Exploring the Nanoworld with Small-Angle Scattering

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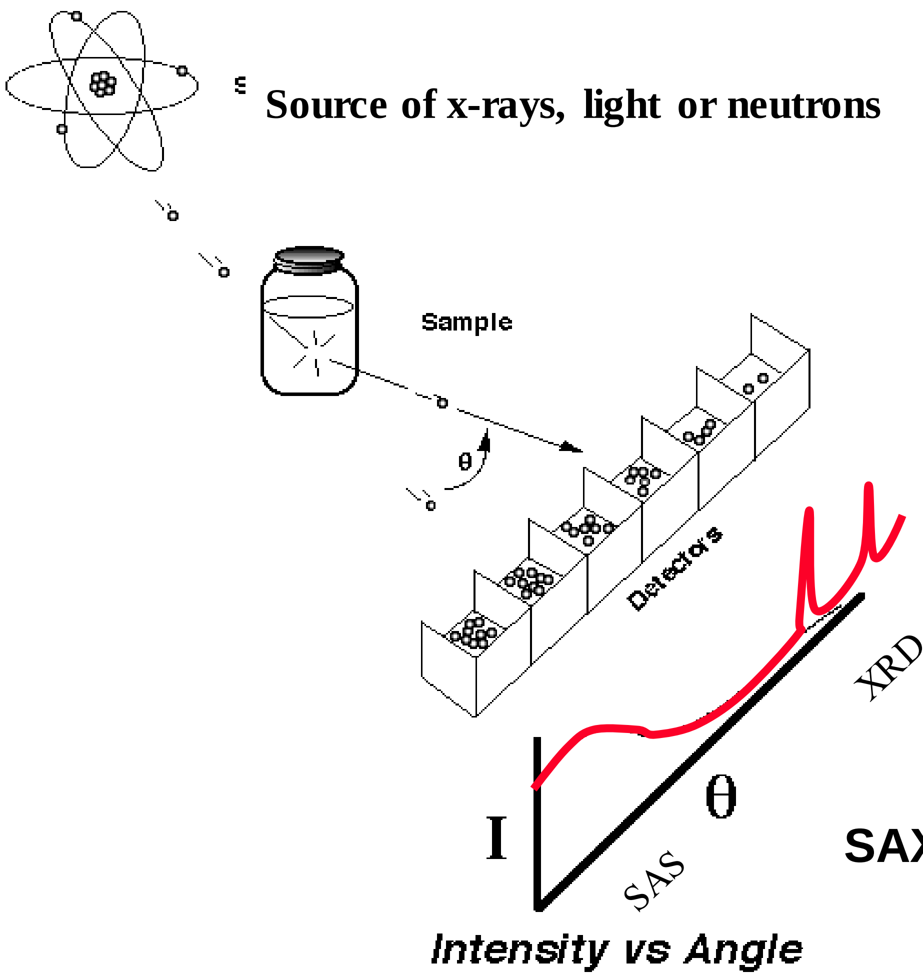
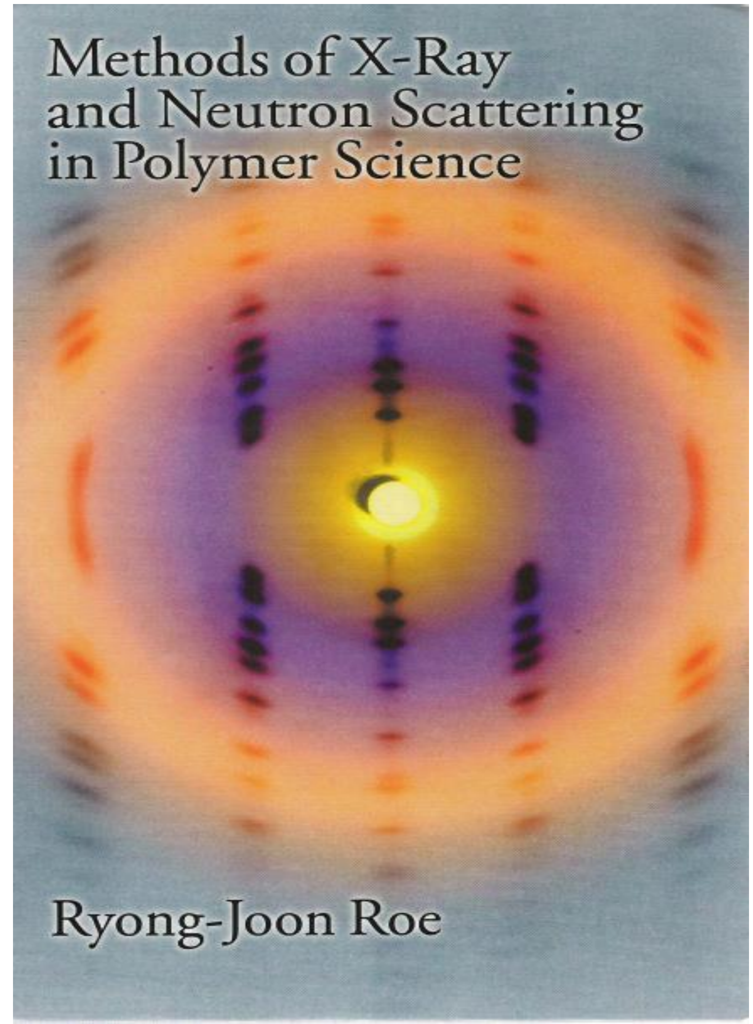
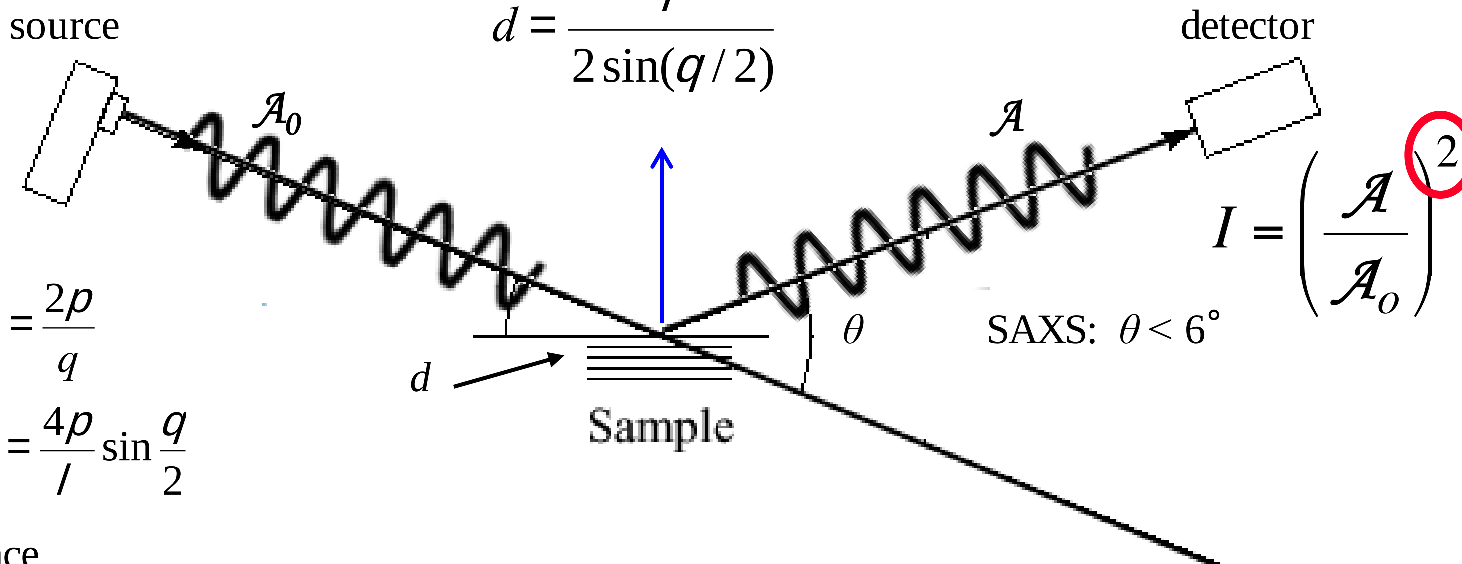




