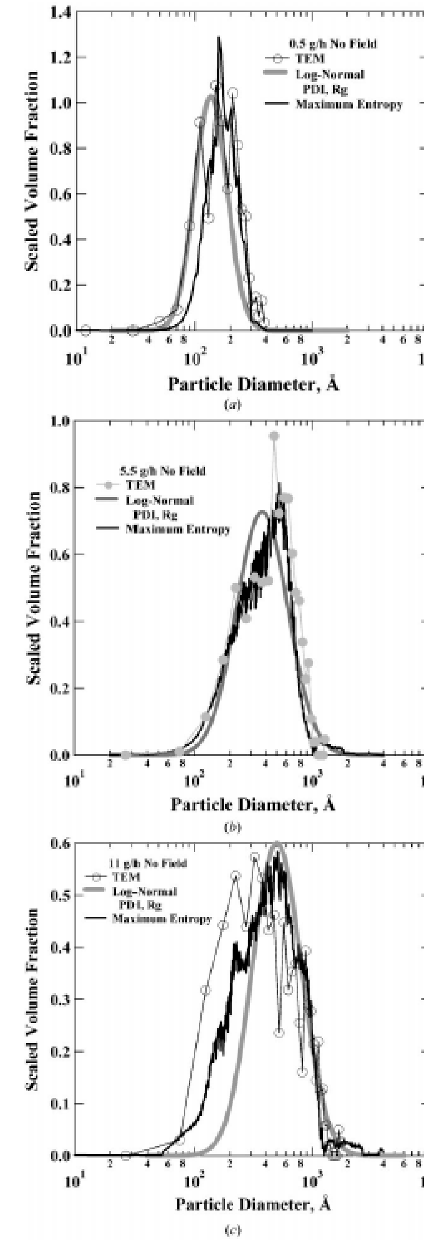


Figure 6
Comparison of particle volume distributions for titania made without an electric field using TEM (circles; Kammler *et al.*, 2003), PDI (grey line) and maximum entropy (black line). (a) 0.5 g h^{-1} [fractal d_{VIS} = 12.1 nm, PDI = 3.52 (σ_g = 1.38), R_g = 8.9 nm, d_f = 1.59, $z_{2:1}$ = 1160, z_{R_g} = 1343]. (b) 5.5 g h^{-1} [d_{VIS} = 37.2 nm, PDI = 20.0 (σ_g = 1.65), R_g = 50.8 nm]. (c) 11 g h^{-1} [d_{VIS} = 46.8 nm, PDI = 15.5 (σ_g = 1.61), R_g = 60.8 nm]. (3 g h^{-1} is shown in Fig. 5.)

Particle Size, d_p

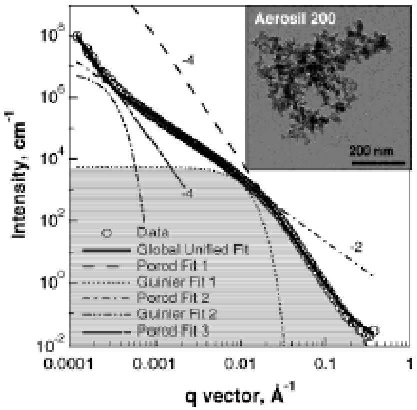


Figure 1. An USAXS pattern of agglomerated fumed silica (Aerosil 200, Degussa AG). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, three Porod regimes (dashed line, dashed−dotted line, and long−short-dashed line) are shown together with the Guinier regimes (dotted line and dashed−double-dotted line). The appearance of the second Porod (weak power-law) regime (0.0005 Å^{-1} < q < 0.01 Å^{-1}) proves that these particles are agglomerated and mass fractal as shown by the TEM insert. The gray shaded area indicates the integral part for determination of d_{VS}.

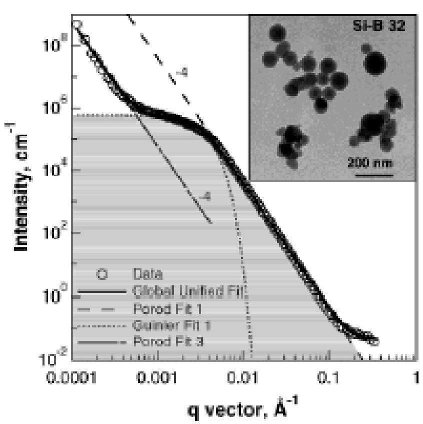


Figure 2. A USAXS plot of a nonagglomerated fumed silica (Si-B 32) made in a 17 g/h sustained premixed flame reactor (ref 18). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, Porod regimes (dashed line and long−short-dashed line) are shown together with the Guinier regime (dotted line). The lack of the Porod (weak power-law) regime at 0.0005 Å^{-1} < q < 0.005 Å^{-1} indicates that the particles are nonagglomerated as shown by the TEM insert. The gray shaded area indicates the integral part for determination of d_{VS}.

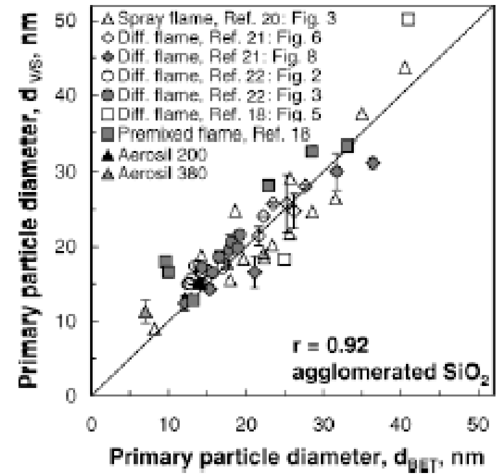


Figure 3. Comparison of d_{VS} and d_{BET} for agglomerated silica powders made in our vapor- or liquid-fed flame aerosol reactors (refs 18 and 20−22) and those of commercially available powders (Aerosil 200 and Aerosil 380, Degussa AG).

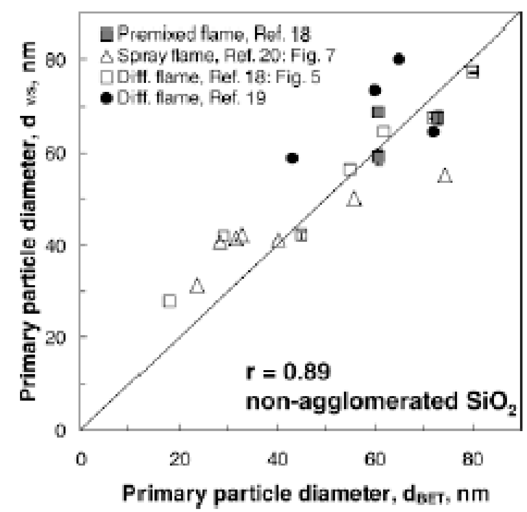
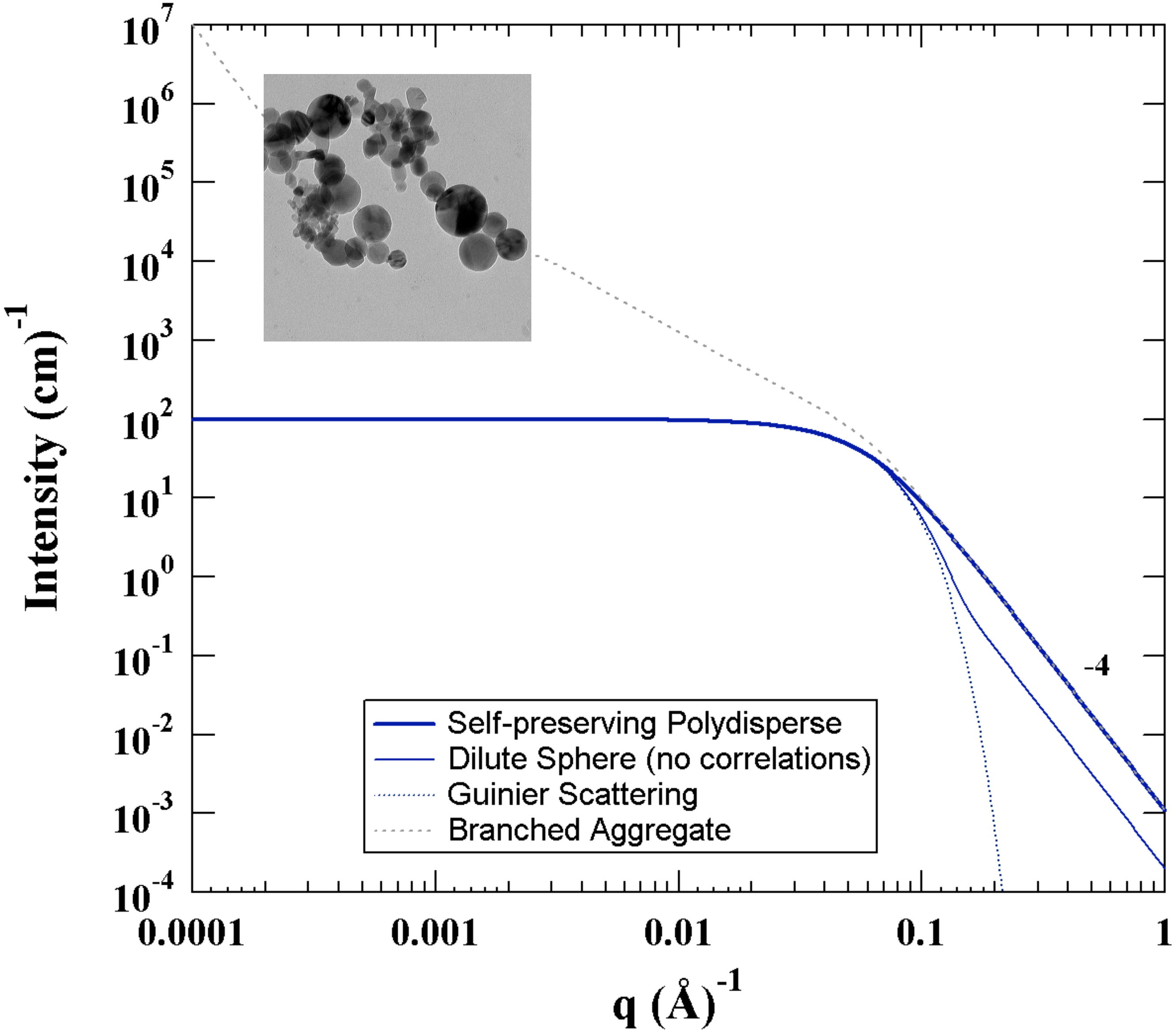
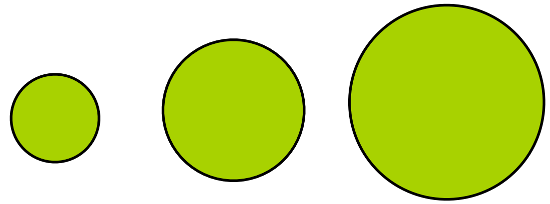


Figure 4. Comparison of d_{VS} and d_{BET} for various nonagglomerated silica powders made in our vapor-fed (refs 18 and 19) and liquid-fed (ref 20) flame aerosol reactors.

