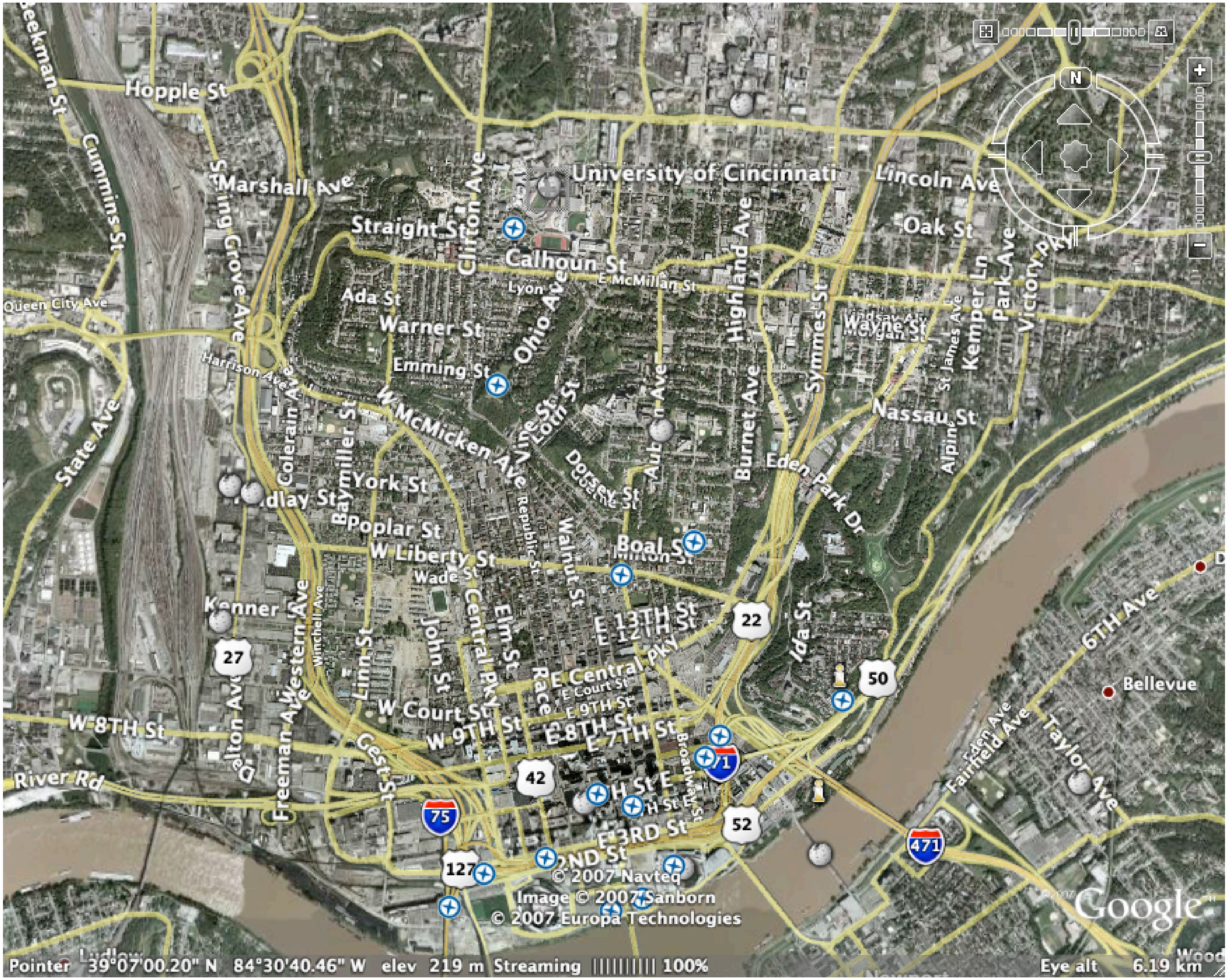
Small-Angle X-Ray (SAXS) and Neutron Scattering to Quantify Nanostructure

Gregory Beaucage
Professor of Chemical and Materials Engineering
University of Cincinnati
Cincinnati OH 45221-0012

20,085 undergraduate students
5,054 full-time graduate
6,739 part-time undergraduate students
3,366 part-time graduate
83.9 percent residents of Ohio

$332.0 million External Grants (2005)
3,000 full time faculty

& 6 SAXS Cameras!!! 6 hrs APS, IPNS, SNS
Roe, Schaefer, Beaucage, Jim Mark etc.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Beekman St
Cummins St
Spring Grove Ave
Marshall Ave
University of Cincinnati
Lincoln Ave
Oak St
Straight St
Clifton Ave
Calhoun St
E McMillan St
Lyon
Ohio Ave
Highland Ave
Symmes St
Queen City Ave
Ada St
Warner St
Emming St
Wayne St
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Park Ave
Victory Pky
Harrison Ave
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Republic St
Dorsey St
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Poplar St
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Milton St
Walnut St
Wade St
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Winchell Ave
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Linn St
John St
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2ND St
6TH Ave
Bellevue
Eden Ave
Fairfield Ave
Taylor Ave
Ludlow
Newport
Wood
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Pointer 39°07'00.20" N 84°30'40.46" W elev 219 m Streaming ||||||||| 100%
Eye alt 6.19 km
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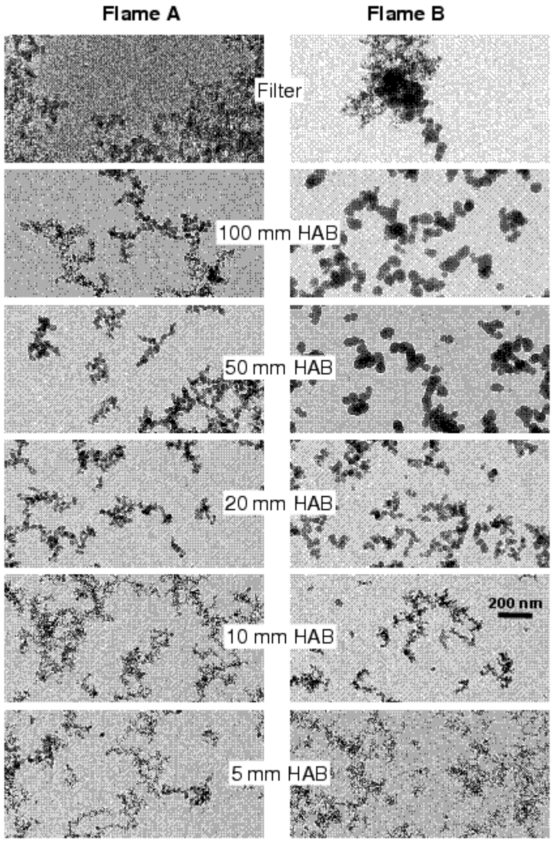
Outline:

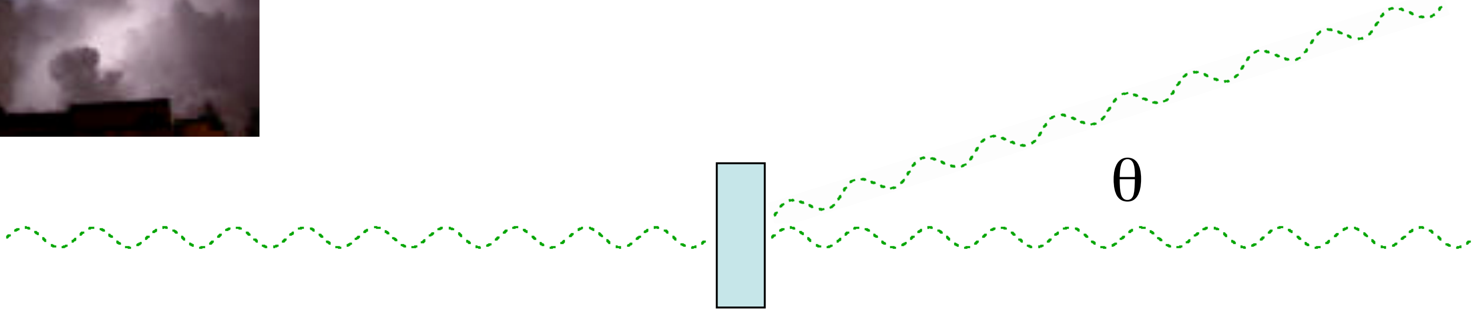
General Background, Instruments, Facilities

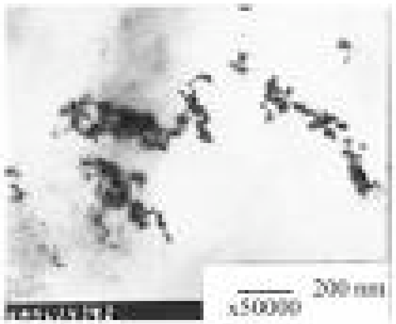
1) Specific Scattering Laws.
2) General Scattering Laws.
   Guinier’s Law; Porod’s Law;
   Unified Scattering
   Fractal Scattering
   Quantification of Branching in Aggregates
3) Polydispersity
4) ASAXS for Catalysts
5) Summary

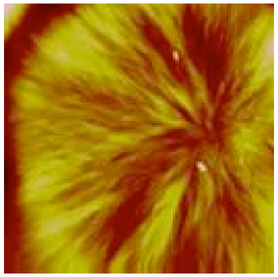


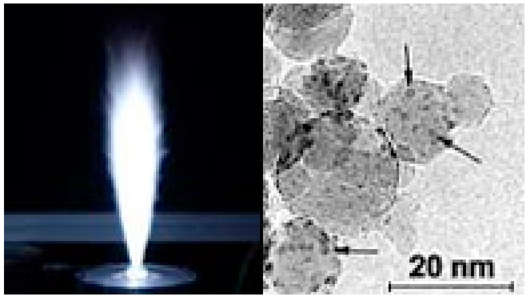
Kammler HK, Beaucage G, Kohls DJ, Agashe N. Ilavsky J
J Appl. Phys. **97**(2005) (Article 054309).

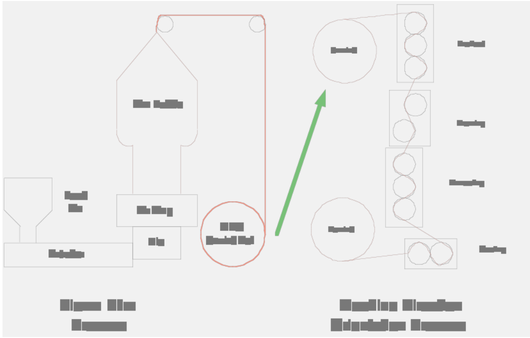
Nanostructure from Small Angle X-ray Scattering



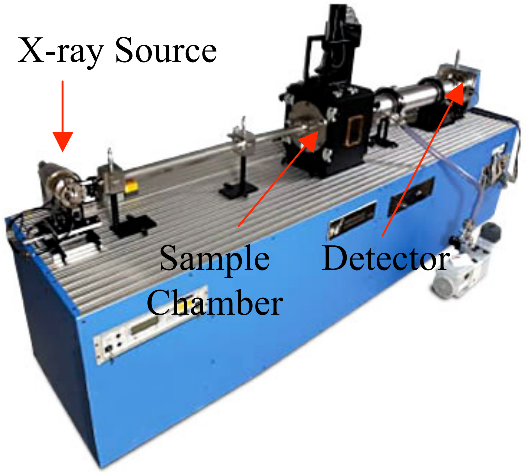






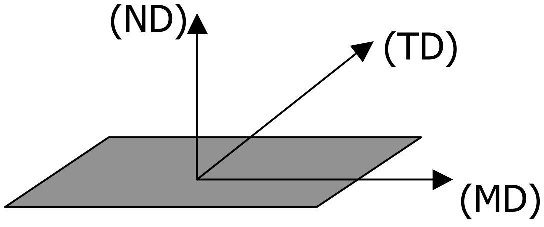


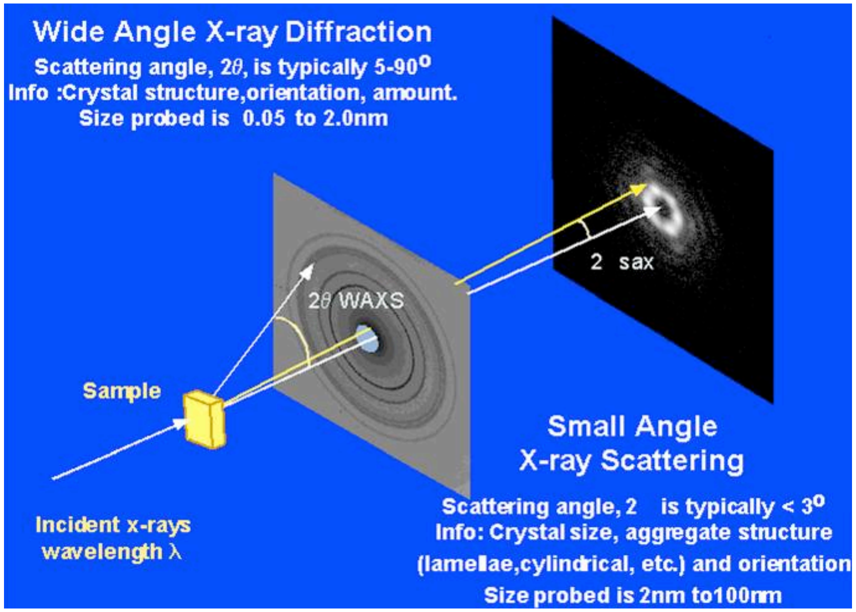
Small- and Wide-Angle X-ray Scattering Measurements



<u>SAXS</u> : pinhole camera : 2-d detector at 1m from the sample

<u>WAXS</u> : pinhole geometry camera : image plate detector at 5cm from the sample

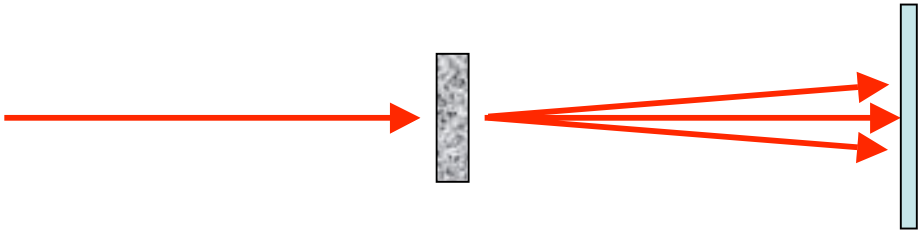




- ❑ 2D measurements are useful in determining both size and relative orientation of various structural components

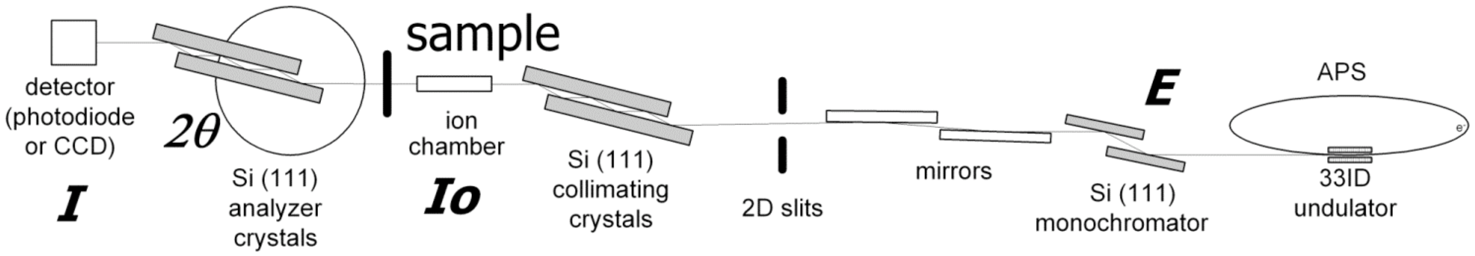
Small-Angle X-ray Scattering, (SAXS)

We Get Intensity as
A Function of Angle
(or radial position)



-Collimated Beam
-Monochromatic Beam
-Coherent Beam
(-Focusing Optics Perhaps)

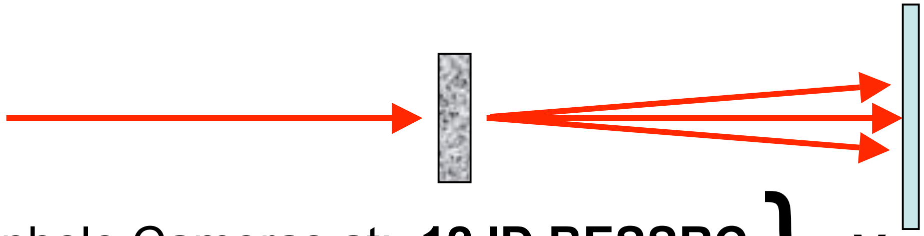
-Longer Distance for Lower Angle
-Large Dynamic Range Detector
-Evacuated Flight Path
-Extend Angle Range with Multiple SDD’s



Crystalline Reflections Can Also Be Used

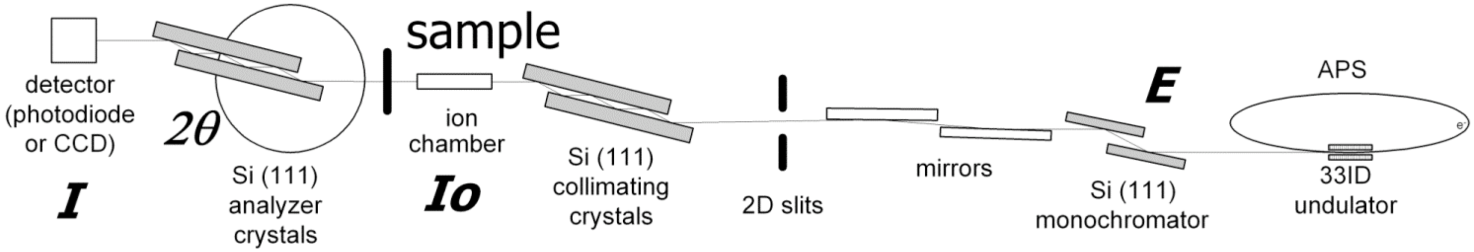
Small-Angle X-ray Scattering at the APS Chicago

We Get Intensity as
A Function of Angle
(or radial position)



Pinhole Cameras at:
- **12 ID BESSRC**
- **5 ID DND**
- **18 ID BIOCAT**
- 15 ID CARS
- 8 ID XOR
- 9 ID CMC-CAT

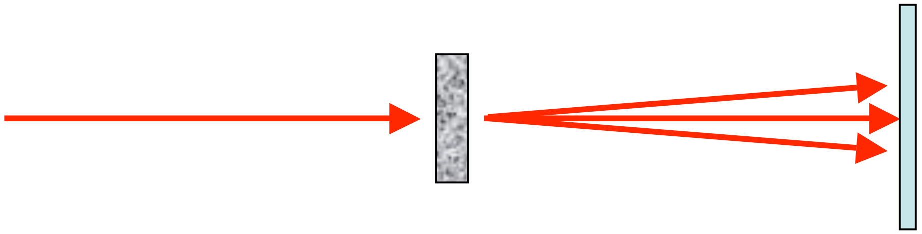
Variants on Build/Tear Down Motif (Inside Traders)



33 ID UNICAT

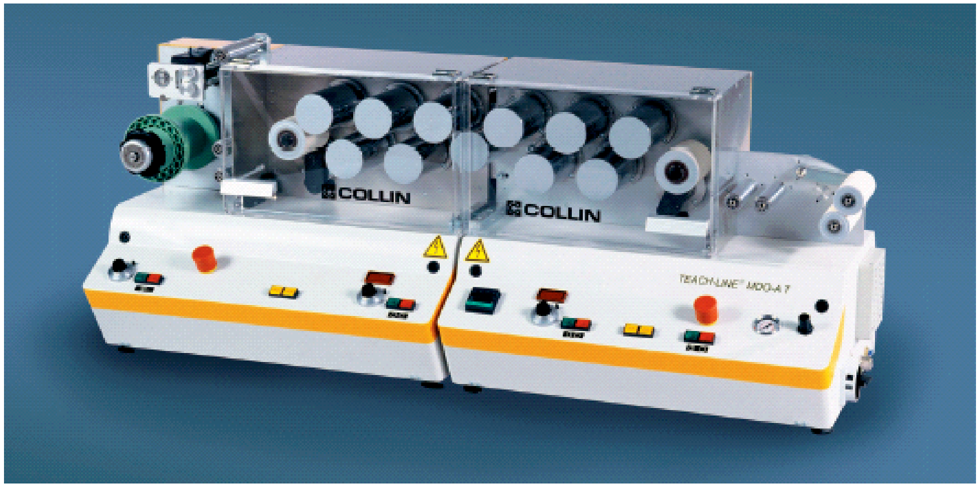
Semi-Permanent (Easily Used)

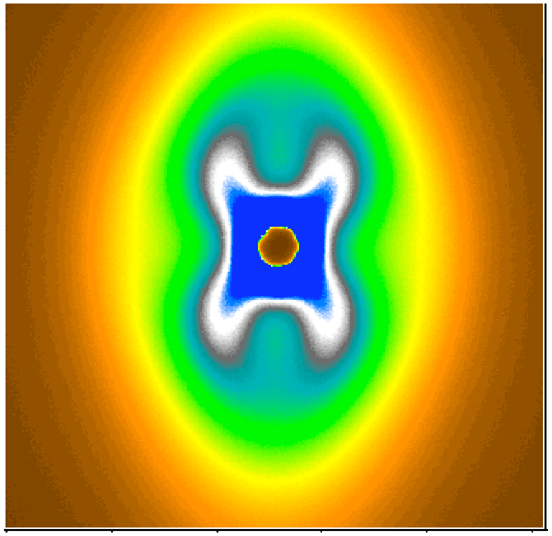
Small-Angle X-ray Scattering at Other Synchrotrons



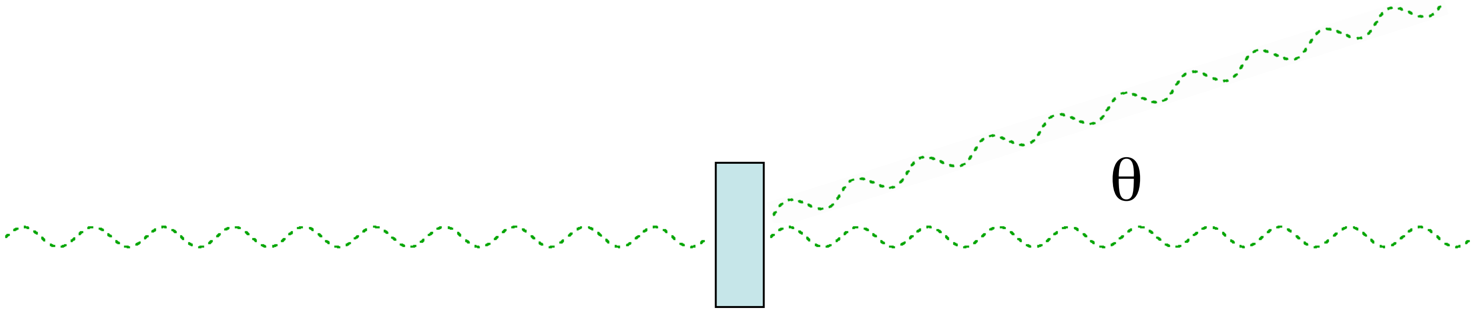
ESRF we use ID2 with T. Naryanan
(Probably the best instrument)

Much easier to get time on smaller synchrotrons
We use SSRL (Stanford); CHESS (Cornell)





Nanostructure from Small Angle X-ray Scattering

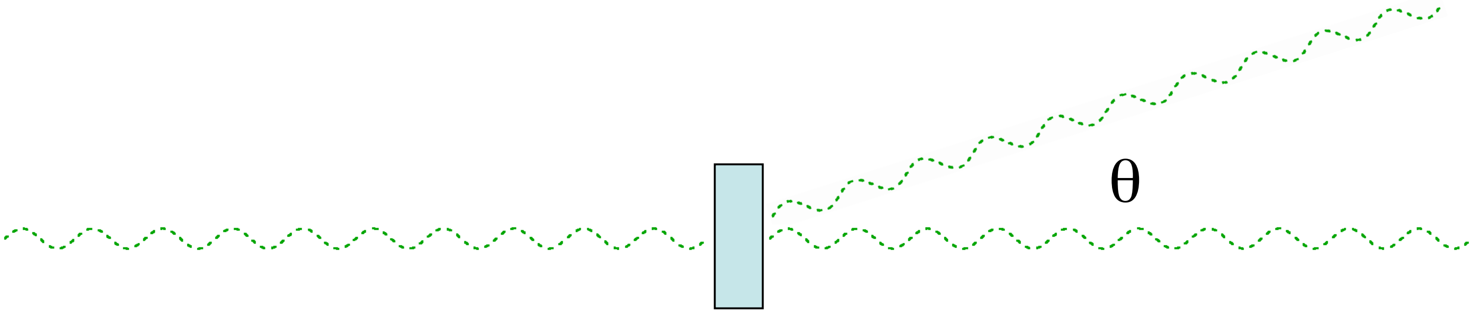


Time Resolution 10 ms (Synchrotron Facility)

For Flow Through Experiment
(Flame/Liquid/Gas Flow) can be 10 μs

Size Resolution 1 Å to 1 μm (Synchrotron Facility)

Nanostructure from Small Angle X-ray Scattering



3-Techinques are similar
SALS/LS, SANS, SAXS

λ = 0.5 μm	λ = 0.1 - 0.5 nm
For light	For x-ray/neutron

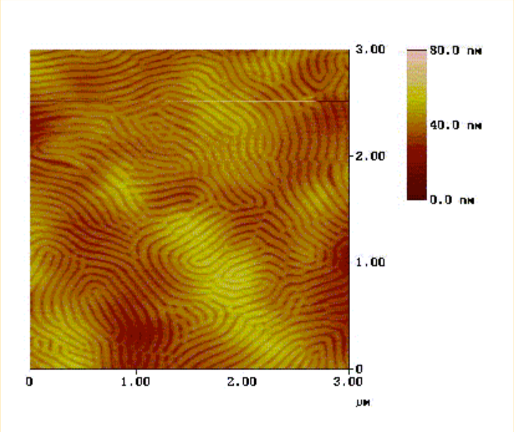
Contrast, index of refraction, electron density, neutron cross section

3-Closely related Techniques:

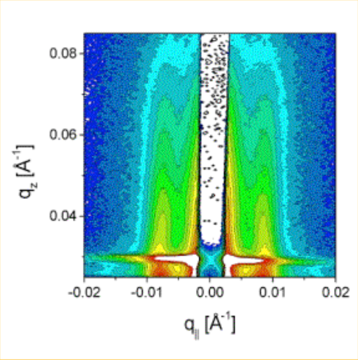
USAXS- Ultra Small Angle Scattering SAXS at 1/1000 º. APS in US and ESRF in Europe.

ASAXS- Anomalous x-ray scattering, vary wavelength leads to change in contrast due to the complex absorption spectra.

GISAXS- Promise of high resolution spectra for surface structures but there are technical issues with data interpretation.



AFM image of a diblock copolymer film displaying vertical lamellae [Busch2]



GISAXS from the polymer film shown on the left. [Smilgies]

http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php

For Small Angle X-ray Scattering (SAXS)

1) Specific Structure

Calculate Pairwise Correlation Function

Calculate Fourier Transform to predict scattering or direct transform of measured data to correlation function and analysis of correlation function.

Svergun (Hamburg) has applied this to protein in native state

Simple application to monodisperse structures

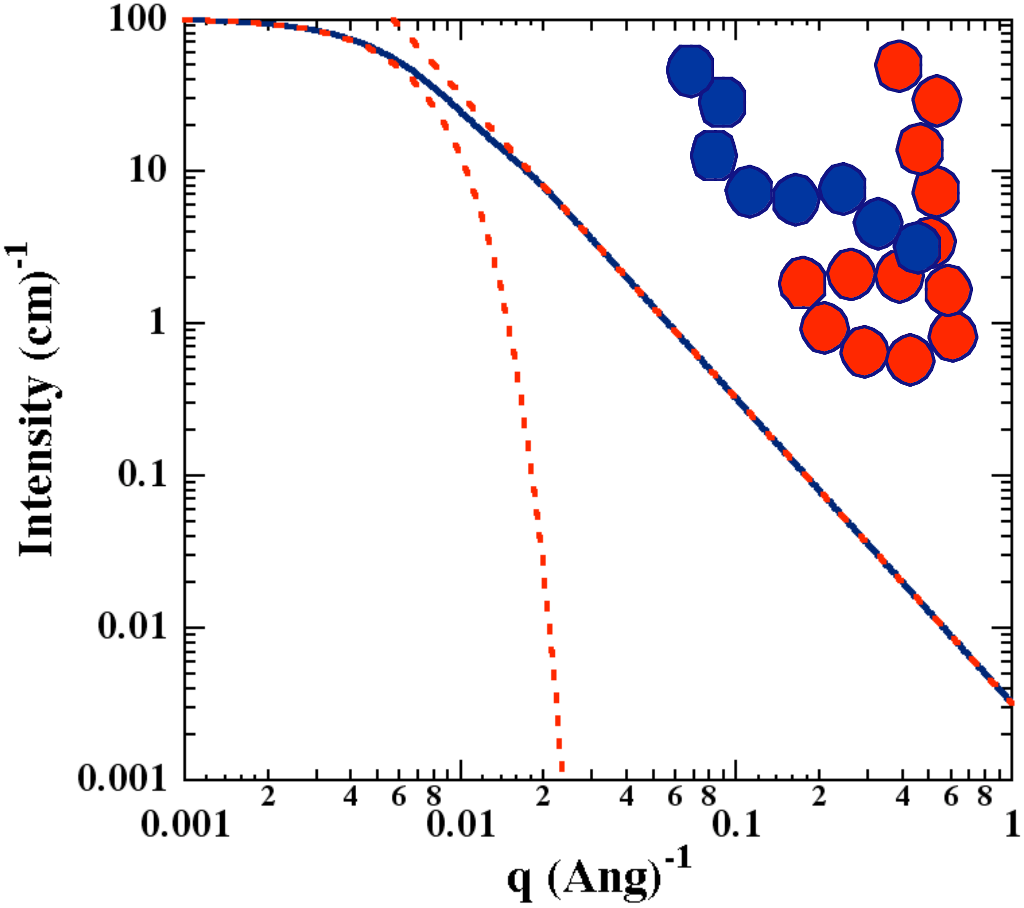
Sphere Function/Rod Function/Cylinder

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2 \qquad G = Nn_e^2$$

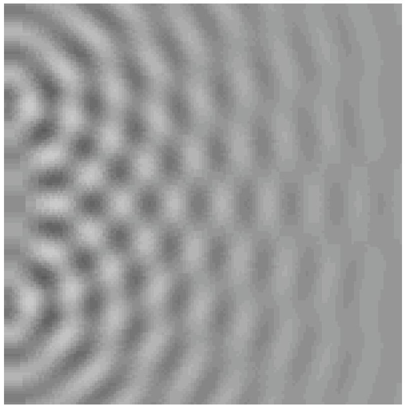
The Debye Scattering Function for a Polymer Coil

$$I(Q) = \frac{2}{Q^2}\left(Q - 1 + \exp\left(-Q\right)\right)$$

$$Q = q^2 R_g^2$$



Binary Interference Yields Scattering Pattern.

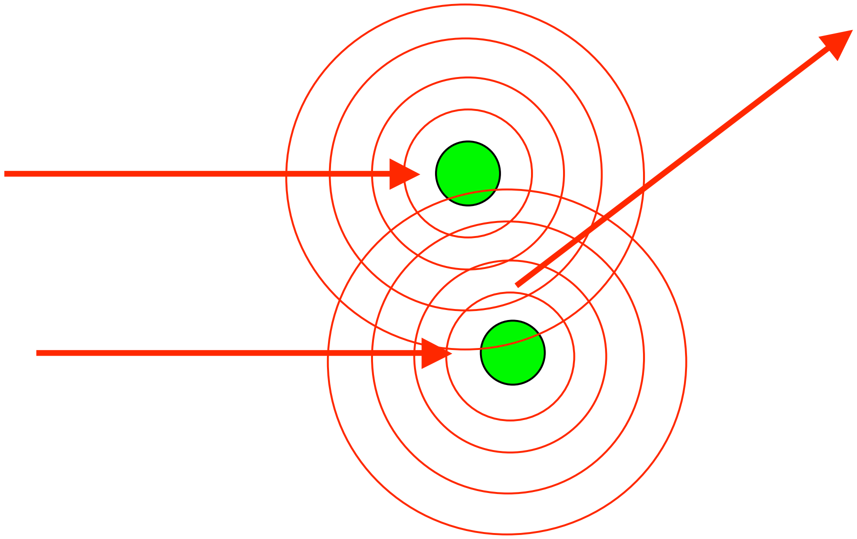


$I(q) \sim N\, n_e^2$

n_e Reflects the density of a Point generating waves

N is total number of points

The Scattering Event



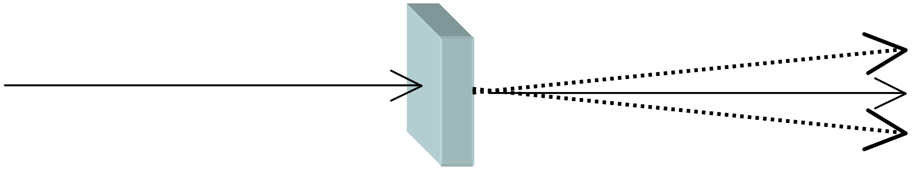
I(θ) is related to amount Nn^2

θ is related to size/distances

$$q = \frac{4\pi}{\lambda}\sin\left(\theta/2\right)$$

$$d = \frac{2\pi}{q}$$

2) Rather than consider specific structures, we can consider *general scattering laws* by which all scatters are governed under the premises that 1) “Particles” have a size and 2) “Particles” have a surface.



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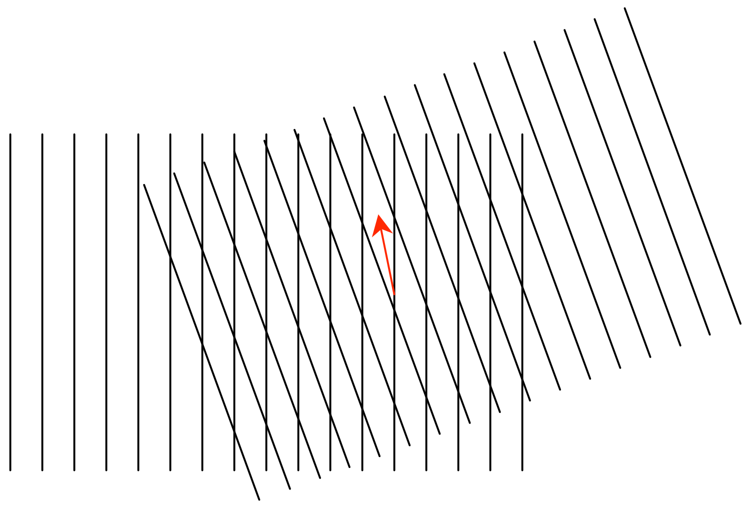


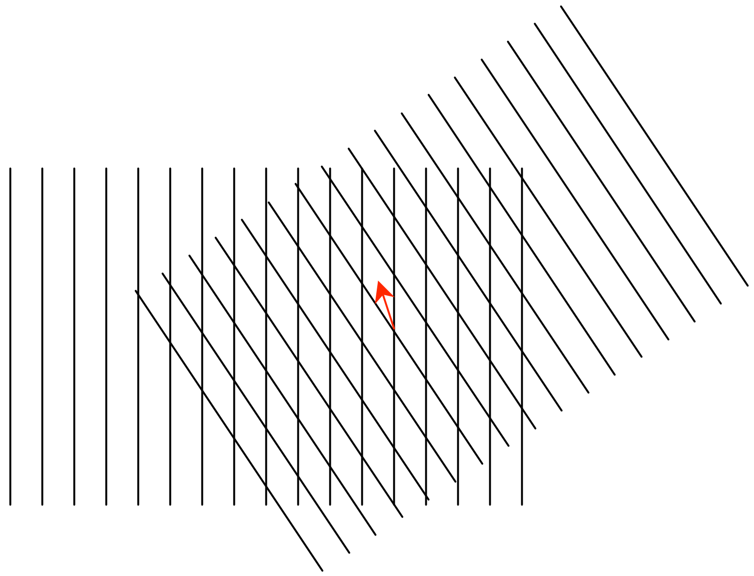
-Consider that an in-phase wave scattered at angle θ was in phase with the incident wave at the source of scattering.