SAXS & SANS: θ ≤ 6°

Crystals: Bragg's Law and the scattering vector, *q*

$$d = \frac{\lambda}{2\sin(\theta/2)}$$

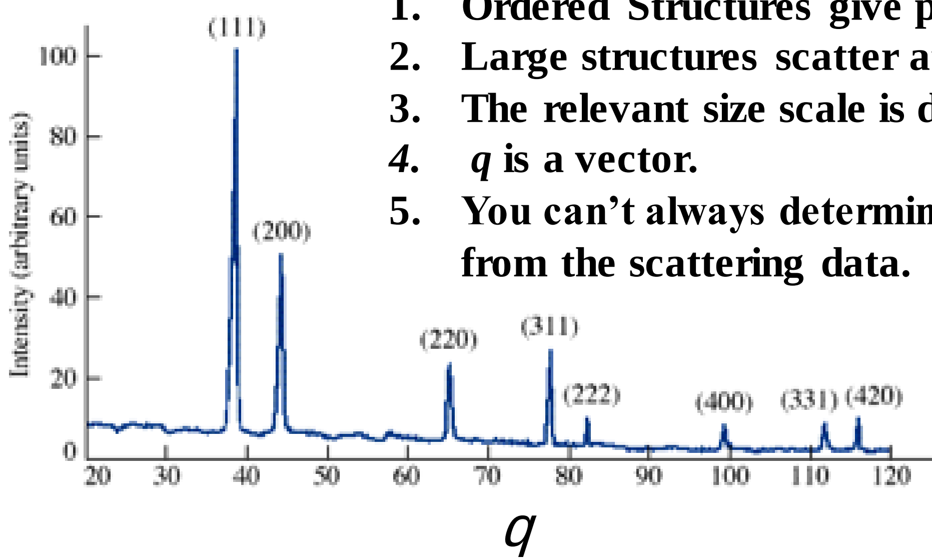


$$I = \left(\frac{\mathcal{A}}{\mathcal{A}_o}\right)^2$$

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

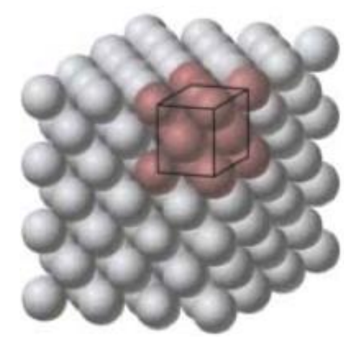
$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

Reciprocal space



1. **Ordered Structures give peaks in "reciprocal" Space.**
2. **Large structures scatter at small angles.**
3. **The relevant size scale is determined by $2\pi/q$**
4. ***q* is a vector.**
5. **You can't always determine the real space structure from the scattering data.**

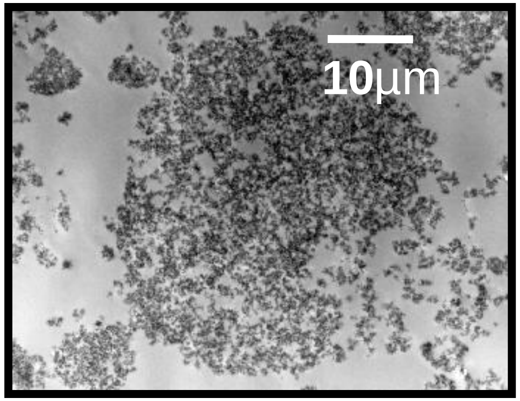
real space



Problem: Nanomaterials are seldom ordered

Disordered Structures in "Real Space"

Agglomerates

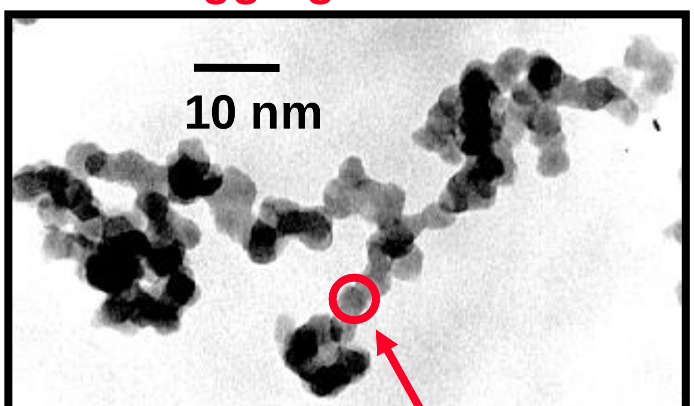


Precipitated Silica

$$\mathbf{(NaO)\,(SiO_2)_{3.3} + HCl \longrightarrow SiO_2 + NaCl}$$

Water Glass

Aggregates



Primary Particles

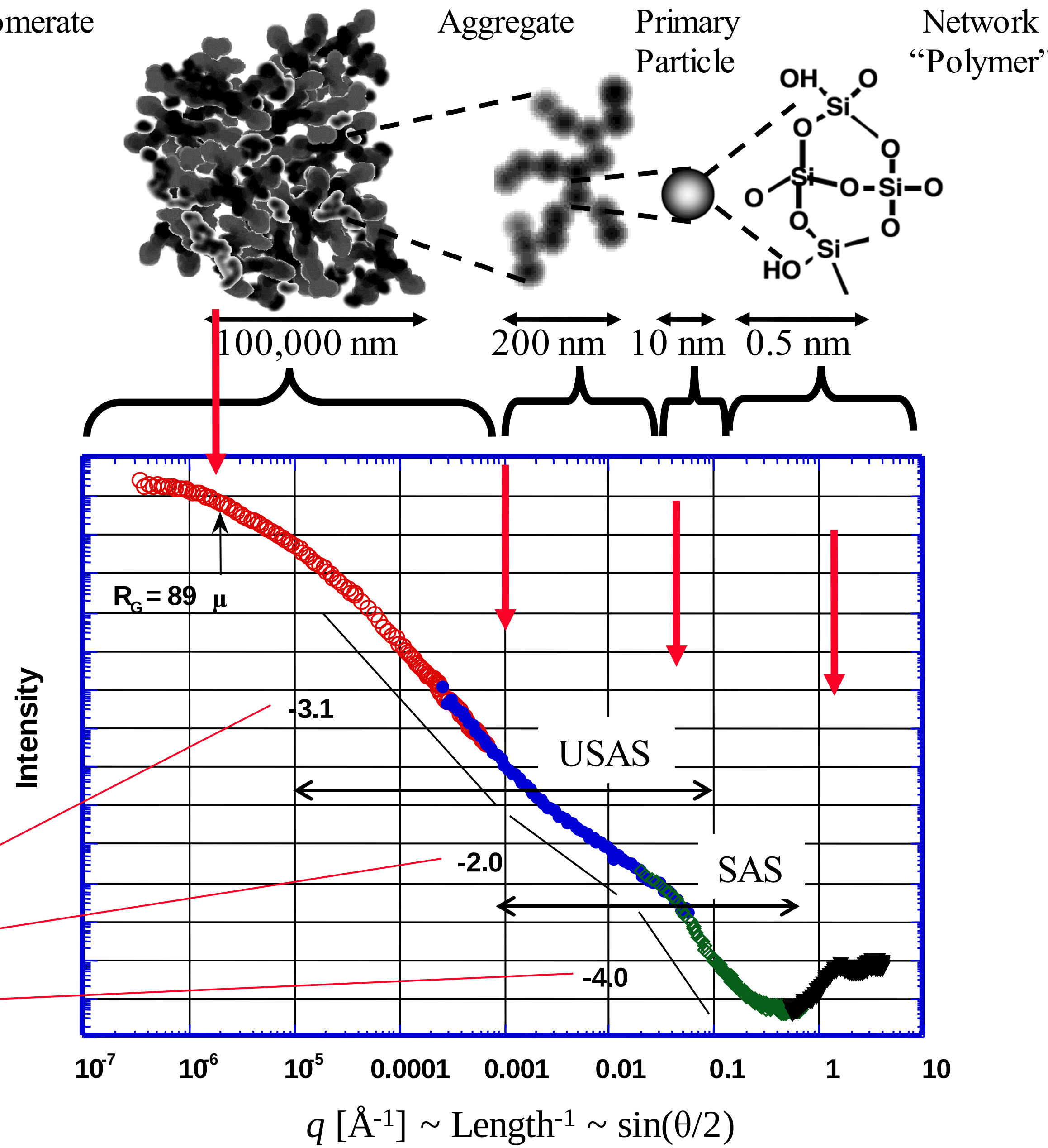
Complex
Hierarchical
Disordered

Difficult to quantify structure from images.

Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

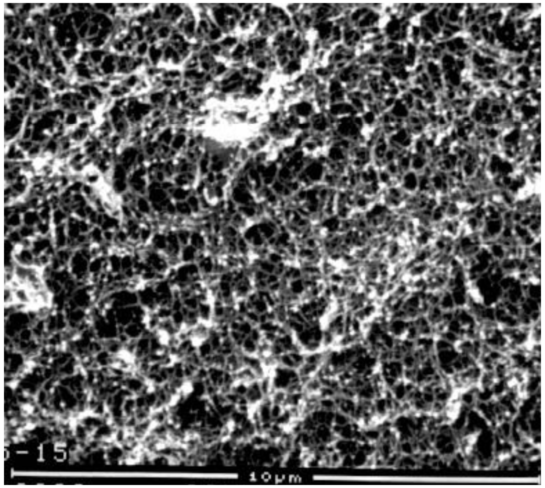
$$q = \frac{2\pi}{d_{Bragg}} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

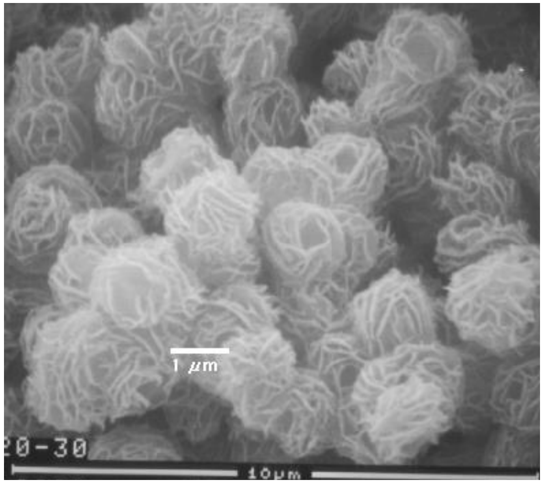


Exponents related to morphology

Why Reciprocal Space?