Structure of flame made silica nanoparticles by ultra-snall-angle x-ray scattering. Kammmler HK, Beaucage G, Mueller R, Pratsinis SE *Langmuir* **20** 1915-1921 (2004).

Polydisperse Particles





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$$\sigma = \ln(\sigma_g) = \left[\frac{\ln(PDI)}{12}\right]^{1/2}$$

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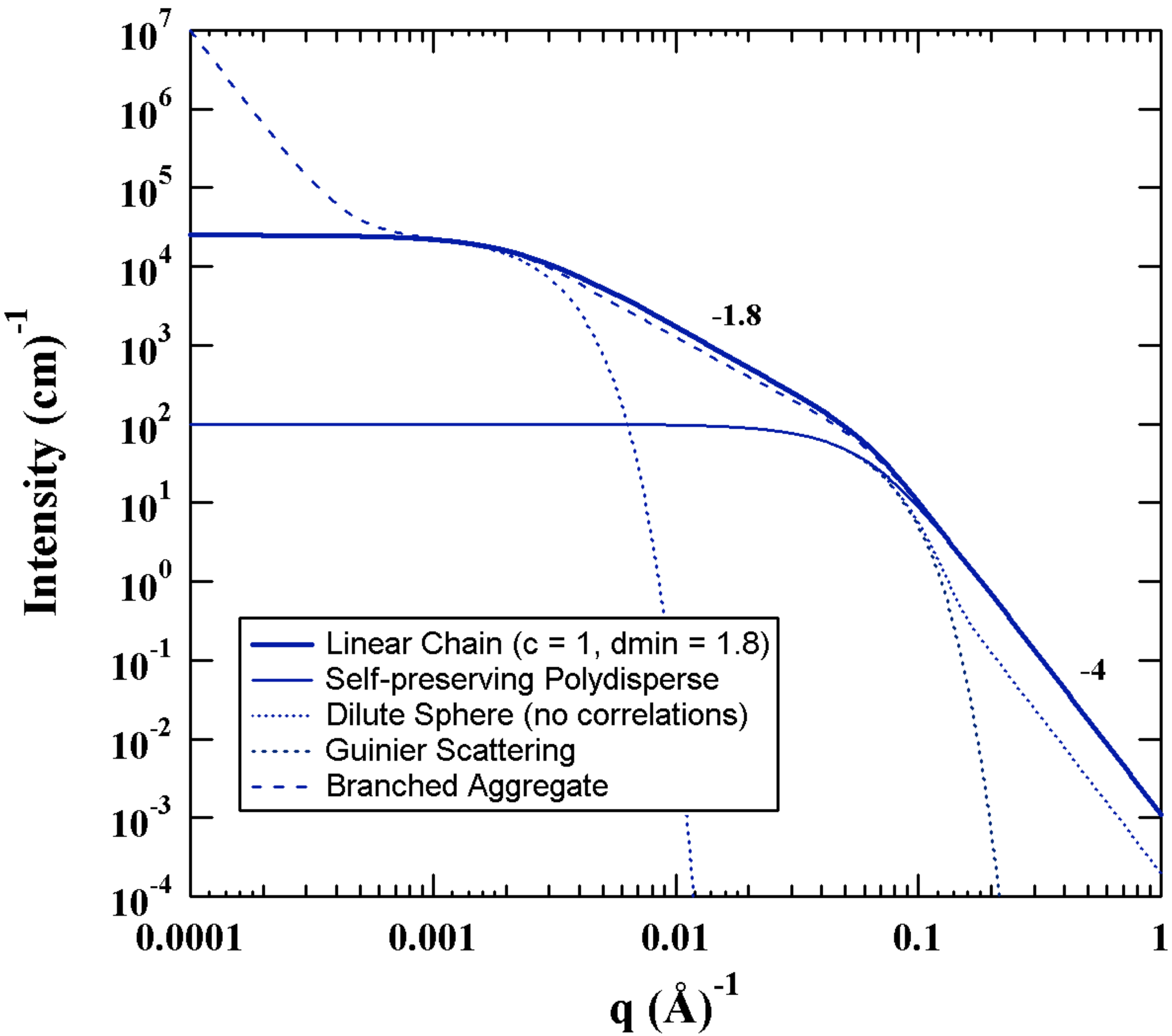
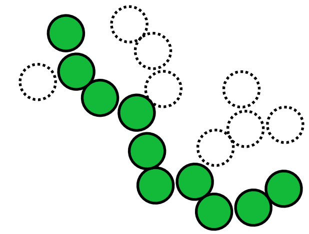
Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

Linear Aggregates





$$I(q) = G_2 \exp\left(\frac{-q^2 \langle R_{g,2}^2 \rangle}{3}\right)$$

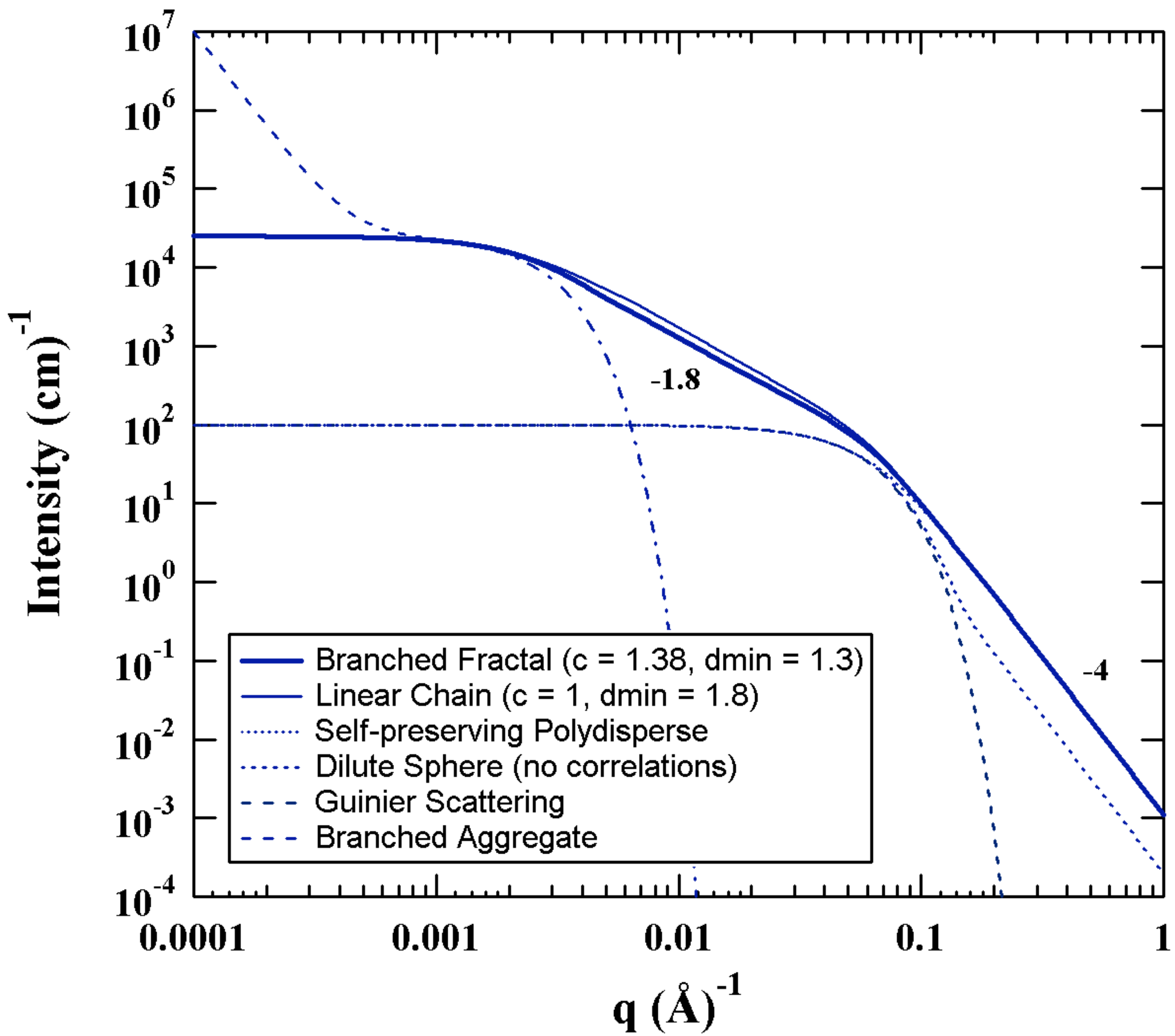
$$z = \frac{G_2}{G_1} = \left(\frac{R_2}{R_1}\right)^{d_f}$$

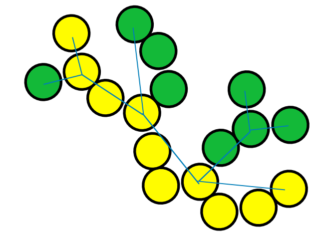
$$I(q) = B_f q^{-d_f}$$

$$B_f = \frac{G_2 d_f}{R_{g,2}^{d_f}} \Gamma\left(d_f/2\right)$$

Beaucage G, Small-angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension, J. Appl. Cryst. 29 134-146 (1996).