-This can occur for points separated by ***r*** such that

|r| = 2π/|q|

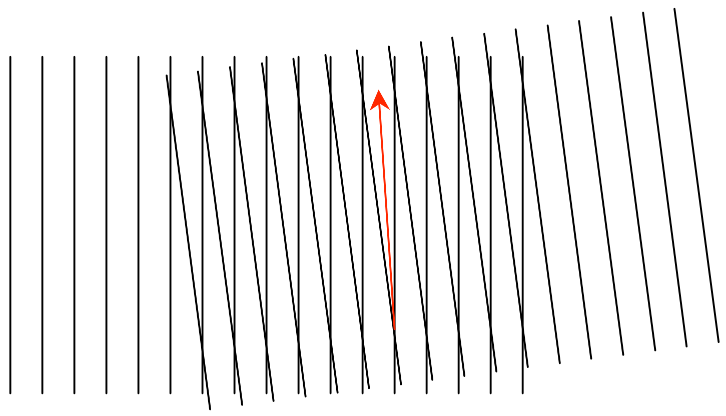
- $q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$

Binary Interference Yields Scattering Pattern.



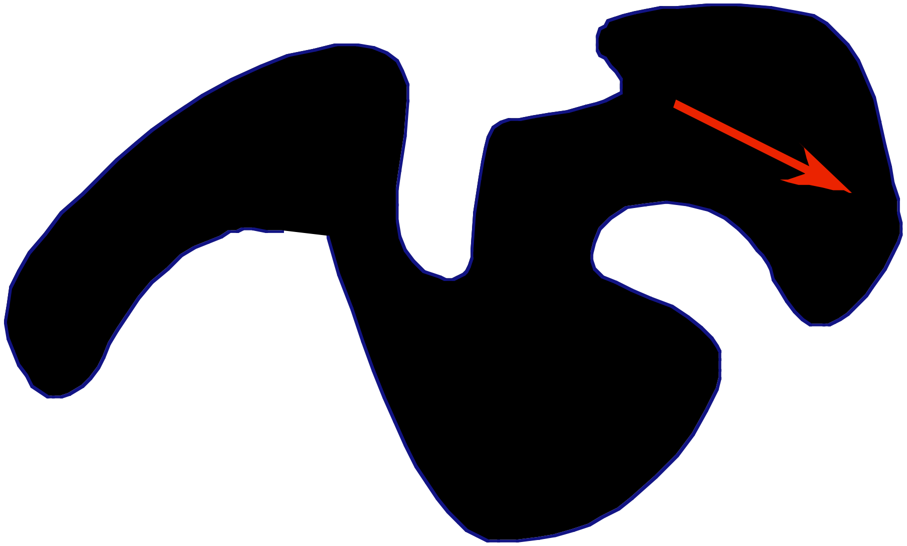
-For high θ, ***r*** is small

Binary Interference Yields Scattering Pattern.



-For small θ, ***r*** is large

For an isotropic sample we consider scattering as arising from the probability of the random placement of a vector ***r*** in the scattering phase.



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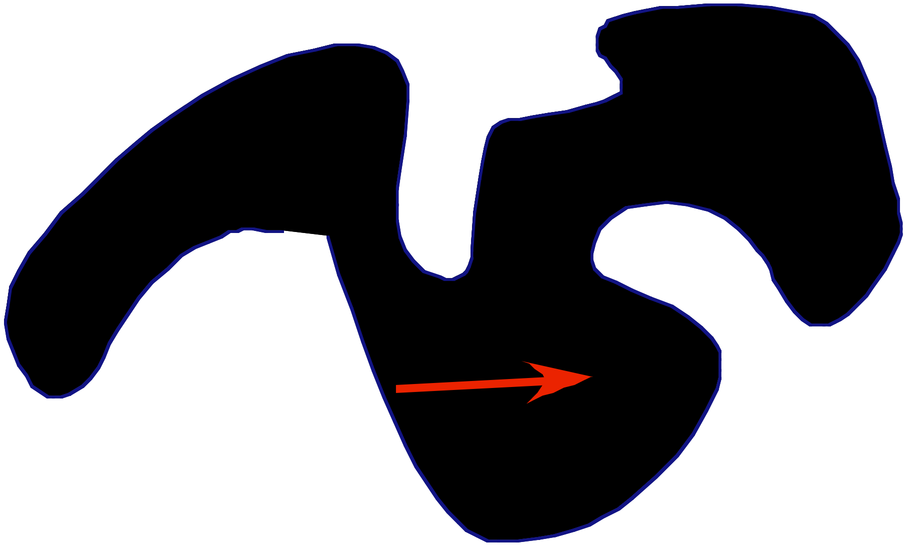

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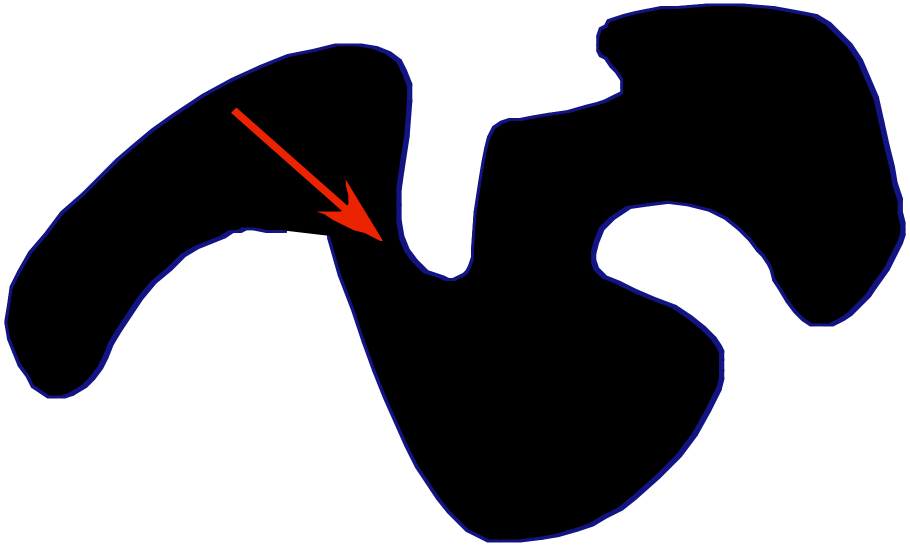

Rather than random placement of the vector we can hold The vector fixed and rotate the particle

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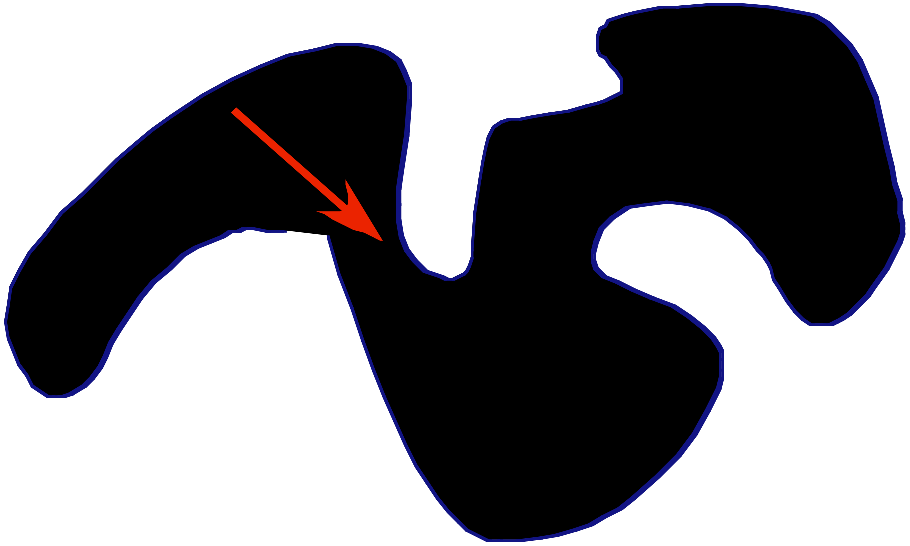

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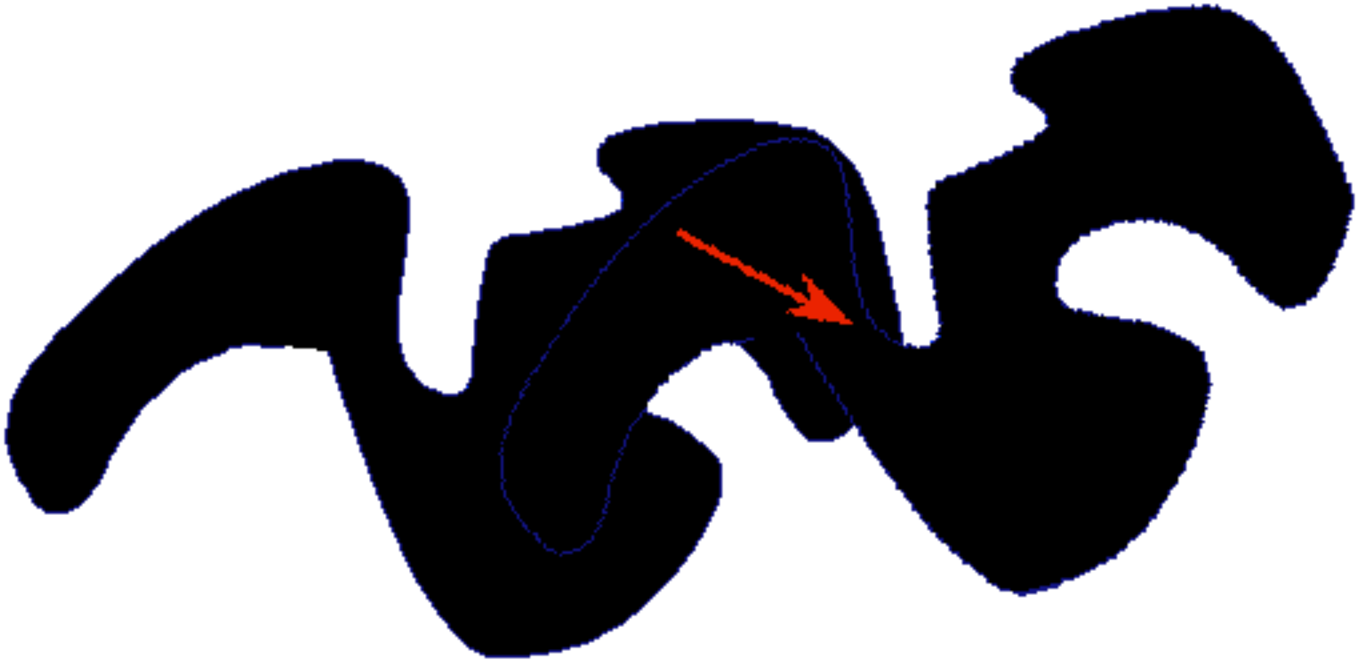

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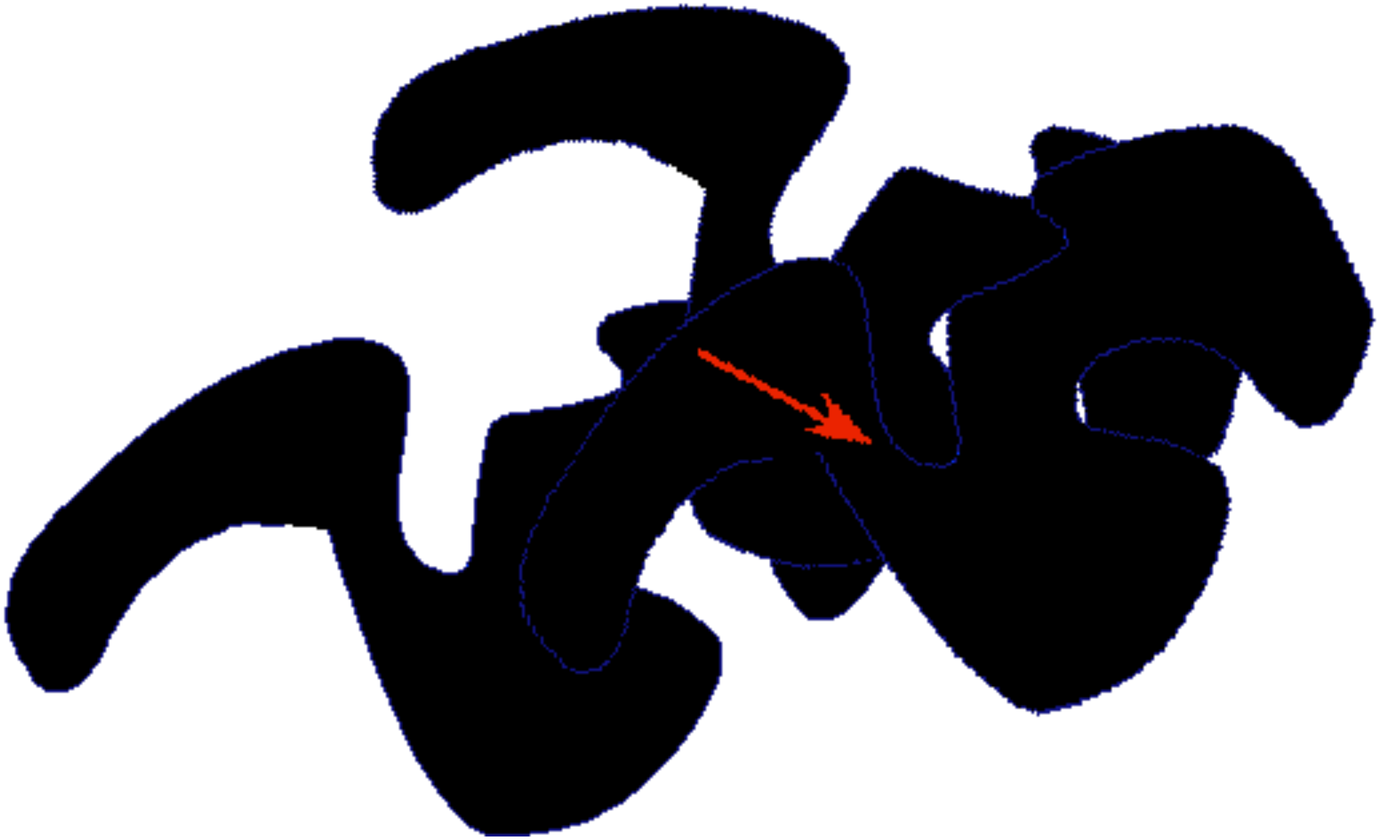
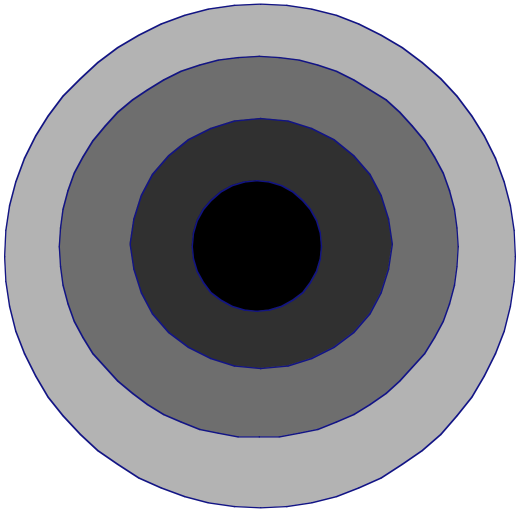


Rather than random placement of the vector we can hold The vector fixed and rotate the particle

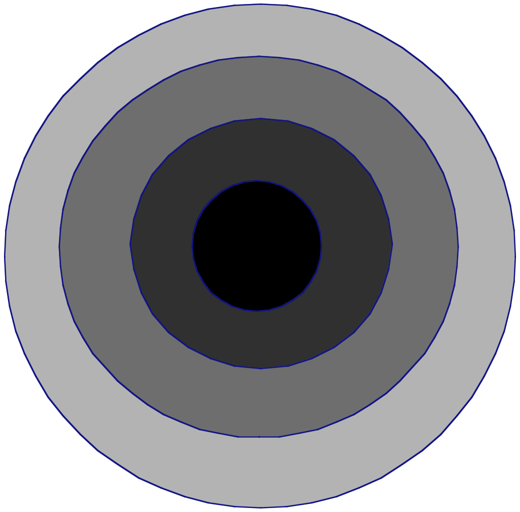
The particle becomes a probability density function from the center of mass.



That follows a Gaussian Distribution.

$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right)$$

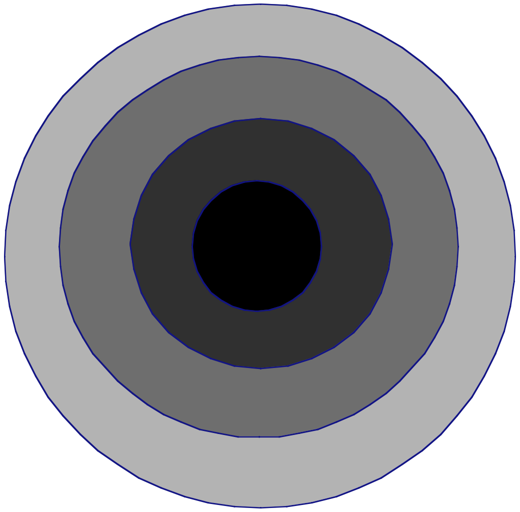
The particle becomes a probability density function from the center of mass.



Whose Fourier Transform is Guinier's Law.

$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right) \quad \Rightarrow \quad \mathrm{I}(\mathrm{q}) = G\exp\left(-\frac{q^2R_g^2}{3}\right)$$

$$\mathrm{G} = \mathrm{N}\mathrm{n}_\mathrm{e}^2$$

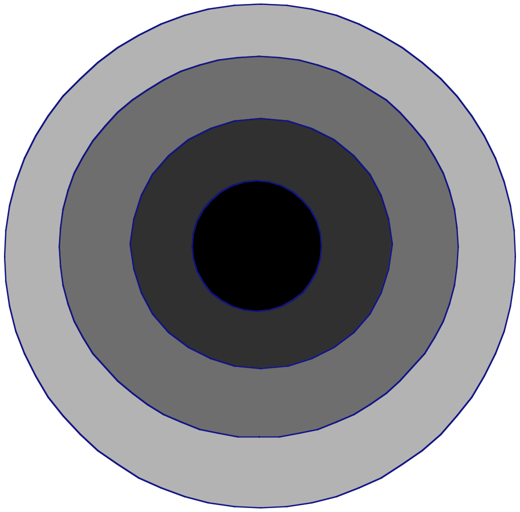


Guinier's Law Pertains to a Particle with no Surface.

$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right) \qquad \Rightarrow \qquad \mathrm{I(q)} = G\exp\left(-\frac{q^2R_g^2}{3}\right)$$

$$\mathrm{G} = \mathrm{Nn_e^2}$$

Any "Particle" can be Approximated as a Gaussian probability distribution in this context.



$$p(r) = \exp\left(\frac{-3r^2}{4R_g^2}\right) \quad \Rightarrow \quad \mathrm{I(q)} = G\exp\left(-\frac{q^2R_g^2}{3}\right)$$

$$\mathrm{G} = \mathrm{Nn}_e^2$$

Guinier's Law can be thought of as the

First Premise of Scattering:

All "Particles" have a size reflected by the radius of gyration.

The Debye Scattering Function for a Polymer Coil

$$I(Q) = \frac{2}{Q^2}\left(Q - 1 + \exp(-Q)\right)$$

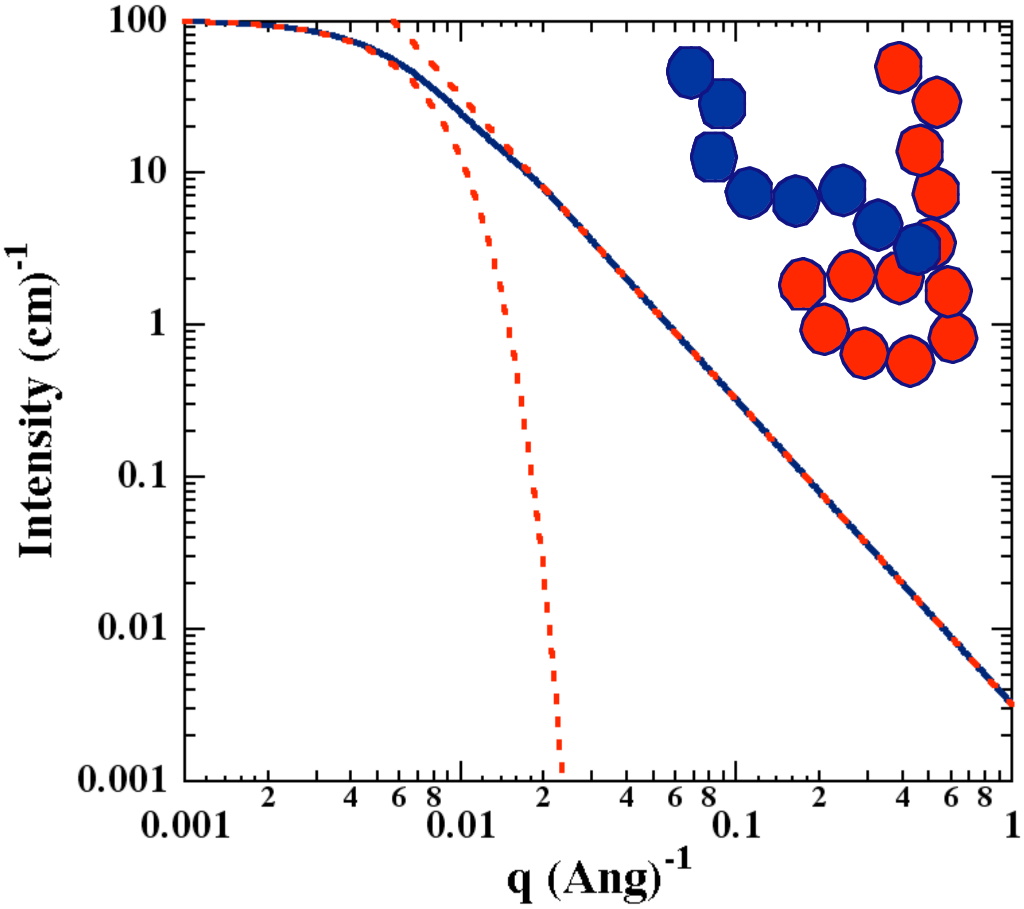
$$Q = q^2 R_g^2$$

For $qR_g << 1$

$$\exp(-Q) = 1 - Q + \frac{Q^2}{2!} - \frac{Q^3}{3!} + \frac{Q^4}{4!} - \dots$$

$$I(q) = 1 - \frac{Q}{3} + \dots \approx \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

Guinier's Law!



$I(q) \sim N n_e^2$

n_e Reflects the density of a Point generating waves

N is total number of points

At the other extreme we consider a surface.

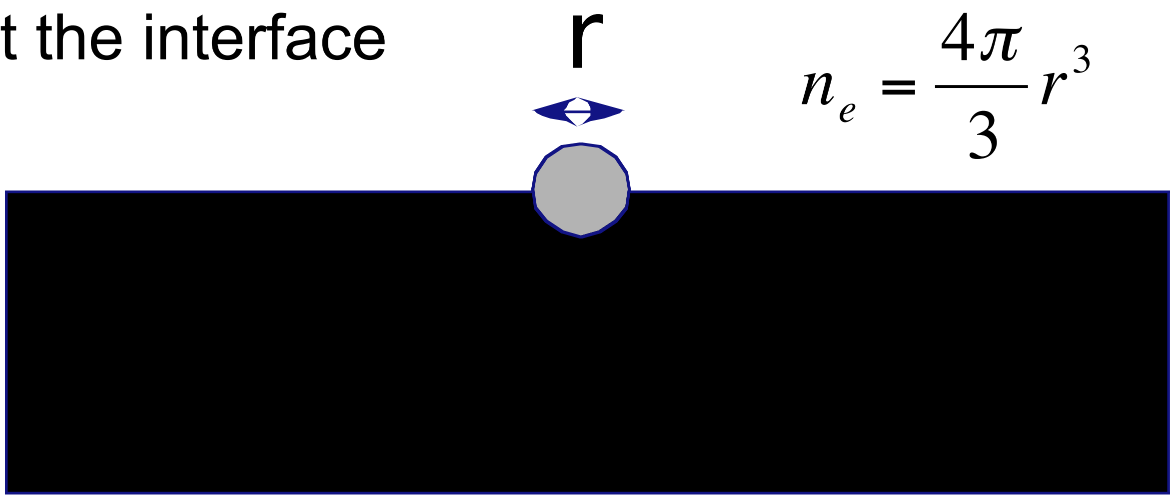
$I(q) \sim N\, n_e^2$

n_e Reflects the density of a Point generating waves

N is total number of points

At the other extreme we consider a surface.

The only location for contrast between phases is At the interface



$$n_e = \frac{4\pi}{3} r^3$$

$I(q) \sim N\, n_e^2$

n_e Reflects the density of a Point generating waves

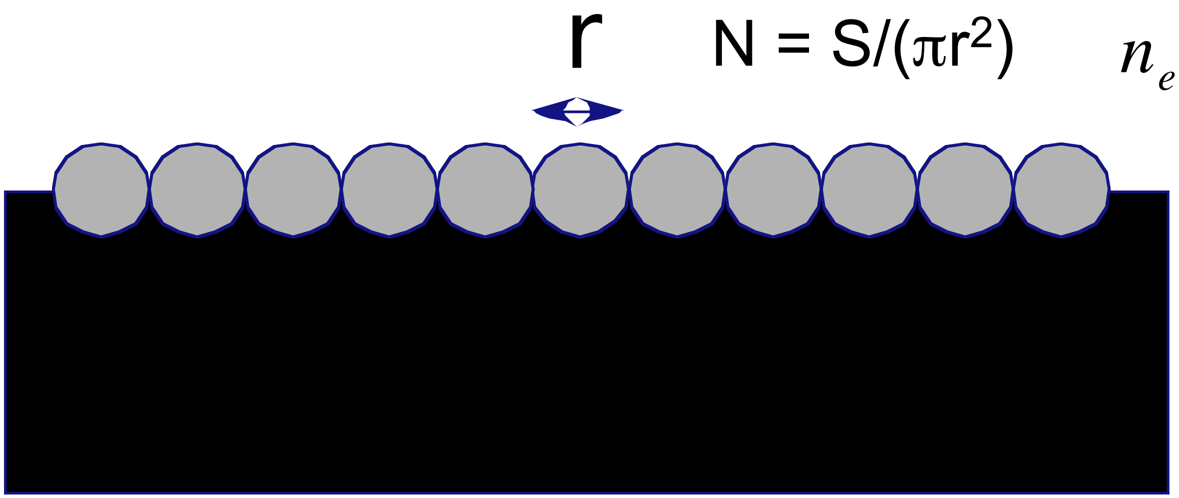
N is total number of points

At the other extreme we consider a surface.

We can fill the interface with spheres of size ***r***

$N = S/(\pi r^2)$

$$n_e = \frac{4\pi}{3} r^3$$



Porod’s Law can be thought of as the

Second Premise of Scattering:

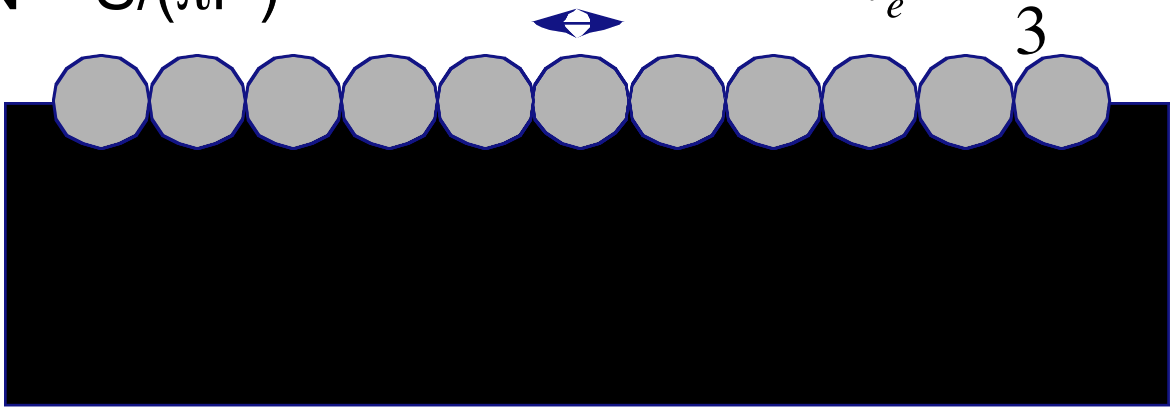
All “Particles” have a surface reflected by S/V.

$(d_p = (S/V)^{-1})$

$$I(q) \sim Nn_e^2 \sim \left(\frac{S}{\pi r^2}\right)\left(\frac{4\pi r^3}{3}\right)^2 \sim \frac{16S\pi r^4}{9} \quad \Rightarrow \quad \frac{2\pi \mathrm{n}_\mathrm{e}^2\left(\frac{S}{V}\right)}{Vq^4}$$

$N = S/(\pi r^2)$

$$n_e = \frac{4\pi}{3} r^3$$

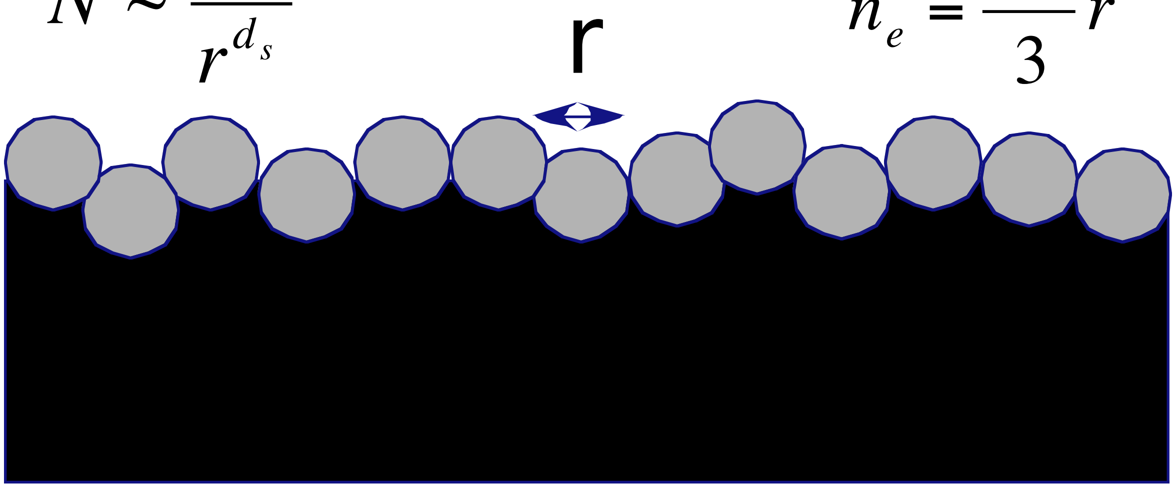


For a Rough Surface: $2 \le d_s < 3$

(This Function decays to Porod's Law at small sizes)

$$I(q) \sim N n_e^2 \sim \left(\frac{S}{r^{d_s}}\right)\left(\frac{4\pi r^3}{3}\right)^2 \sim S r^{6-d_s} \qquad \Rightarrow \qquad \frac{S}{q^{6-d_s}}$$

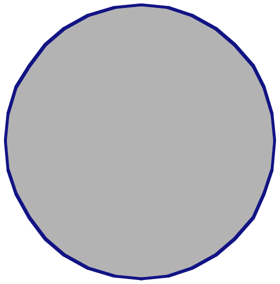
$$N \sim \frac{S}{r^{d_s}} \qquad\qquad n_e = \frac{4\pi}{3} r^3$$



Sphere Function

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$

For $qR >> 1$



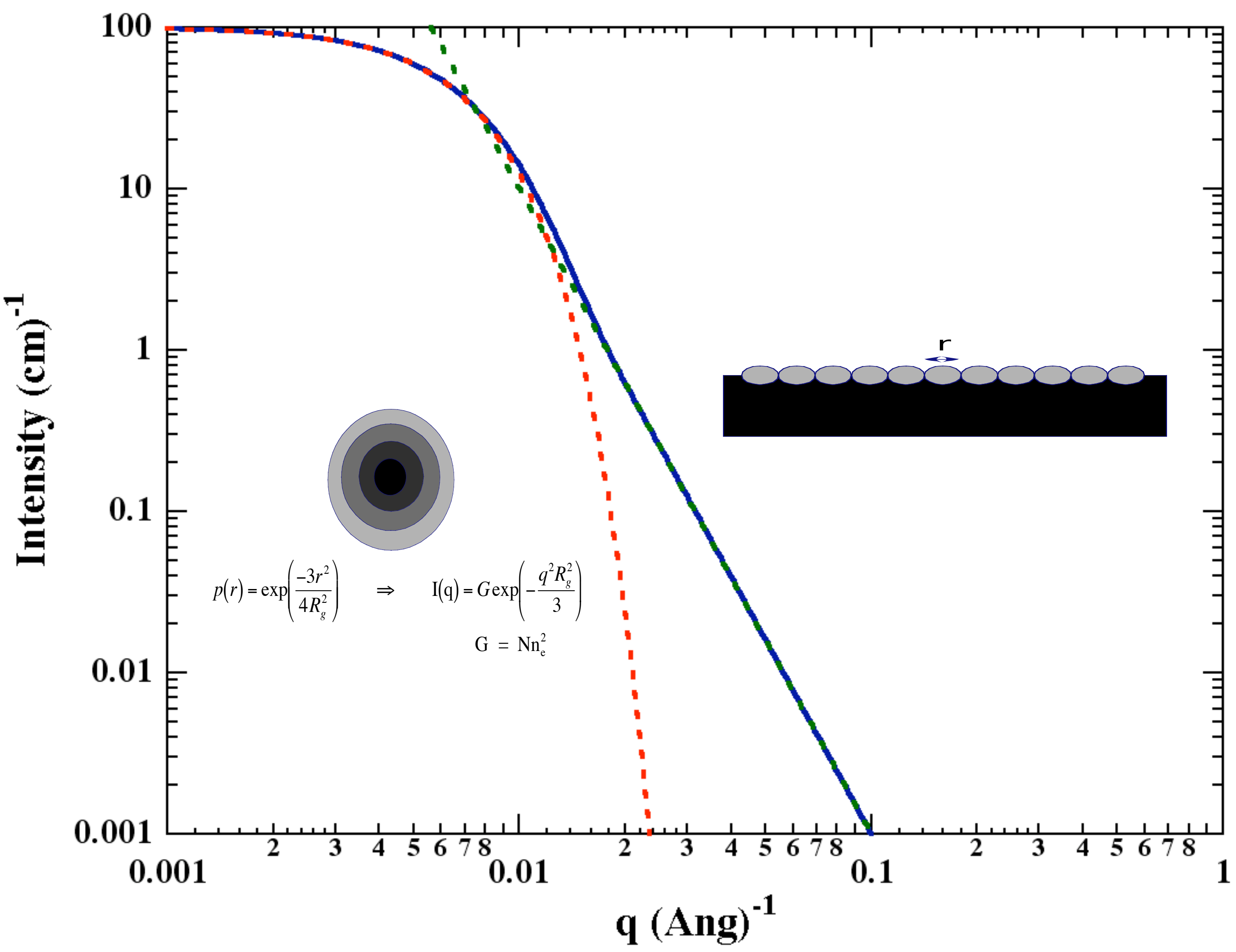
$<\sin qR> \Rightarrow 0$

$<\cos^2 qR> \Rightarrow 1/3$

$$I(q) \approx \frac{G}{q^4 R^4}$$

Porod's Law for a Sphere!

First and Second Premise of Scattering



Particle Size, d_p

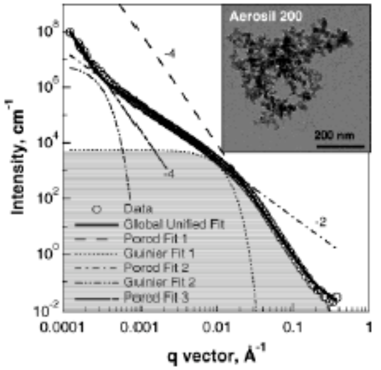


Figure 1. An USAXS pattern of agglomerated fumed silica (Aerosil 200, Degussa AG). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, three Porod regimes (dashed line, dashed−dotted line, and long−short-dashed line) are shown together with the 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}.