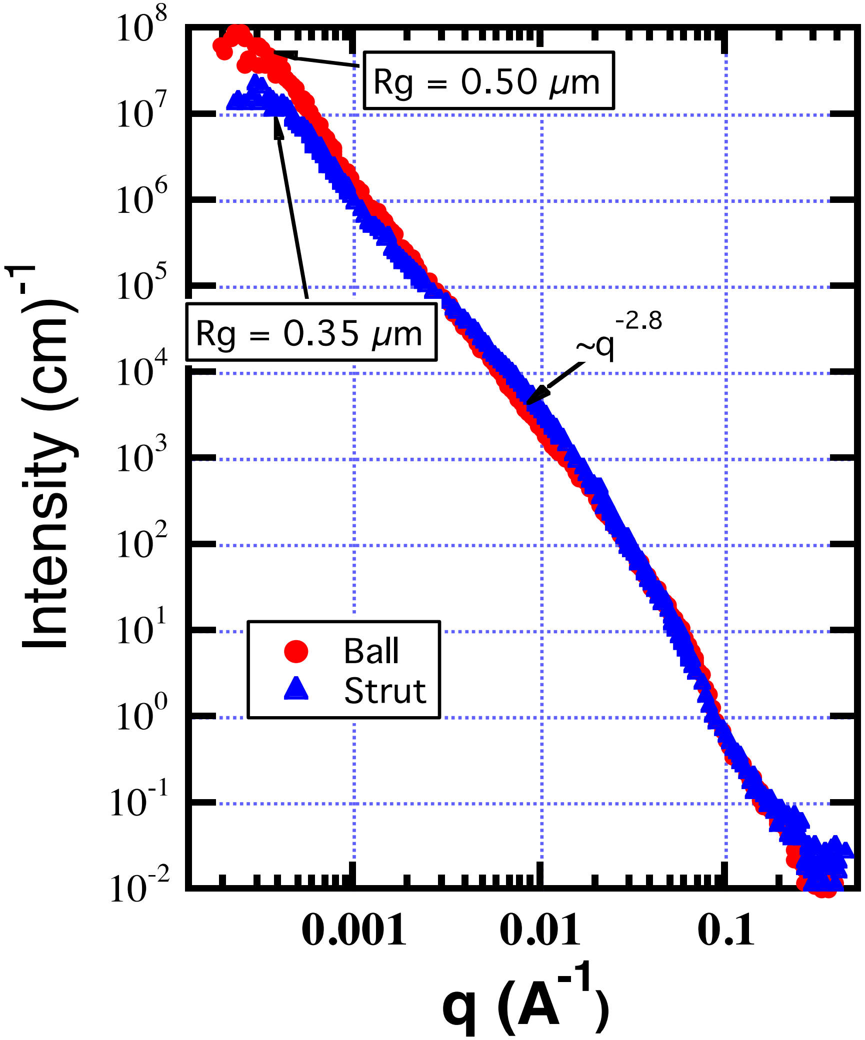
Isotactic polystyrene foams prepared by TIPS





10 μm

Jim Aubert, SNL



Images miss similarity

Ultra-small-angle neutron scattering: a new tool for materials research. Cur. Opinion Sol. State & Mat Sci, 2004. 8(1): p. 39-47.

Characterizing Disordered Systems in Real Space

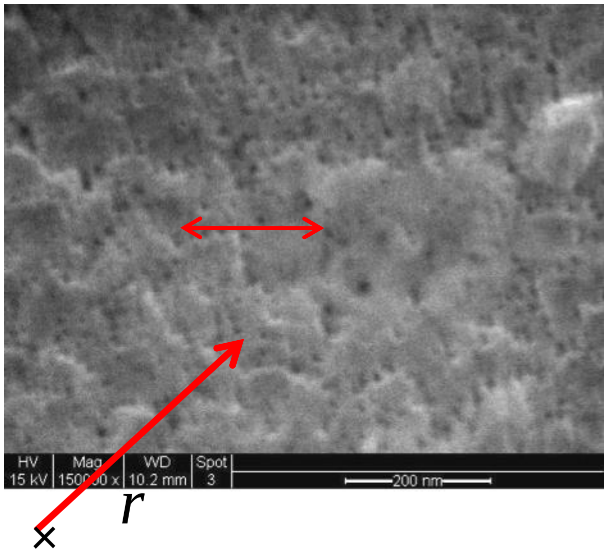
Electron Density Distribution

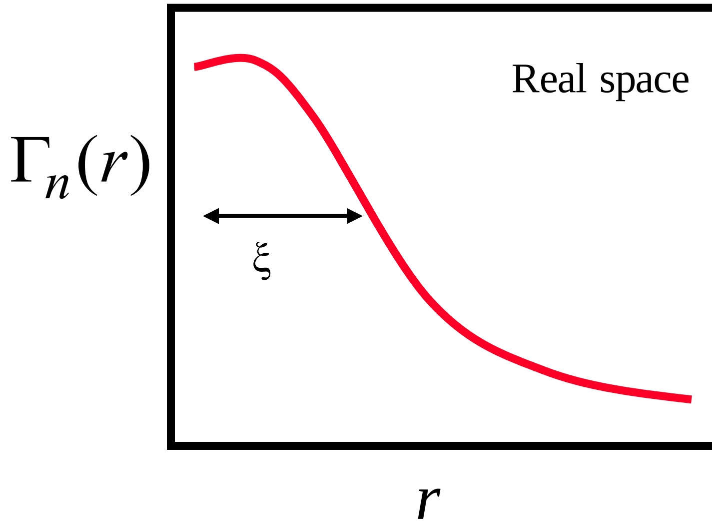
$$n(r)$$

Throw out phase information $\longrightarrow$

Correlation Function of the Electron Density Distribution

$$\Gamma_n(r) = \int n(u)n(u+r)du$$





Depends on latitude and longitude.
Too much information to be useful.

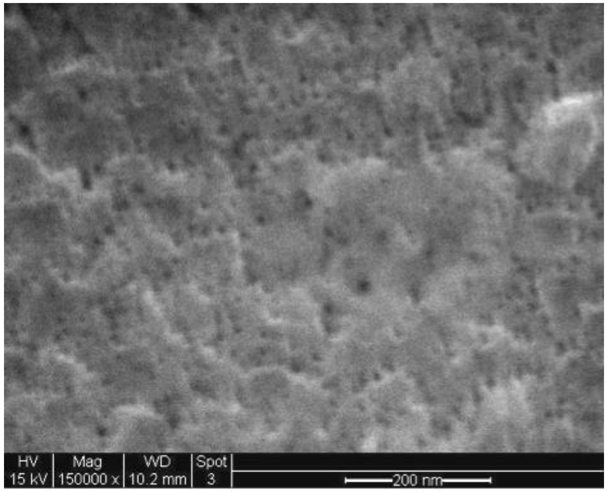
Depends on separation distance.
Retains statistically significant info.