Branched Aggregates





$$z = p^{c} = s^{d_{\min}}$$

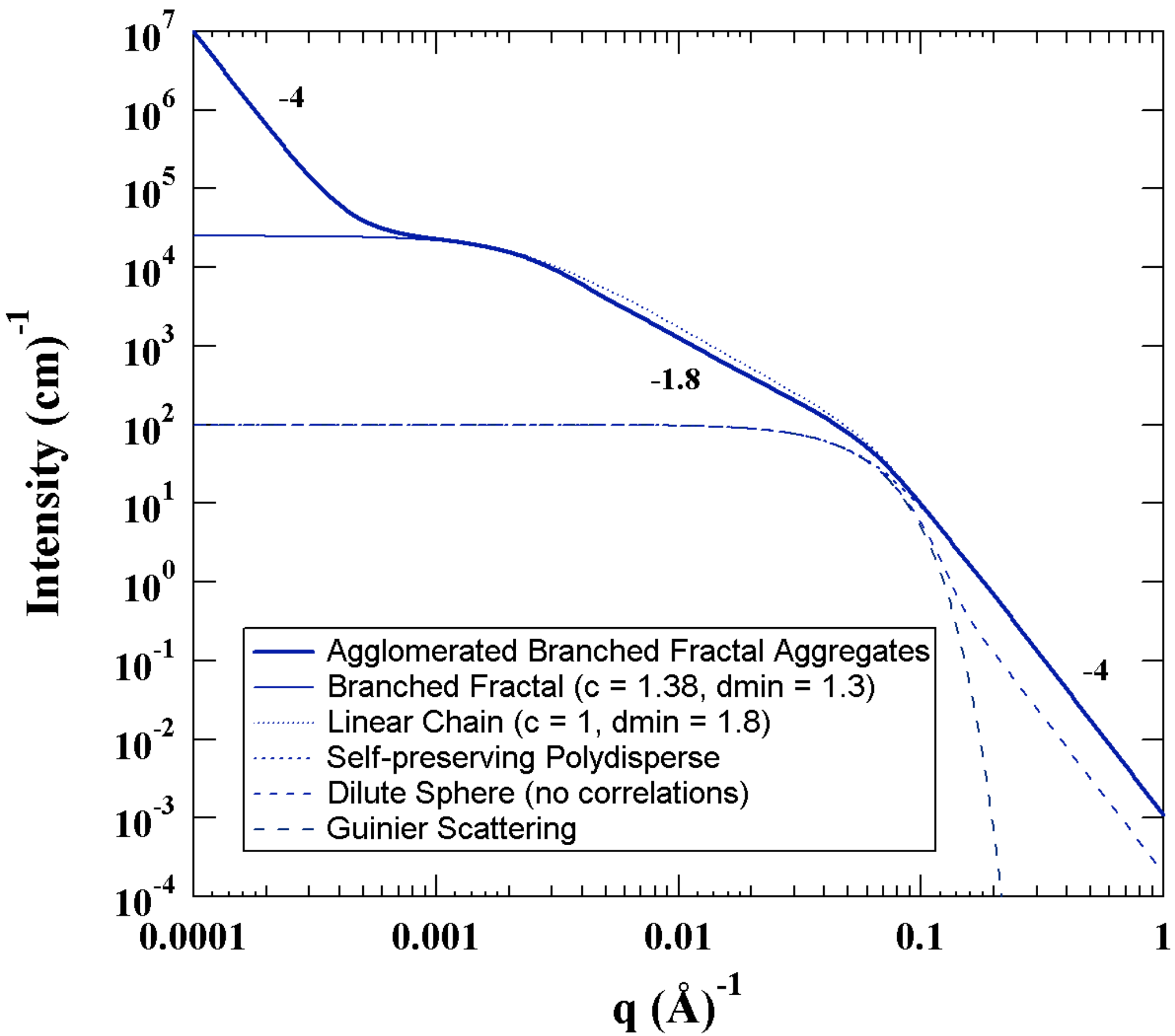
$$d_f = c d_{\min}$$

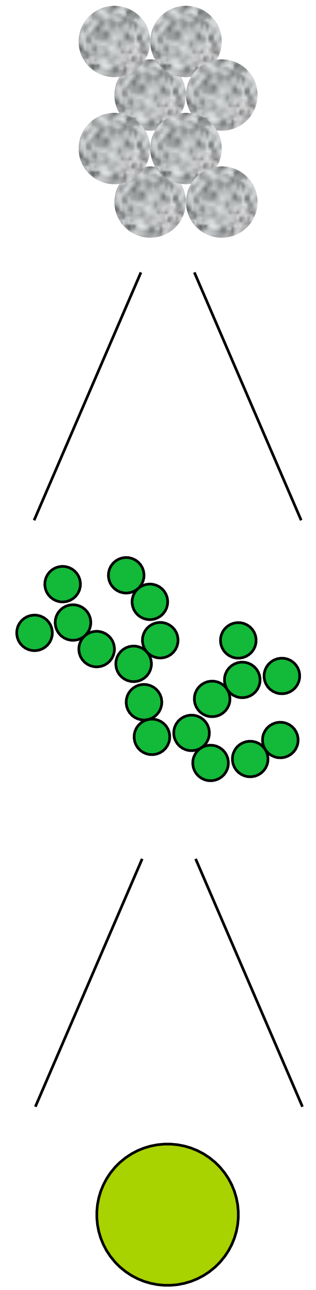
$$\phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c - 1}$$

$$B_f = \frac{G_2 d_{\min}}{R_{g,2}^{d_f}} \Gamma\left(d_f / 2\right)$$

Beaucage G, Determination of branch fraction and minimum dimension of fractal aggregates Phys. Rev. E 70 031401 (2004).