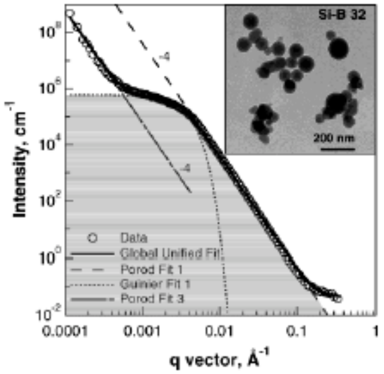


Figure 2. A USAXS plot of a nonagglomerated fumed silica (Si-B 32) made in a 17 g/h sustained premixed flame reactor (ref 18). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, Porod regimes (dashed line and long−short-dashed line) are shown 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}.

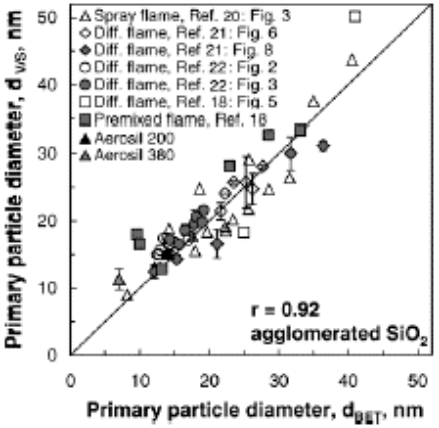


Figure 3. Comparison of d_{VS} and d_{BET} for agglomerated silica powders made in our vapor- or liquid-fed flame aerosol reactors (refs 18 and 20−22) and those of commercially available powders (Aerosil 200 and Aerosil 380, Degussa AG).

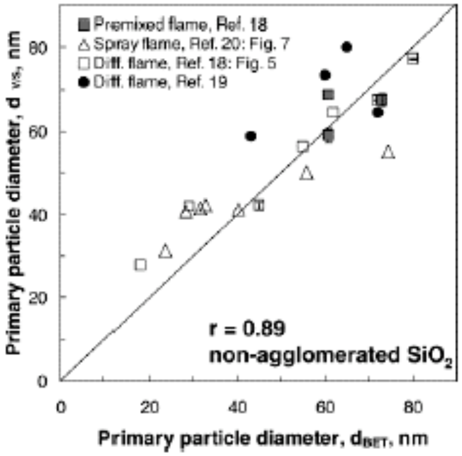
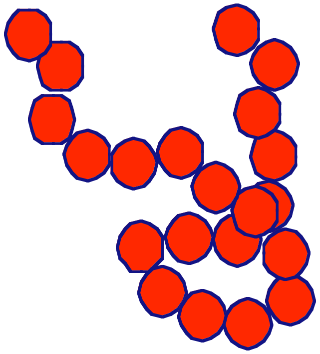


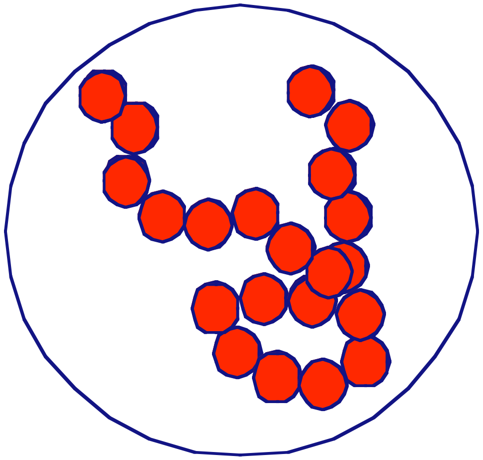
Figure 4. Comparison of d_{VS} and d_{BET} for various nonagglomerated silica powders made in our vapor-fed (refs 18 and 19) and liquid-fed (ref 20) flame aerosol reactors.

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).

Many Things can Happen between the “Particle” Size
And the “Particle” Surface. Consider a “Linear” Aggregate.

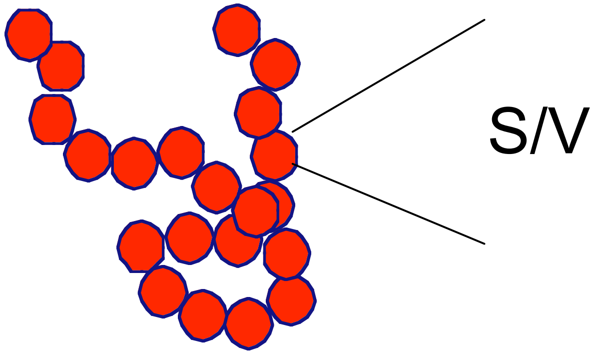


Many Things can Happen between the “Particle” Size
And the “Particle” Surface. Consider a “Linear” Aggregate.



Overall R_g

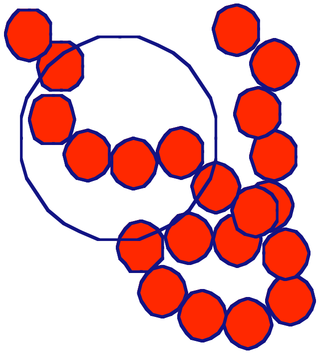
Many Things can Happen between the “Particle” Size
And the “Particle” Surface. Consider a “Linear” Aggregate.



Overall Surface Area (Sum of Primaries)

Many Things can Happen between the “Particle” Size And the “Particle” Surface. Consider a “Linear” Aggregate.

At intermediate sizes the chain is “self-similar”

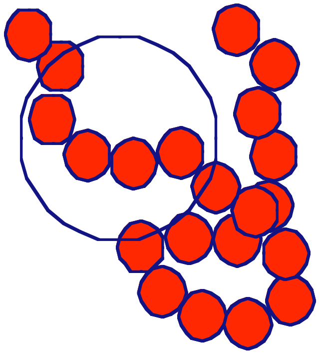


$$Mass \sim Size^{d_f}$$

$$z \sim \left(\frac{R_2}{R_1}\right)^{d_f}$$

Many Things can Happen between the "Particle" Size And the "Particle" Surface. Consider a "Linear" Aggregate.

At intermediate sizes the chain is "self-similar"



I(q) ~ N n_e^2

N = Number of Intermediate Spheres in the Aggregate

n_e = Mass of inter. sphere

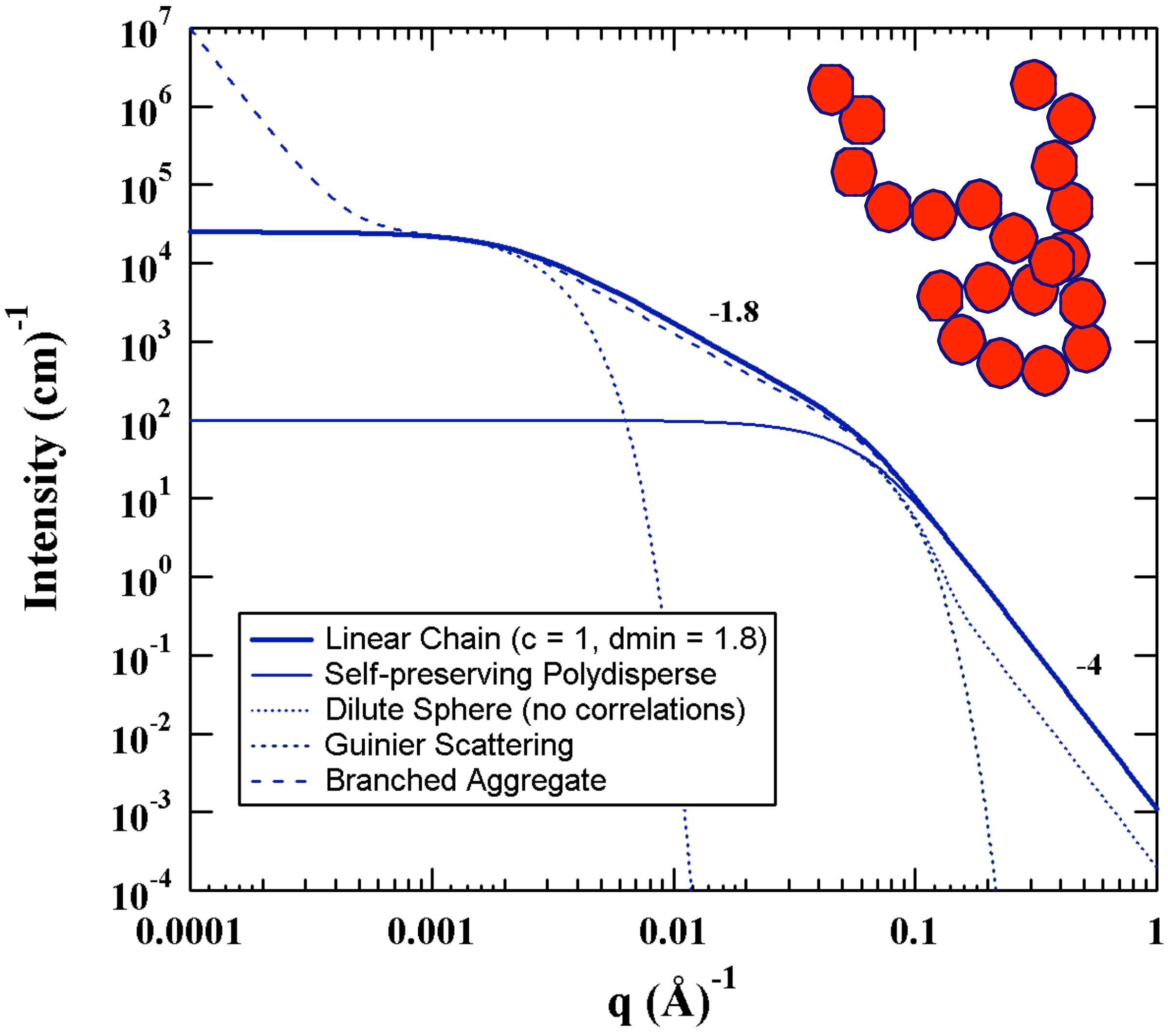
I(q) ~ N n_e^2

$$N \sim \left(\frac{R_2}{r_{\text{int}}}\right)^{d_f}$$

$$n_e \sim \left(\frac{r_{\text{int}}}{R_1}\right)^{d_f}$$

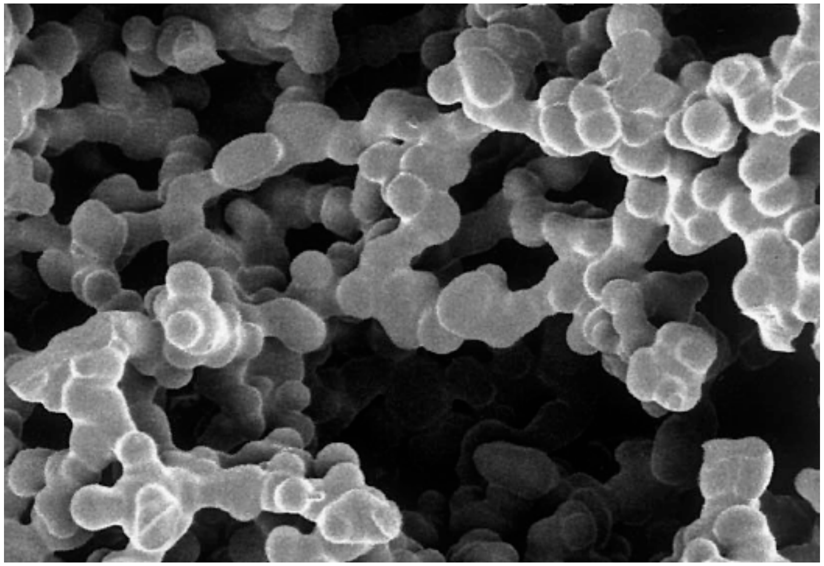
$$Nn_e^2 \sim \left(\frac{r_{\text{int}}}{R_1}\right)^{d_f}\left(\frac{R_2}{R_1}\right)^{d_f} \quad \Rightarrow \quad \mathrm{I}(\mathrm{q}) \sim \left(\frac{R_2}{R_1^2}\right)^{d_f} q^{-d_f}$$

Linear Aggregates



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

Branched Structures



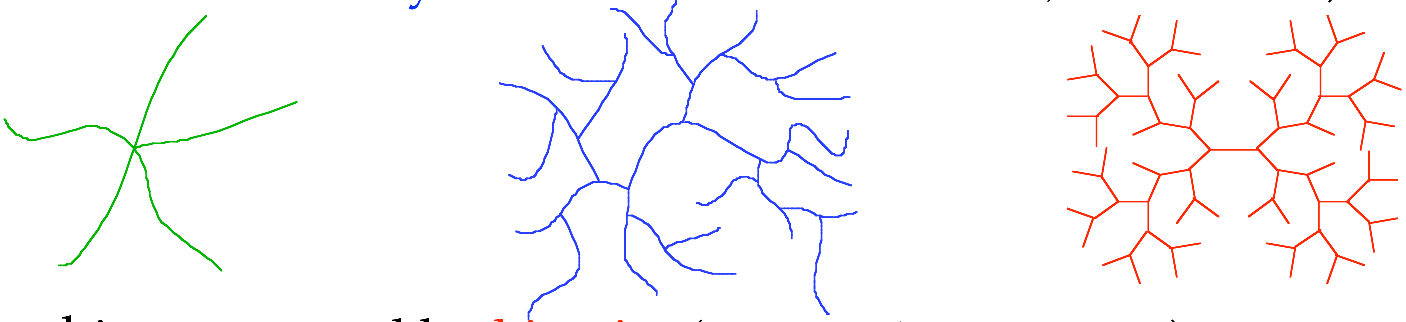
PDMS/Silica Hybrid Material

Guo L, Hyeon-Lee J, Beaucage G *J. Non-Cry. Solids* **243** 61-69 (1999)

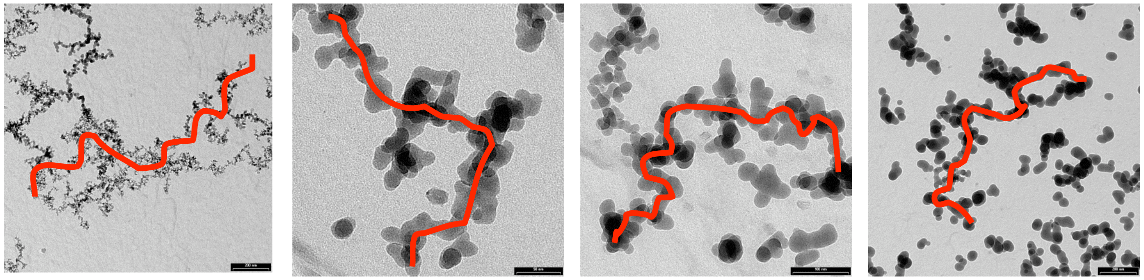
Branching in different systems

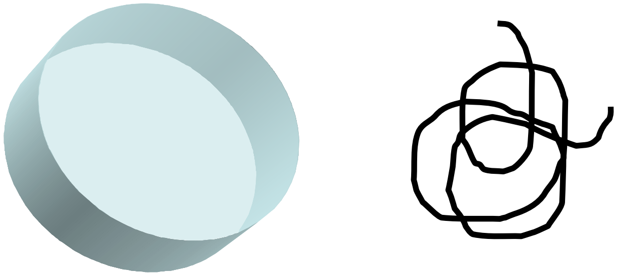
- Long Chain and Short Chain

- Model Branched Polymers (Stars, Hyperbranched, Dendrimers)



- Branching governed by kinetics (nano-scale aggregates)





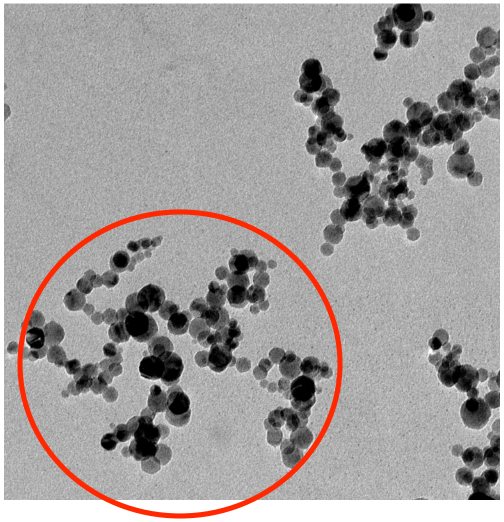
1) Mass Fractal dimension, d_f.

$$z = \alpha\left(\frac{2R}{d_p}\right)^{d_f}$$

z is mass/DOA
d_p is bead size
R is coil size

Random aggregation (right) $d_f \sim 1.8$;
Randomly Branched Gaussian $d_f \sim 2.5$;
Self-Avoiding Walk $d_f = 5/3$

Problem:
Disk $d_f = 2$
Gaussian Walk $d_f=2$

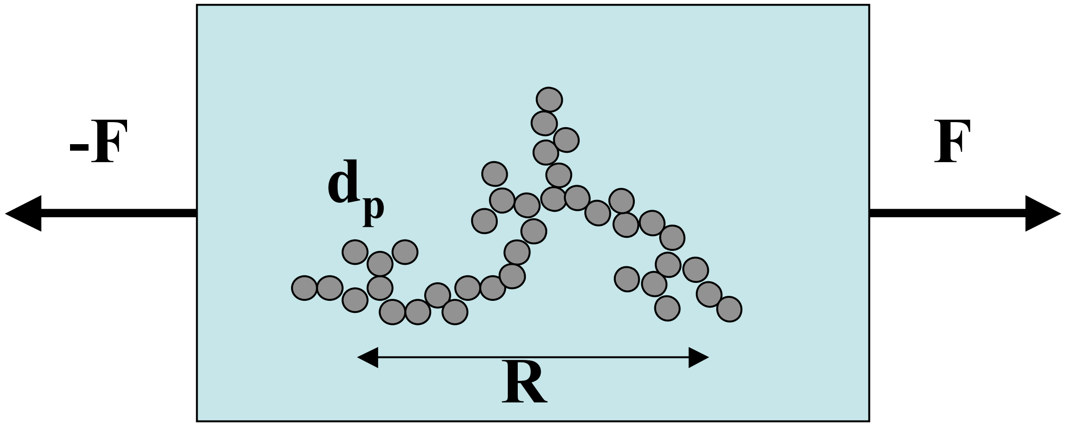


Nano-titania from Spray Flame

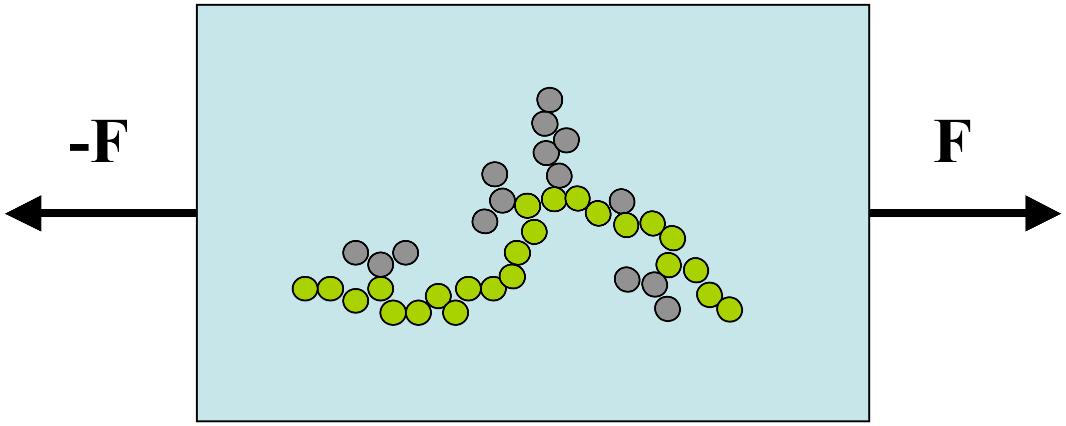
$2R/d_p = 10$, $\alpha \sim 1$, $z \sim 220$
$d_f = \ln(220)/\ln(10) = 2.3$

A Measure of Branching is not Given.

2) Fractal dimensions (d_f, d_{min}, c) and degree of aggregation (z)



$$z \sim \left(\frac{R}{d_p}\right)^{d_f}$$



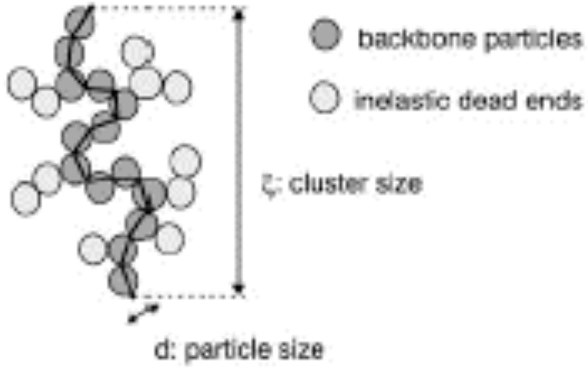
$$p = z_{\min} \sim \left(\frac{R}{d_p}\right)^{d_{\min}}$$

$$z \sim p^c = p^{d_f/d_{\min}}$$

d_{min} should effect perturbations & dynamics, transport electrical conductivity & a variety of important features.

Beaucage G, *Determination of branch fraction and minimum dimension of frac. agg.* Phys. Rev. E **70** 031401 (2004).
Kulkarni, AS, Beaucage G, *Quant. of Branching in Disor. Mats.* J. Polym. Sci. Polym. Phys. **44** 1395-1405 (2006).

Fractal aggregates are springs



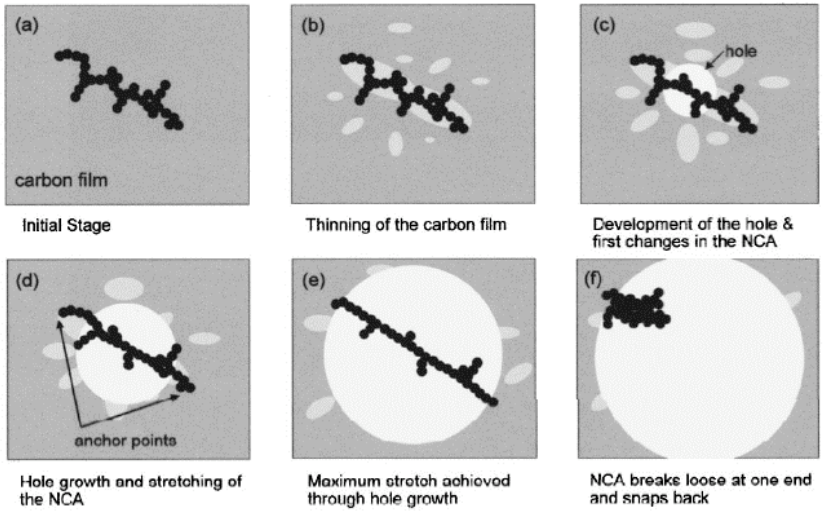


FIG. 7. Schematics of hole formation and stretching.

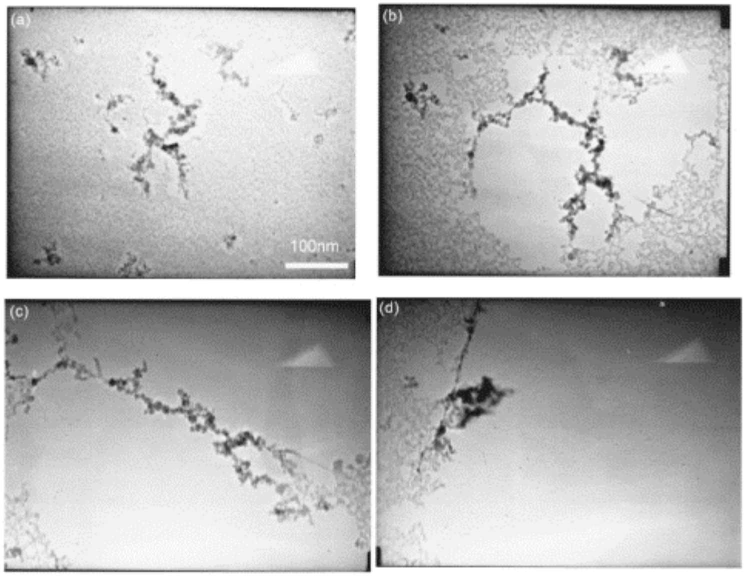
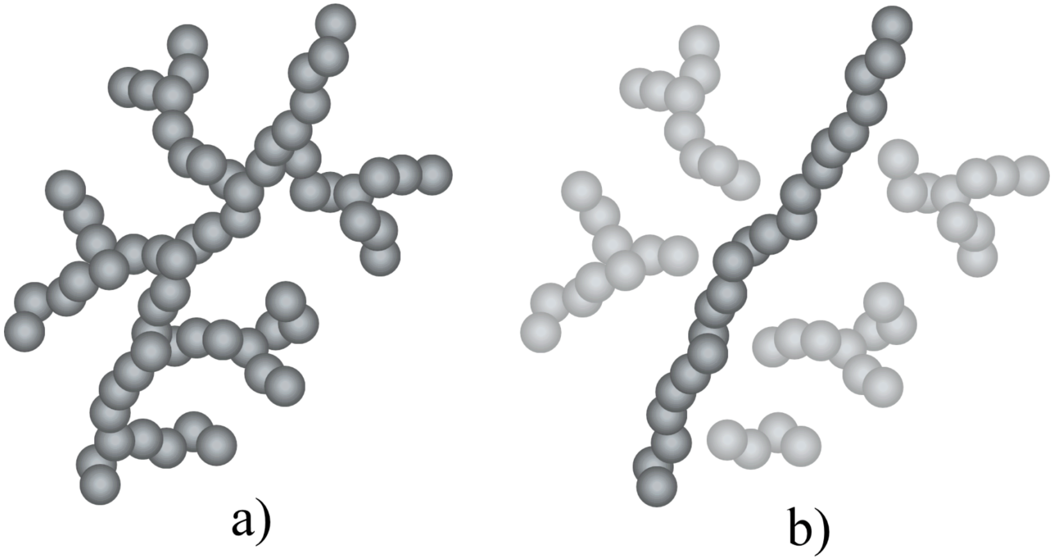


FIG. 9. Elastic behavior of titania NCA. (a) Initial shape of NCA on an ultrathin carbon film. (b) The NCA began to stretch as a hole developed in the carbon film after 7.5 min. (c) The NCA stretched by 36% after 10 min. (d) Contracted NCA after the anchor point to the film (bottom right) broke at 11.3 min.

Ogawa K, Vogt T., Ullmann M, Johnson S, Friedlander SK, *Elastic properties of nanoparticulate chain aggregates of* TiO_2*,* Al_2O_3 *and* Fe_2O_3 *generated by laser ablation*, J. Appl. Phys. **87**, 63-73 (2000).

A Scaling Model for Branched Structures Including Polyolefins



$$\phi_{Br} = \frac{42}{64} = 0.66$$

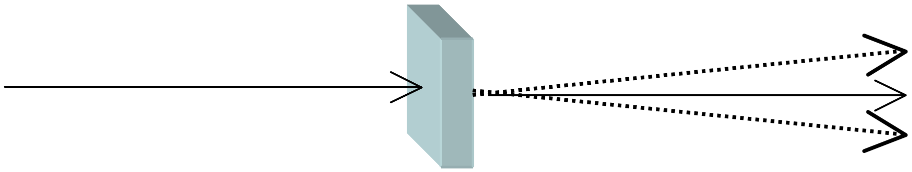
$$\phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c-1}$$

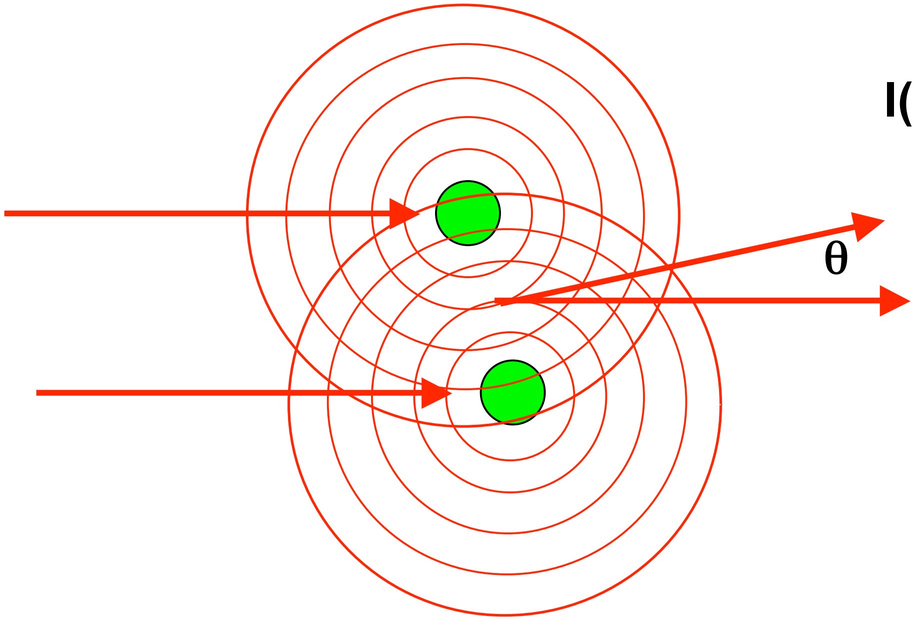
Mole Fraction of Branches

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

3) Neutron & X-ray Scattering

We can "Build" a Scattering Pattern from Structural Components using Some Simple Scattering Laws