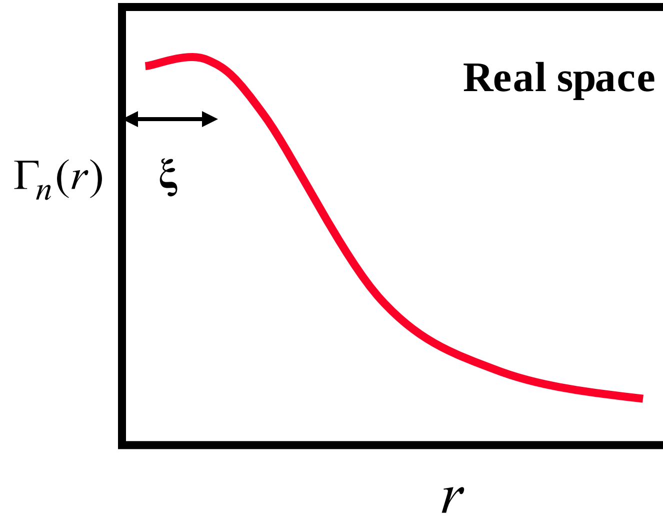
Resolution problems at small r
Opacity problems for large r
2-dimensional
Operator prejudice

Problems with real space analysis

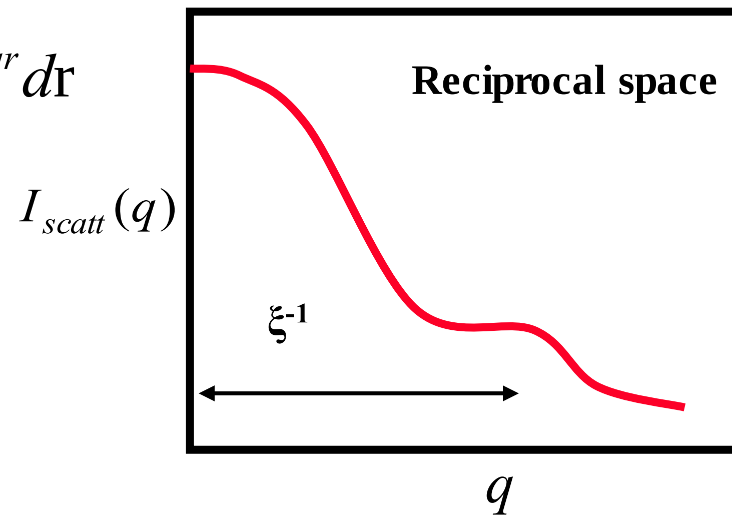
Imaging vs. Scattering

$$\Gamma_n(r) = \int n(u)n(u+r)du$$





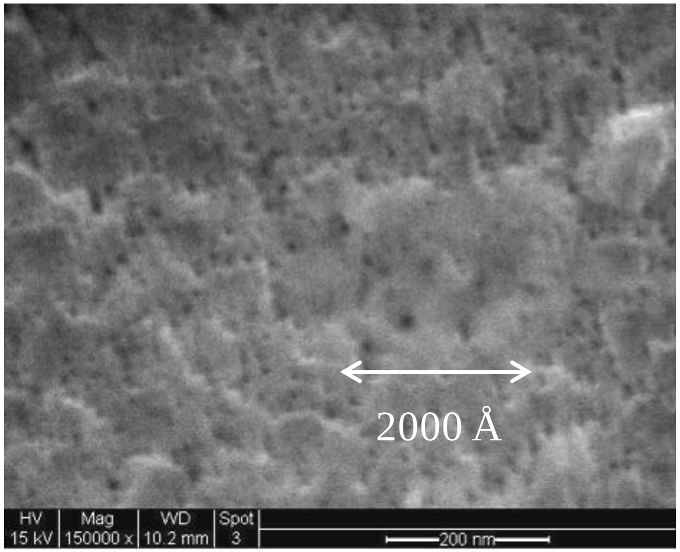
$$I_{scatt} \cong \int \Gamma_n(r)\, e^{-iqr} dr$$

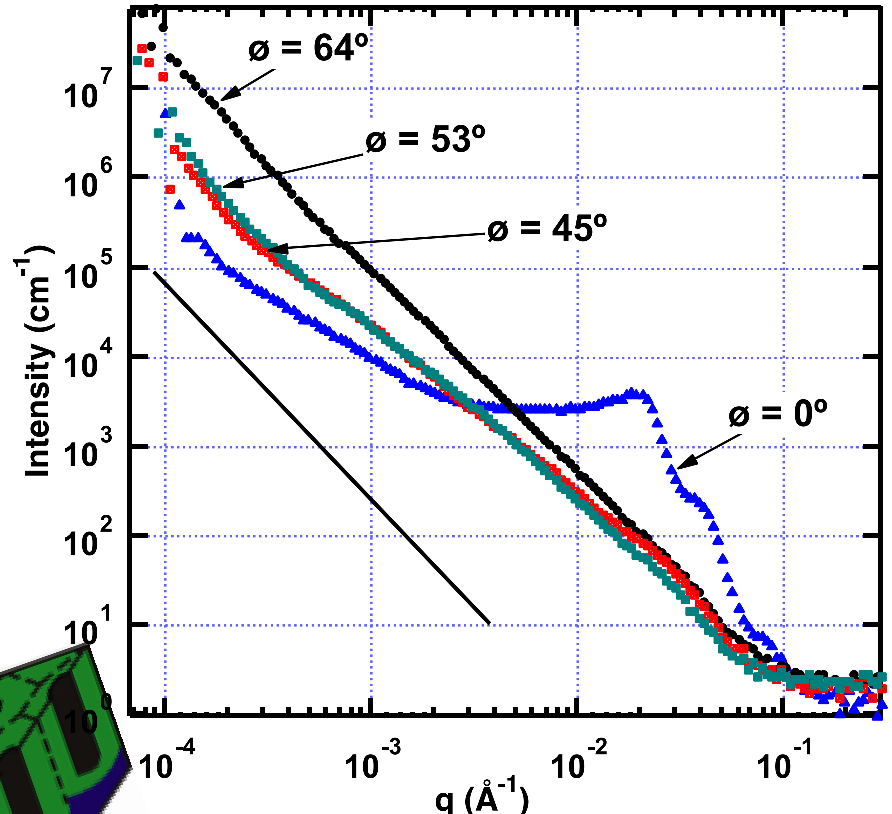


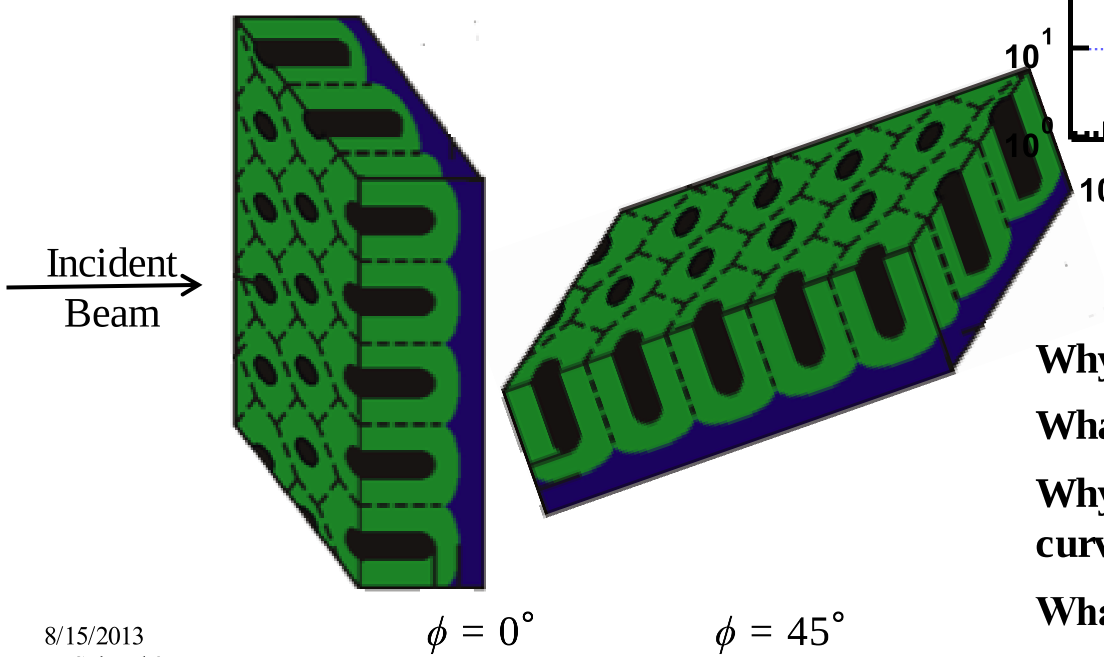
Schaefer, D. W. & Agamalian, M. Ultra-small-angle neutron scattering: a new tool for materials research. *Curr Opin Solid St & Mat Sci* 8, 39-47, (2004).

Pegel, S., Poetschke, P., Villmow, T., Stoyan, D. & Heinrich, G. Spatial statistics of carbon nanotube polymer composites. *Polymer* 50, 2123-2132, (2009).