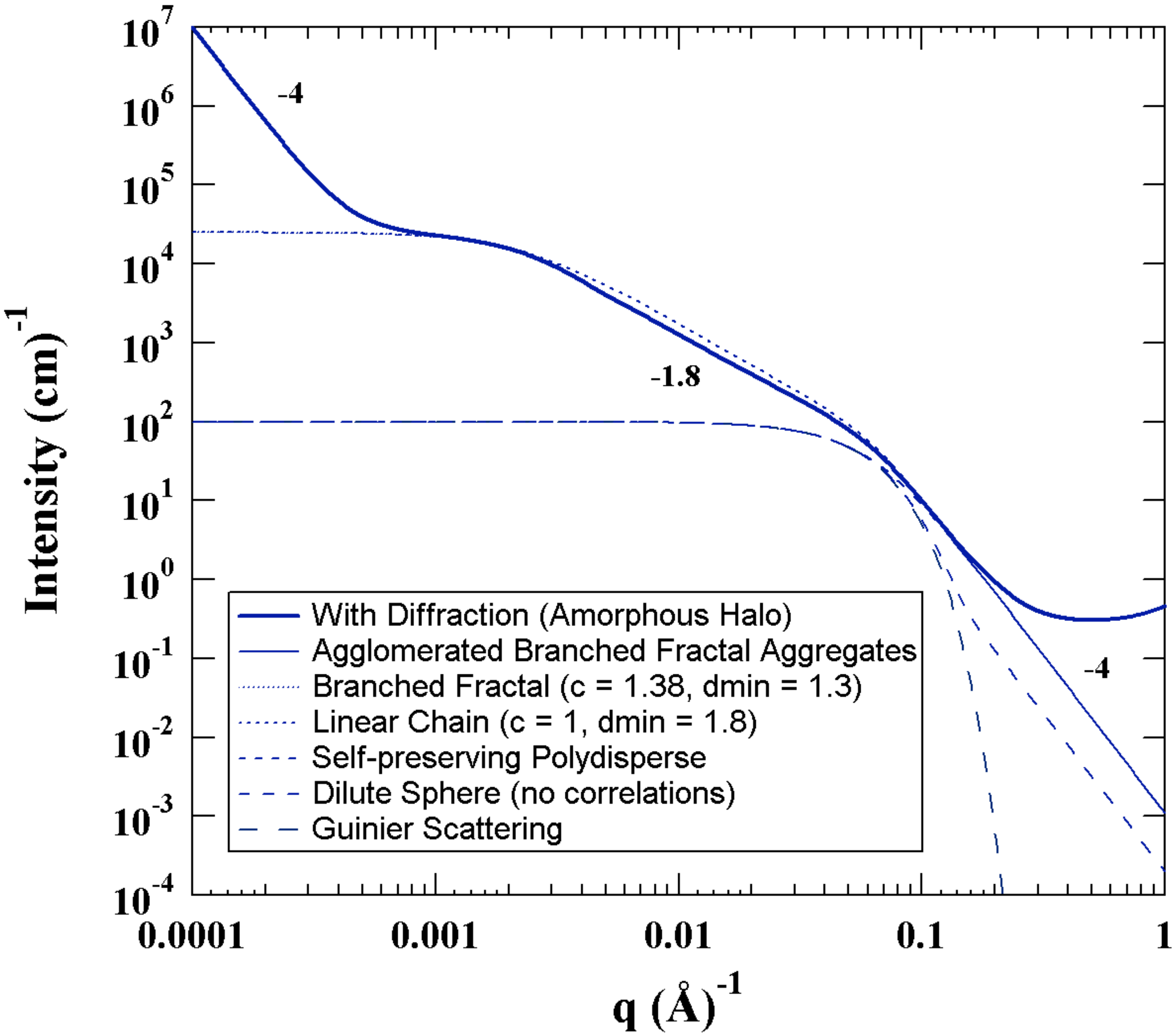
Large Scale (low-q) Agglomerates

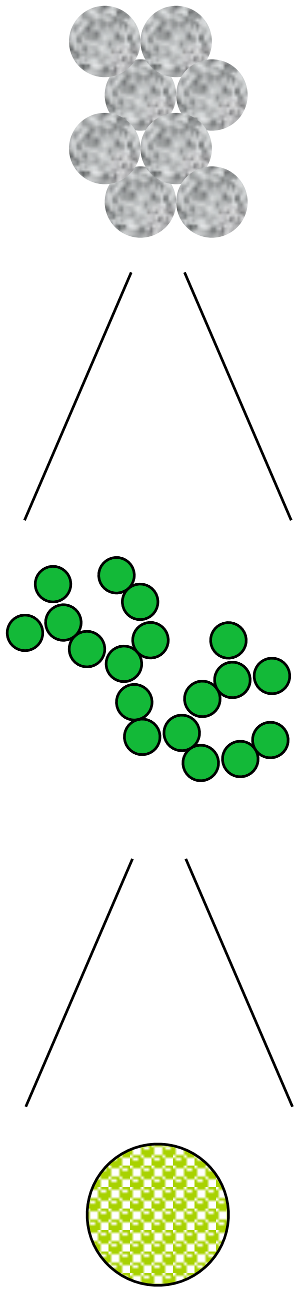




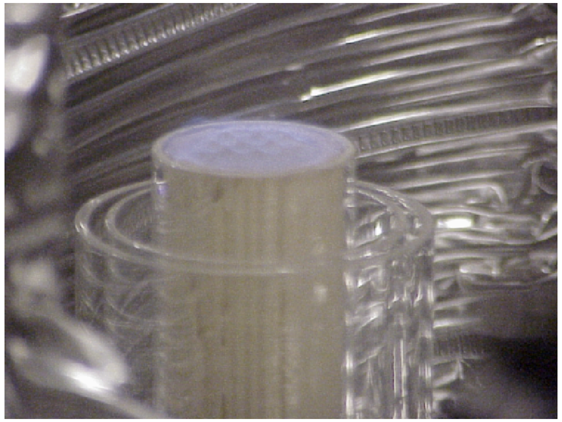
$$I(q) = B_P q^{-4}$$

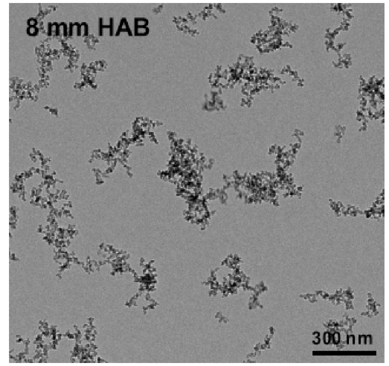
Small-scale Crystallographic Structure





Branched Aggregates





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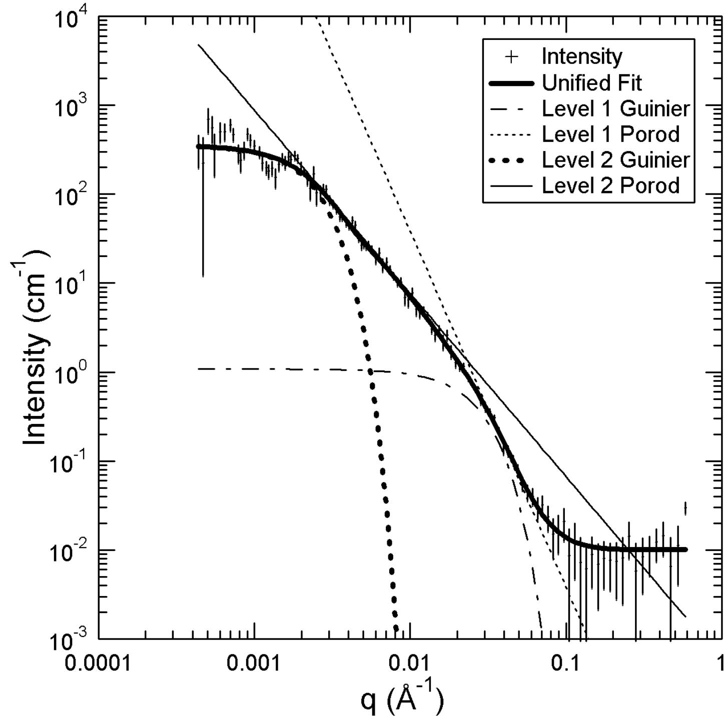
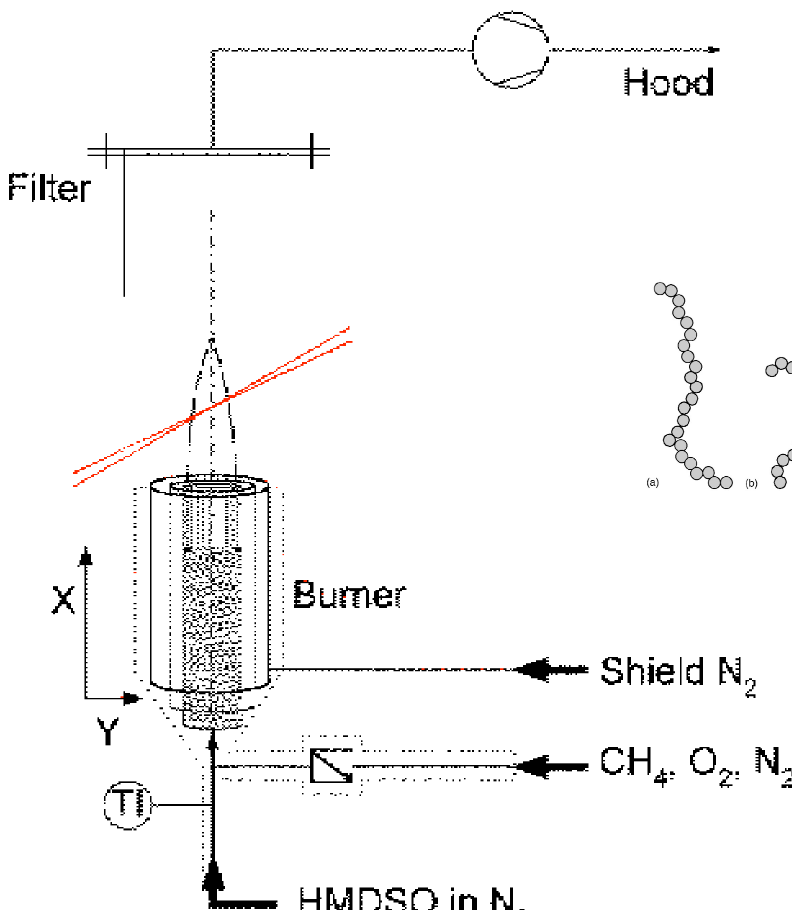
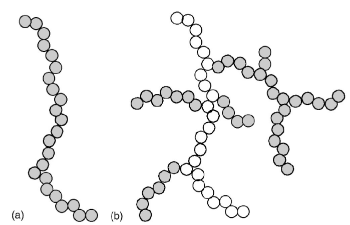
Silica Premixed Flames
J. Appl. Phys 97 054309 Feb 2005



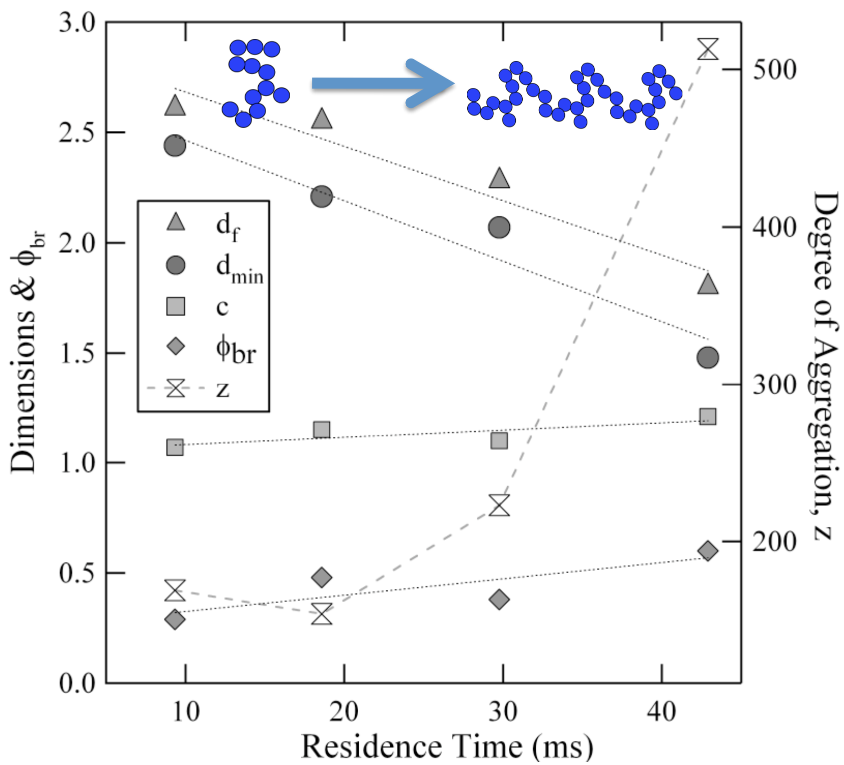




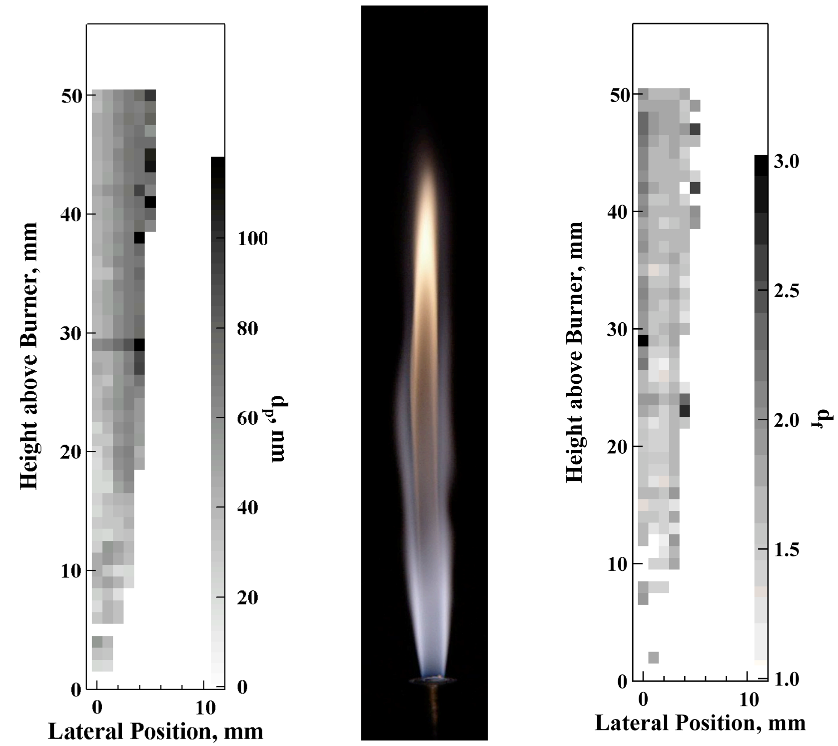
5mm LAT 16mm HAB
Typical Branched Aggregate
$\mathbf{d_p = 5.7\ nm}$
$\mathbf{z = 350}$
$\mathbf{c = 1.5,\ d_{min} = 1.4,\ d_f = 2.1}$
$\mathbf{\phi_{br} = 0.8}$

Beaucage G, *Determination of branch fraction and minimum dimension of fractal aggregates* Phys. Rev. E 70 031401 (2004).

Examples of Application to In Situ Studies of Flame Made Nanoparticles



Sztucki M, Narayanan T, Beaucage G, *In situ study of aggregation of soot particles in an acetylene flame by small-angle x-ray scattering* J. Appl. Phys. **101**, 114303 (2007).

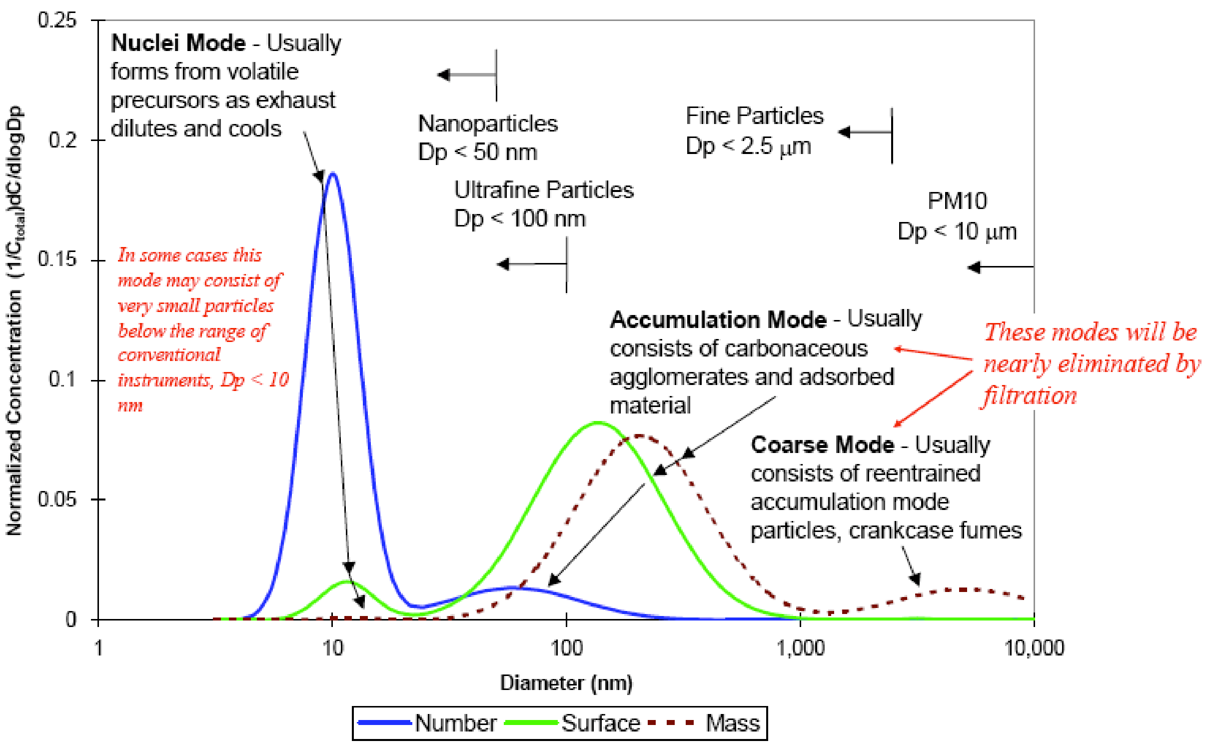


Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J *J Appl. Phys.* **97**(2005) (Article 054309).