I(θ) is related to amount Nn^2

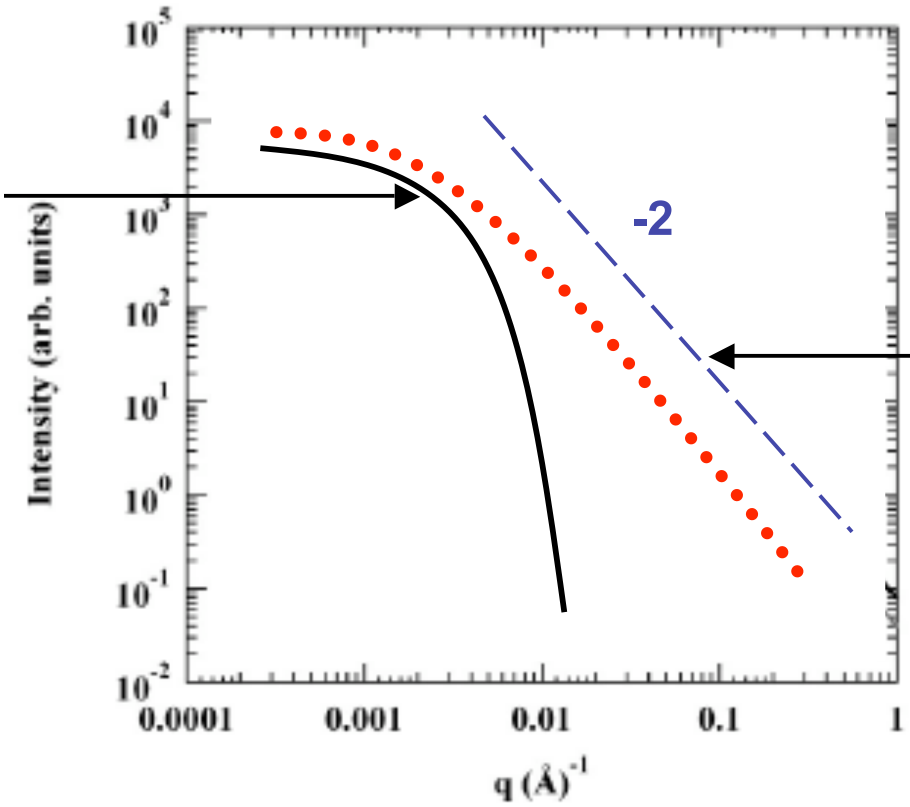
θ is related to size/distances

$$q = \frac{4\pi}{\lambda}\sin\left(\theta/_2\right)$$

$$d = \frac{2\pi}{q}$$

Guinier's Law

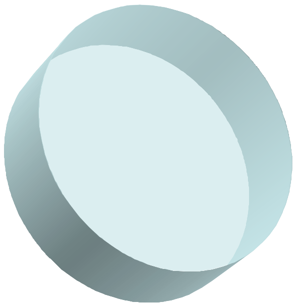
$$I(q) = G e^{\frac{(-qR_g)^2}{3}}$$



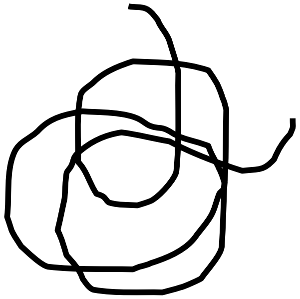
Power Law

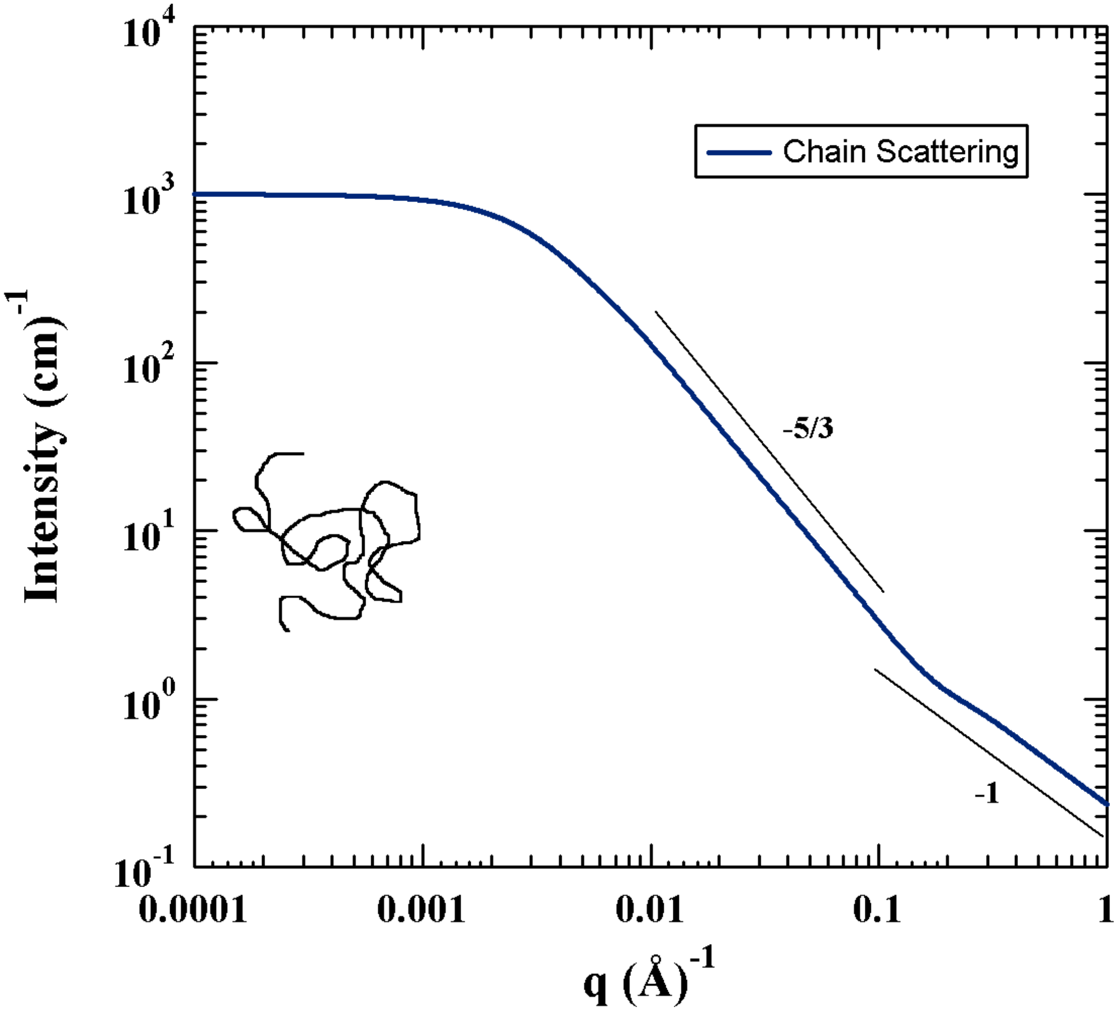
$$I(q) = B_f\, q^{-d_f}$$

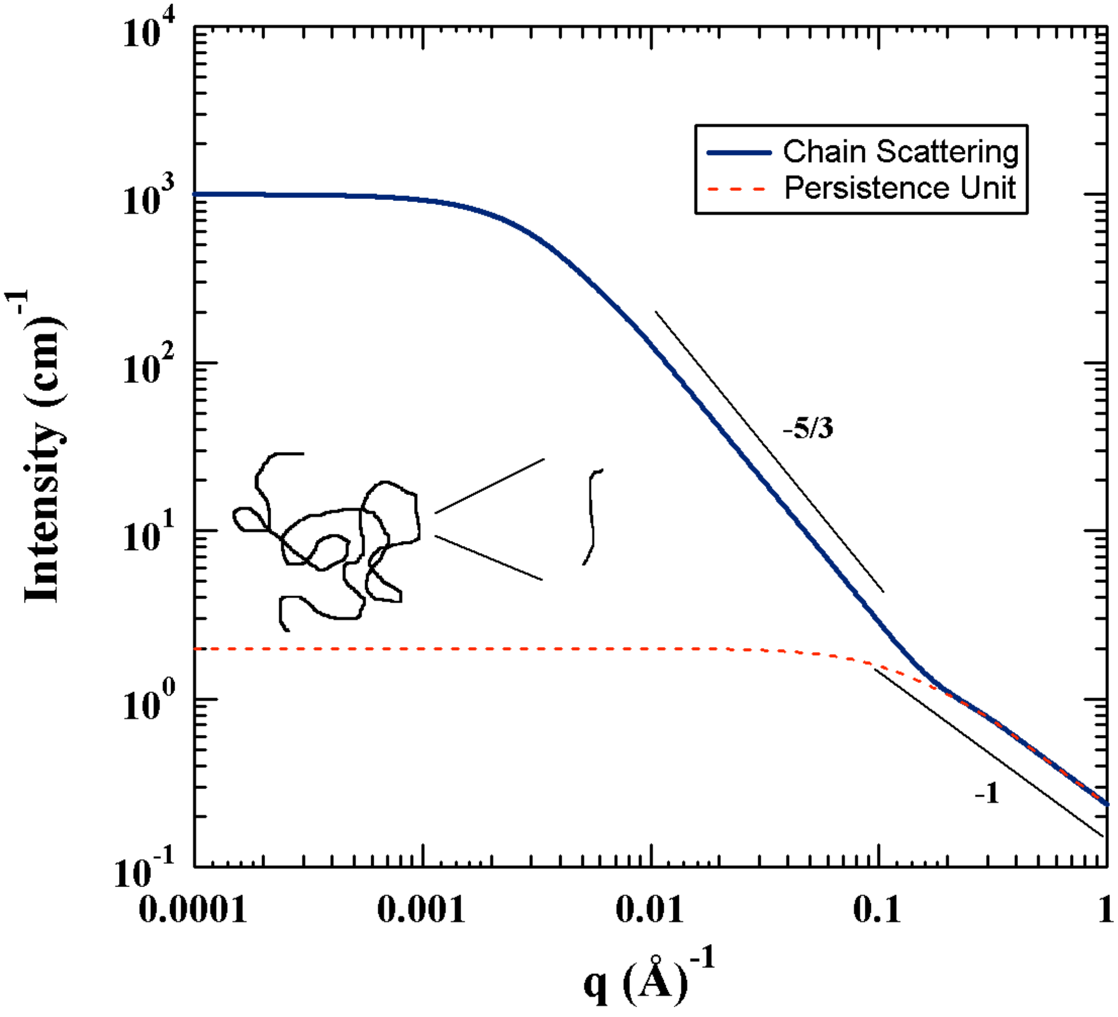
Thin Disk



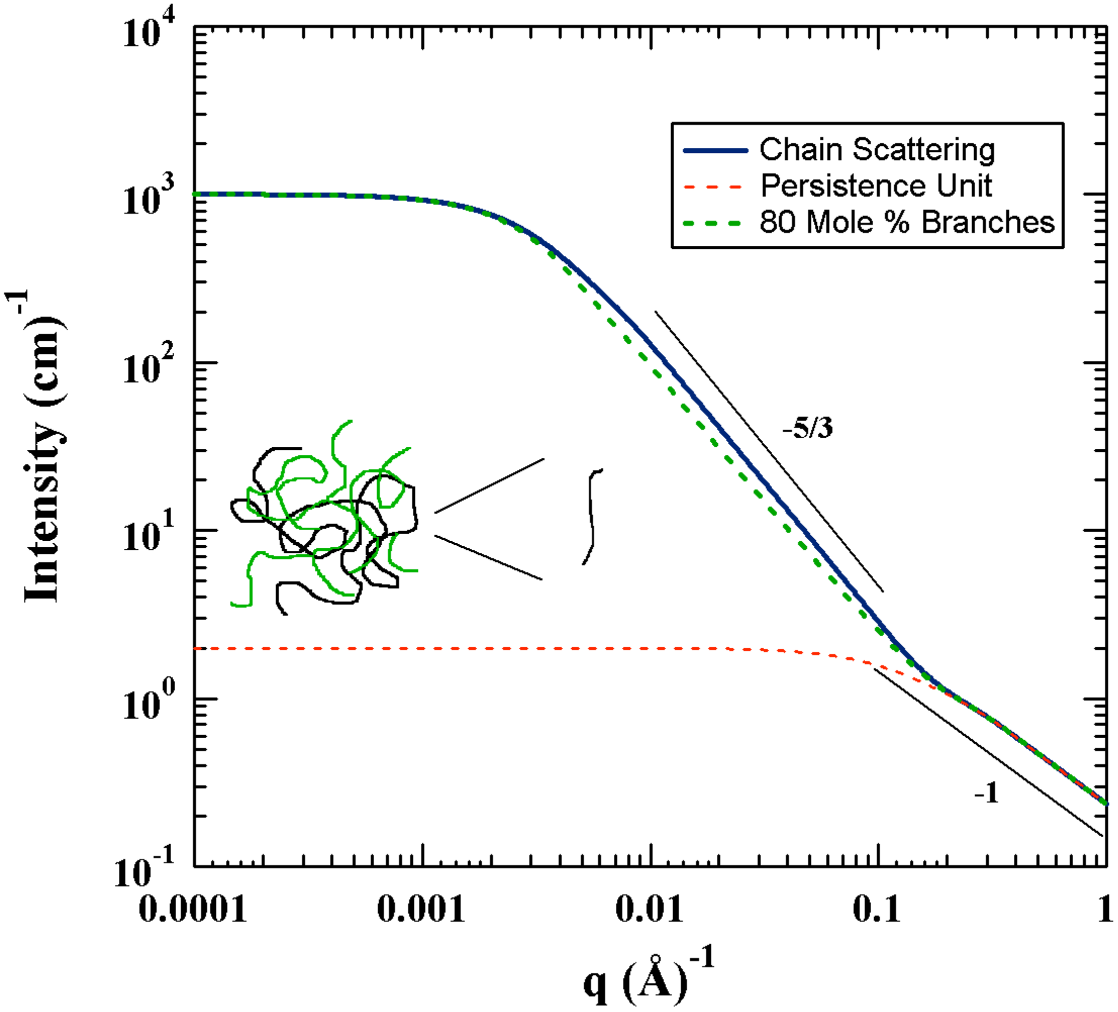
Gaussian Chain



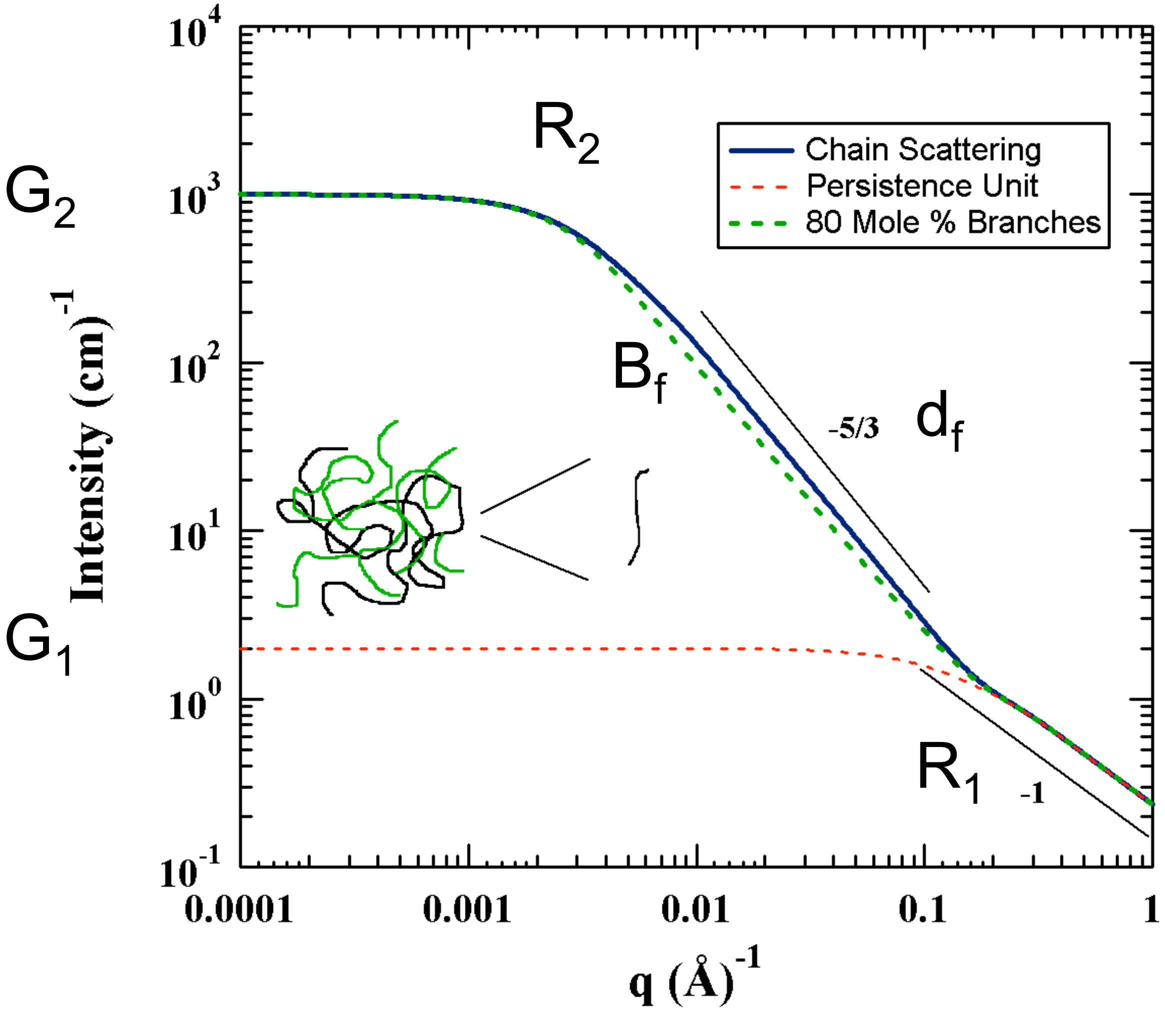

Chain Scattering
-5/3
-1
Intensity (cm)$^{-1}$
q (Å)$^{-1}$
10^4
10^3
10^2
10^1
10^0
10^{-1}
0.0001
0.001
0.01
0.1
1



Persistence is distinct from chain scaling

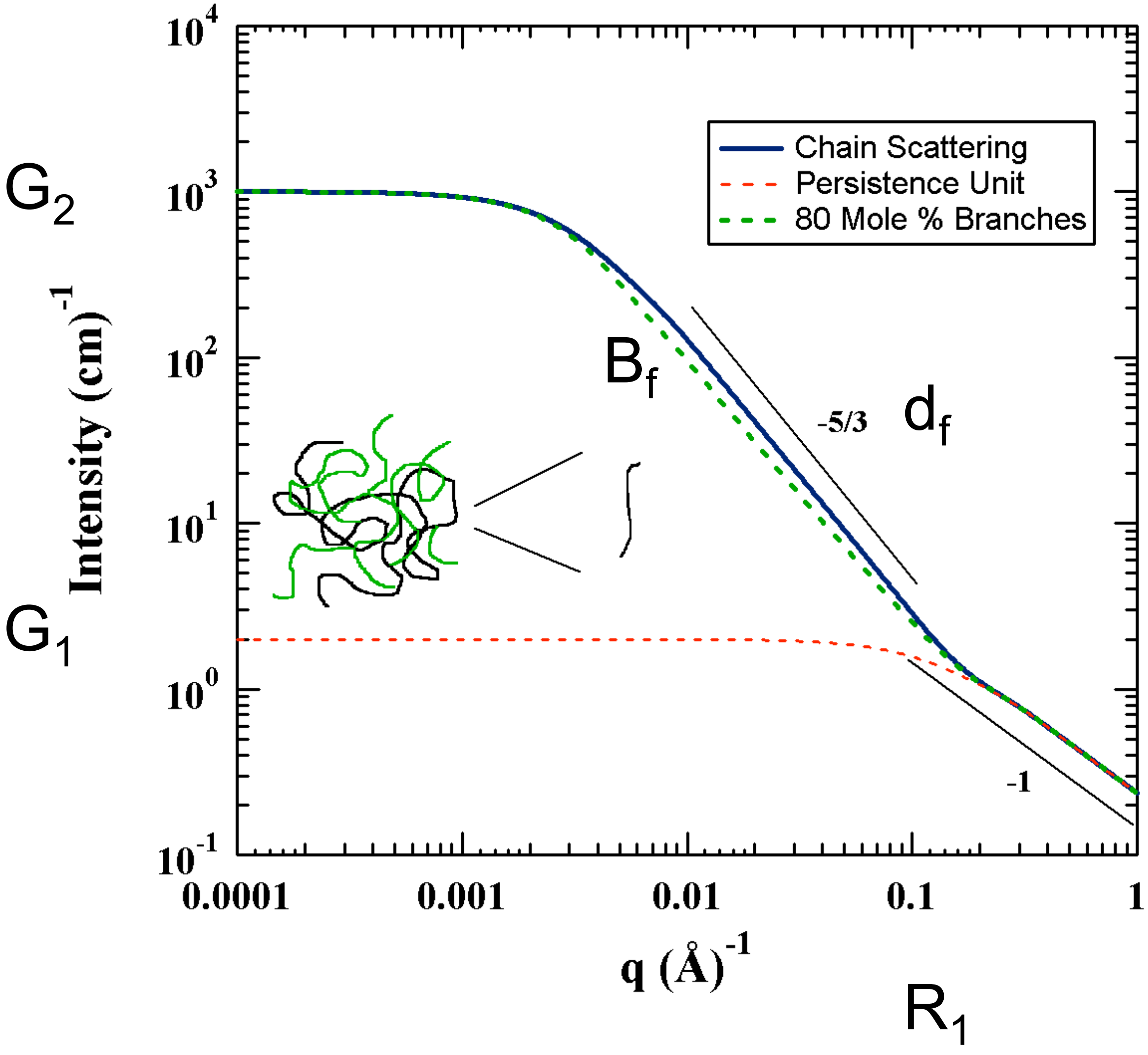


Branching has a quantifiable signature.



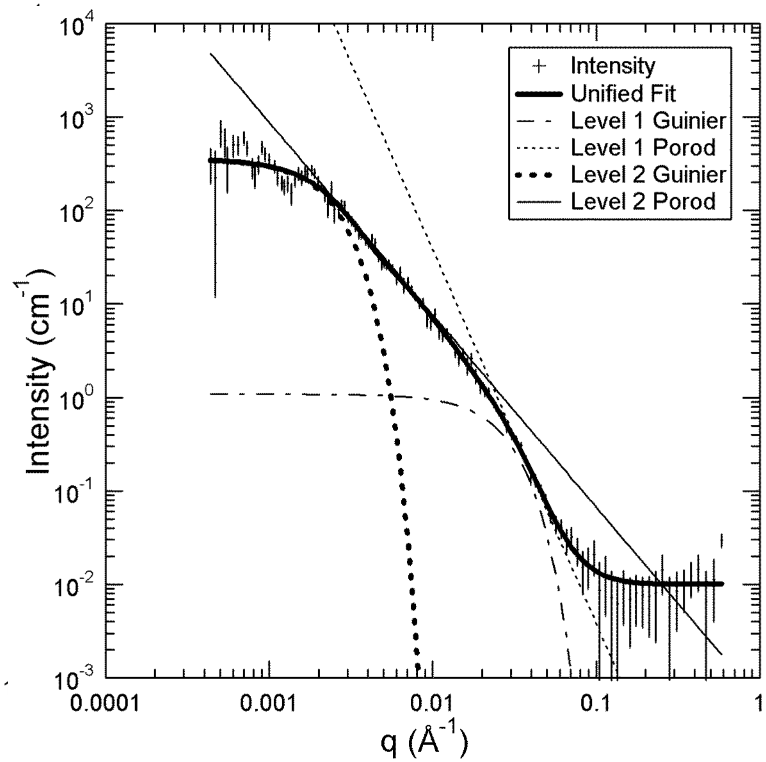
G_2
R_2
Chain Scattering
Persistence Unit
80 Mole % Branches
B_f
-5/3
d_f
G_1
R_1
-1
Intensity (cm)$^{-1}$
10^4
10^3
10^2
10^1
10^0
10^{-1}
0.0001
0.001
0.01
0.1
1
q (Å)$^{-1}$

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

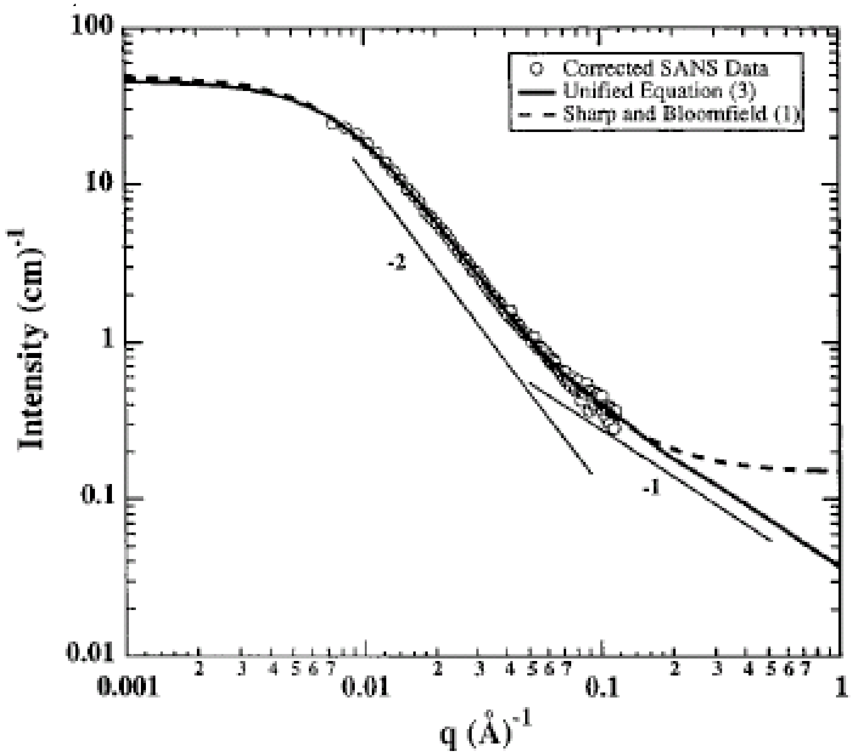


Branching dimensions are obtained by combining local scattering laws

Small Angle Scattering



Silica Aggregates



Deuterated-PHB

Guinier's Law

$$I(q) = G \exp\left(\frac{(-q R_g)^2}{3}\right)$$

Power Law

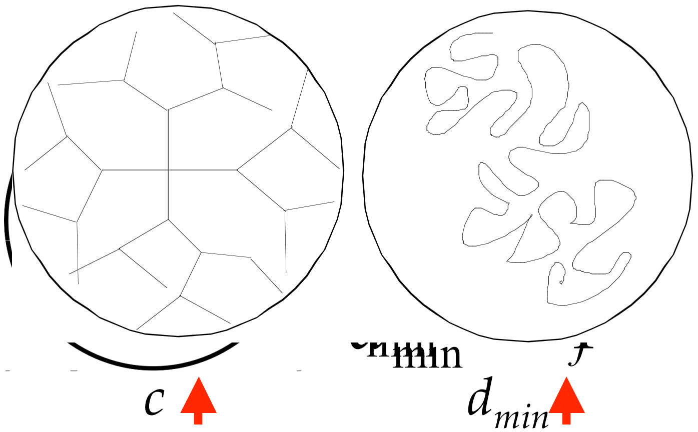
$$I(q) = B_f\, q^{-d_f}$$

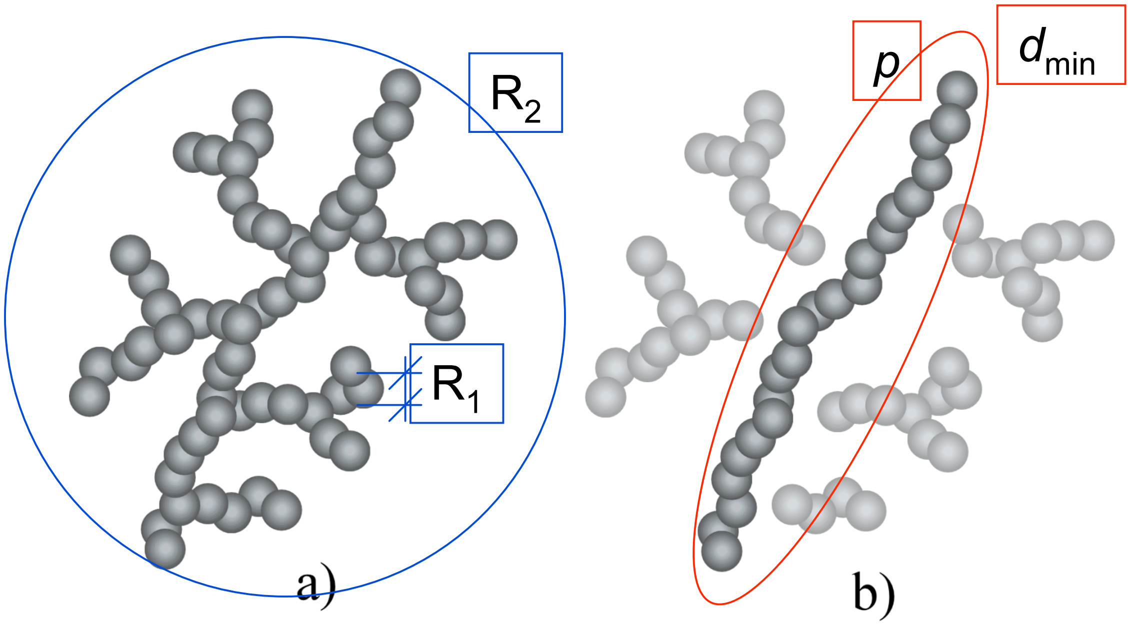
Scattering Vector, *q*

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

Branch Content from Scattering

$$p^{c} \sim z \sim \left(\frac{R_2}{R_1}\right)^{d_f}$$





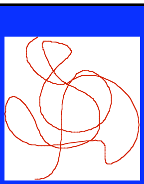
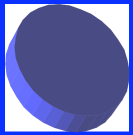
$$z = \frac{G_2}{G_1}$$

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

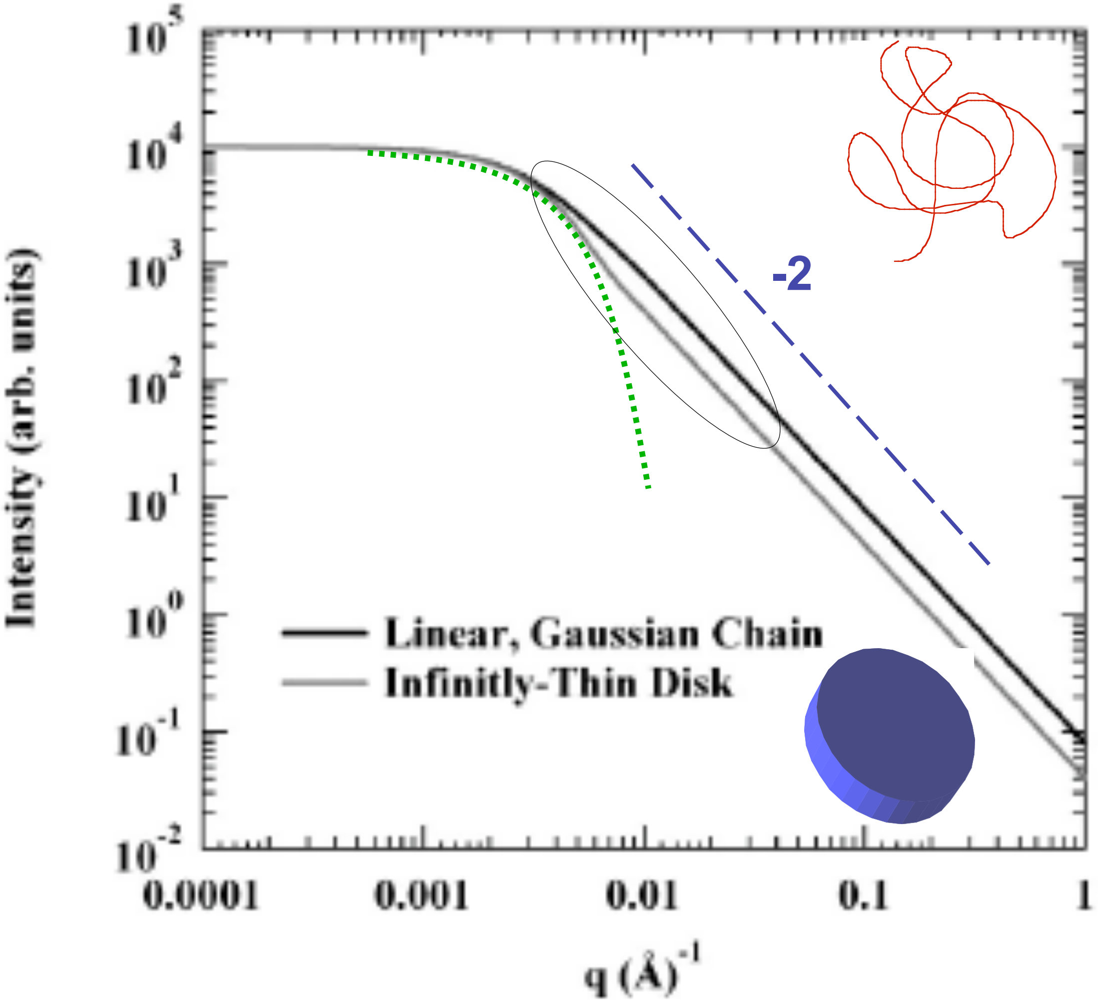
$$\phi_{br} = \frac{z-p}{z} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{\min}-d_f}$$

G Beaucage, Physical Review E (2004)

A S Kulkarni and G Beaucage, Journal of Polymer Science, Part B: Polymer Physics (2006)

			$d_f = c \times d_{\min}$
$d_{\min}$	2	1	2
c	1	2	2

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

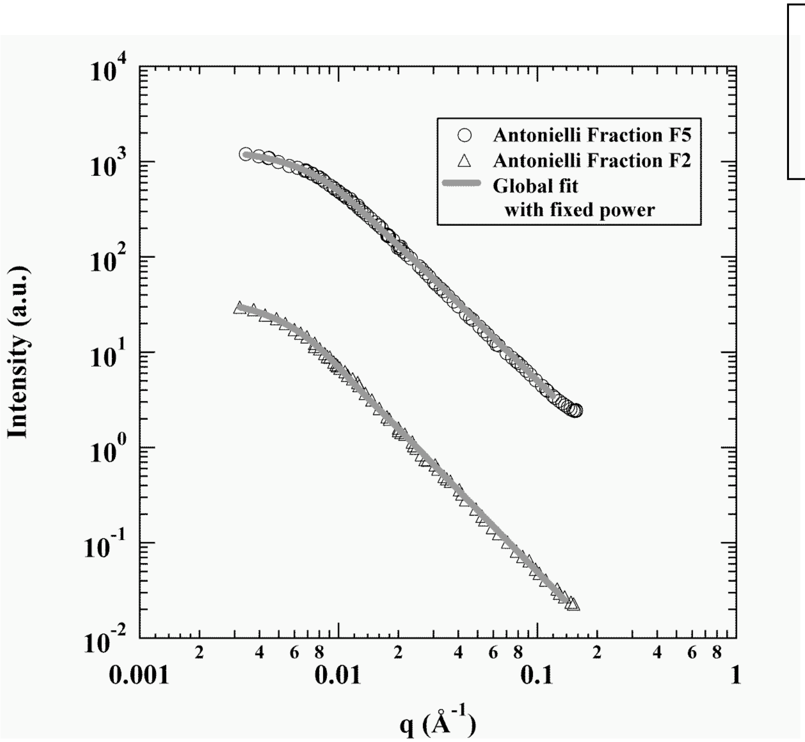


Topological information can be extracted from this feature arising from combining Local Scattering Laws

G Beaucage, Physical Review E, **70**, 031401 (2004)

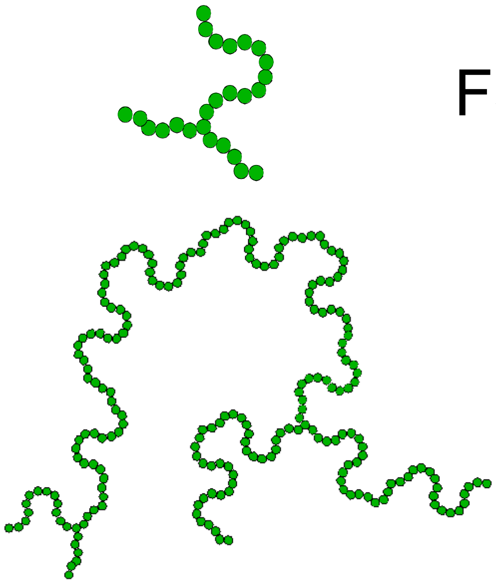
AS Kulkarni, G Beaucage, J Polym Sci, Part B: Polym Phy, **44**, 1395 (2006)

4) Branched Polymers at Thermal Equilibrium: Model Systems for LCB



PDI ~ 1.05

“2D Slice”



	F5	F2
M_w (g/mol)	2×10^6	18×10^6
G (arb. units)	1376 ± 8	38 ± 1
R_g (Å)	197 ± 1	268 ± 10
B_f	0.0448 ± 0.0004	0.00035
d_f	2.05	2.15
$d_{\min}$	1.67	1.64
c	1.23	1.36
z	19 200	173 000
ϕ_{br}	0.84	0.94

For Polymers $d_{\min}$ is the Thermodynamically Relevant Dimension (5/3 = 1.67 or 2)

$d_f = d_{\min}\ c$

~ thermo x branching

Mole fraction of Branches

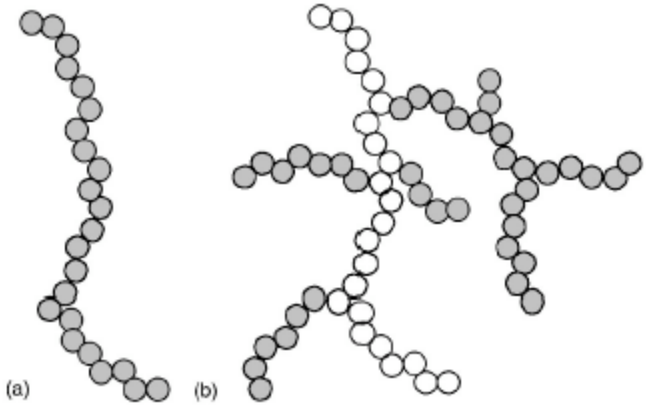
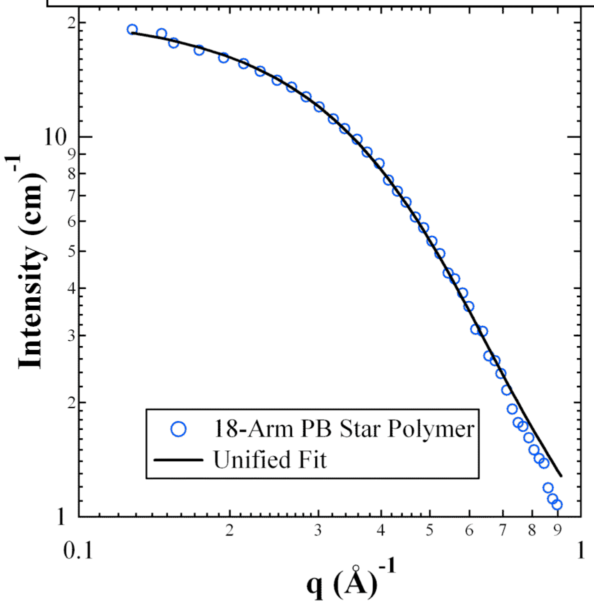
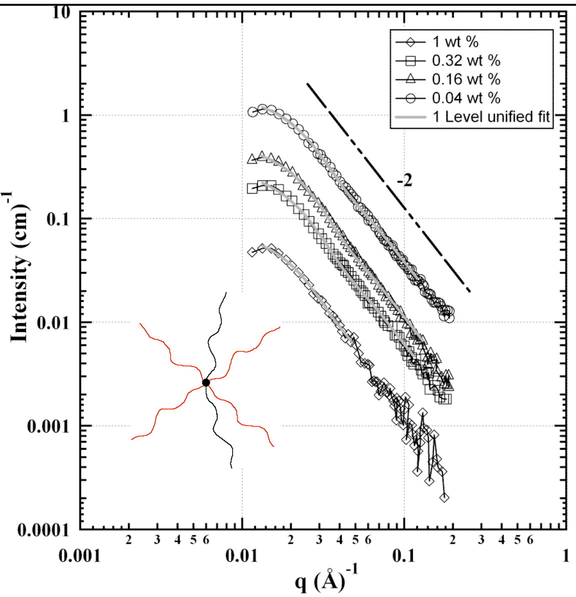


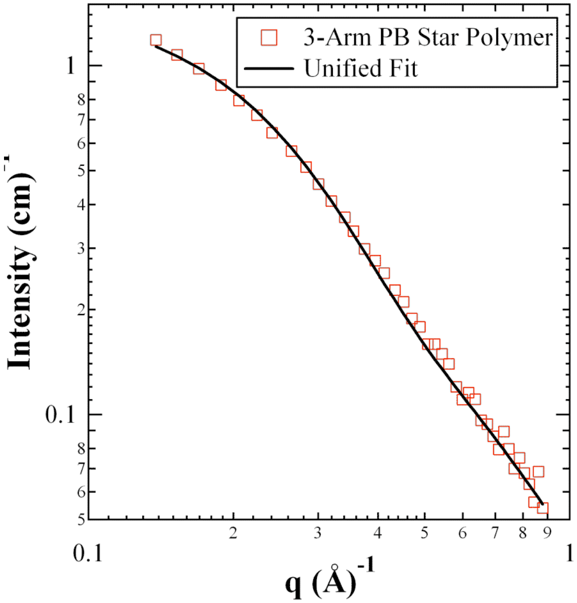
FIG. 1. 2D schematic sketches of aggregates with similar R_g. (a) Linear aggregate and (b) a branched fractal aggregate of identical p but different z and d_f, as described in the text.

$$\phi_{\mathrm{br}} = \frac{z-p}{z} = 1 - z^{1/c-1} = 1 - \left(\frac{R_{g,2}}{R_{g,1}}\right)^{d_{\min}-d_f}$$

Multi-Arm Star Polymers





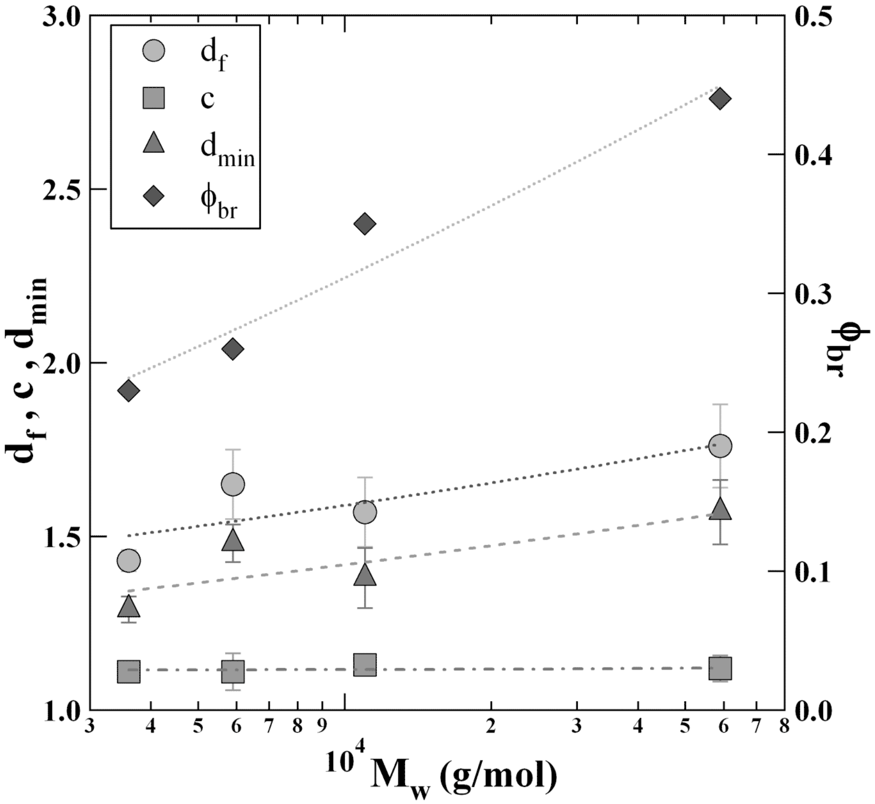


Horton et al., Macromolecules, 22, 681 (1989)
US Jeng, TL Lin, LY et al. *App Phys A*, **74**, S487 (2002).