Anodized Aluminum







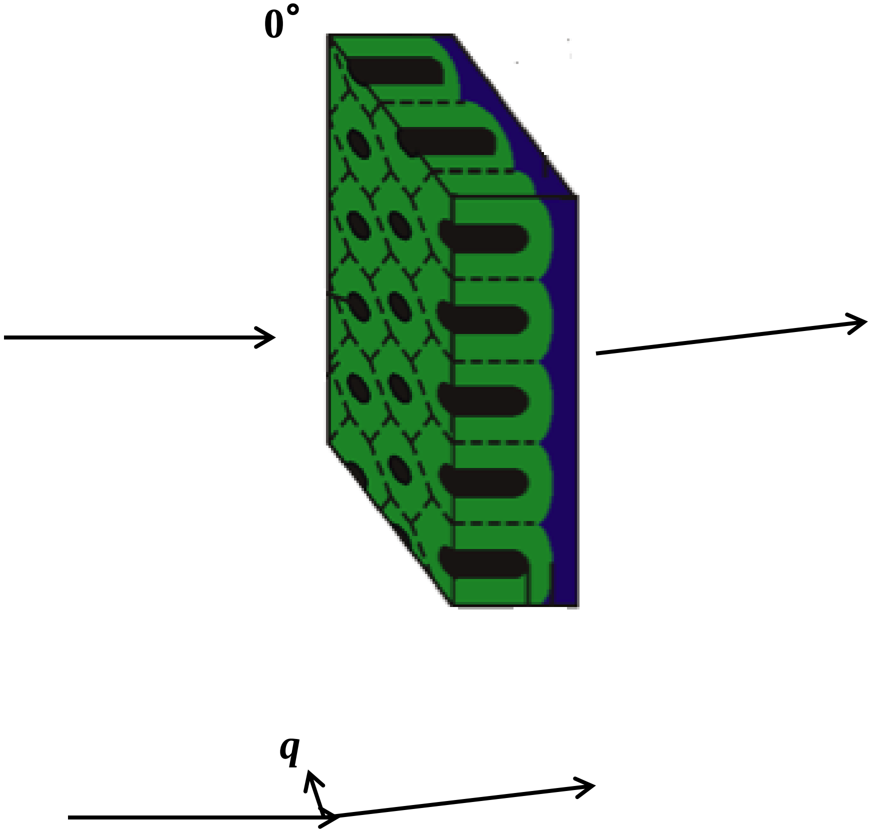
Why is there a peak?

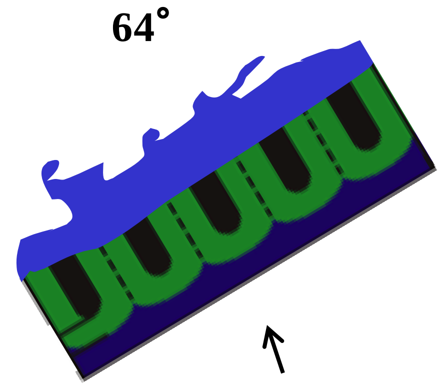
What is the meaning of the peak position?

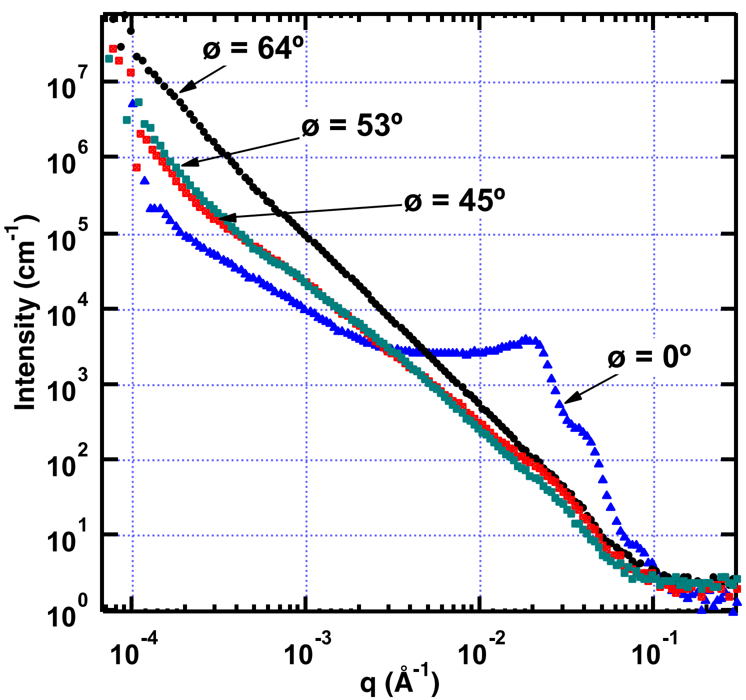
Why did the peak disappear for the 64° curve.

What is the meaning of "Intensity (cm^{-1})"

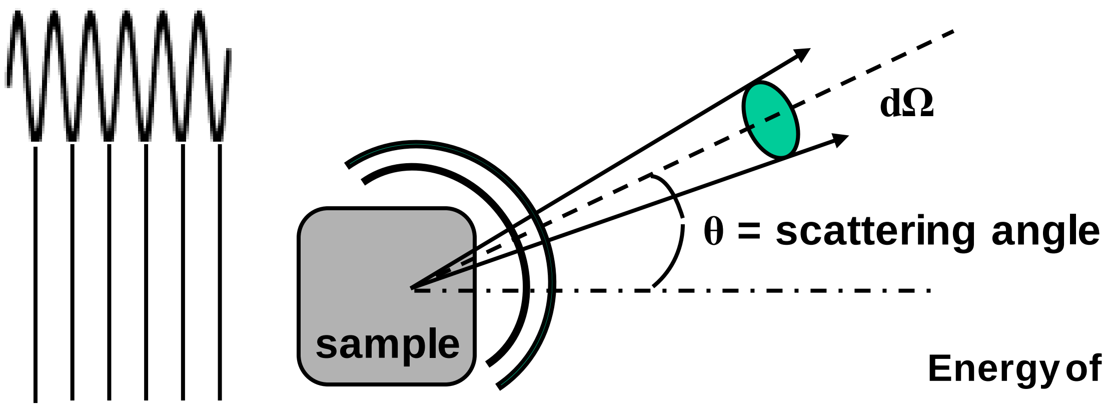
Angle dependence







Intensity and Differential Scattering Cross Section



Plane wave
$\mathbf{J_0}$

Spherical wave
$\mathbf{J_\Omega}$

Energy of a wave ~ Intensity ~ Amplitude^2 = $|\mathcal{A}|^2$

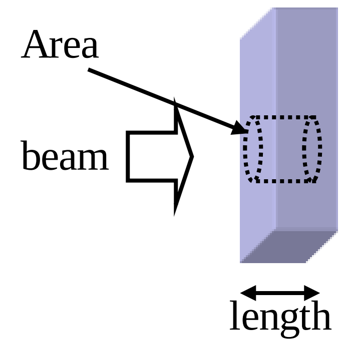
Spherical wave:	**Flux J_Ω =**	**energy/unit solid angle/s**	**or**	**photons/ unit solid angle /s**
Plane wave:	**Flux J_0 =**	**energy/unit area/s**	**or**	**photons/unit area/s**

$$\frac{J_\Omega}{J_0} \equiv \frac{d\sigma}{d\Omega}\left(\frac{\mathrm{cm}^2}{\mathrm{str}}\right) \quad \text{differential scattering cross section}$$

What is “Intensity?” What do we really measure?

$$\frac{J_\Omega}{J_A} \equiv \frac{d\sigma}{d\Omega}\left(\frac{\text{cm}^2}{\text{str}}\right) = \frac{\text{detected photons/ solid angle/s}}{\text{incident photons/area/s}} = \frac{\text{cm}^2}{\text{str}} \sim V = \textit{sample volume}$$

$$\frac{J_\Omega(q)}{J_A V} = \frac{J_\Omega(q)}{J_A \cdot \text{area} \cdot \text{length}} = \frac{\text{detected photons/str/s}}{\text{incident photons} \cdot \text{area} \cdot \text{length/s/area}} = \frac{1}{\text{length} \cdot \text{str}}$$



$$= \frac{\text{fraction of the photons scattered into unit solid angle}}{\text{unit sample length}}$$

$$= \text{cross section / unit sample volume/ unit solid angle}$$

$$= \frac{d\sigma(q)}{V d\Omega}\left[cm^{-1}\right]$$ **Often called the scattering cross section or the intensity**

$$\text{Intensity} = \frac{J}{J_0} \equiv \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\left(\frac{\text{cm}^2}{\text{str}}\right)$$ Roe

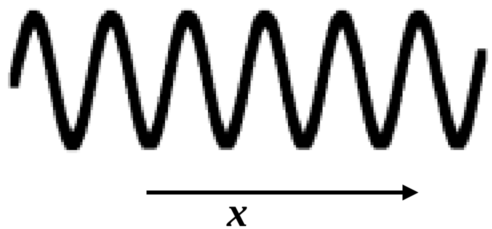
$$\text{Intensity} = \frac{J}{VJ_0} = \frac{\mathrm{d}\sigma}{V\mathrm{d}\Omega}\left(\frac{1}{\text{cm}}\right)$$ Experimentalists, Irena, Indra

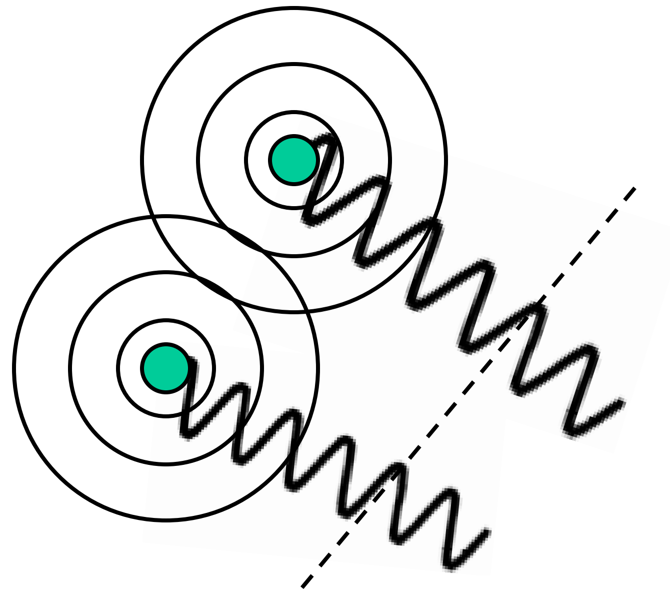
$$\text{Intensity} = \left(\text{arbitrary constant}\right) \times J$$ Common Usage

Generalized Bragg's Law for Disordered System

What is the relationship between real space and reciprocal space when there are no crystal planes?