Beaucage, G., H. K. Kammler, S. E. Pratsinis, T. Narayanan... *Probing the dynamics of nanoparticle growth in a flame using synchrotron radiation. Nature Mater.*, **3**, 370-373 (2004).

SAXS and DMA Comparison

Typical Diesel Particle Size Distributions, Number, Surface Area, and Mass Weightings Are Shown



Engines and Nanoparticles a Review, Kittelson DA, *J. Aerosol Sci.* **29** 575-588 (1998) as modified in a talk online.

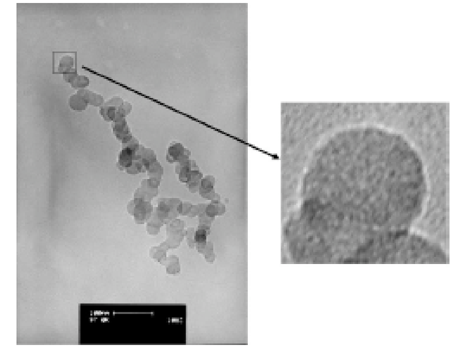
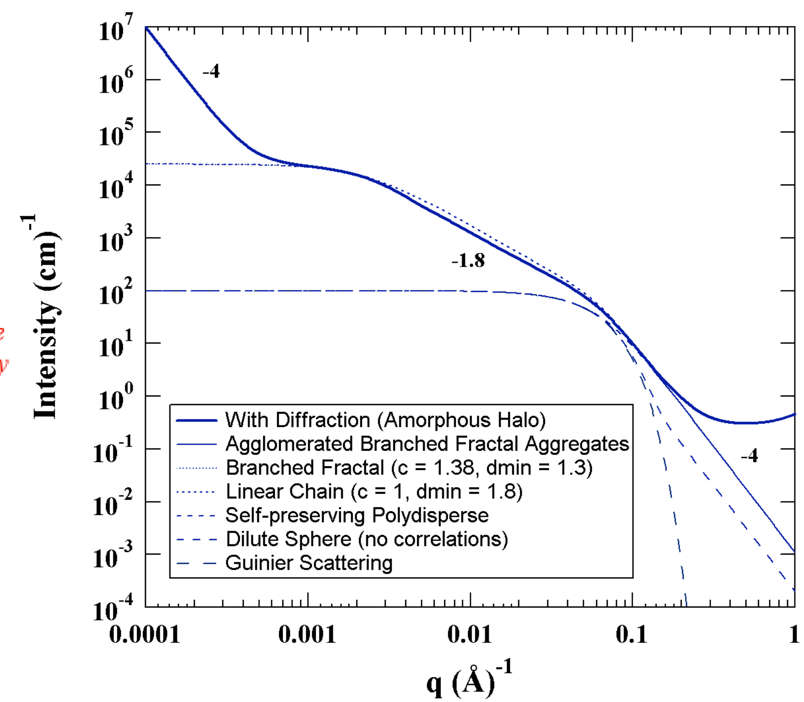
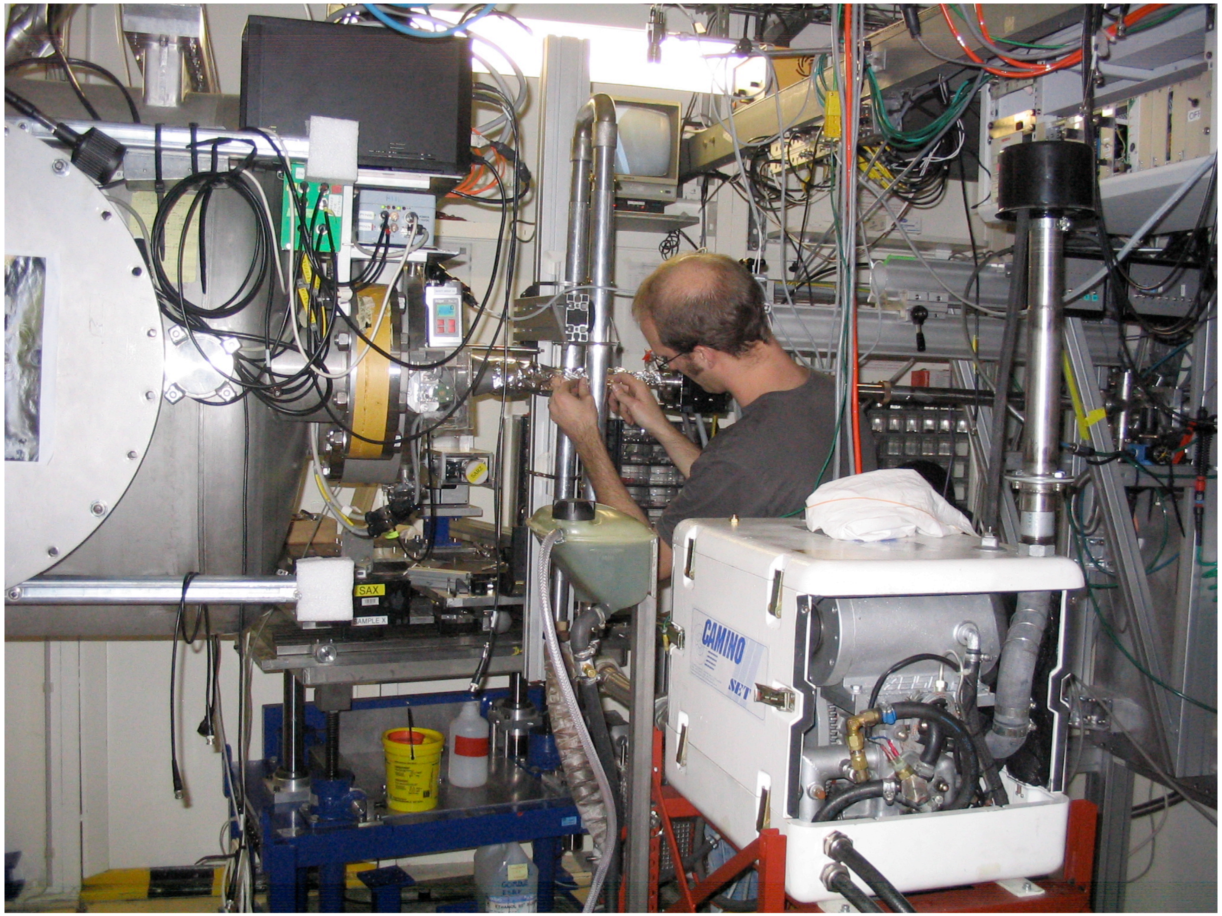


Fig. 1. Diesel soot agglomerate composed of spherical primary particles.

Lapuerta M, Ballesteros R, Martos FJ, *J. Col. And Interf. Sci.* ***303****, 149-158 (2006).*



Experimental Setup for in situ Exhaust SAXS Measurement



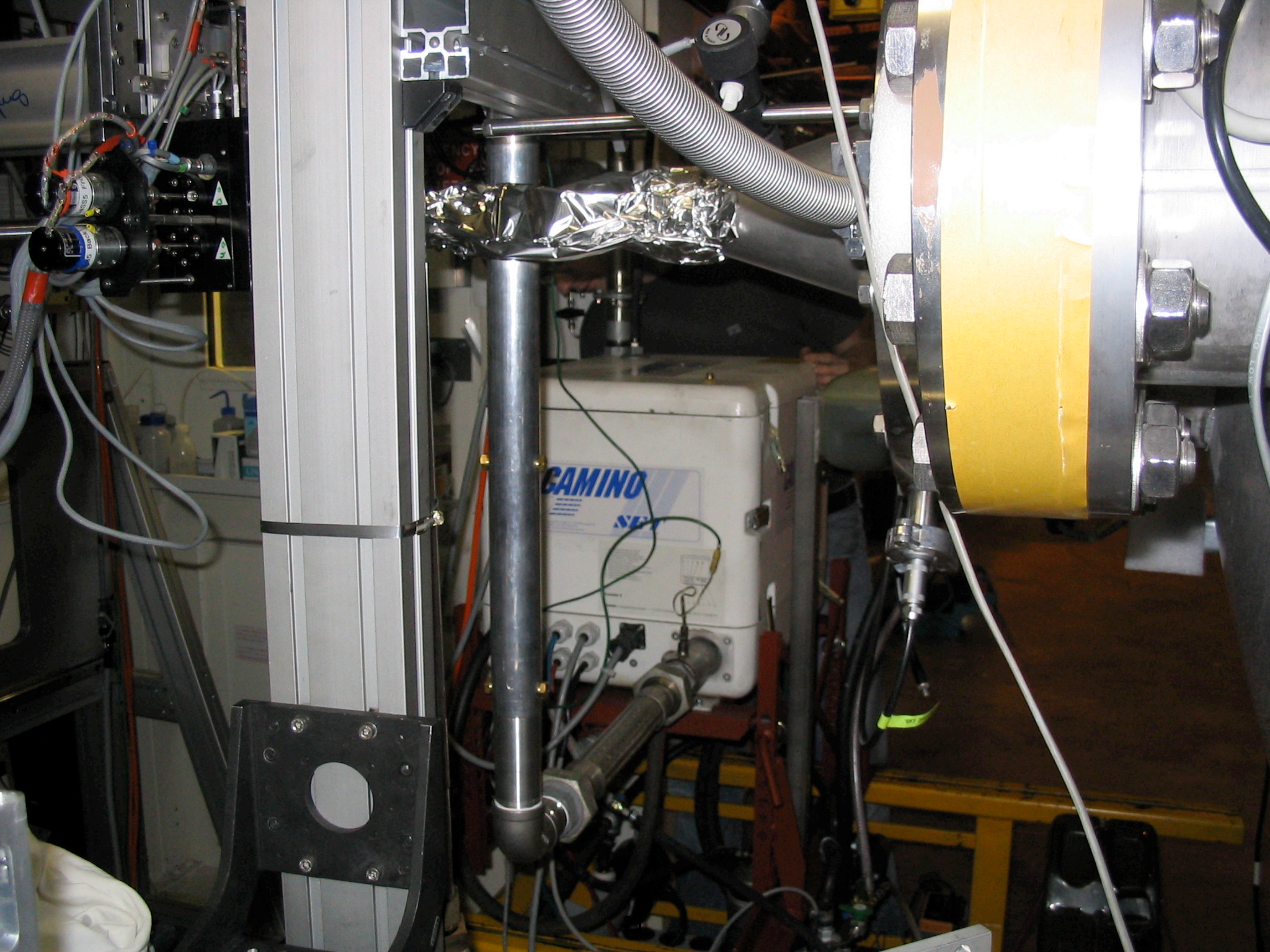
<u>Camino Generator Set</u>
4- Stroke Direct Injection
Water Cooled
Single Cylinder
Bore: 65 mm, Stroke: 62 mm
210 cc displacement
2.95 kW
2,600 RPM (Constant)
No Turbocharger
Fixed Fuel Feed Rate
Exhaust Temperature 271-194 °C
Vary Load Using Water Heater
Measure 1.5 m in Steel Exhaust Pipe