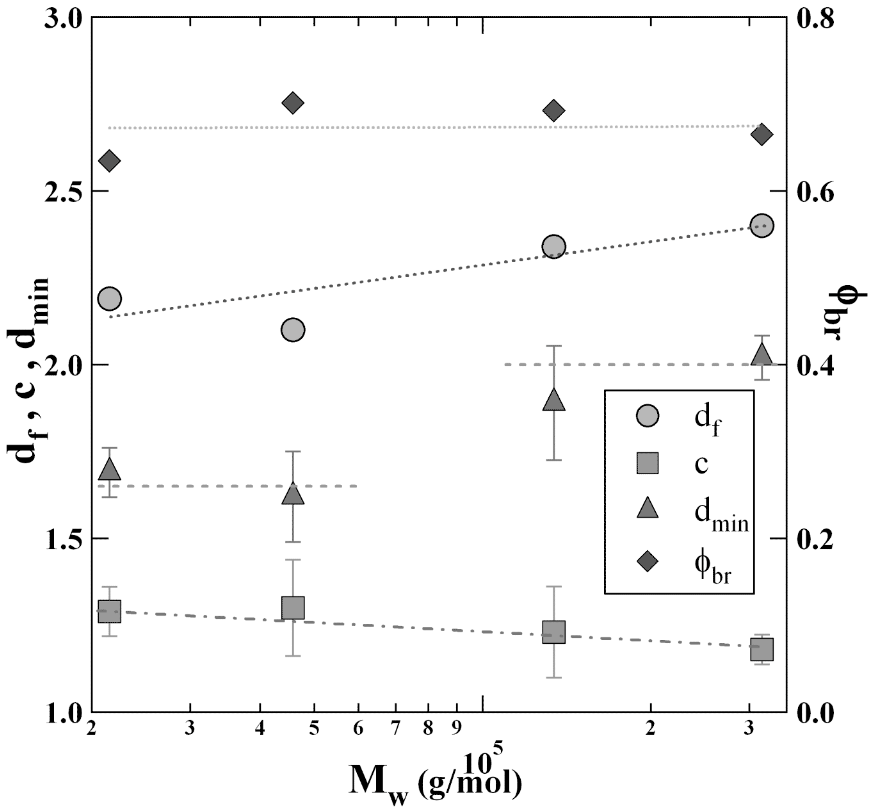
#	Sample	R_g (Å)	d_f	d_{min}	c	ϕ_{br}	Theoretical ϕ_{br}
1	3 Arm Star	6.87	2.00	1.33	1.49	0.39	0.33
2	6 Arm Star	78.27	2.00	1.25	1.59	0.71	0.67
3	18 Arm Star	4.37	2.27	1.61	1.40	0.81	0.88

Hyperbranched Polymers

SANS on Hyperbranched Polymers: Beaucage model correctly describes transition from good-solvent to Θ - solvent collapsed state for the minimum path dimension.



a)



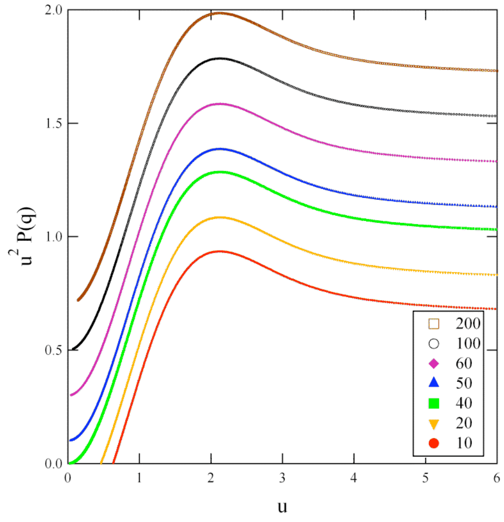
b)

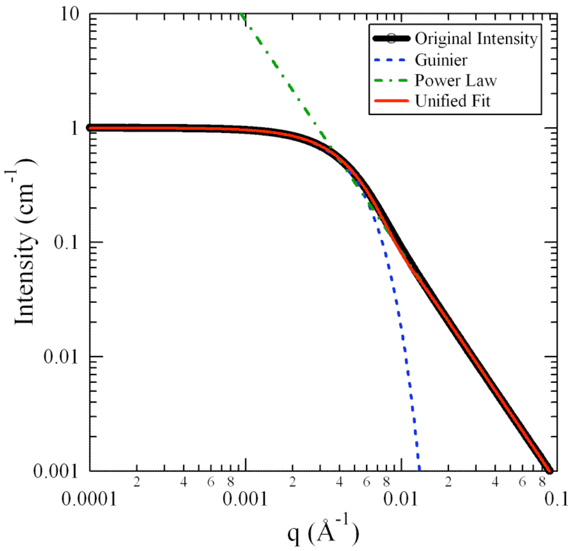
E. De Luca, R. W. Richards, I. Grillo, and S. M. King, J. Polym. Sci.: Part B: Polym. Phys. **41**, 1352 (2003).
Geladé, E. T. F.; Goderis, B.; et al. Macromolecules, **34**, (2001).
AS Kulkarni, G Beaucage, Macromolecular Rapid Communications, accepted, (2007).

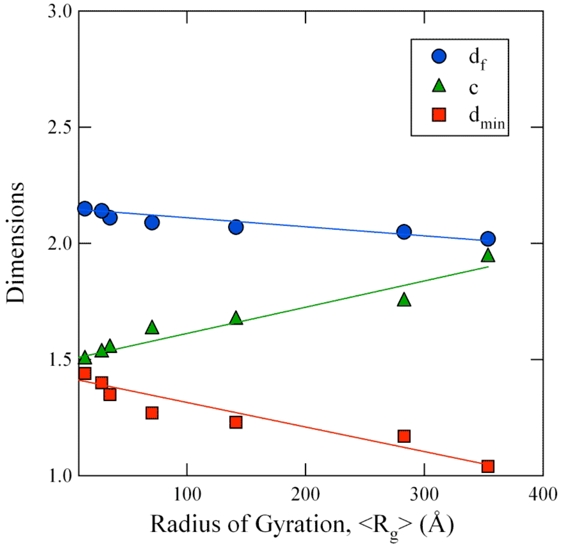
Cyclic Polymers

Casassa Equation

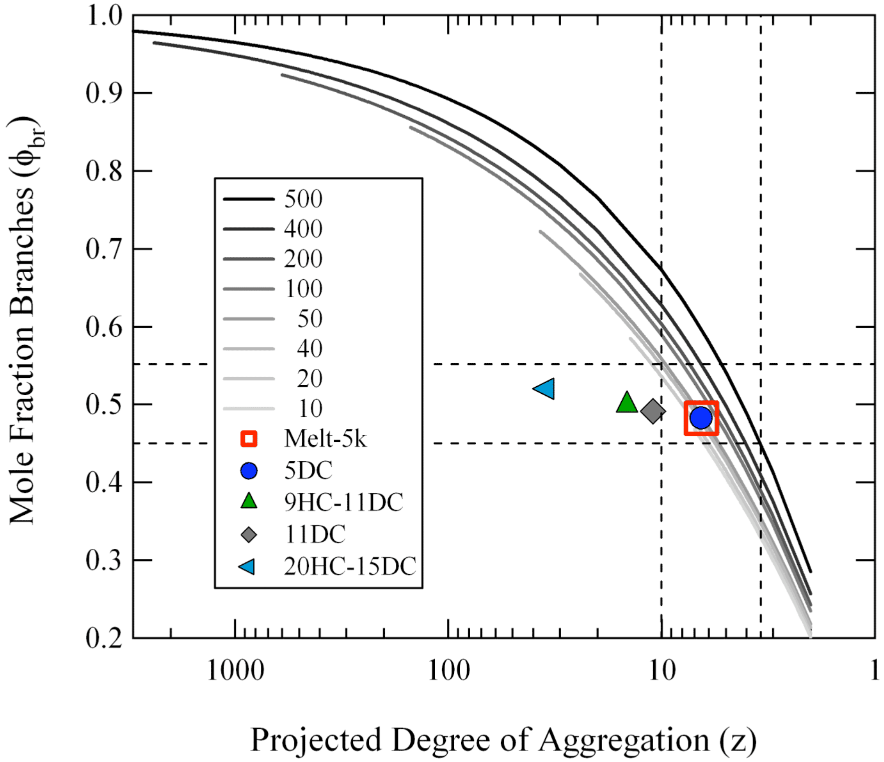
$$P(q) = \frac{2}{q\,R_g}\exp\left(\frac{-q^2R_g^2}{4}\right)\int_0^{qR_g/2}\exp\left(x^2\right)dx$$

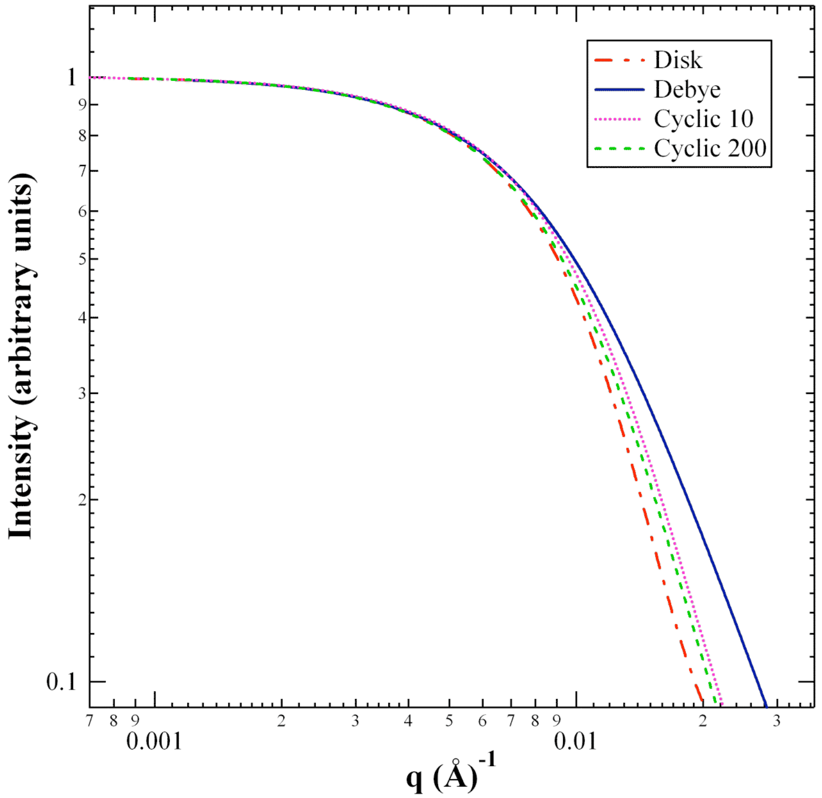






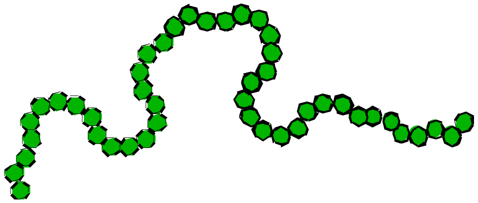
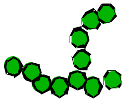
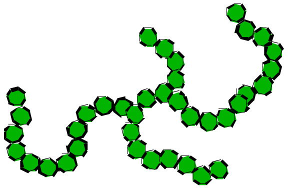
E F Casassa, Journal of Polymer Science: Part A, 3, 605, (1965)





V Arrighi, S Gagliardi et al., Macromolecules, 37, (2004)
S Gagliardi, V Arrighi et al., Applied Physics A, (2002)
S Gagliardi, V Arrighi et al., Journal of Chemical, 122 (2005)

This Approach Can Quantify LCB in Polyolefins.
(Talk by Kulkarni/Beaucage Tomorrow T34 0668 3:30)

	M_n (g/mol)	Index LCBI	Mole Fraction of Branches ϕ_{br}	NMR $n_{br}/10^4$ C	Model Based on Mole Fraction of Branches
PE 0	**46,500**	**0.04**	**0**	**0**	
PE 2	**11,500**	**0.91**	**0.39±0.005**	**0.36**	
PE 3	**37,900**	**2.27**	**0.63±0.004**	**0.91**	

4) Model Polydisperse Simulations

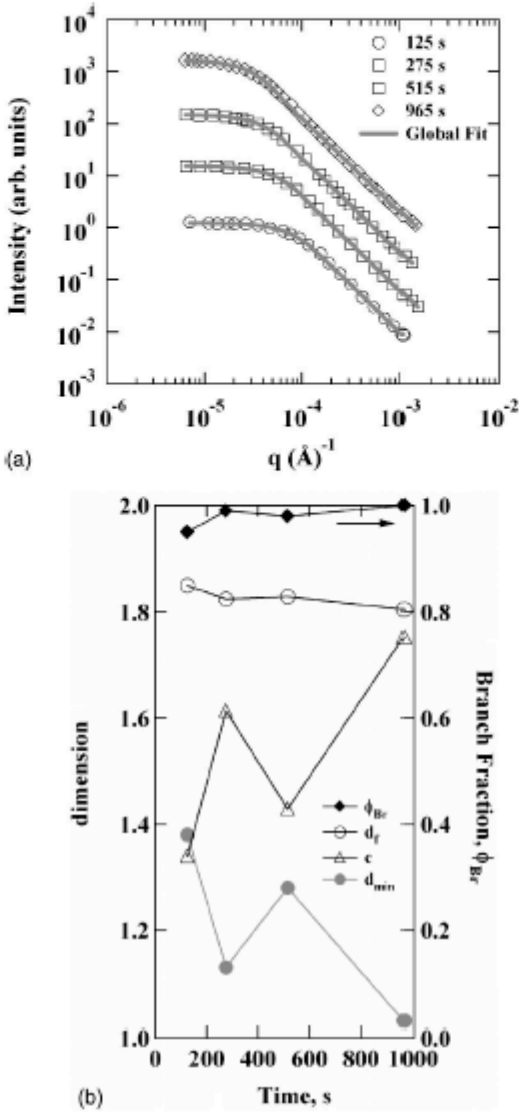


FIG. 6. (a) Lattuada time series simulation results (scattering data agree with experimental results in Ref. [42]). The simulations are for diffusion-limited aggregation with polydisperse aggregates. (b) Branch fraction, c, d_f, and d_{min} versus time from unified fits shown in (a).

$M_w/M_n \sim 4$
Large aggregates
Growth kinetics show
d_{min} => 1
d_f => 1.8 for RLCA
Predicted previously
by Meakin

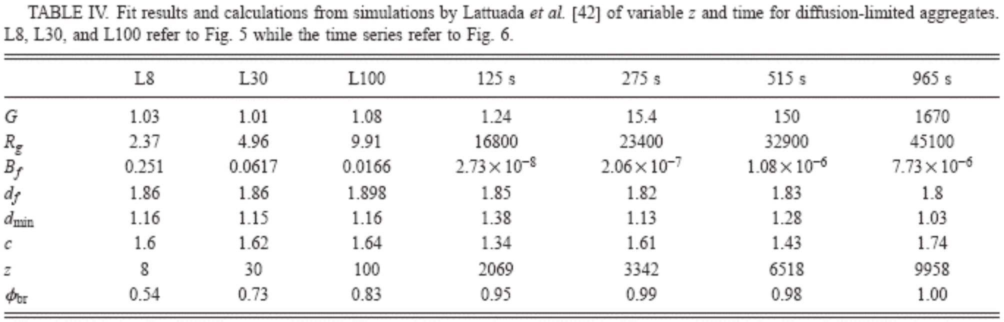
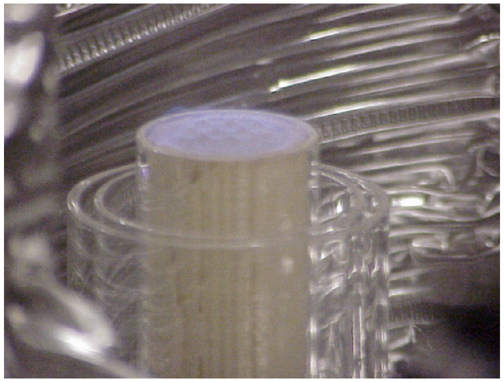


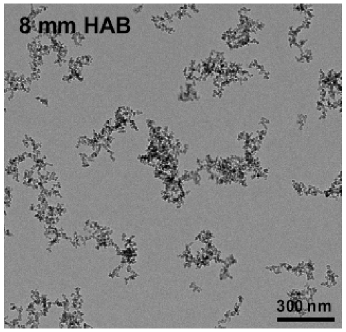
TABLE IV. Fit results and calculations from simulations by Lattuada *et al.* [42] of variable z and time for diffusion-limited aggregates. L8, L30, and L100 refer to Fig. 5 while the time series refer to Fig. 6.

	L8	L30	L100	125 s	275 s	515 s	965 s
G	1.03	1.01	1.08	1.24	15.4	150	1670
R_g	2.37	4.96	9.91	16800	23400	32900	45100
B_f	0.251	0.0617	0.0166	2.73×10^{-8}	2.06×10^{-7}	1.08×10^{-6}	7.73×10^{-6}
d_f	1.86	1.86	1.898	1.85	1.82	1.83	1.8
d_{min}	1.16	1.15	1.16	1.38	1.13	1.28	1.03
c	1.6	1.62	1.64	1.34	1.61	1.43	1.74
z	8	30	100	2069	3342	6518	9958
ϕ_{br}	0.54	0.73	0.83	0.95	0.99	0.98	1.00

[42] M. Lattuada, H. Wu, and M. Morbidelli, J. Colloid Interface Sci. **268**, 106 (2003).

Branched Aggregates





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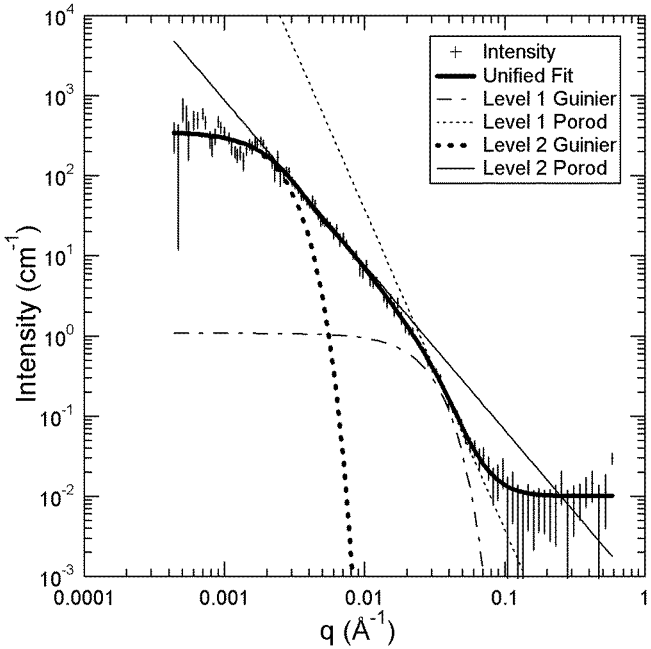
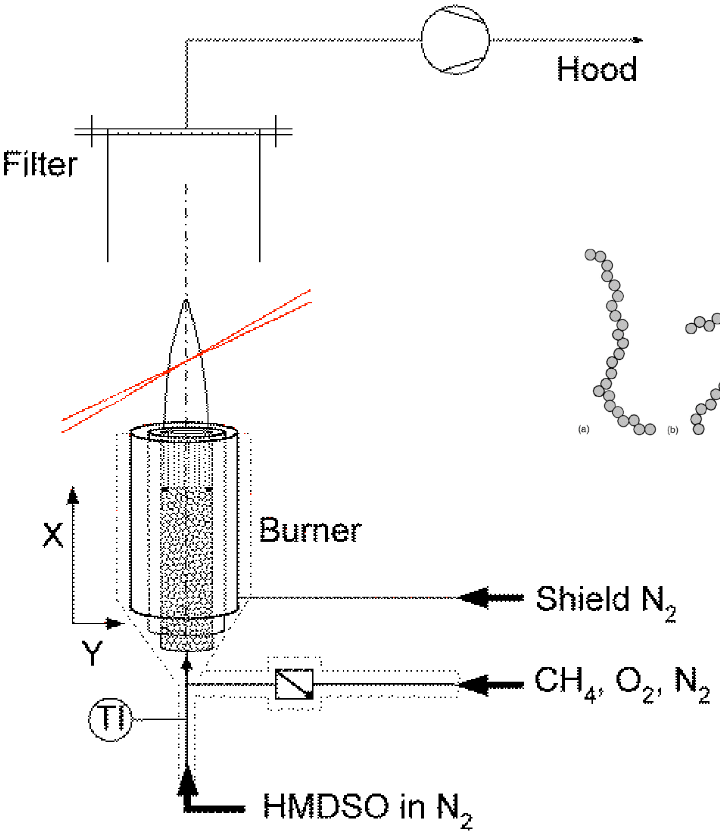
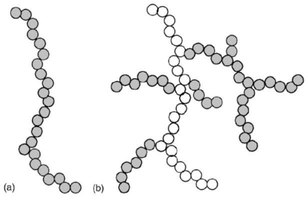
J. Appl. Phys 97 054309
Feb 2005

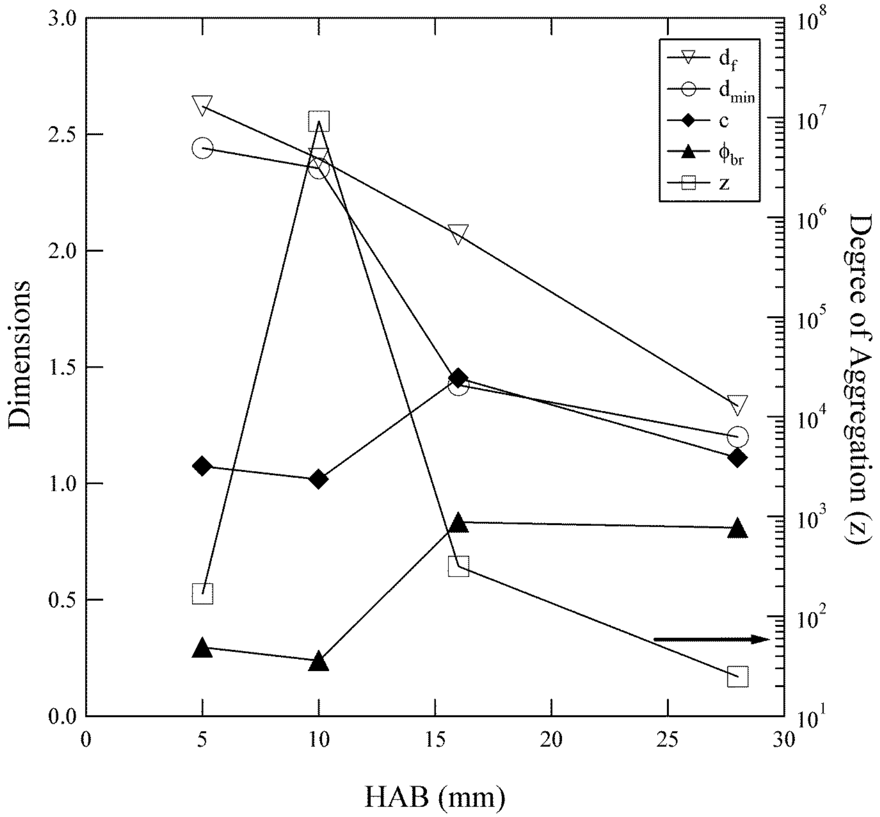


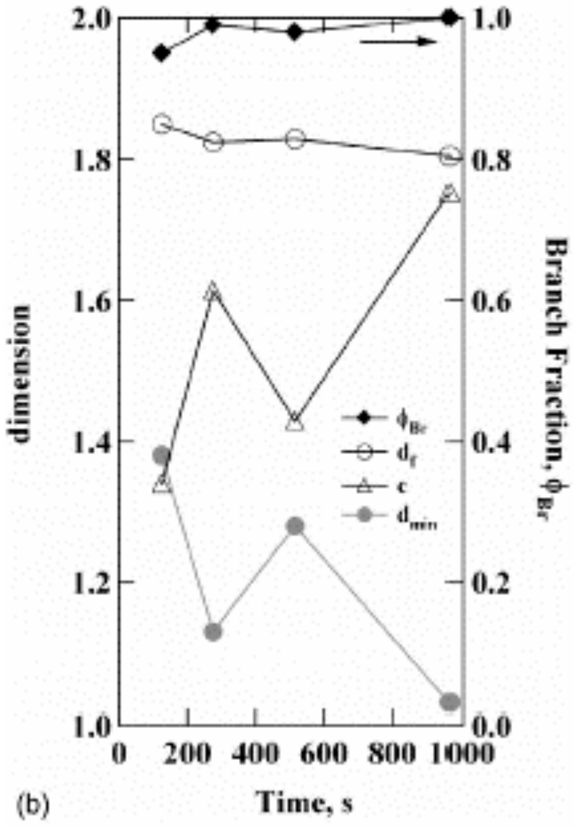


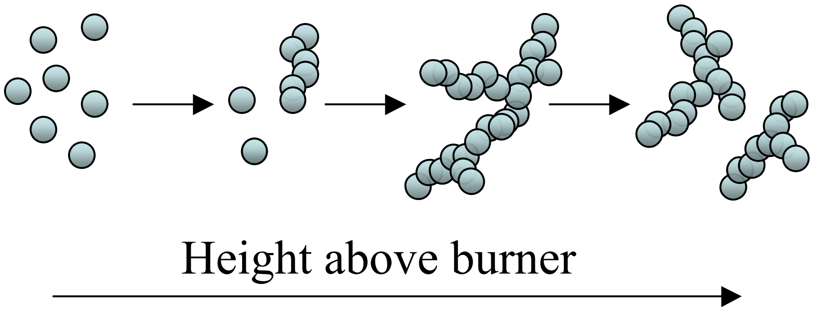


5mm LAT 16mm HAB
Typical Branched Aggregate
$d_p = 5.7$ nm
$z = 350$
$c = 1.5$, $d_{min} = 1.4$, $d_f = 2.1$
$\phi_{br} = 0.8$

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





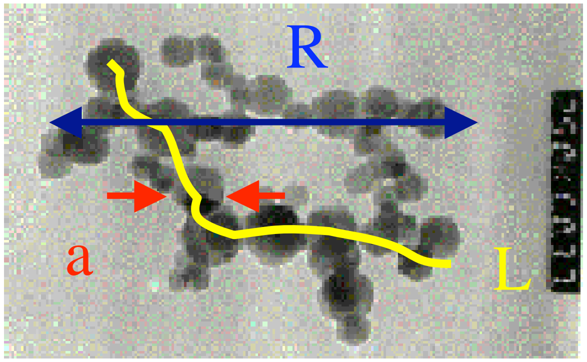


- Behavior is Similar to Simulation
  d_f drops due to branching

- Aggregate Collapse

- Entrainment High in the Flame

Mechanics Depend on Structure Structure on Growth Chemistry



Mean Primary Particle Size, "a"

Mean Aggregate Size, "R"

Specific Surface Area related to 1/a

"R" is related to "a", "N", and Structure

"Structure" is Related to Growth Mechanism
"a" is Related to Early Stage
"N" and "R" to Later Stage

$N = \alpha (R/a)^{d_f}$ How Dense?

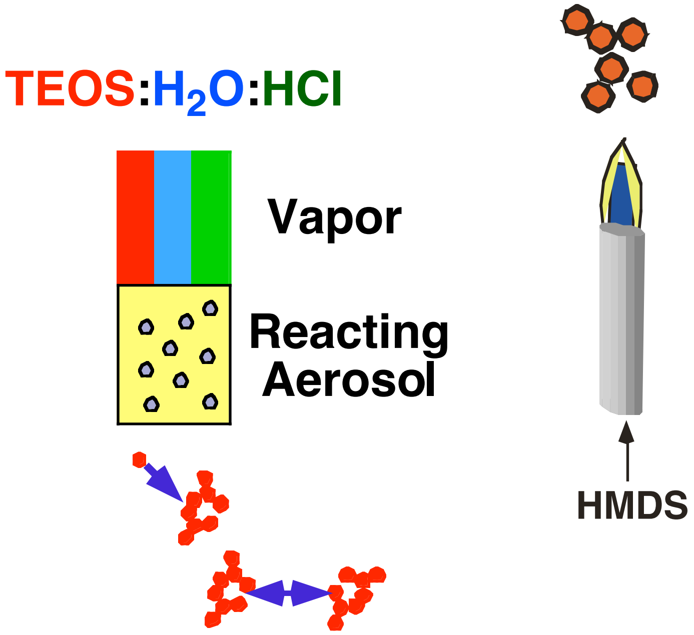
$1 \le d_f \le 3$

$(L/a) = (R/a)^{d_{min}}$ Minimum Path Dim.

$1 \le d_{min} \le d_f$

$C = d_f/d_{min}$ How Branched?

Linear $C = 1$; Reg. $C = d_f$



TEOS:H_2O:HCl

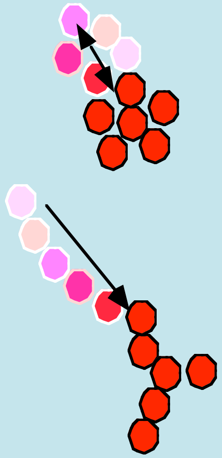
Vapor

Reacting Aerosol

HMDS

Particle/Cluster, Denser

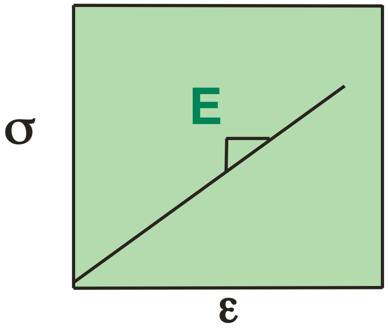
Cluster/Cluster, Looser



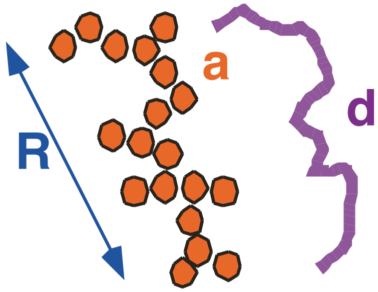
If Particles Don't Stick Well Packing is Dense "Reaction Limited"

If Particles Stick Immediately Packing is Loose "Diffusion Limited"

Nano-Aggregates Can Act as Springs

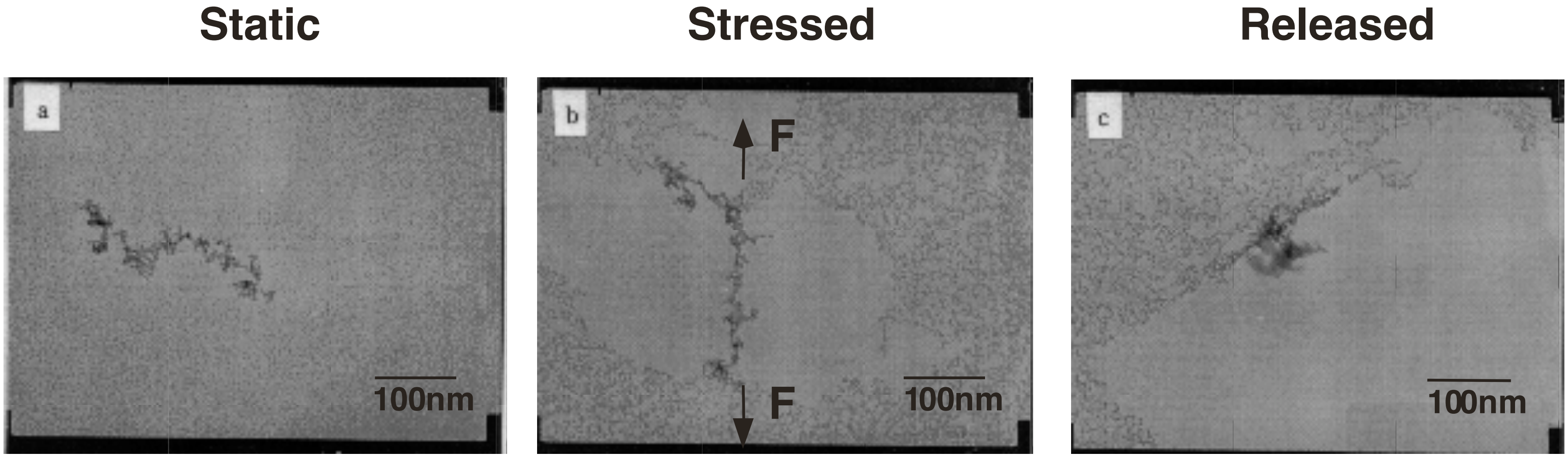


$$E_{Aggregate} = E_{Oxide}(a/R)^{3+d_{min}}$$



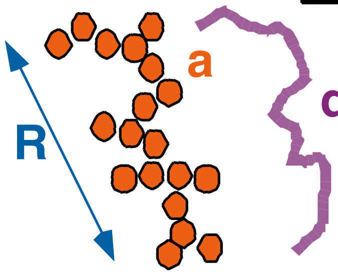
d_{min} is Dimension of Stressed Path

From: *T. A. Witten, M. Rubinstein, R. H. Colby*
J. Phys. II France 3, 367 (1993).


Static
Stressed
Released

From: *S. K. Friedlander, H. D. Jang, K. H. Ryu*
Appl. Phys. Lett. 72 173 (1998).