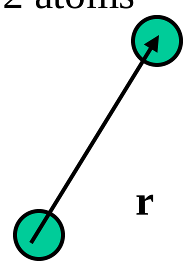
$$\mathcal{A}e^{i2\pi(\upsilon t - x/\lambda)}$$



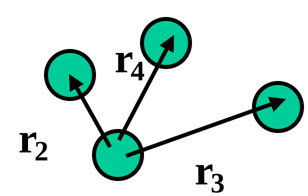


Scattering from 2 atoms

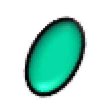
2 atoms



many atoms

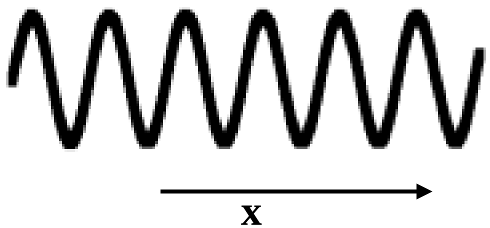


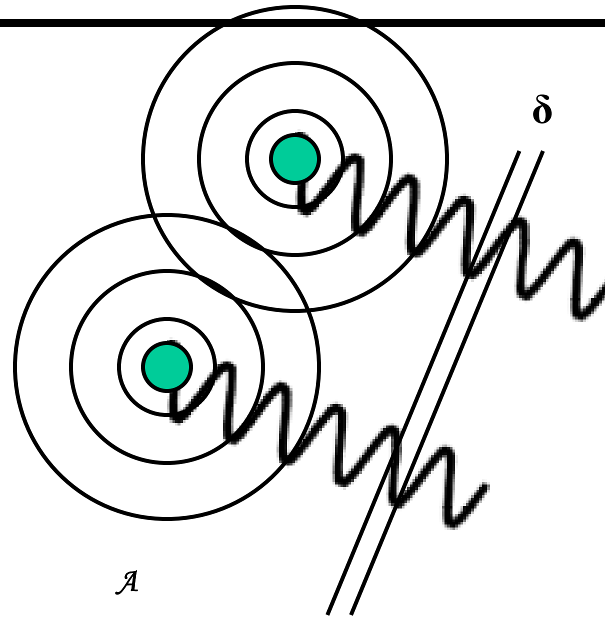
dΩ



Scattering from two atoms

$$\mathcal{A}_o e^{i2\pi(\upsilon t - x/\lambda)}$$





Difference in path length

$$\frac{const \times \mathcal{A}_o}{r} e^{i2\pi(\upsilon t - (x+\delta)/\lambda)}$$

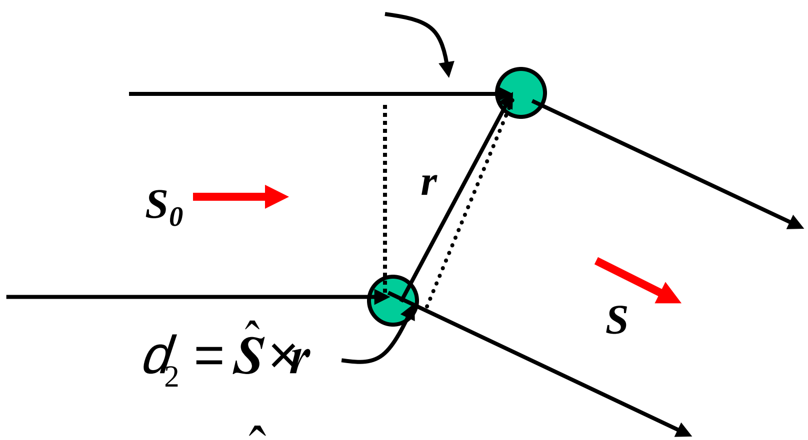
$$\Delta\phi = \frac{2\pi}{\lambda}\delta$$

$$\frac{const \times \mathcal{A}_o}{r} e^{i2\pi(\upsilon t - x/\lambda)}$$

What are the units of const?

unit vector

$$d_1 = \hat{S}_0 \cdot r$$



Instrument (q)

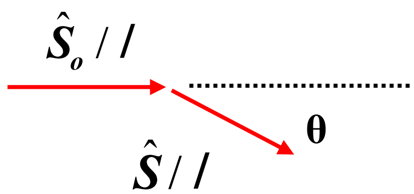
$$\Delta\phi = \frac{2\pi}{\lambda}\left(\hat{S}_0 \cdot r - \hat{S} \cdot r\right)$$

Sample (r)

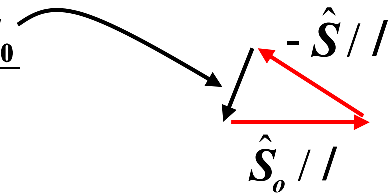
Scattering vectors *s* and *q*

$$\mathrm{D}f = \frac{2p}{l}\left(\hat{\boldsymbol{S}}_0 \cdot \boldsymbol{r} - \hat{\boldsymbol{S}} \cdot \boldsymbol{r}\right) \equiv -2p\boldsymbol{s} \cdot \boldsymbol{r}$$

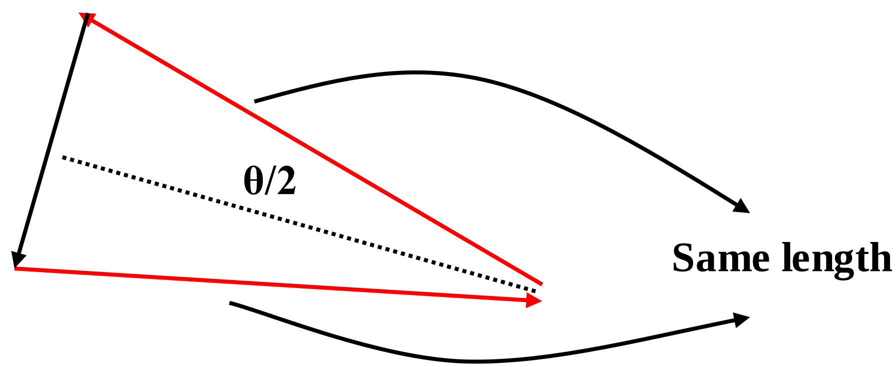
$$\boldsymbol{s} = \frac{\hat{\boldsymbol{S}} - \hat{\boldsymbol{S}}_0}{l}$$ Called the scattering <u>vector</u>



$$\boldsymbol{s} = \frac{\hat{\boldsymbol{S}} - \hat{\boldsymbol{S}}_0}{\lambda}$$



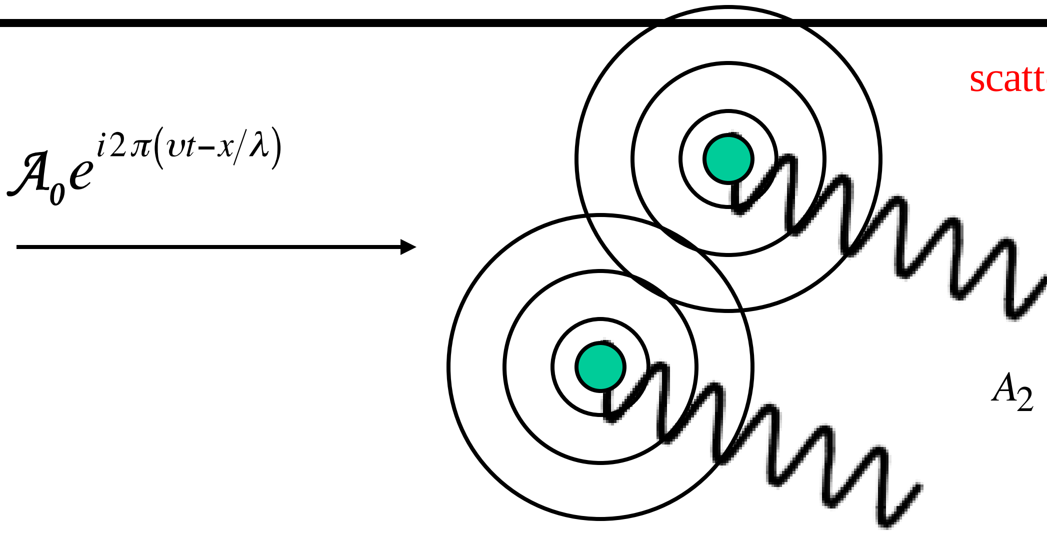
$$|\mathbf{s}| = s = \frac{|\hat{\mathbf{S}} - \hat{\mathbf{S}}_0|}{\lambda} = \frac{2\sin\theta/2}{\lambda}$$