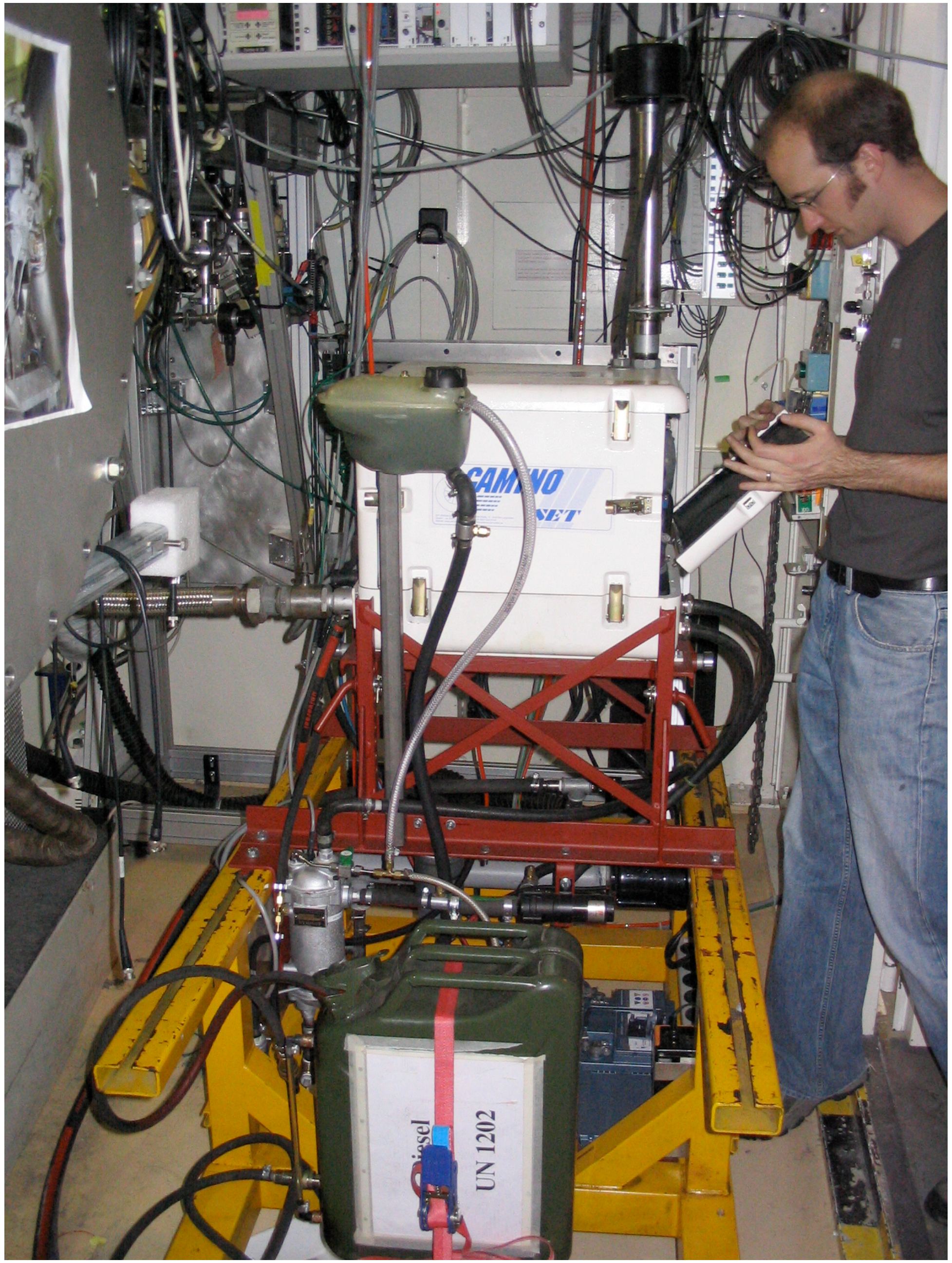
<u>We consider here two fuels</u>

1) "Regular" Diesel (UN 1202)
   Centane Number 43
   Sulfur <10.0 mg/kg
   ρ = 829 kg/m^3; η /ρ = 2.33 mm^2/s at 40°C
   Boiling Point 336 °C
2) Kerosene
   Centane Number 51
   Sulfur 9.5 mg/kg
   ρ = 776 kg/m^3; η/ρ = 1.07 mm^2/s at 40°C
   Boiling Point 226 °C

The Influence of additives on the size distribution and composition of particles produced by diesel engines. Skillas G, Qian Z, Baltensperger U, Matter U & Burtscher H, *Combust. Sci. and Tech.* **154** 159-273 (2000). & Skillas G Dissertation ETHZ (1999) *Carbon Nanostructures from Combustion: Morphology, Density and Applications.*

Similar to generator set used by:
Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, Robinson AL, Pandis SN et al. *Science* **315** 1259-1262 (2007).