Summary of Witten/Rubinstein/Colby Theory for Mechanics of Springy Aggregates in Elastomers



d_{min} is Dimension of Stressed Path

$$E_{Aggregate} = E_{Oxide}(a/R)^{3+d_{min}}$$

Aggregates are only Effective below a Critical Size, $R_{critical}$

$$R_{critical} = a(E_{Oxide}/E_{Rubber})^{1/(3+d_{min})}$$

A Critical Concentration is Predicted Beyond which There is No Higher Reinforcing Effect, $\phi_{critical}$

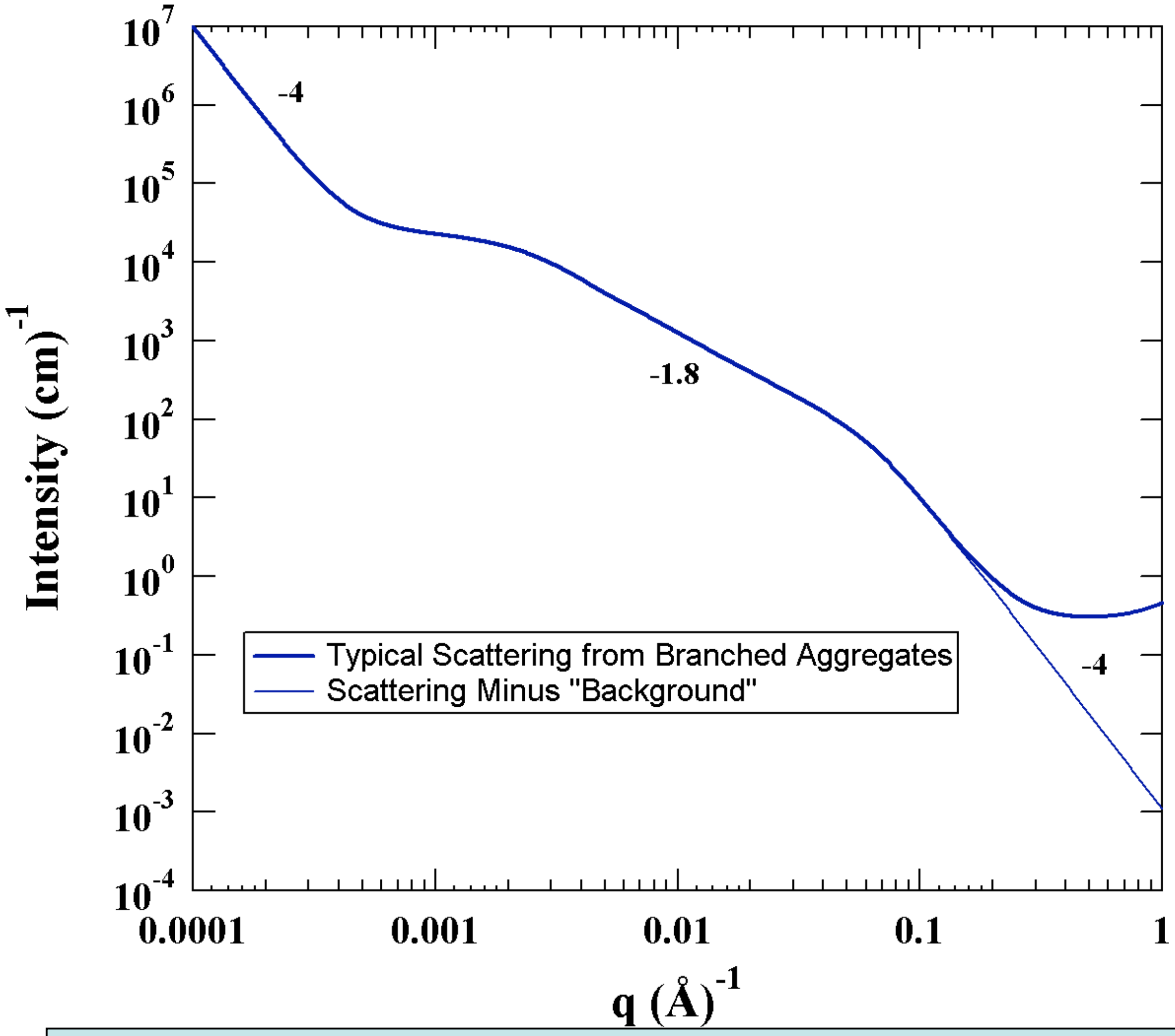
$$\phi_{critical} = (R/a)^{d_f-3}$$

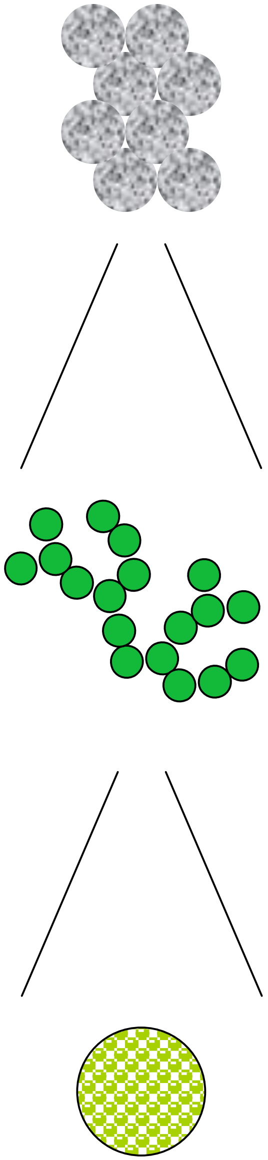
The Modulus for a Critical Concentration Composite, $E_{composite}$ is given by:

$$E_{composite} = E_{Oxide}\ \phi_{critical}^{(3+d_{min})/(3-d_f)}$$

Test these Propositions using Tuned Nano-Composites

Complex Scattering Pattern (Unified Calculation)



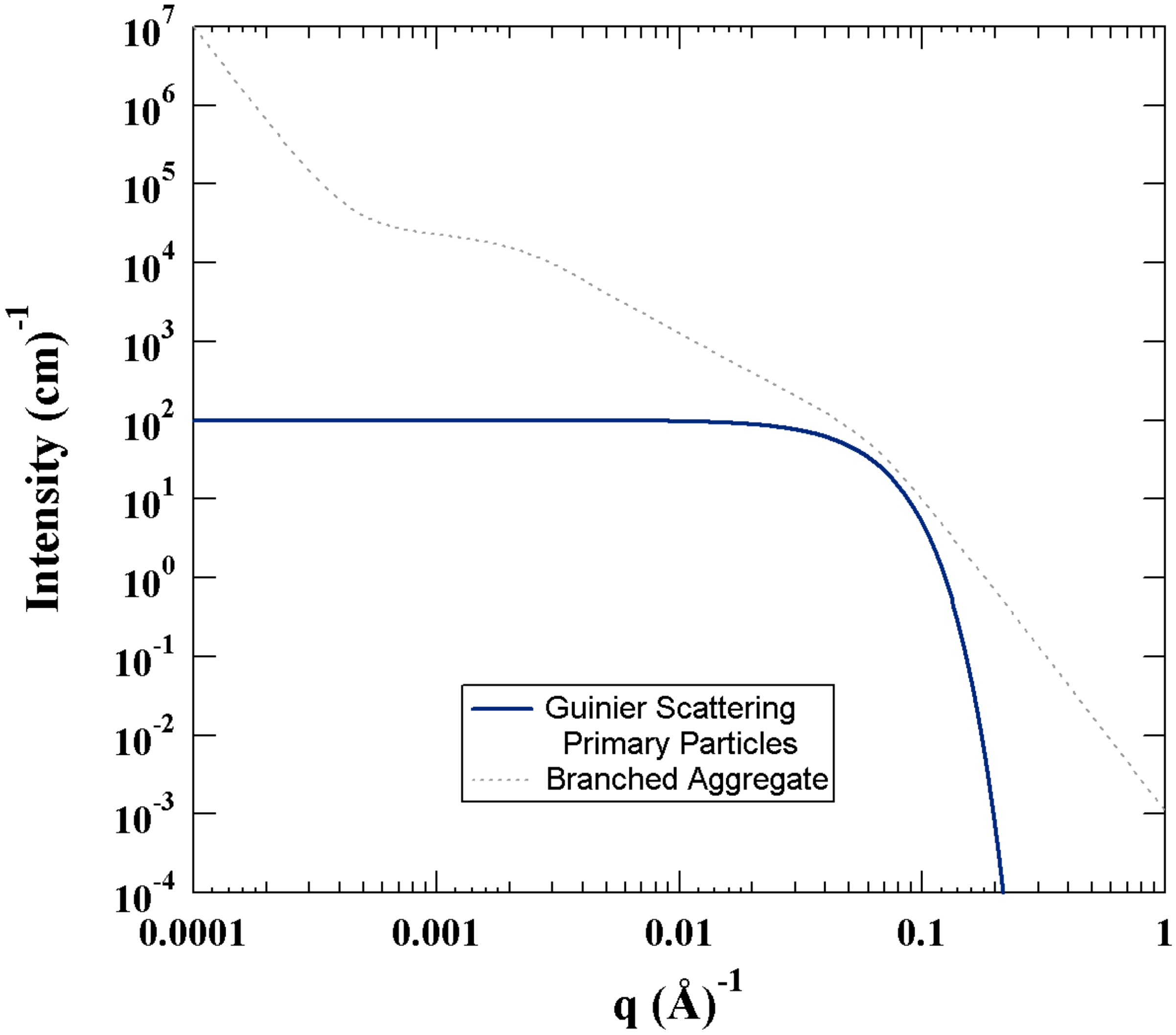


$$q = \frac{2\pi}{d} \qquad I(q) = N(d)\,n_e^2(d)$$

N = Number Density at Size "d"

n_e = Number of Electrons in "d" Particles

Guinier's Law



Particle with No Interface

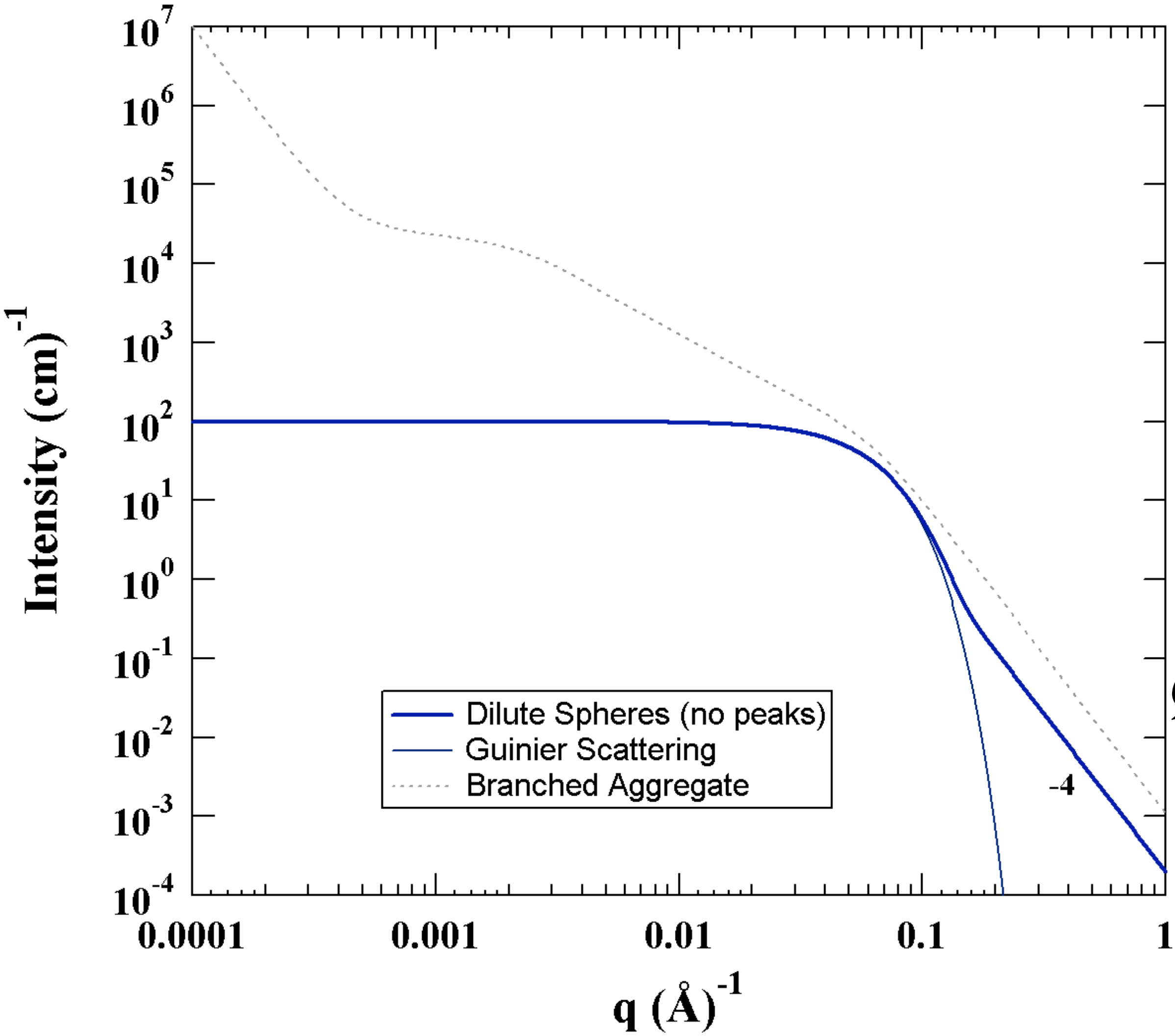
$$I(q) = N(d)n_e^2(d)$$

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

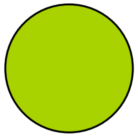
$$G = N\rho_e^2\left\langle V^2\right\rangle \sim \left\langle \mathrm{R}^6\right\rangle$$

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

Guinier and Porod Scattering



Spherical Particle
With Interface (Porod)



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

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

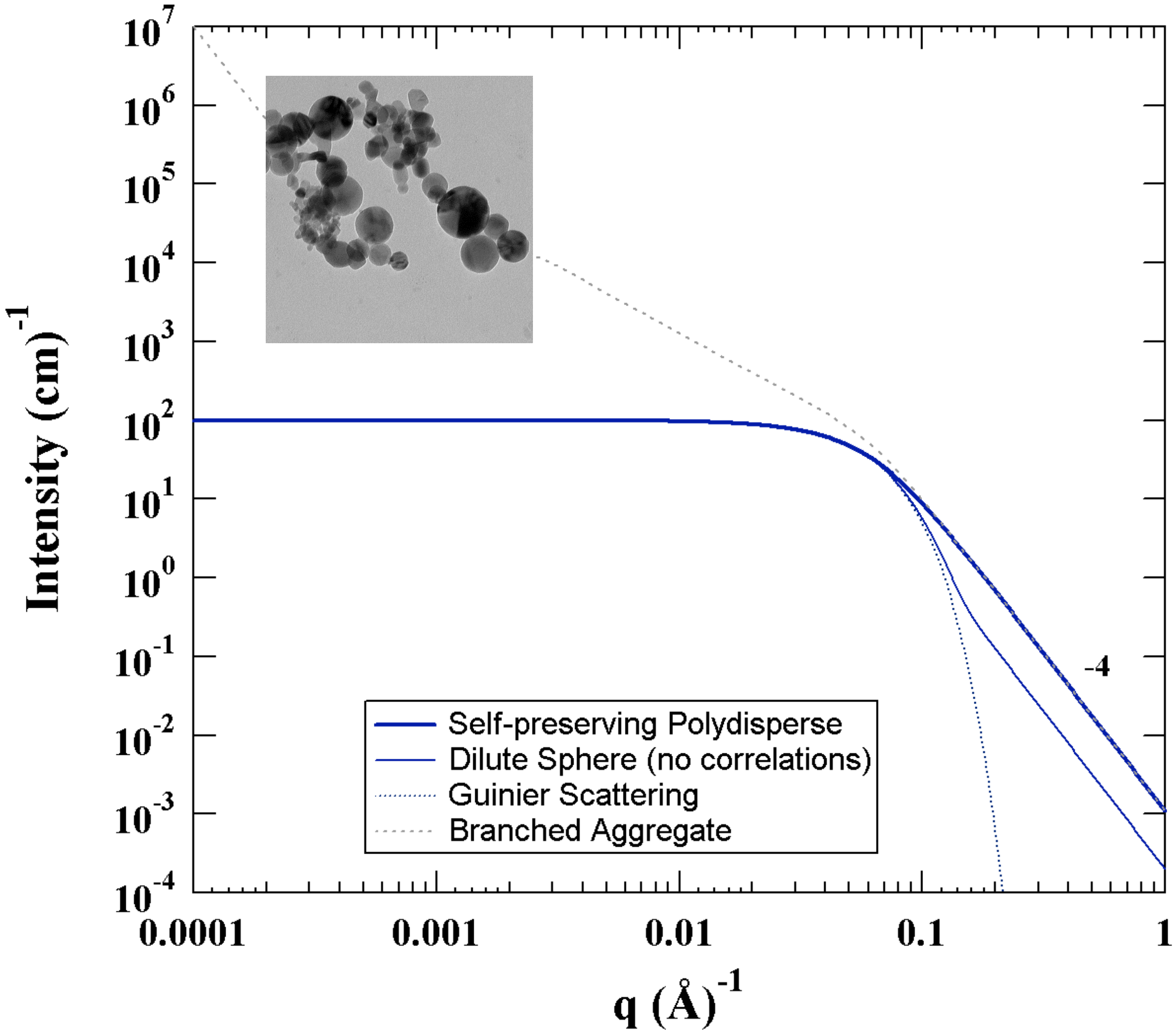
$$\langle S \rangle \sim \langle R^2 \rangle$$

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

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

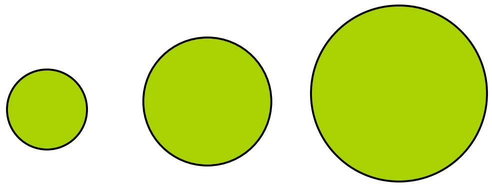
Structure of Flame Made Silica Nanoparticles
By Ultra-Small-Angle X-ray Scattering
Kammler/Beaucage Langmuir 2004 20 1915-1921

Polydispersity Index, PDI



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

Polydisperse Particles

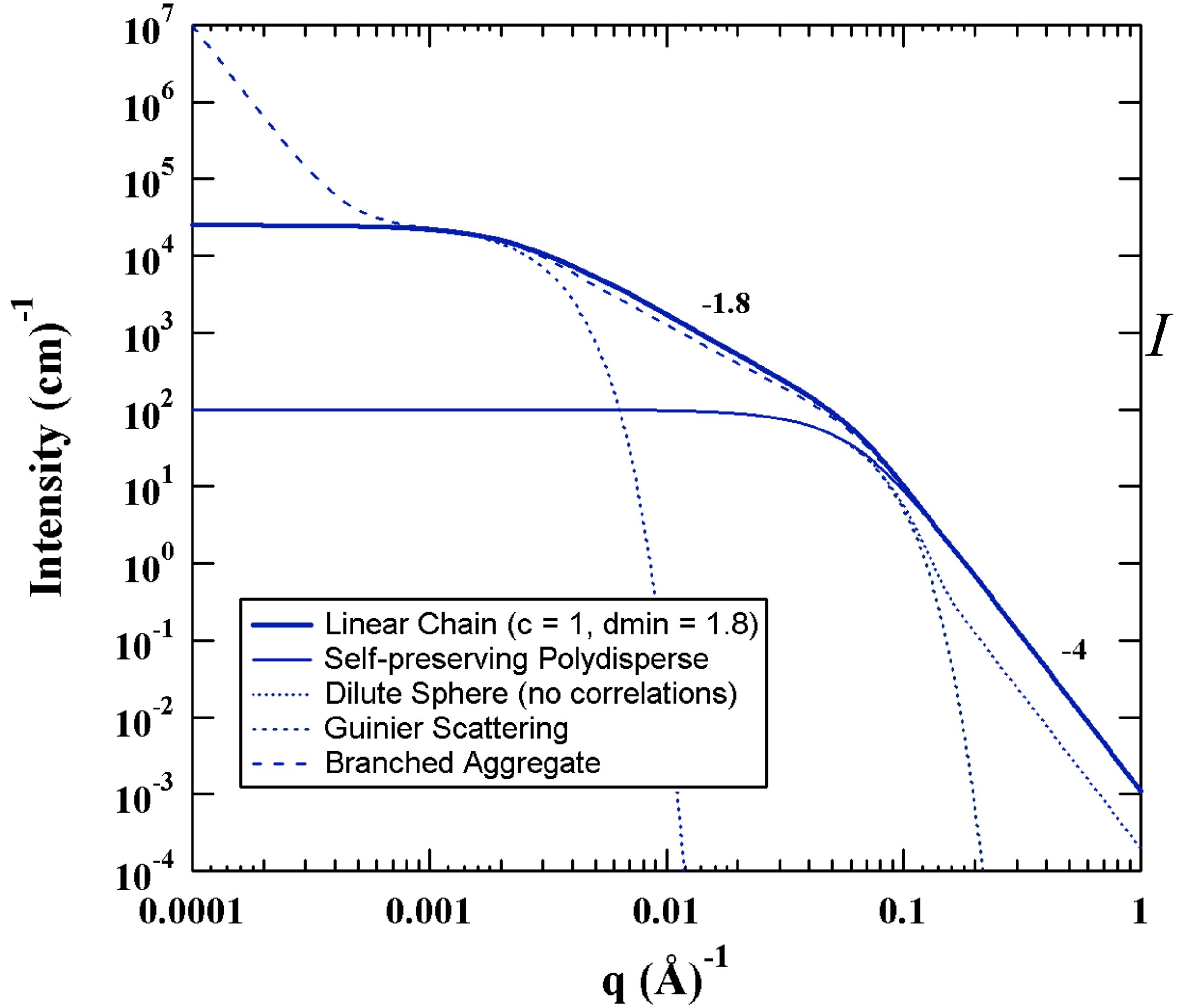


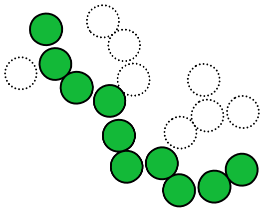
$$PDI = \frac{B_P R_g^4}{1.62G}$$

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

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

Linear Aggregates





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

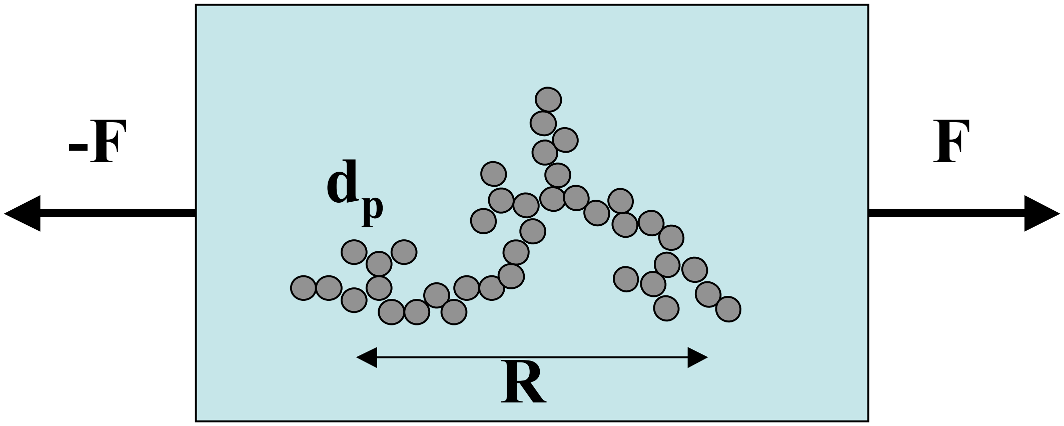
$$z = \frac{G_2}{G_1} = \left(\frac{R_2}{R_1}\right)^{d_f}$$

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

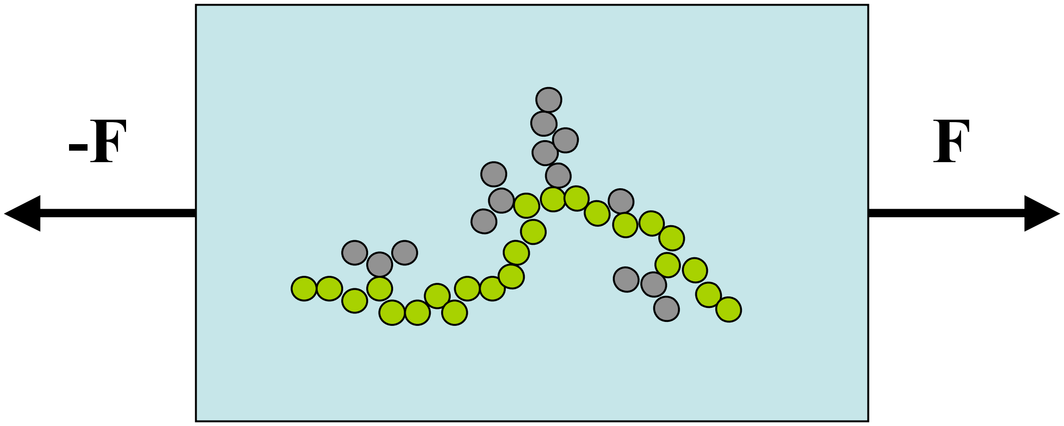
$$B_f = \frac{G_2 d_f}{R_{g,2}^{d_f}} \Gamma\left(d_f/2\right)$$

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

1) Fractal dimensions (d_f, d_{min}, c) and degree of aggregation (z)



$$z \sim \left(\frac{R}{d_p}\right)^{d_f}$$



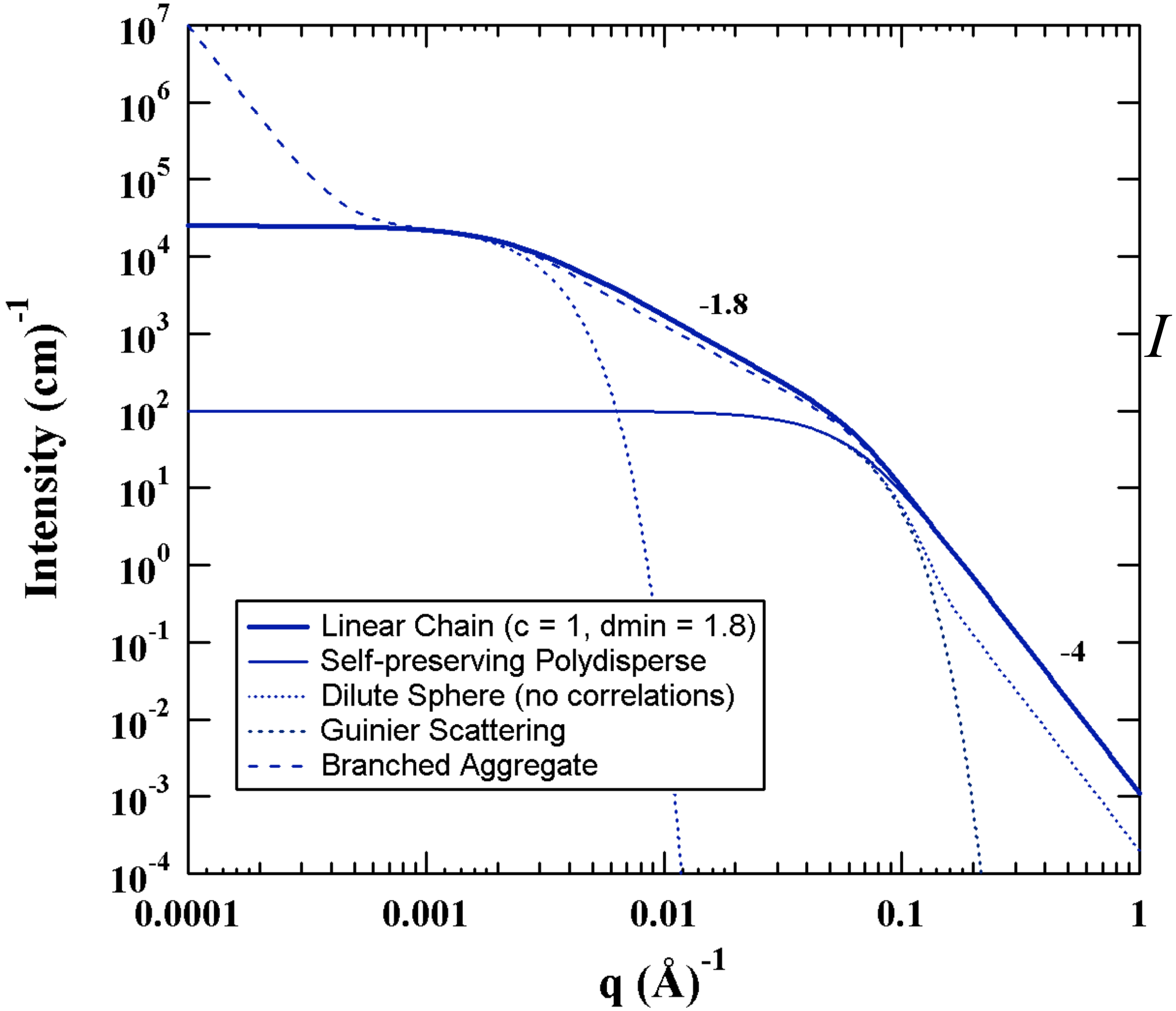
$$p = z_{\min} \sim \left(\frac{R}{d_p}\right)^{d_{\min}}$$

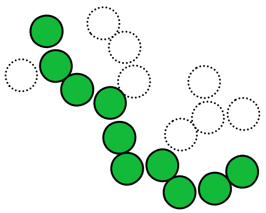
$$z \sim p^{c} = p^{d_f/d_{\min}}$$

d_{min} should effect perturbations & dynamics.

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

Linear Aggregates





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

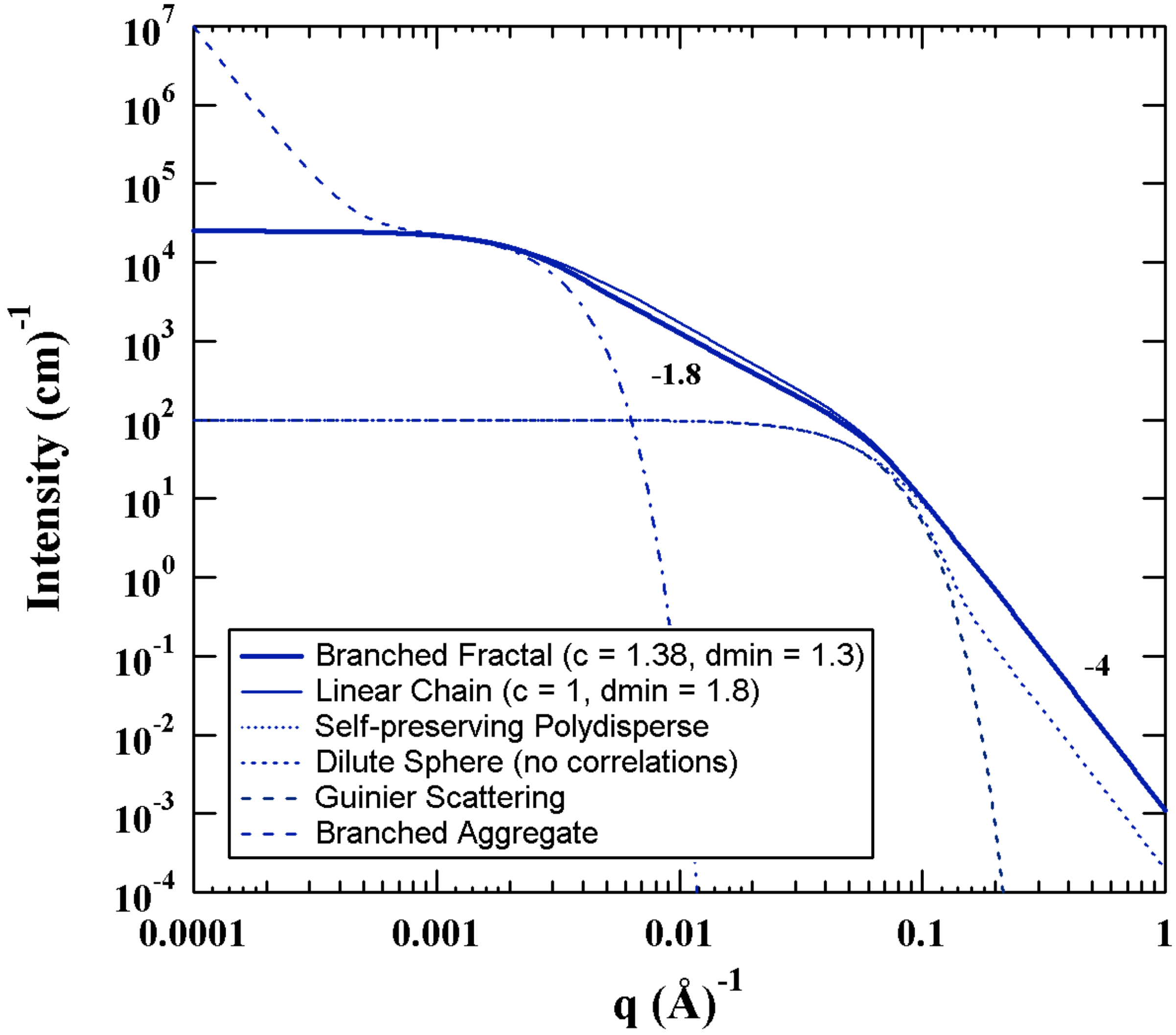
$$z = \frac{G_2}{G_1} = \left(\frac{R_2}{R_1}\right)^{d_f}$$

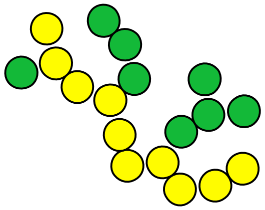
$$I(q) = B_f q^{-d_f}$$

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

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

Branched Aggregates





$$p = \left(\frac{R_2}{R_1}\right)^{d_{\min}} = z^{1/c}$$

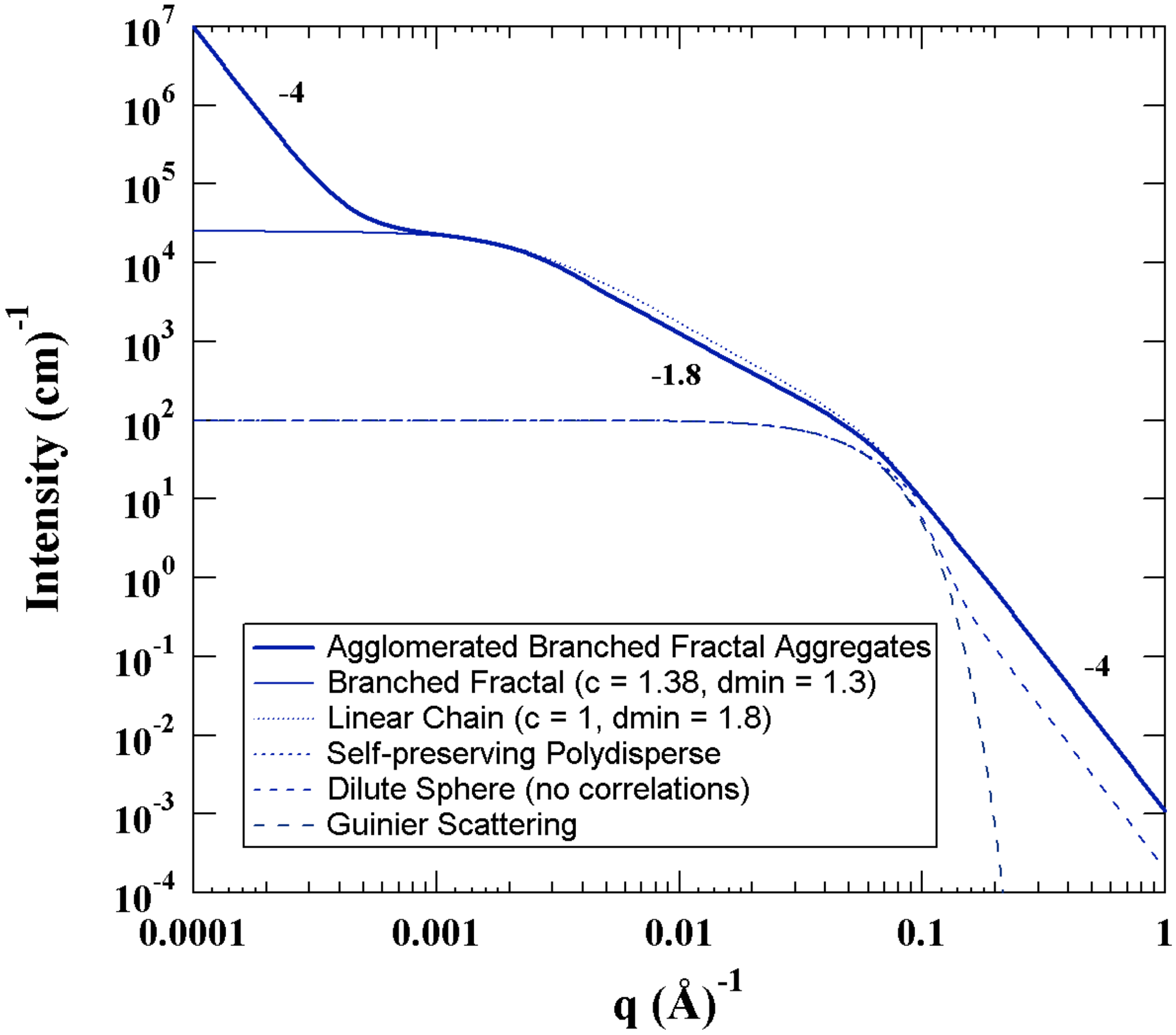
$$c = \frac{d_f}{d_{\min}}$$

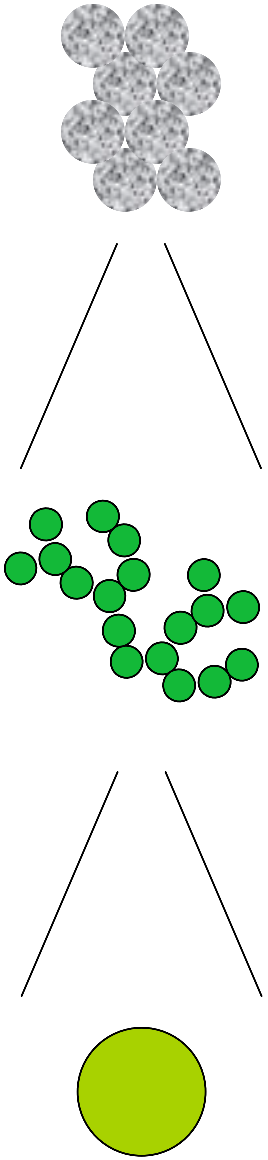
$$\phi_{Br} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{\min} - d_f}$$