SAXS
$$\left\{\begin{array}{l} \boldsymbol{q} = 2\pi\boldsymbol{s} \quad \text{Also called the scattering } \underline{\text{vector}} \\ q = 2ps = \dfrac{4p}{l}\sin\dfrac{q}{2} \end{array}\right.$$

Combine the two waves

$$\mathcal{A}_0 e^{i2\pi(\upsilon t - x/\lambda)}$$



scattering power, *b*, of an atom has the units of length

$$A_2 = \frac{b}{R}\mathcal{A}_0\, e^{i2\pi(\upsilon t - x/\lambda) - \overbrace{2\pi s\cdot r}^{\Delta\varphi}}$$

$$A_1 = \frac{b}{R}\mathcal{A}_0\, e^{i2\pi(\upsilon t - x/\lambda)}$$

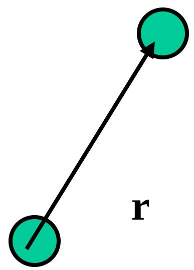
Total Scattered Wave

$$\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2 = \frac{b}{R}\mathcal{A}_0 e^{i2\pi(\upsilon t - x/\lambda)} + \frac{b}{R}\mathcal{A}_0 e^{i2\pi(\upsilon t - x/\lambda) - i2\pi s\cdot r}$$

$$= \frac{b}{R}\mathcal{A}_0 \underbrace{e^{i2\pi(\upsilon t - x/\lambda)}}_{\text{drops out}} \left(1 + e^{-i2\pi s\cdot r}\right)$$

$$J = \mathcal{A}\mathcal{A}^* = (b\mathcal{A}_0)^2 \left(1 + e^{-i2\pi s\cdot r}\right)\left(1 + e^{i2\pi s\cdot r}\right)$$

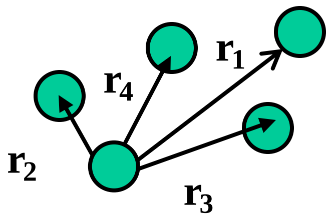
Adding up the Phases



$$\mathcal{A}(\mathbf{s},\mathbf{r}) = (b\mathcal{A}_0) \times \left(1 + e^{-i2\pi\mathbf{s}\cdot\mathbf{r}}\right)$$ Two electrons

x and t terms suppressed

$$\mathcal{A}(\mathbf{s},\mathbf{r}_{1....N}) = (b\mathcal{A}_0)\sum_{j=0}^{N} e^{-i2\pi\mathbf{s}\cdot\mathbf{r}_j}$$ Many electrons



$$\mathcal{A}(\mathbf{s},\mathbf{r}_{1....N}) = \mathcal{A}_0\int_V bn(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$\sum \rightarrow \int$

$\boldsymbol{q} = 2\pi \boldsymbol{s}$

$$= \mathcal{A}_0\int_V \rho(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$\rho(\boldsymbol{r}) = bn(\boldsymbol{r})$

Amplitude is the Fourier transform of the SLD distribution (almost)

Electron density distribution
$n(\boldsymbol{r})$ = number of atoms in a volume element $d\mathbf{r} = dx\,dy\,dz$ around point **r.**

$$\frac{atoms}{cm^3}$$

Scattering length density distribution
$\rho(\boldsymbol{r})$ = scattering length in a volume element $d\mathbf{r} = dx\,dy\,dz$ around point **r.**

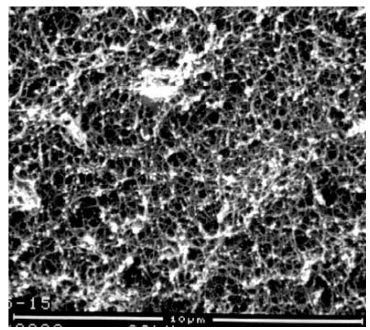
$$\frac{atoms}{cm^3}, \frac{cm}{atom} = cm^{-2}$$

Scattering Length Density (SLD) Distribution

Fourier transform of the scattering length density distribution

$$\frac{\mathcal{A}(\boldsymbol{q})}{\mathcal{A}_0} = \int \underbrace{b(\boldsymbol{r})n(\boldsymbol{r})}_{\rho(\boldsymbol{r})}\, e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \int \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

Can't be measured



$\rho(\boldsymbol{r})$

$$\boxed{I_{scatt}(\boldsymbol{q}) = \frac{J_\Omega(\boldsymbol{q})}{J_0} = \left|\mathcal{A}(\boldsymbol{q})\right|^2 = \left|\int \rho(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}\right|^2}$$

Can't be inverted

What we measure: Square of the Fourier transform of the SLD distribution

$$I_{scatt} = \int \Gamma_n(\mathrm{r})\, e^{-iqr} d\mathrm{r} \qquad \Gamma_n(r) = \int n(u)n(u+r)du$$

$$q \neq 0$$

See slide 43

Scattering from Spherical Particle(s)

$$\mathcal{A}_1(\boldsymbol{q}) = \frac{A(\boldsymbol{q})}{A_0} = \int \rho(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d\mathbf{r}$$

$$= \int_0^\infty \rho(r) 4\pi r^2 \frac{\sin qr}{qr} dr \qquad \textbf{B-50}$$

$$= \frac{\rho_0 4\pi}{q} \int_0^R r \sin(qr)\, dr$$

$$= \rho_0 4\pi R^3 \frac{(\sin qR - qR\cos qR)}{(qR)^3}$$

v = particle volume

$$= \rho_0 \overbrace{\frac{4\pi R^3}{3}}^{v} \frac{3(\sin qR - qR\cos qR)}{(qR)^3}$$

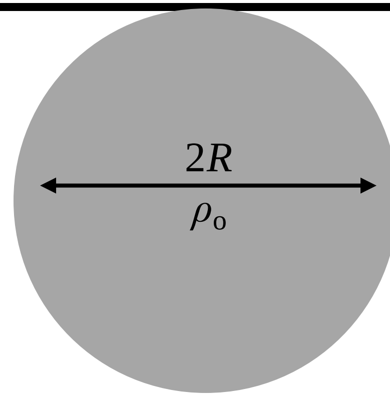
$$= \rho_0 v \frac{3(\sin qR - qR\cos qR)}{(qR)^3}$$

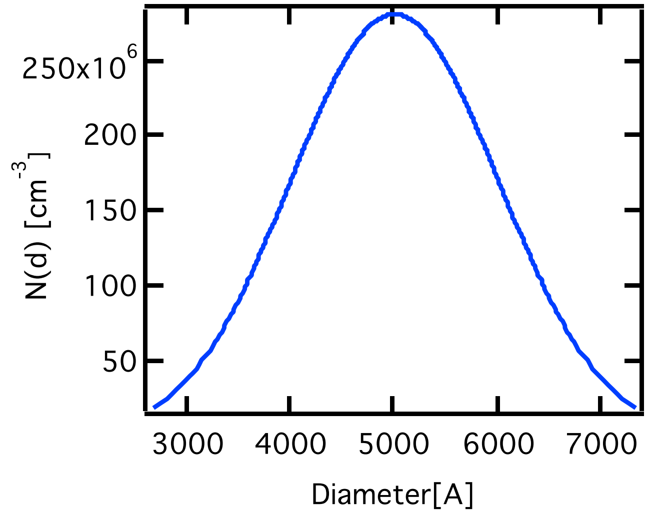
$$I_N(q) = N\rho_o^2 v^2 \left[\frac{3(\sin qR - qR\cos qR)}{(qR)^3}\right]^2$$