CAMINO


UN 1202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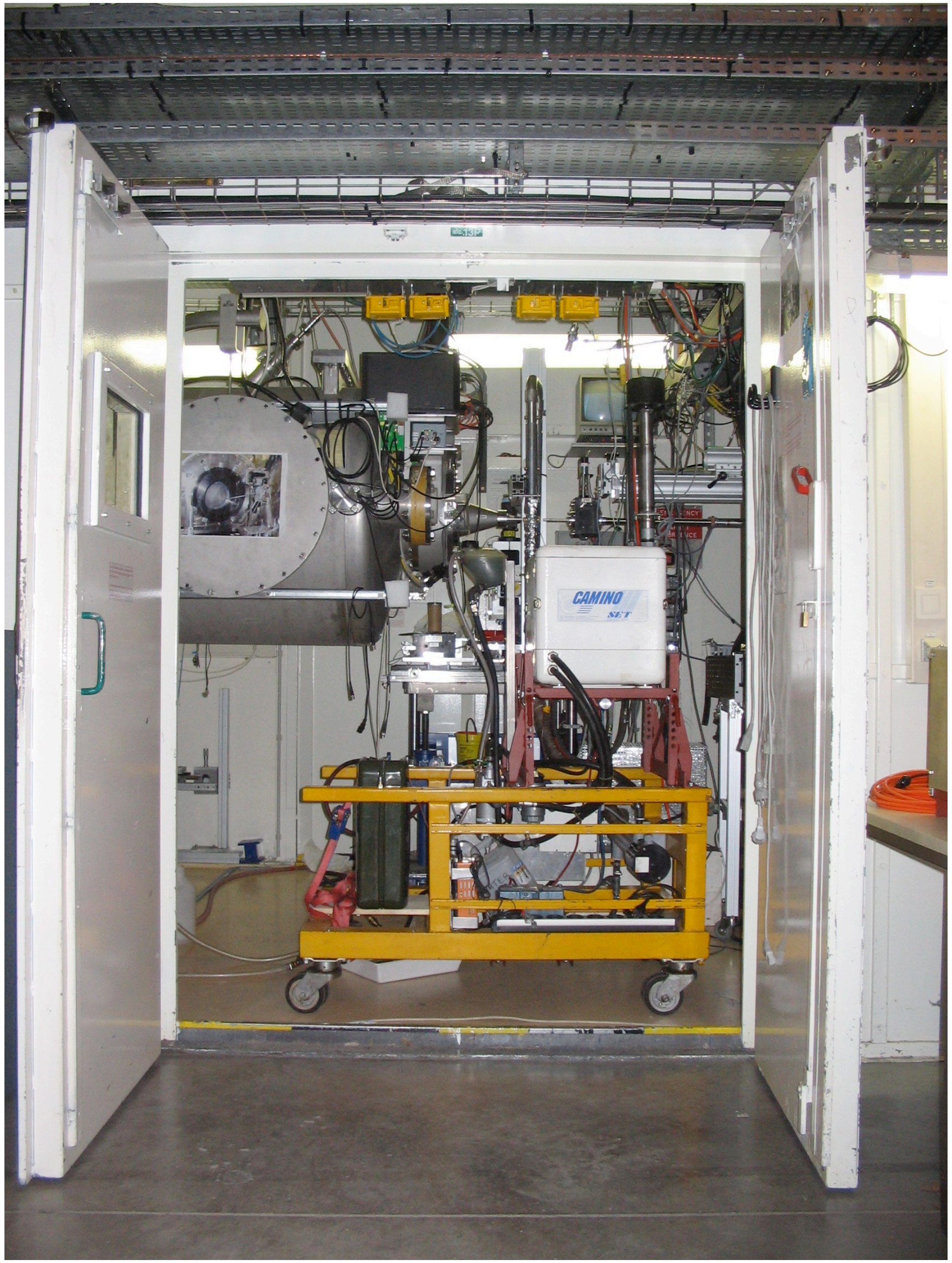
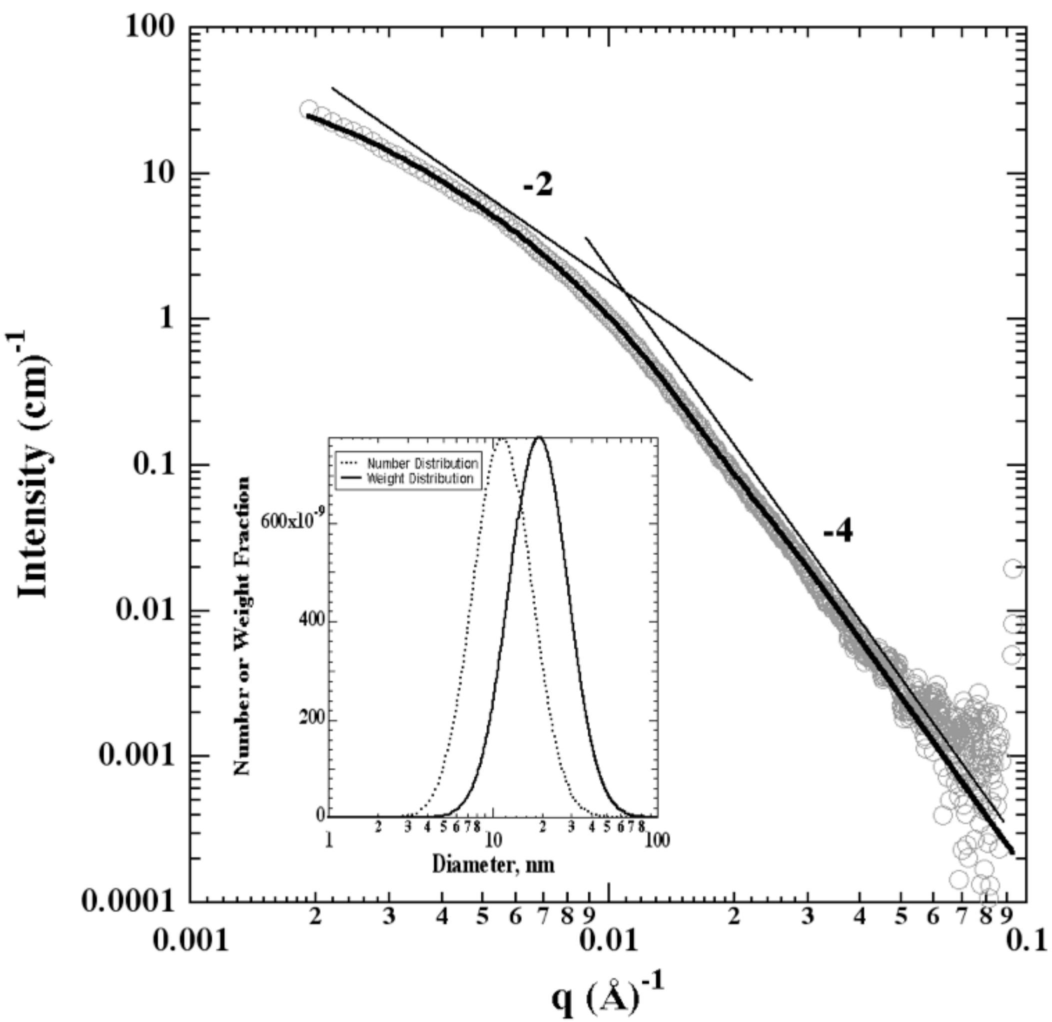
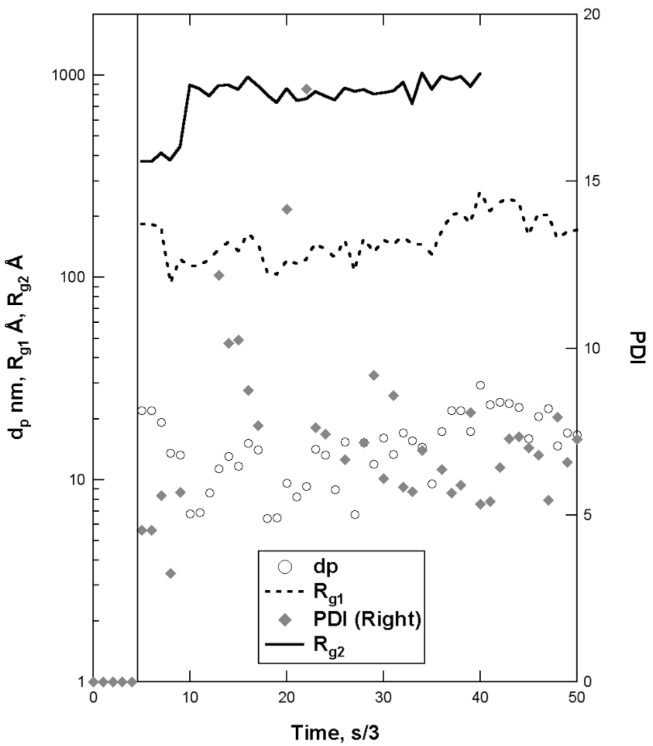

CAMINO
SET

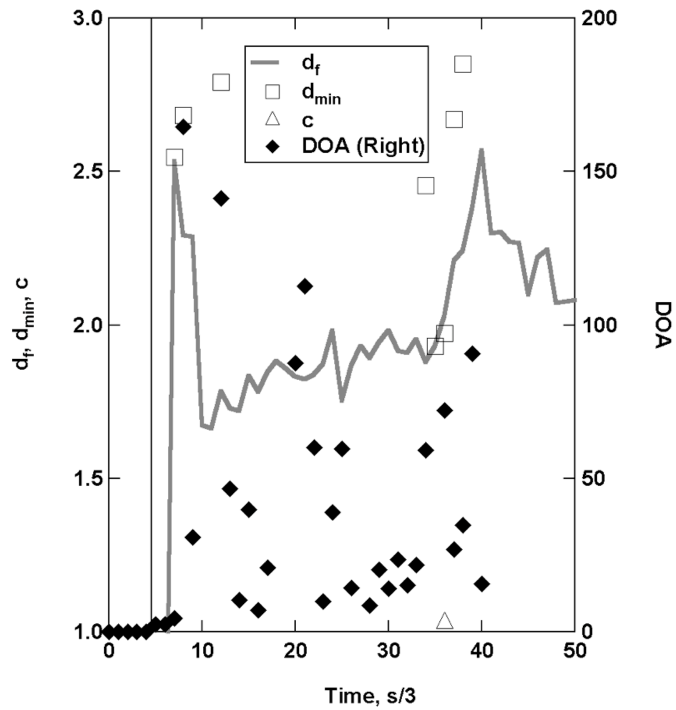
In Situ Exhaust Measurement
20 ms Exposure on Exhaust Stream

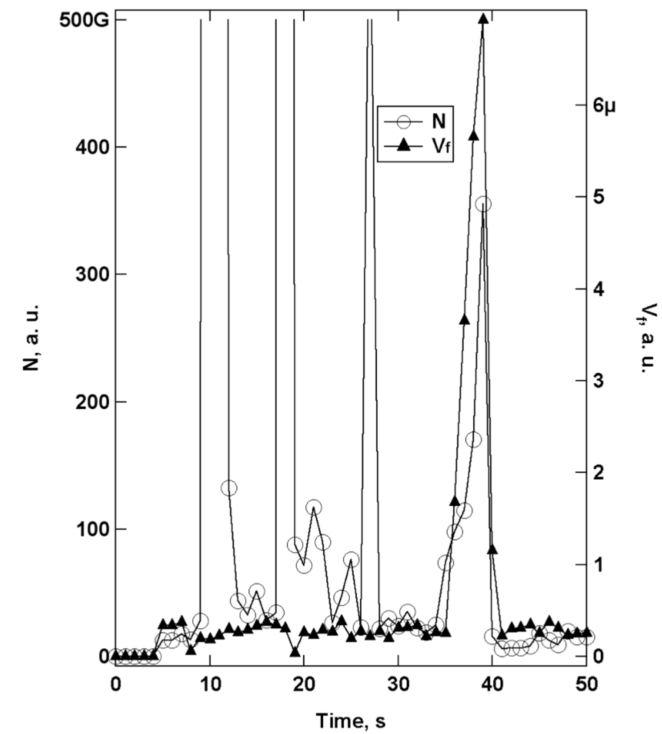


d_p = 19.2 nm
σ_g = 1.48 (PDI = 6.40)
d_f = 2.10, c= 1.03
z = 43.6
ϕ_{Br} = 0.104