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

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

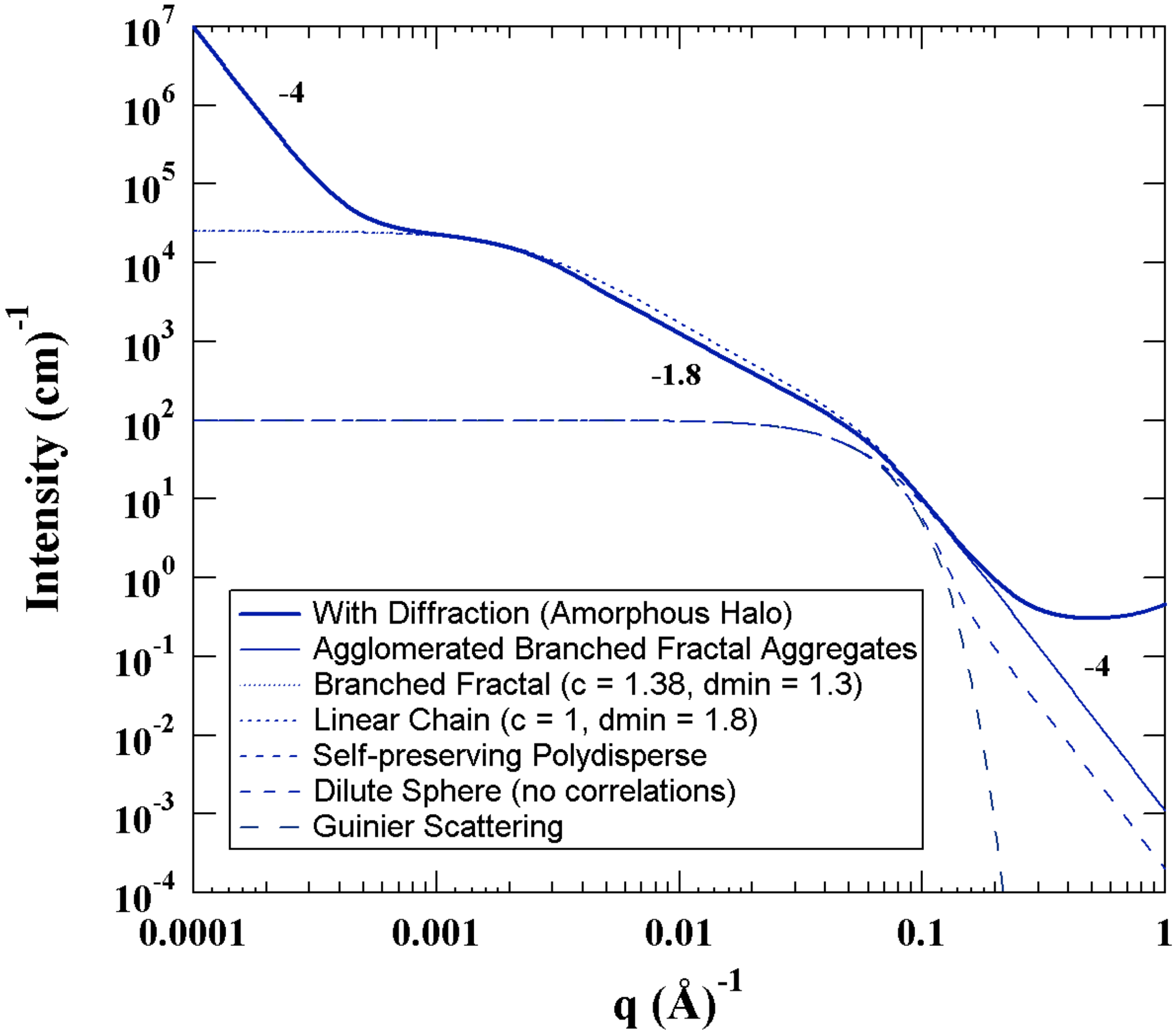
Large Scale (low-q) Agglomerates

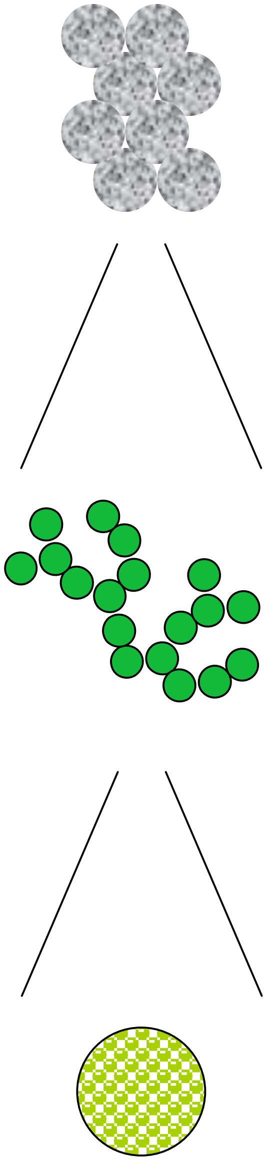




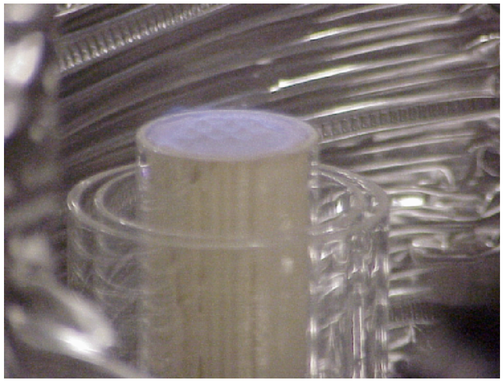
$$I(q) = B_P q^{-4}$$

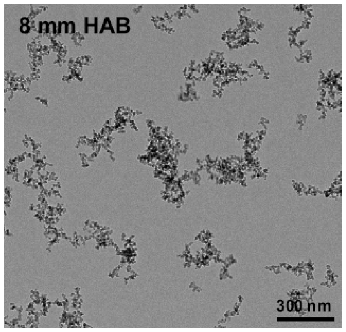
Small-scale Crystallographic Structure





Branched Aggregates





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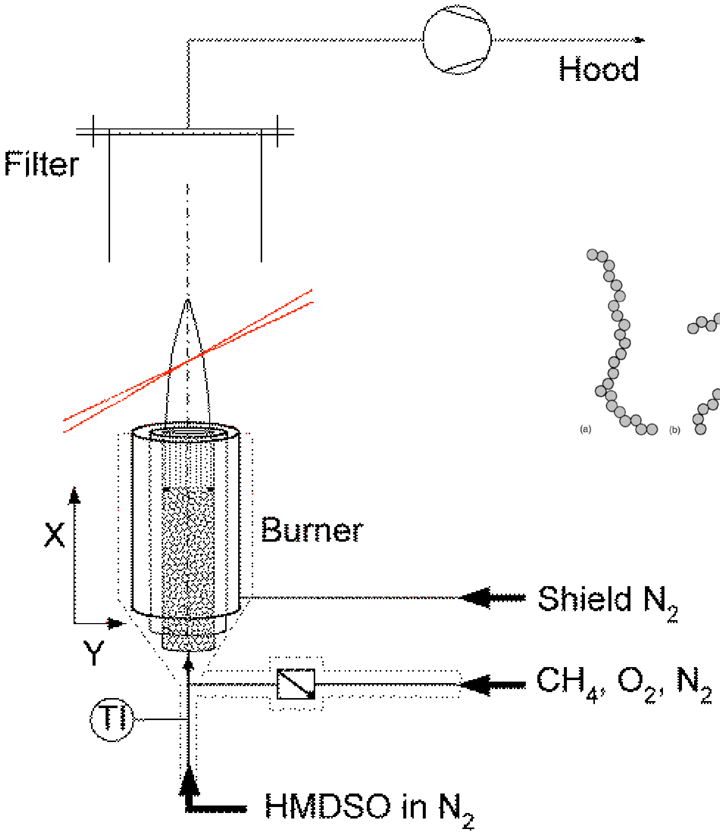
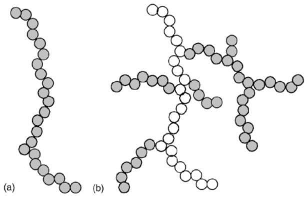
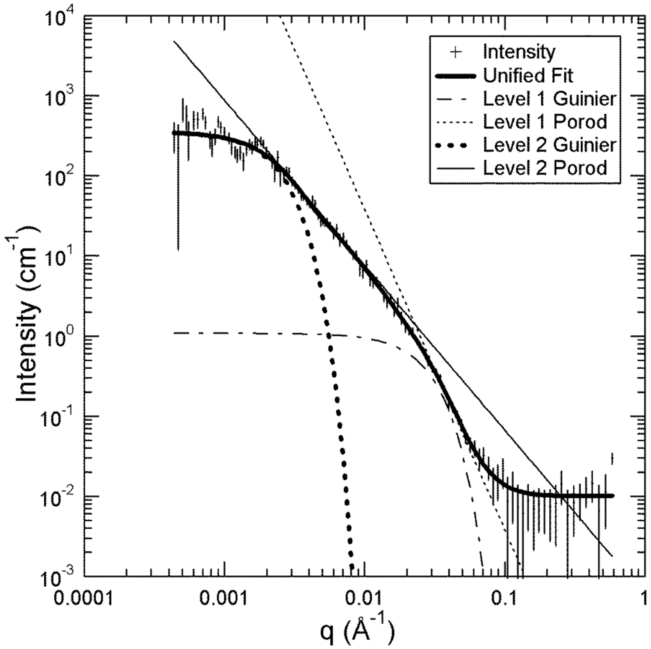
Silica Premixed Flames
J. Appl. Phys 97 054309
Feb 2005







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

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

Supported Catalysts

Nobel Metals (Gold) Become Reactive Catalysts When of 1-6 nm Size

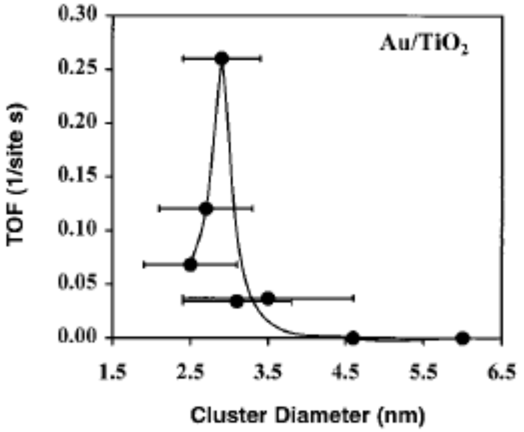


Fig. 1. CO oxidation turnover frequencies (TOFs) at 300 K as a function of the average size of the Au clusters supported on a high surface area TiO$_2$ support (*7*). The Au/TiO$_2$ catalysts were prepared by deposition-precipitation method, and the average cluster diameters were measured by TEM. The solid line serves merely to guide the eye.

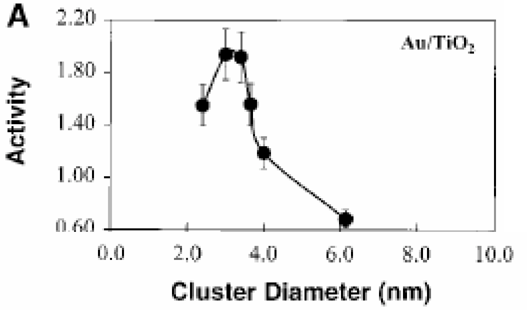
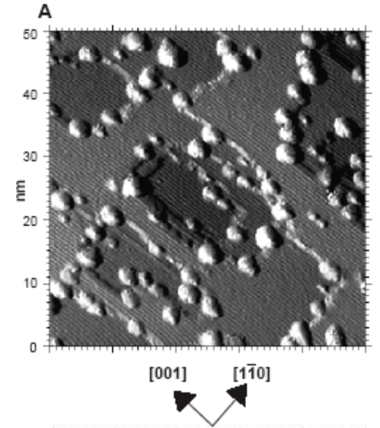


Fig. 3. (**A**) The activity for CO oxidation at 350 K as a function of the Au cluster size supported on TiO$_2$(110)-(1×1) assuming total dispersion of the Au. The CO:O$_2$ mixture was 1:5 at a total pressure of 40 Torr. Activity is expressed as (product molecules) × (total Au atoms)$^{-1}$ s^{-1}. (**B**) Cluster band gap measured by STS as a



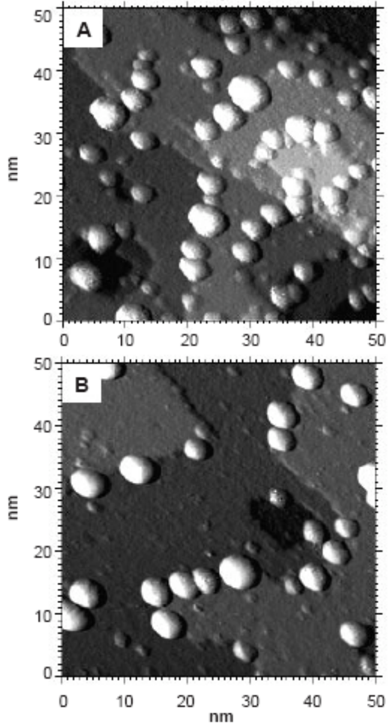


Fig. 4. A series of CCT STM images of Au/TiO$_2$(110)-(1×1) as prepared in Fig. 2 (**A**) after 120 min of O$_2$ exposure at 10 Torr, and (**B**) after 120 min of CO:O$_2$ (2:1) exposure at 10 Torr. The Au coverage was 0.25 ML, and the sample was annealed at 850 K for 2 min before the exposures. All of the exposures are given at 300 K. The size of the images is 50 nm by 50 nm.

Onset of catalytic activity of gold clusters on titania with the appearance of non-metallic properties.
Valden M, Lai X, Goodman DW
Science 281, 1647-1650 (1998).

Solution Method For Au/Support Oxide (Using $HAuCl_4$)

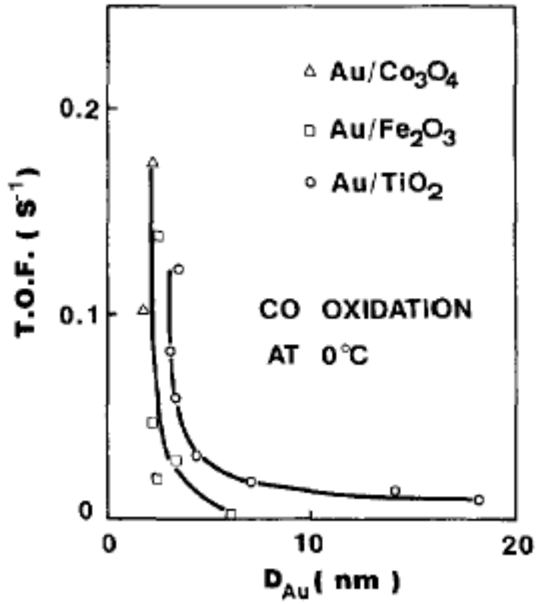
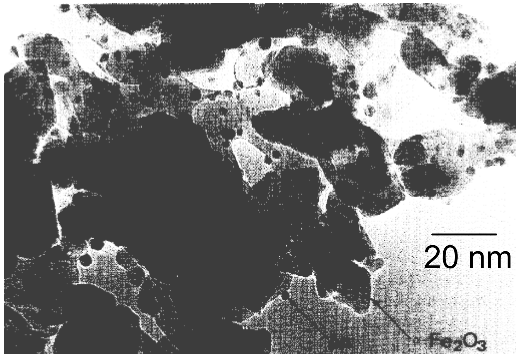


Fig. 4. Turnover frequencies based on surface exposed gold atoms as a function of the mean particle diameters of gold in CO oxidation at 0°C. △, Au/Co_3O_4; □, $Au/\alpha\text{-}Fe_2O_3$; ○, Au/TiO_2.

Size- and support-dependency in the catalysis of gold. **Haruta M, Catalysis Today 36, 153-166 (1997).**

592 Citations



Gold Catalysts Prepared by coprecipitation for low-temperature oxidation of hydrogen and of Carbon Monoxide.
Haruta M, Yamada N, Kobayashi T, Iijima S, J. Of Catalysis 115, 301-309 (1989).

480 Citations

Consider Support Particle with Deposited Domains

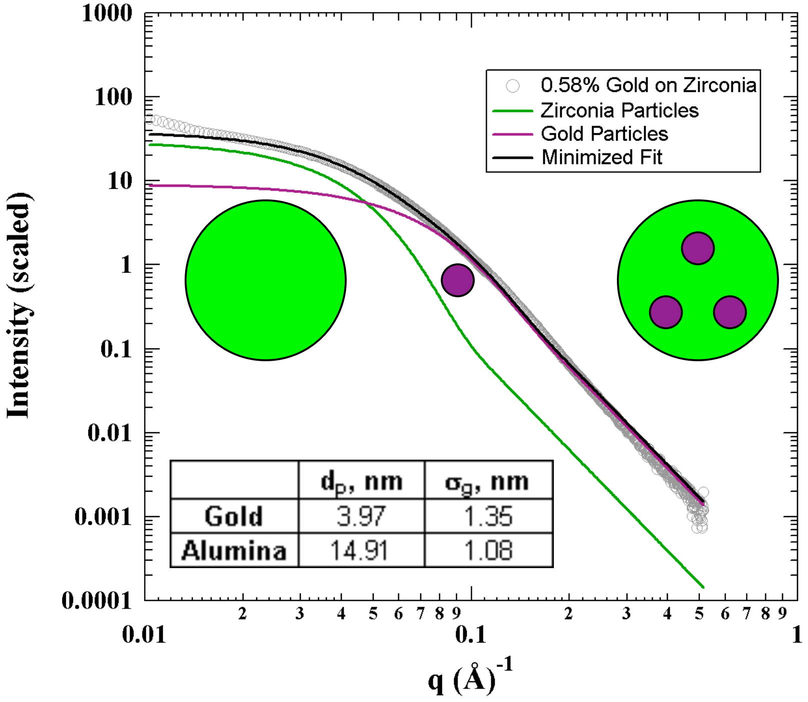
We can obtain: Mean Size,
Polydispersity,
State of Aggregation
For Both Particle Types.

This can be done *in situ* in almost
any environment that can be brought to the synchrotron.

Measurements with ETHZ (Eveline Bus, Jereon Van Bokhoven)
ESRF (T. Narayanan)

Option 1: Brute Force/Lab Source

d_p, nm	σ_g
3.97	1.35
14.9	1.08



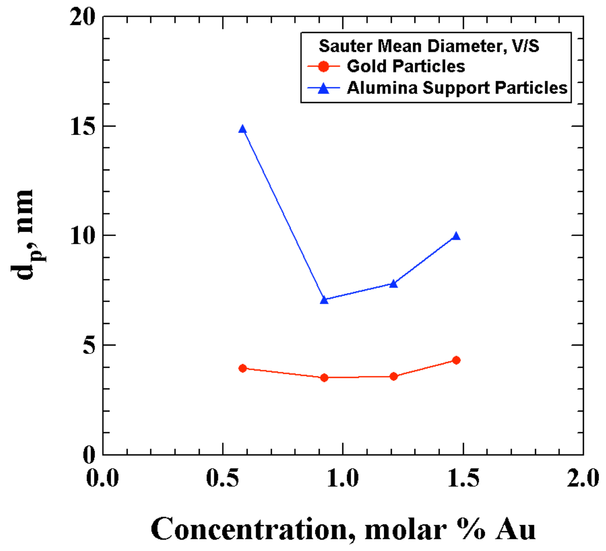
	d_p, nm	σ_g, nm
Gold	3.97	1.35
Alumina	14.91	1.08

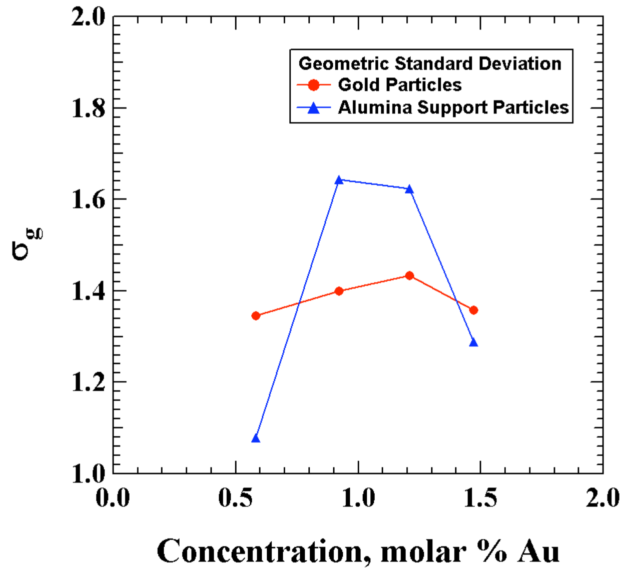
Consider Support Particle with Deposited Domains

Option 1: Brute Force

How do the particles vary with concentration gold?

Measurements with ETHZ (Eveline Bus, Jereon Van Bokhoven)
ESRF (T. Narayanan)



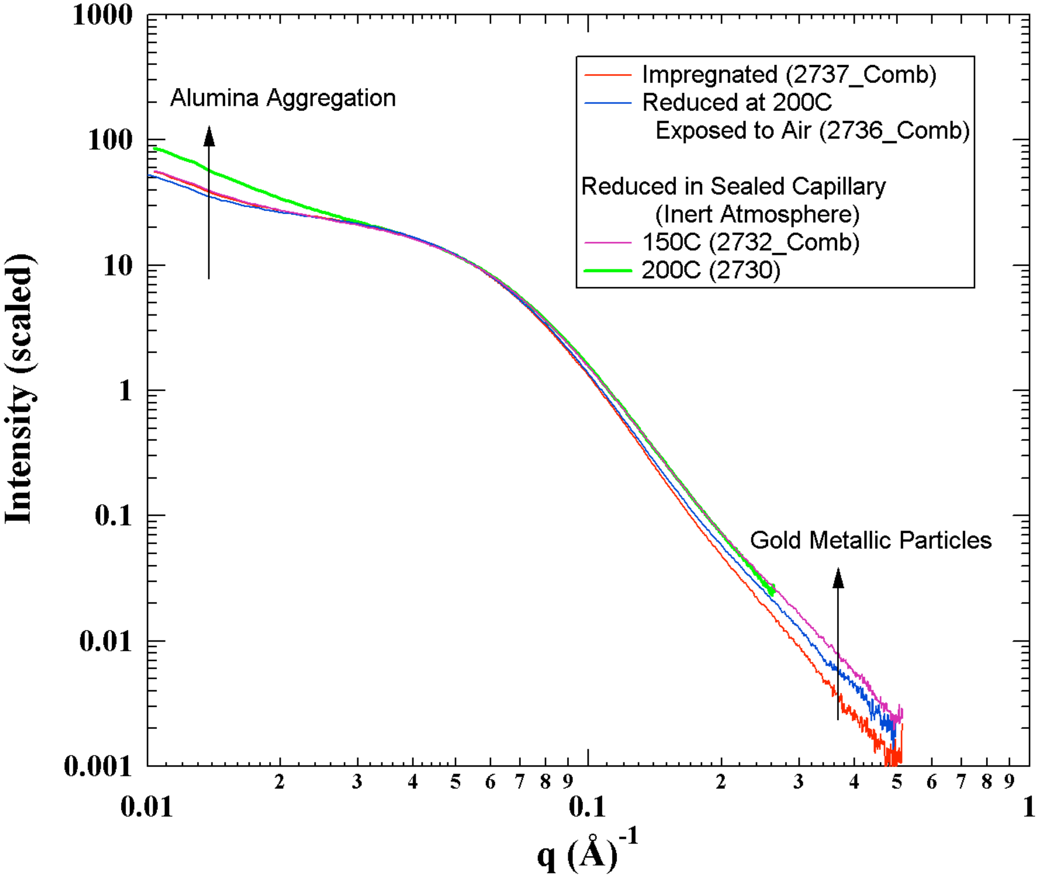


Consider Support Particle with Deposited Domains

Option 1: Brute Force

In situ versus ex situ measurements.

Measurements with ETHZ (Eveline Bus, Jereon Van Bokhoven)
ESRF (T. Narayanan)

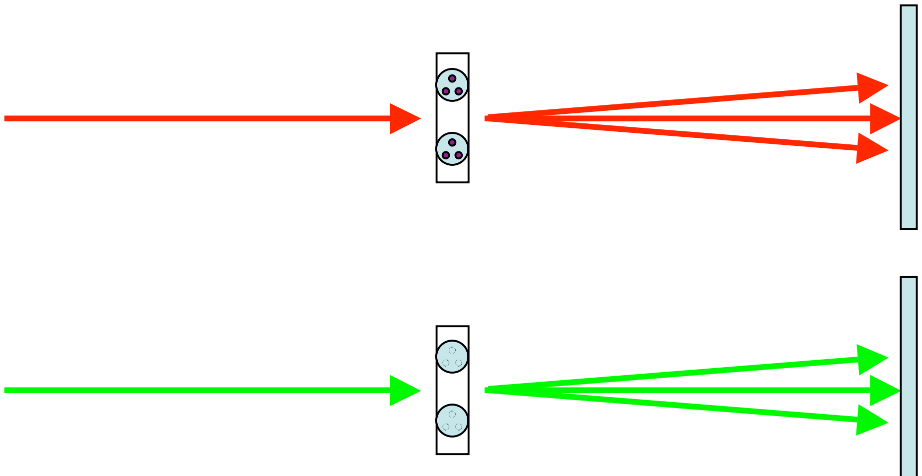


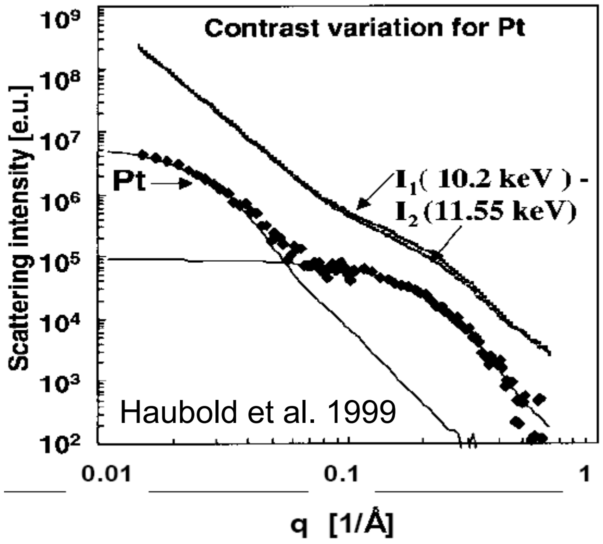
Desirable: In Situ Study/Contrast variation for Gold

Consider Support Particle with Deposited Domains

Option 2: Anomalous Scattering/Synchrotron

In situ anomalous small-angle x-ray scattering from metal particles in supported-metal catalysts. I Theory and II Results. Brumberger H, Hagrman D, Goodisman J, Finkelstein KD, J. Appl. Cryst. 38 147-151 and 324-332 (2005).





Haubold et al. 1999

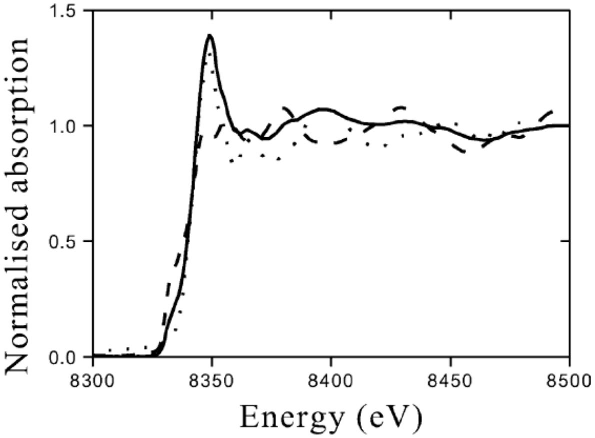
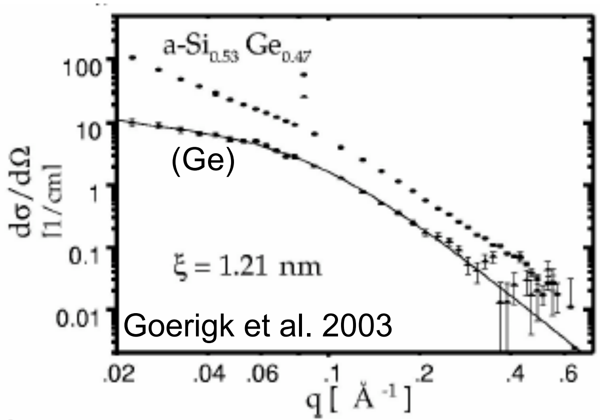


Fig. 5. Normalized absorption spectra of the fresh nickel catalyst (full line). The spectra of Ni (long dash) and NiO (short dash) references are also shown.



Goerigk et al. 2003

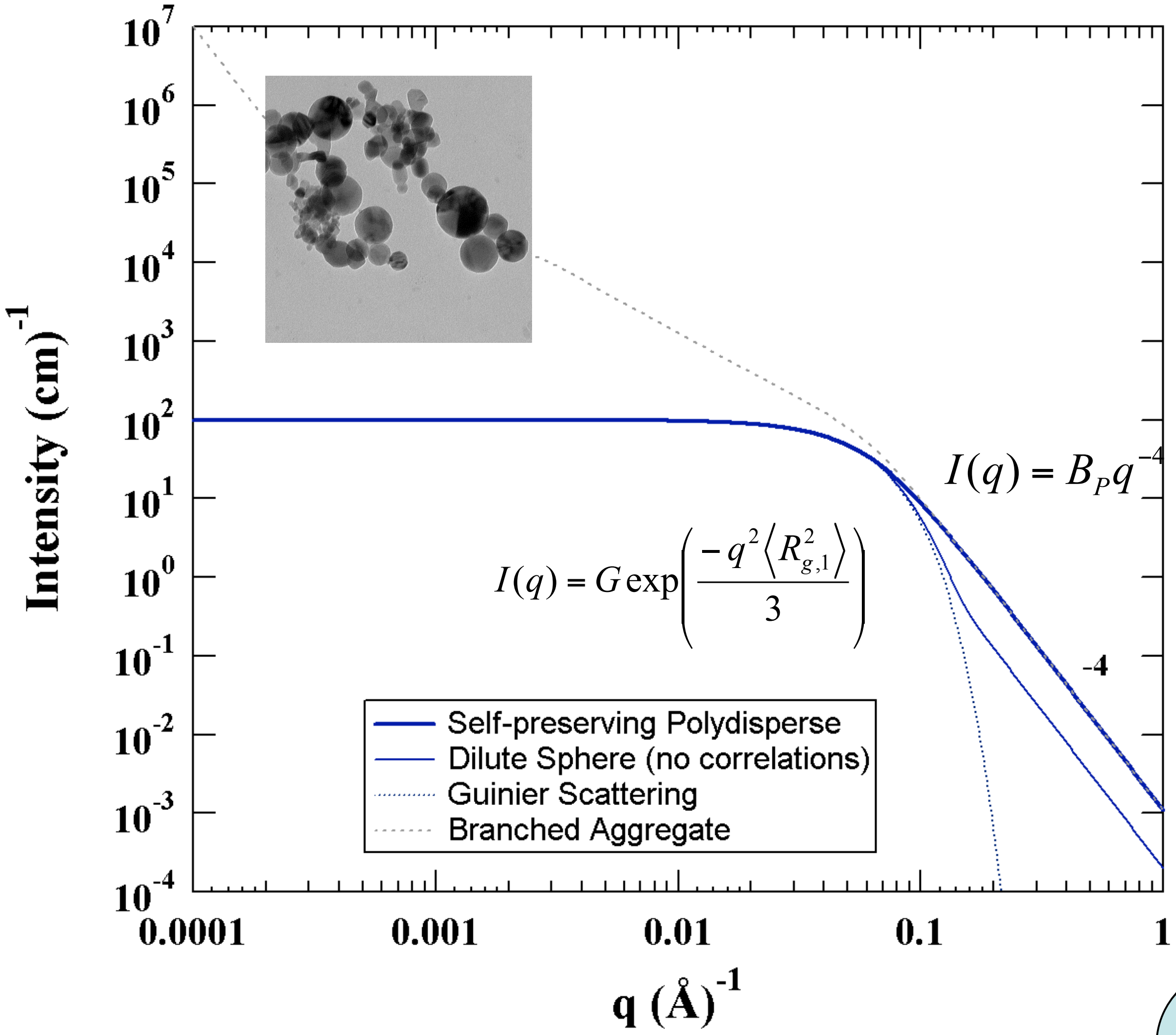
Figure 4

Total (upper curve) and separated scattering curve of an amorphous silicon-germanium alloy.

G.Goerigk and D.L.Williamson

http://www.desy.de/~jusifa/solarzellentechnik.htm

Scattered Intensity Depends on Contrast, G (For Each Phase)

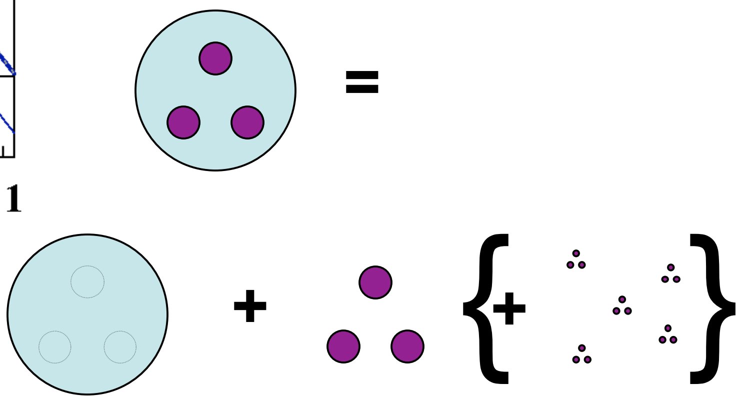


Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. 37 523-535 (2004).