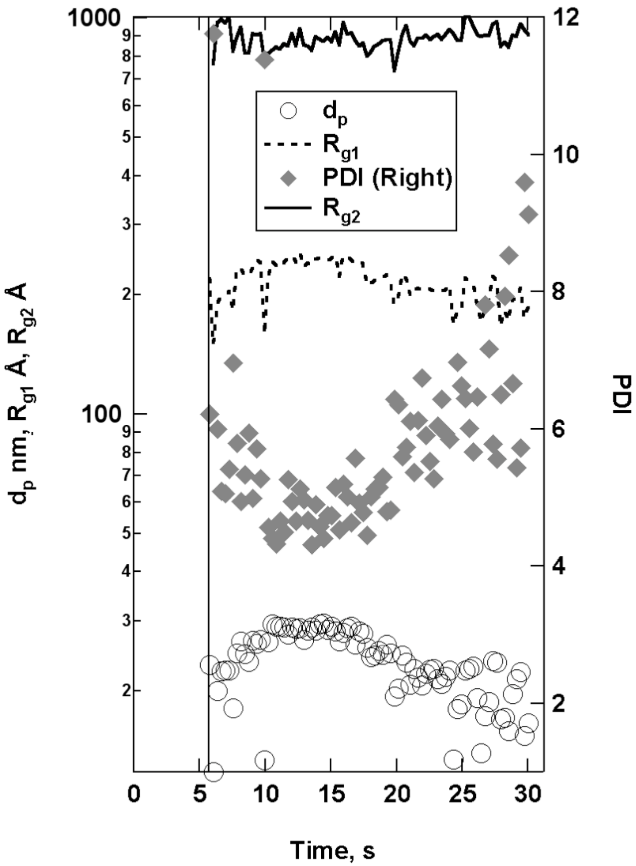
Startup Regular Diesel

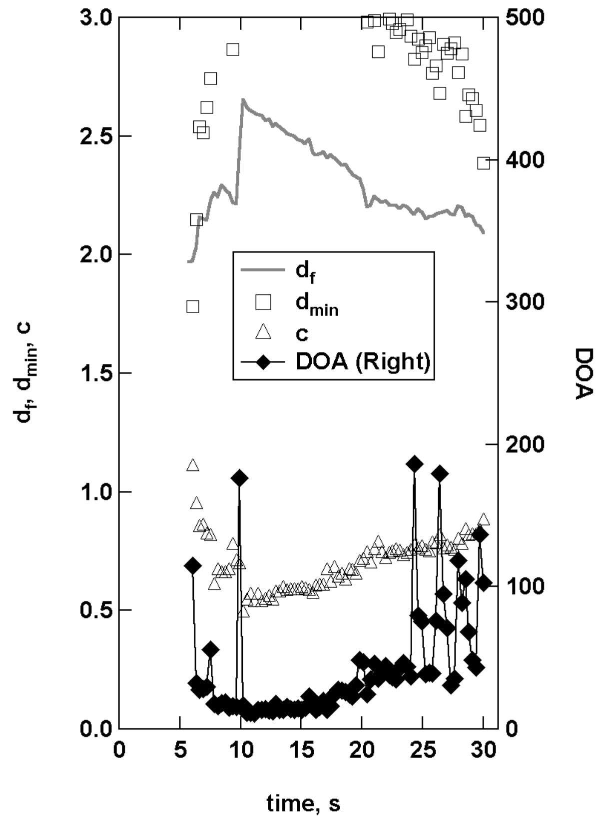


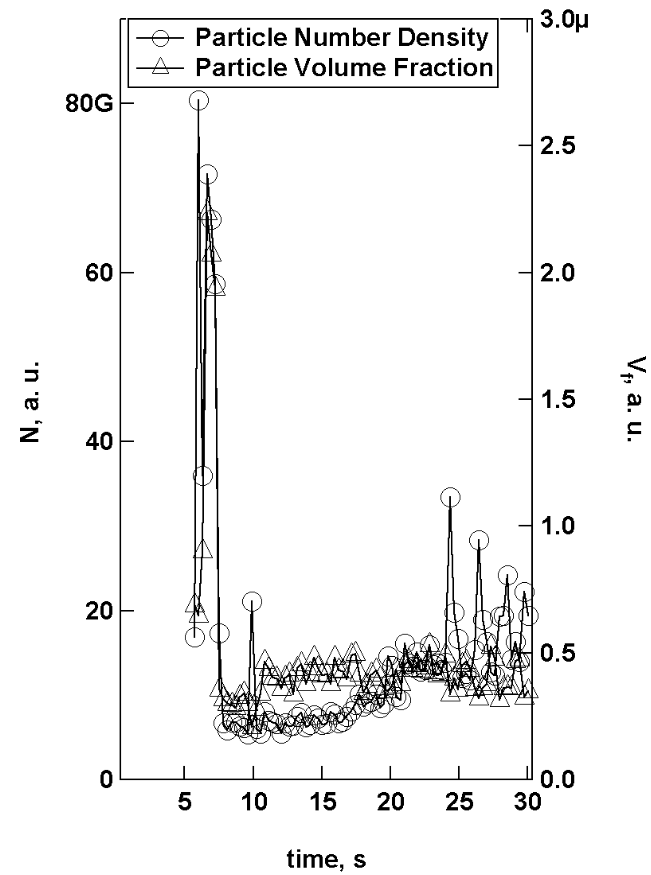




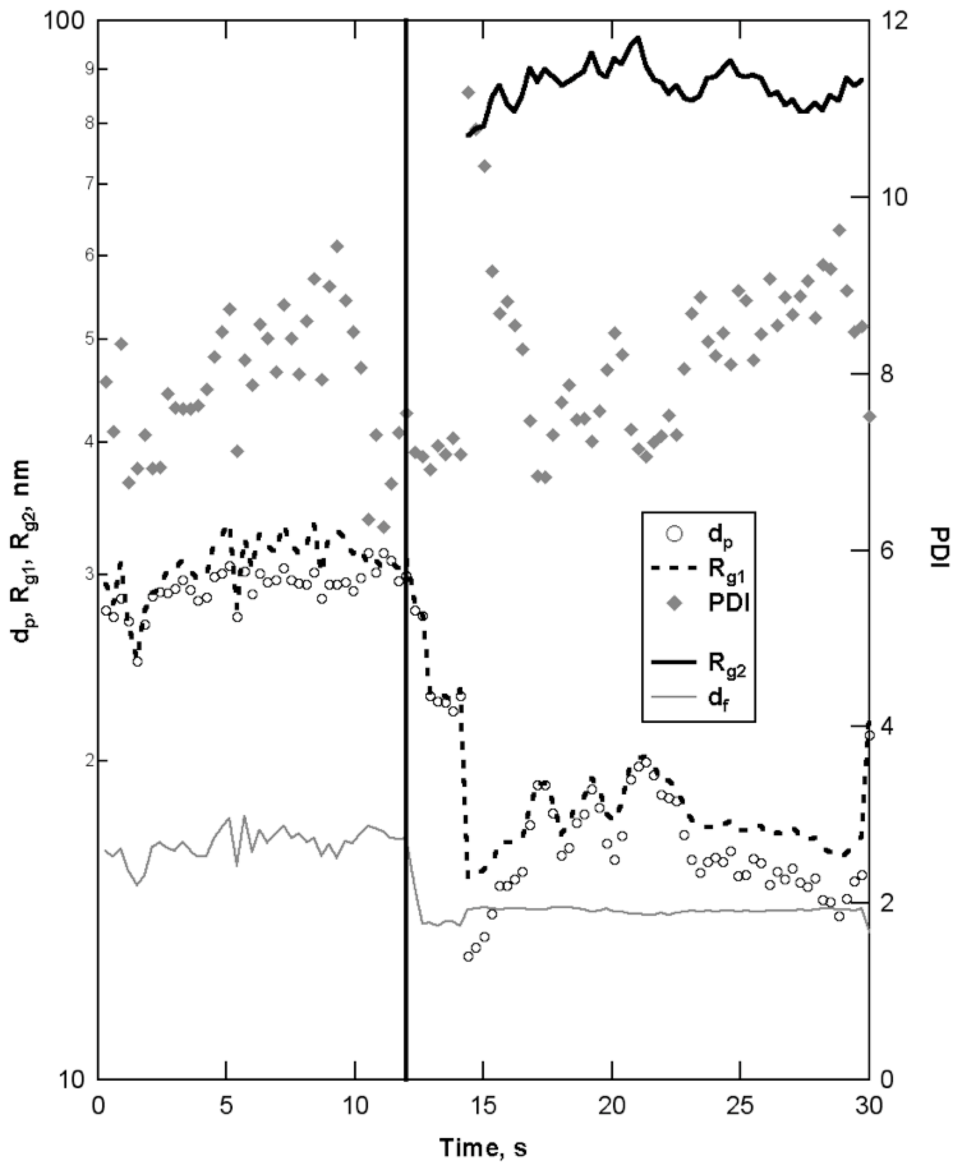
Startup Kerosene

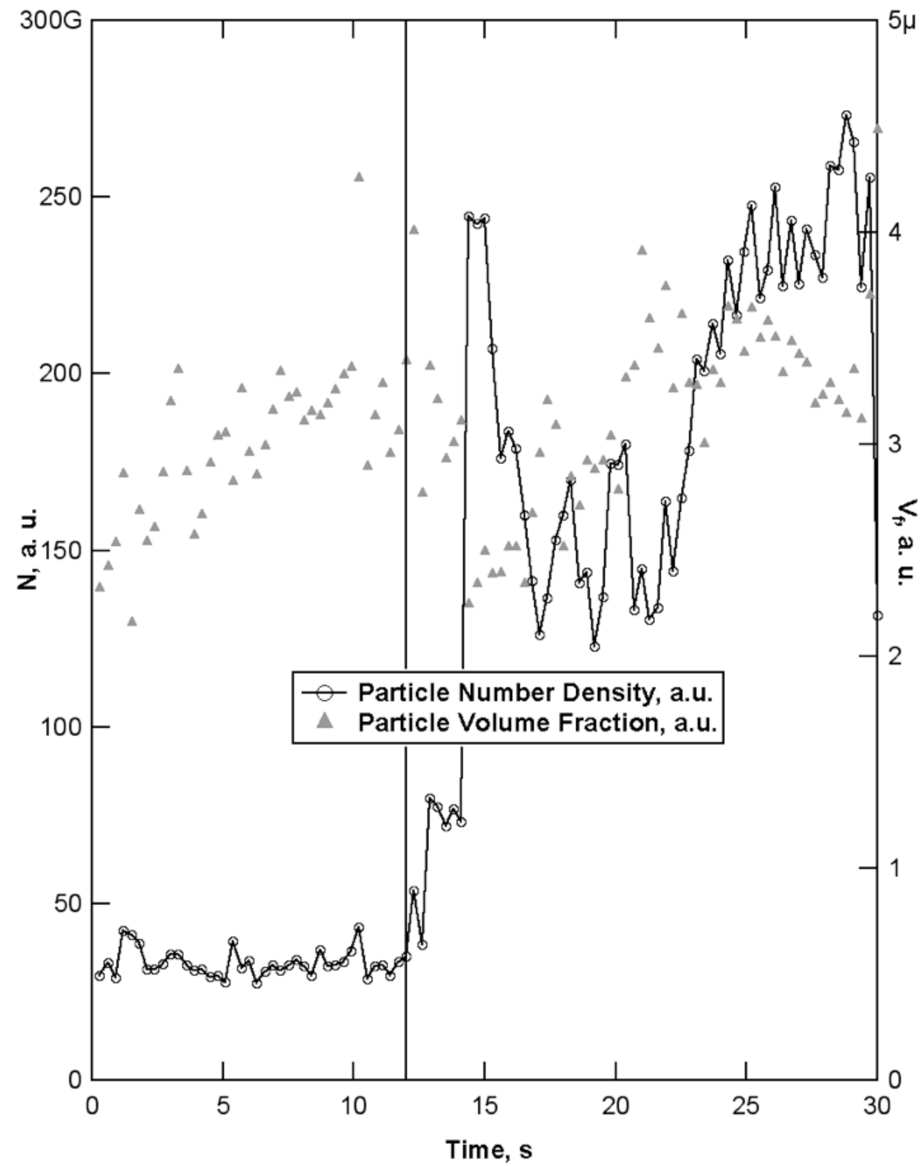






Full Load Removed Regular Diesel at 12 s





Why you might be interested in SAXS:

-In situ observation of soot & inorganic nanostructure with no dilution
(calibrate/verify DMA)
-Measure from ~ 1 Å to 1 μm (direct observation of all possible nucleation modes)
-Wide sample concentration range solid powder to exhaust aerosol
-Volatile, semi-volatile, and solid particles (no dilution, charging or denuding)
-Unique details of aggregate structure including mass fractal dimension, branch content
-Volume and number density as well as primary particle size distribution
-20 ms measurement (possibility of observation within engine cycle)

Why you might *not* be interested in SAXS

-Requires a synchrotron for in situ aerosol measurements
(powders can be measured in the lab)
-Non-portable measurement
-More or less requires a specialist (involved data anaylsis)
-Composition is more difficult than structure (electron density or use anomalous SAXS)
-New method (This is the pioneering study and is still in preparation for publication)

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	Reference	Fuel 2
Density (kg/m^3):	829	776
Evaporation Temperature (°C)	336	226
Cetane Number (-)	51	43
Sulfur Content (mg/kg)	9.5	< 10.0
Aromatic Content (Mass %)	18.6	1.9
Viscosity (mm^2/s at 40°C)	2.33	1.07