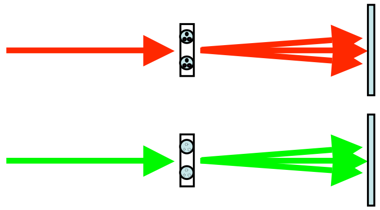
$$G = N\rho_e^2\langle V^2\rangle$$

$$B_P = G\left(\frac{1.62PDI}{R_g^4}\right)$$

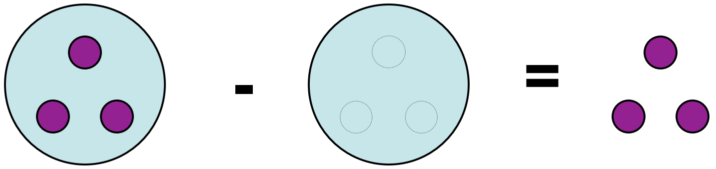
$$\rho_e^2(E) = \left[n_1 f_1(E) - n_2 f_2(E)\right]^2$$



“f” Depends on Wavelength



Sintering of Ni/Al_2O_3 catalysts studied by anomalous small angle x-ray scattering.
Rasmussen RB, Sehested J, Teunissen HT, Molenbroek AM, Clausen BS
***Applied Catalysis A.* 267, 165-173 (2004).**



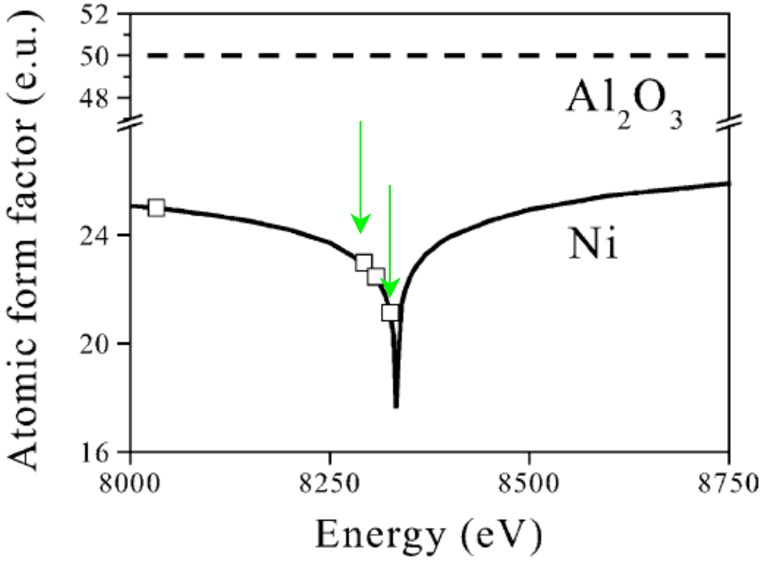


Fig. 1. The magnitude of the atomic form factors of Ni and Al_2O_3 in electron units [30]. The atomic form factor of Ni (full line) has a strong energy dependence close to the K-absorption edge of Ni (8333 eV), whereas the atomic form factor of Al_2O_3 (dashed line) is constant. The squares mark the four X-ray energies used in this study.

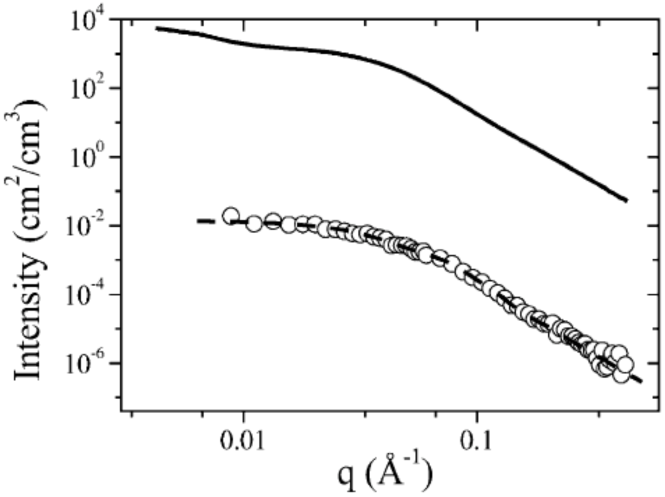
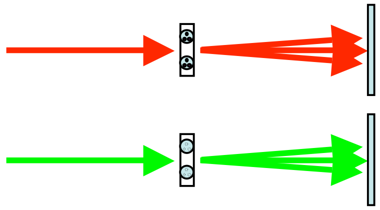


Fig. 7. ASAXS scattering curve measured at 8308 eV on the fresh catalyst (full line). The circles represent the separated scattering curve ($KI(q)$) obtained by subtracting the normalized scattering curves measured at 8308 and 8326 eV. The dashed line represent the best fit to the data using the approach described in the text.

Particle Size Distributions
From SAXS

Particle Size Distribution Curves From SAXS



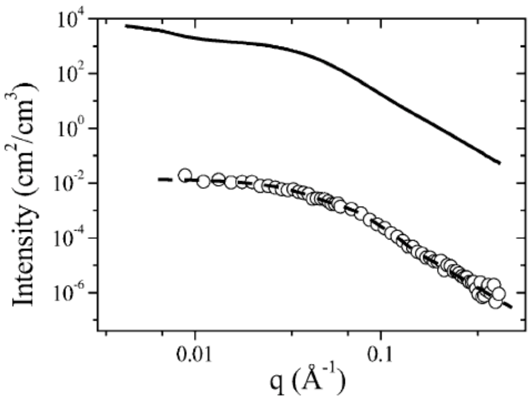


Fig. 7. ASAXS scattering curve measured at 8308 eV on the fresh catalyst (full line). The circles represent the separated scattering curve ($KI(q)$) obtained by subtracting the normalized scattering curves measured at 8308 and 8326 eV. The dashed line represent the best fit to the data using the approach described in the text.

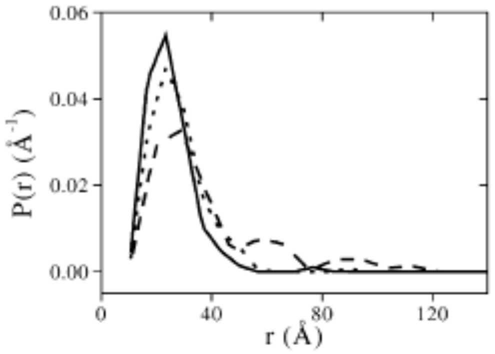


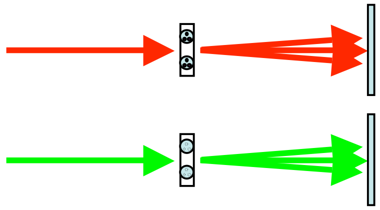
Fig. 8. Normalized nickel number particle size distributions of catalysts sintered at 650 °C obtained by ASAXS as described in the text. The nickel particles are assumed to be spherical with radius r, but otherwise no assumption on the shape of the distribution is made. The full line is the distribution of the fresh catalyst. The short dash (long dash) is the distribution after sintering for 5 h (100 h).

Assumption Method

i) Assume a distribution function.
ii) Assume a scattering function (sphere)
iii) Minimize calculation

$$I(q) = 9G\left[\frac{\sin qR - qR\cos qR}{(qR)^3}\right]^2$$

Particle Size Distribution Curves From SAXS



Assumption Method.
- i) Assume a distribution function.
- ii) Assume a scattering function (sphere)
- iii) Minimize calculation

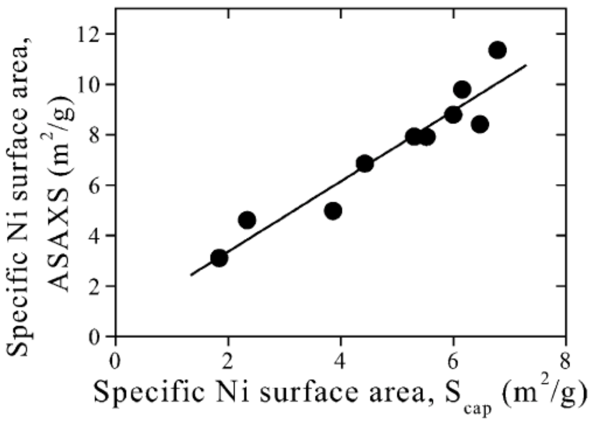


Fig. 11. Comparison of specific nickel surface areas derived from the sulfur chemisorption capacity (S_{cap}) and ASAXS (Tables 3 and 4). The line is the result of a linear regression ($S_{ASAXS} = 1.4(0.2)S_{S_{cap}} + 0.6(0.8)$), where the number in parentheses is the standard deviation of the fit.

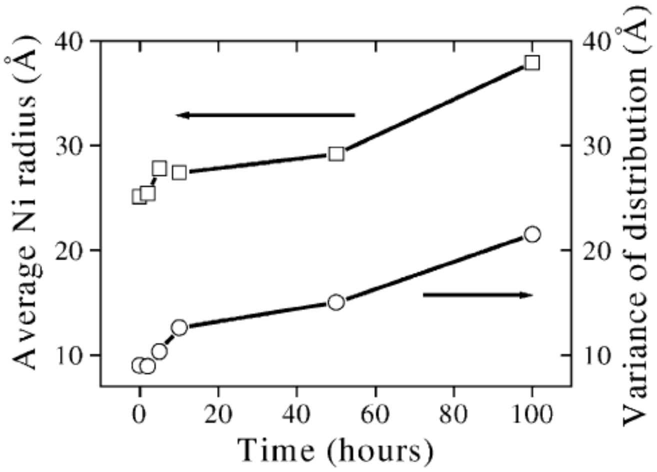


Fig. 10. Average nickel particle radius (squares) and variance (circles) of distribution determined by ASAXS after sintering at 650 °C.

Sintering of Ni/Al$_2$O$_3$ catalysts studied by anomalous small angle x-ray scattering.
Rasmussen RB, Sehested J, Teunissen HT, Molenbroek AM, Clausen BS
***Applied Catalysis A.* 267, 165-173 (2004).**

Not unique &
Based on assumptions
But widely used & easy to understand

Particle Size Distribution Curves From SAXS

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

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

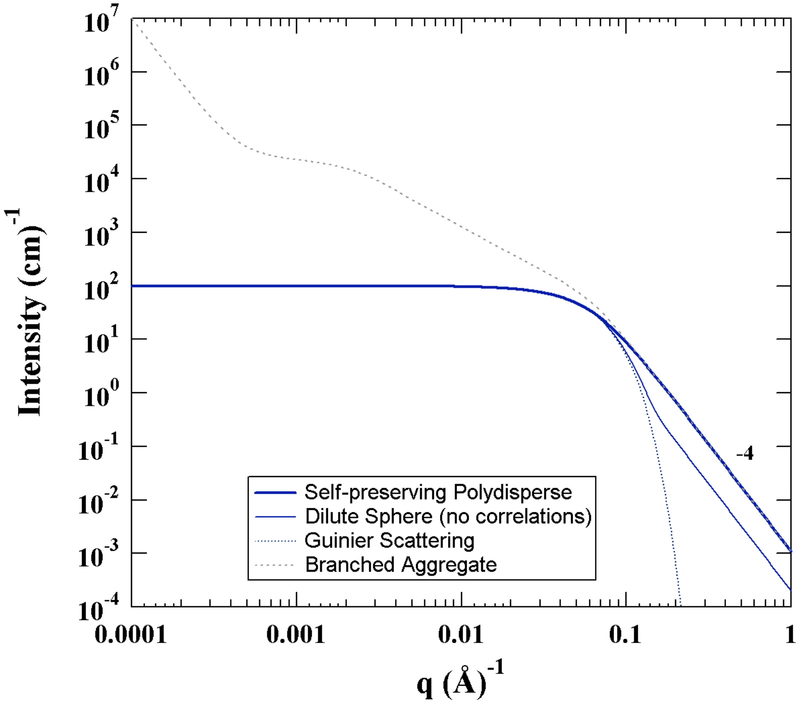
$$m = \left[\frac{5R_g^2}{3e^{14\sigma^2}}\right]^{1/2}$$

Unified Method

- **i) Global fit for B_P and G.**
- **ii) Calculate PDI (no assumptions & unique “solution”)**
- **iii) Assume log-normal distribution for σ_g and distribution curve (or other models)**
- **iv) Data to unique solution**
  Solution to distribution

Advantages

- Generic PDI (asymmetry also)
- Global fit (mass fractal etc.)
- Direct link (data => dispersion)
- Use only available terms
- Simple to implement



Particle Size Distribution Curves from SAXS

PDI/Maximum Entropy/TEM Counting

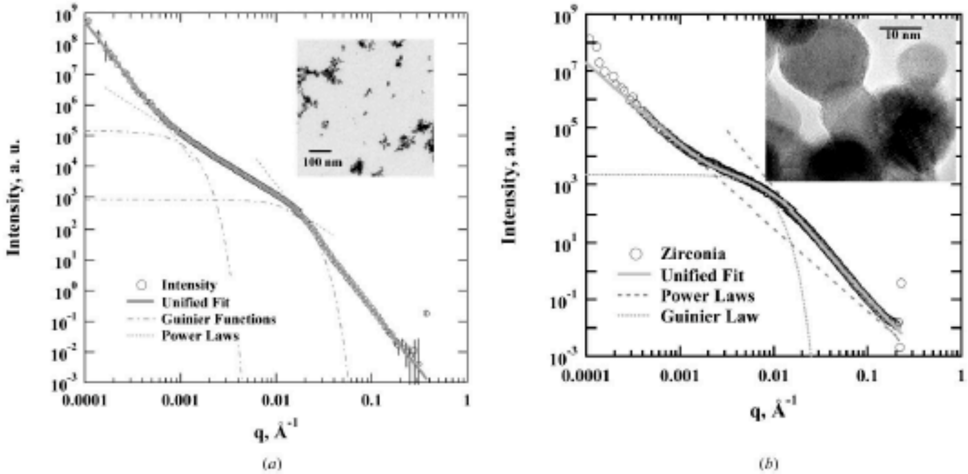


Figure 2
USAXS data from aggregated nanoparticles (circles) showing unified fits (bold grey lines), primary particle Guinier and Porod functions at high q, the intermediate mass fractal scaling regime and the aggregate Guinier regime (dashed lines). (a) Fumed titania sample with multi-grain particles and low-q excess scattering due to soft agglomerates. $d_{V/S} = 16.7$ nm (corrected to 18.0 nm), PDI = 3.01 ($\sigma_g = 1.35$), $R_g = 11.2$ 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. $d_{V/S} = 20.3$ nm, PDI = 10.8 ($\sigma_g = 1.56$), $R_g = 26.5$ nm, $d_f = 2.90$. From gas adsorption, $d_p = 19.7$ nm.

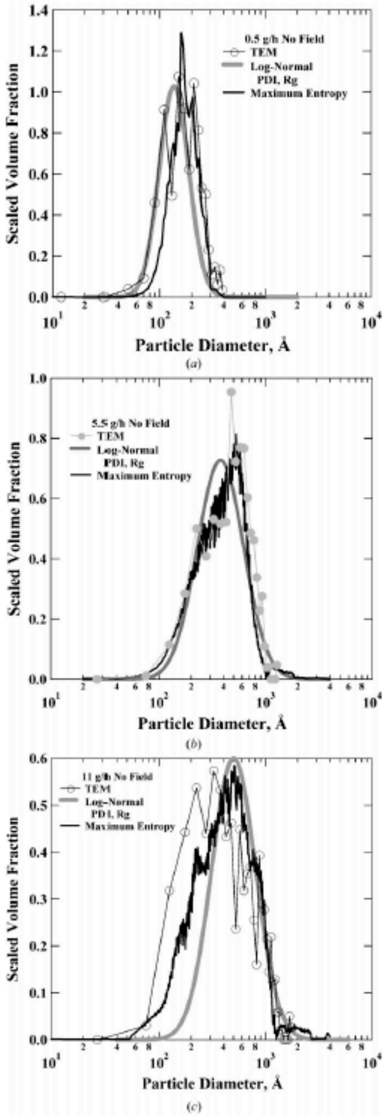


Figure 6
Comparison of particle volume distributions for titania made without an electric field using TEM (circles; Kammler *et al.*, 2003), PDI (grey line) and maximum entropy (black line). (a) 0.5 g h^{-1} [fractal $d_{V/S} = 12.1$ nm, PDI = 3.52 ($\sigma_g = 1.38$), $R_g = 8.9$ nm, $d_f = 1.59$, $z_{2:1}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

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

Particle Size Distribution Curves From SAXS

Maximum Entropy Method

i) Assume sphere or other scattering function

ii) Assume most random solution

iii) Use algorithm to guess/compare/calculate

iv) Iterate till maximum "entropy"

Advantages

- No assumption concerning distribution function
- No assumption for number of modes
- Matches detail PSD's well

Related Alternatives

- Regularization

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

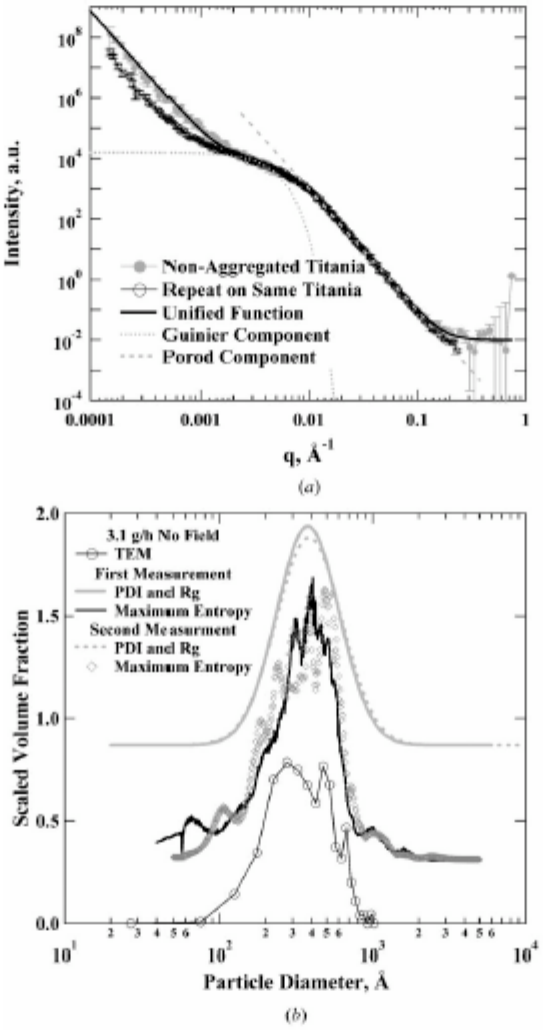


Figure 5
3.1 g h^{-1} titania. (*a*) Repeat USAXS runs on a non-aggregated titania powder (Fig. 1). (*b*) Particle size distributions from TEM (circles; Kammler *et al.*, 2003), equations (1), (2), (17) and (18) using PDI and R_g, and using the maximum-entropy program of Jemian (Jemian *et al.*, 1991). Distribution curves are shifted vertically for clarity. $d_{VIS} = 34.9$ nm, PDI = 14.4 ($\sigma_g = 1.60$), $R_g = 44.2$ nm.

Software for My Collaborators/Students (And Me)

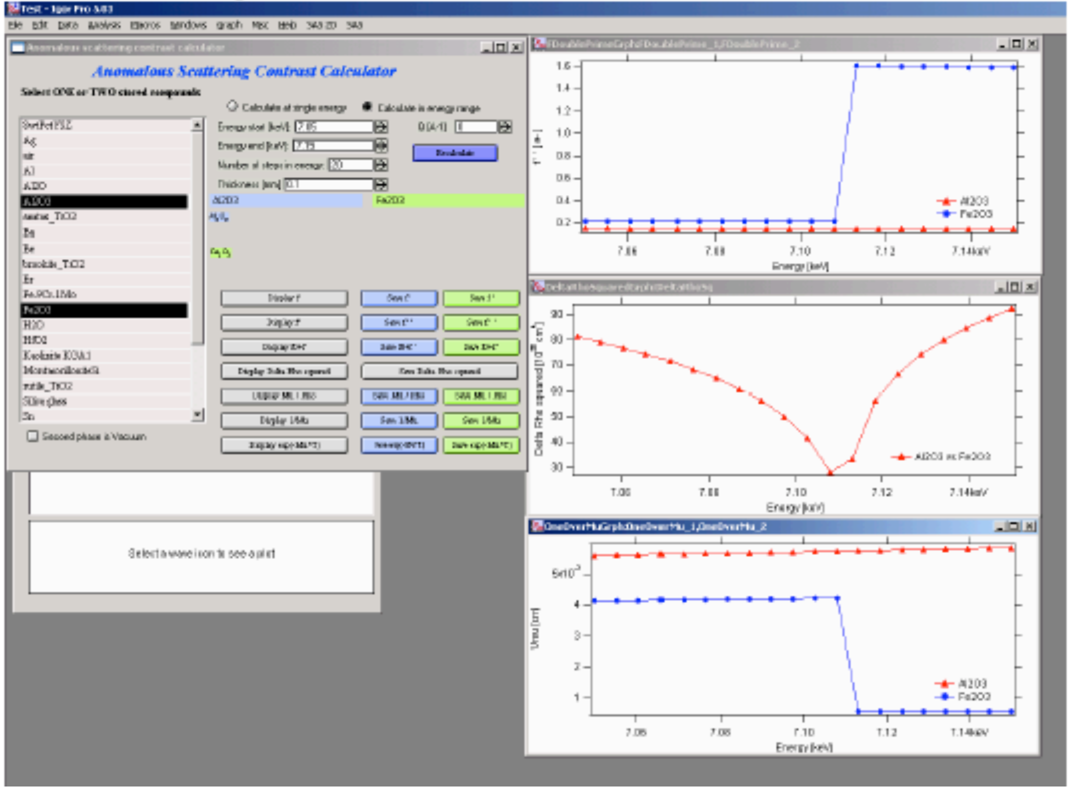
Particle Size Distribution Curves From SAXS

All Methods are available in Jan Ilavsky's Igor Code

http://www.uni.aps.anl.gov/usaxs/

Anomalous Scattering

Irena manual, version August 2004



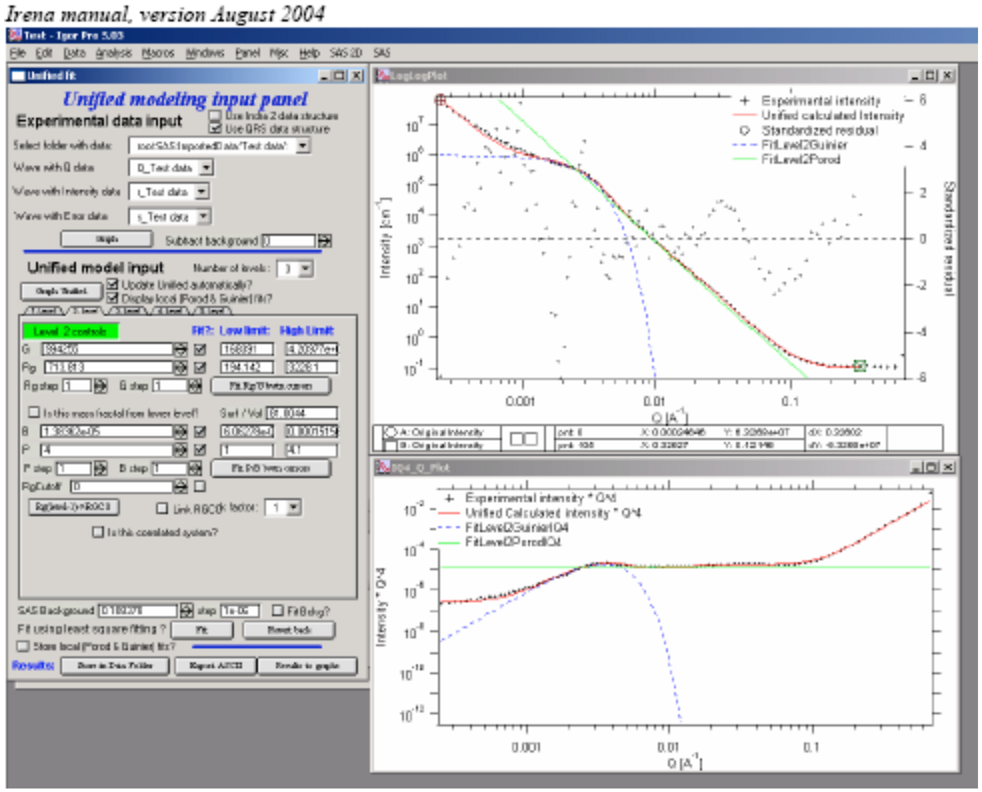
Energy start [keV]: 7.05
Energy end [keV]: 7.15
Number of steps in energy: 20
Thickness [cm]: 0.1
● Calculate in energy range

Particle Size Distribution Curves From SAXS

All Methods are available in Jan Ilavsky's Igor Code

http://www.uni.aps.anl.gov/usaxs/

Unified Fit (Not all implemented)


Irena manual, version August 2004

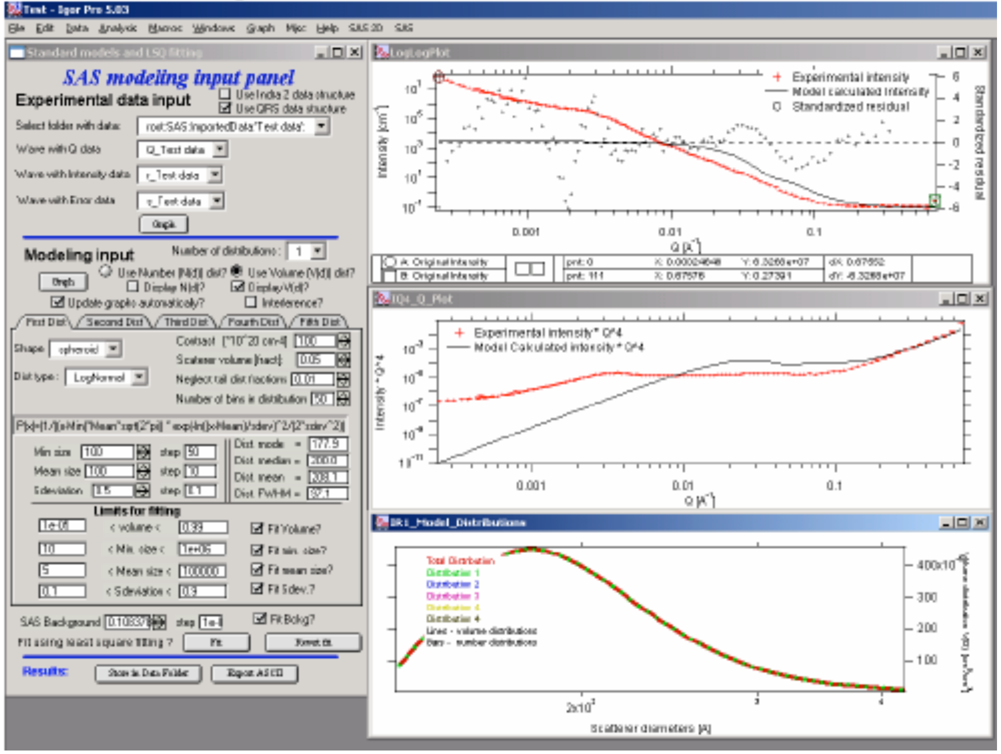
Particle Size Distribution Curves From SAXS

All Methods are available in Jan Ilavsky's Igor Code

http://www.uni.aps.anl.gov/usaxs/

Sphere (or any thing you could imagine) Distributions

Irena manual, version August 2004



SAS modeling input panel

Experimental data input

☐ Use Indra 2 data structure

☑ Use QRS data structure

Select folder with data: root:SAS:ImportedData:'Test data':

Wave with Q data: Q_Test data

Wave with Intensity data: r_Test data

Wave with Error data: s_Test data

Modeling input

Number of distributions: 1

○ Use Number (N(d)) dist? ● Use Volume (V(d)) dist?

☐ Display N(d)? ☑ Display V(d)?

☑ Update graphs automatically? ☐ Interference?

Shape: spheroid

Dist type: LogNormal

Contrast [*10^20 cm-4]: 100

Scatterer volume [fract]: 0.05

Neglect tail dist fractions: 0.01

Number of bins in distribution: 50

P(x)=(1/((x-Min)*Mean*sqrt(2*pi)) * exp(-ln((x-Mean)/sdev)^2/(2*sdev^2))

Min size: 100 step: 50

Mean size: 100 step: 10

Sdeviation: 0.5 step: 0.1

Dist. mode = 177.9

Dist. median = 200.0

Dist. mean = 208.1

Dist. FWHM = 92.1

Limits for fitting

1e-06 < volume < 0.99 ☑ Fit Volume?

10 < Min. size < 1e+05 ☑ Fit min. size?

5 < Mean size < 100000 ☑ Fit mean size?

0.1 < Sdeviation < 0.9 ☑ Fit Sdev.?

SAS Background: 0.10837 step: 1e-6 ☑ Fit Bckg?

Fit using least square fitting?

Results:

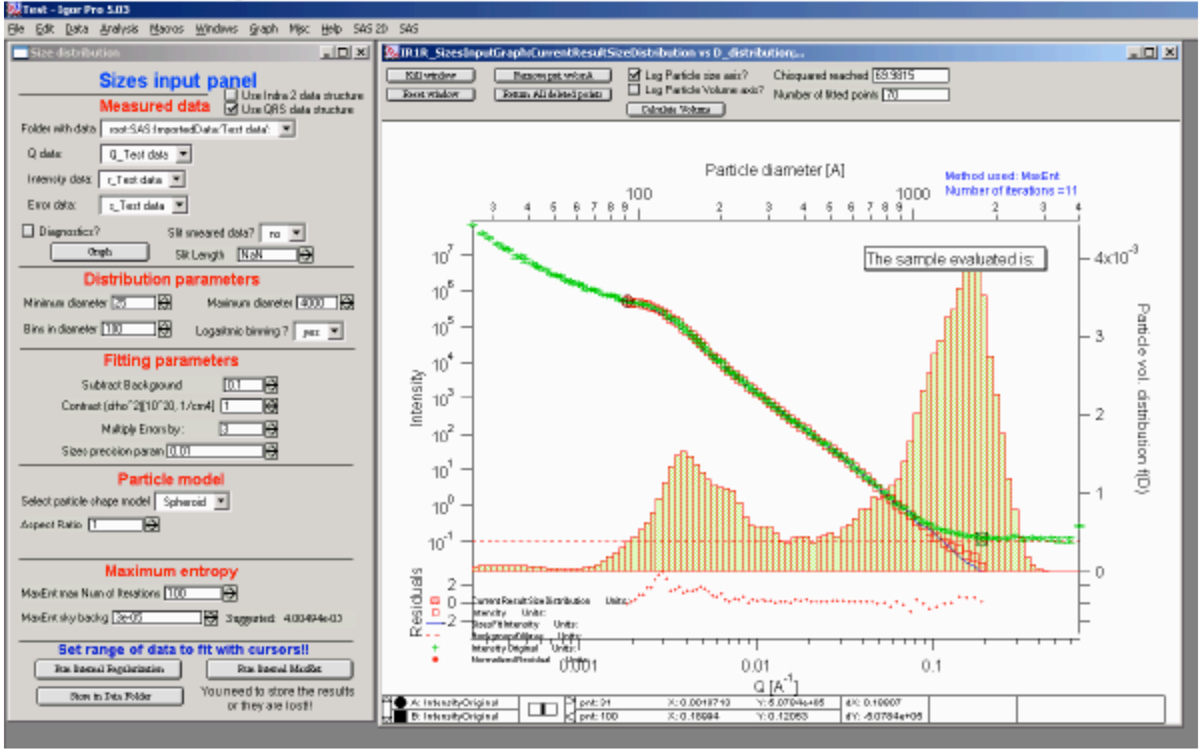
Particle Size Distribution Curves From SAXS

All Methods are available in Jan Ilavsky’s Igor Code

http://www.uni.aps.anl.gov/usaxs/

Maximum Entropy/Regularization Code (Jemian)

Irena manual, version August 2004



Sizes input panel

Measured data

☐ Use Indra 2 data structure
☑ Use QRS data structure

Folder with data: root:SAS:ImportedData:Test data:
Q data: Q_Test data
Intensity data: r_Test data
Error data: s_Test data
☐ Diagnostics?
Slit smeared data? no
Slit Length: NaN

Distribution parameters

Minimum diameter: 25
Maximum diameter: 4000
Bins in diameter: 100
Logaritmic binning ? yes

Fitting parameters

Subtract Background: 0.1
Contrast (drho^2)[10^20, 1/cm4]: 1
Multiply Errors by: 3
Sizes precision param: 0.01

Particle model

Select particle shape model: Spheroid
Aspect Ratio: 1

Maximum entropy

MaxEnt max Num of Iterations: 100
MaxEnt sky backg: 3e-05 Suggested: 4.00494e-03

Set range of data to fit with cursors!!

You need to store the results or they are lost!!

☑ Log Particle size axis?
☐ Log Particle Volume axis?
Chisquared reached: 69.9815
Number of fitted points: 70

A: IntensityOriginal pnt: 31 X: 0.0018713 Y: 5.07046e+05 dX: 0.16007
B: IntensityOriginal pnt: 100 X: 0.16894 Y: 0.12063 dY: -5.0704e+05

Zeolites/Spherical Colloids
Many Other Parts to Scattering
Are Not Covered
For Instance:

Zeolites:

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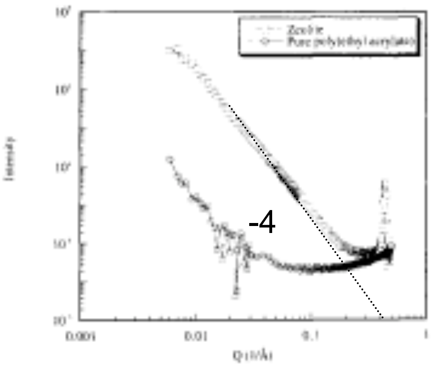


Figure 1. Scattering profiles for pure zeolite powder and pure poly(ethyl acrylate), in which Q is the scattering vector (in reciprocal angstroms).

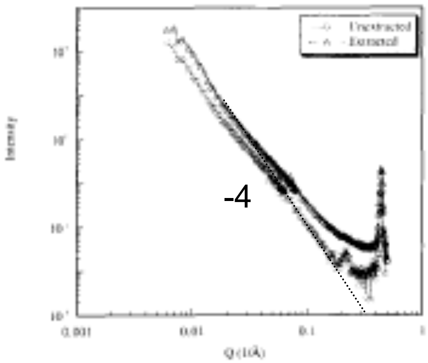


Figure 2. Scattering profiles for the unextracted and extracted zeolite/poly(ethyl acrylate) composites.

- -Pore Structure
- -Nano-Structure
- -Micron Structure

Ethyl acrylate
Benzyl Peroxide
Zeolite 13X

→

Polyethylacrylate
in
Zeolite Pores

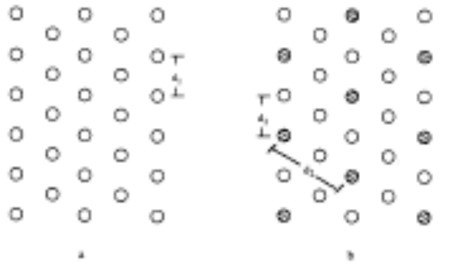


Figure 4. A tentative pore distribution model for (a) pure zeolite, and (b) zeolite/poly(ethyl acrylate) composites. Open circles represent empty pores, while filled circles represent pores containing either ethyl acrylate monomer and/or poly(ethyl acrylate) repeat units.

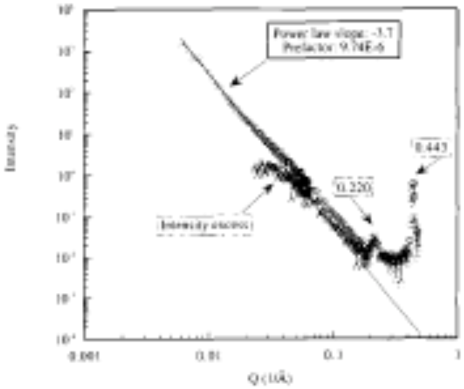
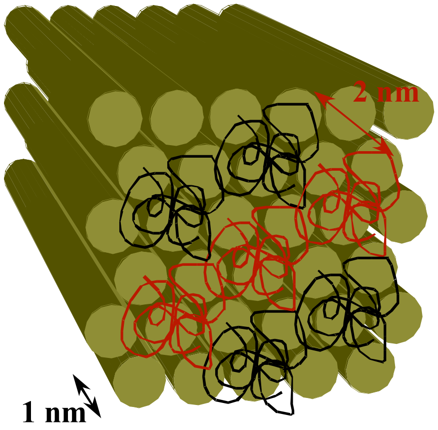
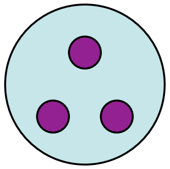


Figure 3. Excess scattering intensities for the composites, as estimated from Porod's Law.



Pu Z, Mark JE, Beaucage G, Maaref S, Frisch HL, *SAXS Investigation of PEA Composites* J. Polym. Sci., Polym. Phys. 34 2657 (1996).

Keep in Mind:



-SAXS Measurement is Generally Easy

-SAXS Analysis is Generally Difficult

-A Reasonable Model is Mostly Needed

-You will Generally Have to Understand
What is going on.

(-This is not a good Technique for Those
Interested only in Verifying)