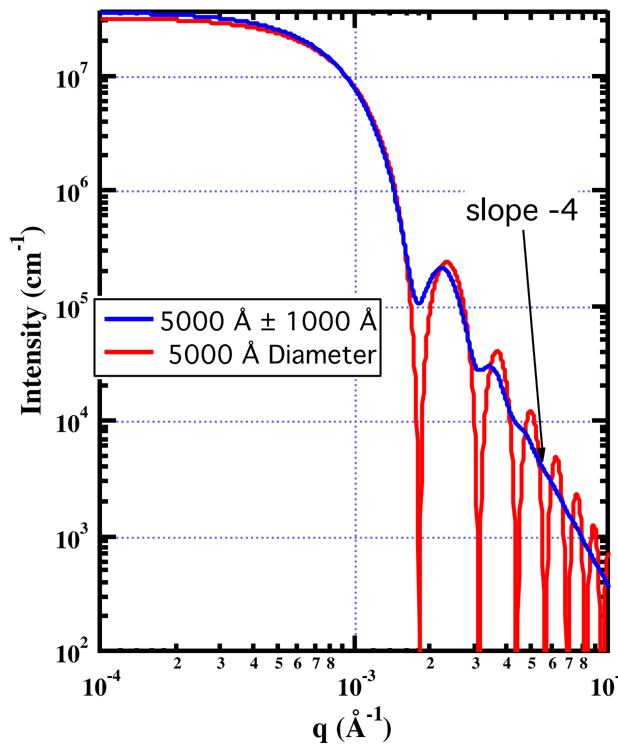
N particles

$I(q) \sim N(\rho - \rho_o)^2 v^2 P(q) \leftarrow$ Form Factor

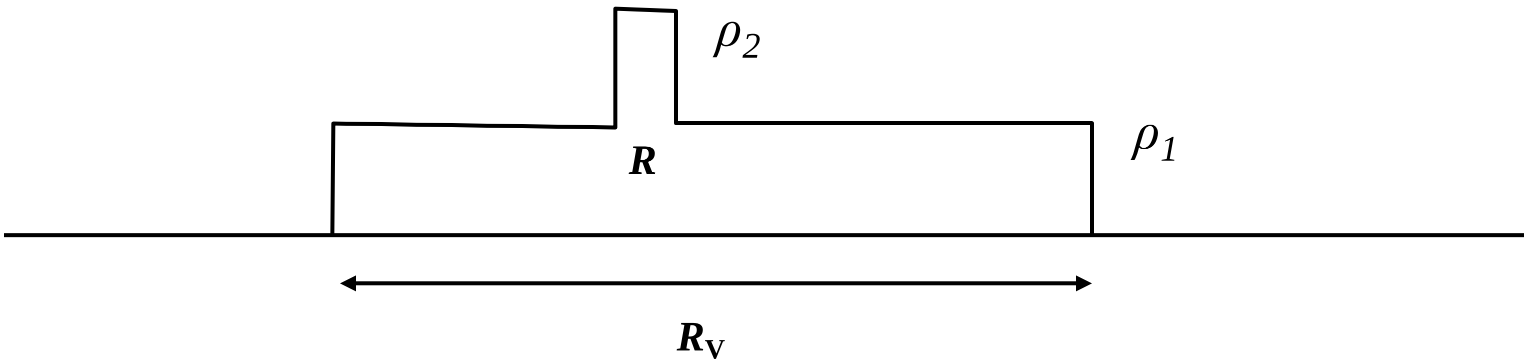
solvent SLD







Particle in Dilute Solution



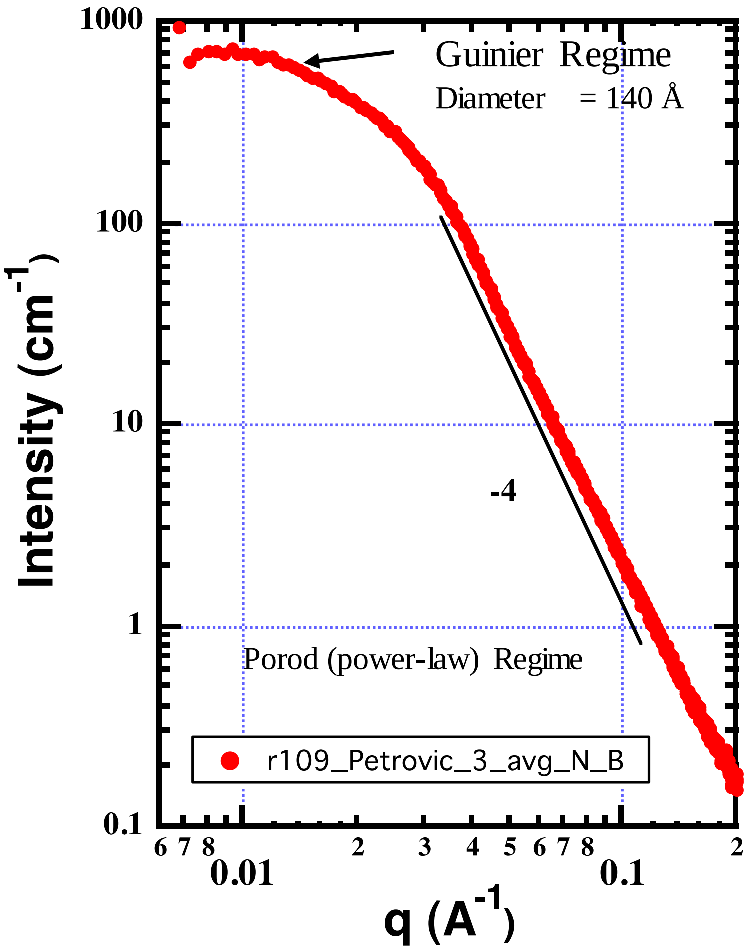
$$\mathcal{A}(q) = \frac{4\pi}{q}(\rho_2 - \rho_1)\int_0^R r\sin(qr)\,dr + \rho_1\int_0^{R_V} r\sin(qr)\,dr$$

$$= \underbrace{(\rho_2 - \rho_1)}_{\substack{\text{contrast}\\ \Delta\rho}}\, v\,\frac{3(\sin qR - qR\cos qR)}{(qR)^3} + \rho_1 V \cancel{\underbrace{\frac{3(\sin qR_V - qR_V\cos qR_V)}{(qR_V)^3}}_{=0 \text{ unless } qR\leq 1}}$$

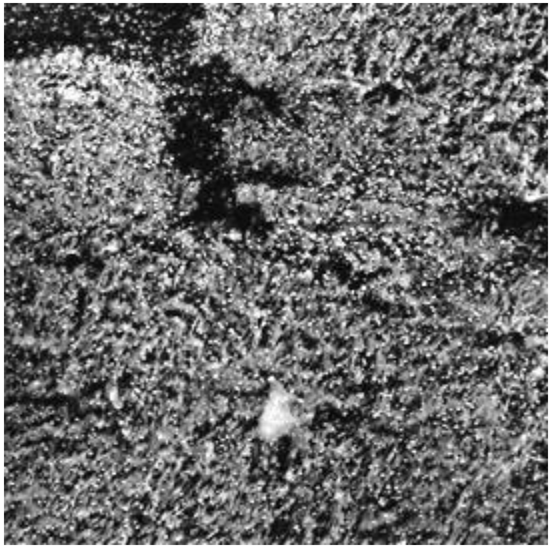
Small-Angle Scattering from Spheres

$$\sin\theta = \frac{\lambda}{2d} \xrightarrow{d>>\lambda} \theta$$

Large object scatter at small angles



Silica in Polyurethane



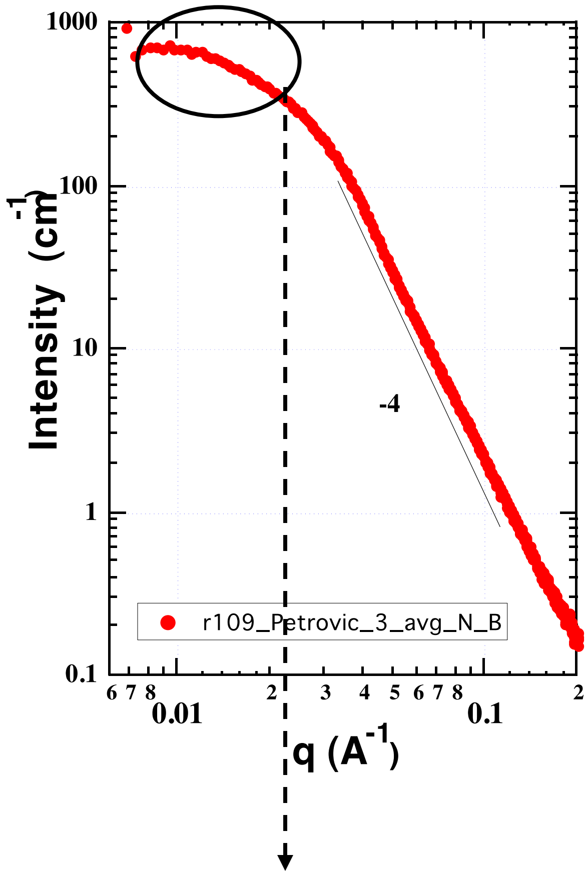
3 µm

AFM

Petrovic, Z. S. *et al.* Effect of silica nanoparticles on morphology of segmented polyurethanes. *Polymer* 45, 4285-4295, (2004)

Guinier Radius

Initial curvature is a measure of length



$\mathrm{R_g} \sim 1/q$

$$\mathcal{A}(q) = \frac{A(q)}{A_0} = \int \Delta\rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

Derived in 5.2.4.1

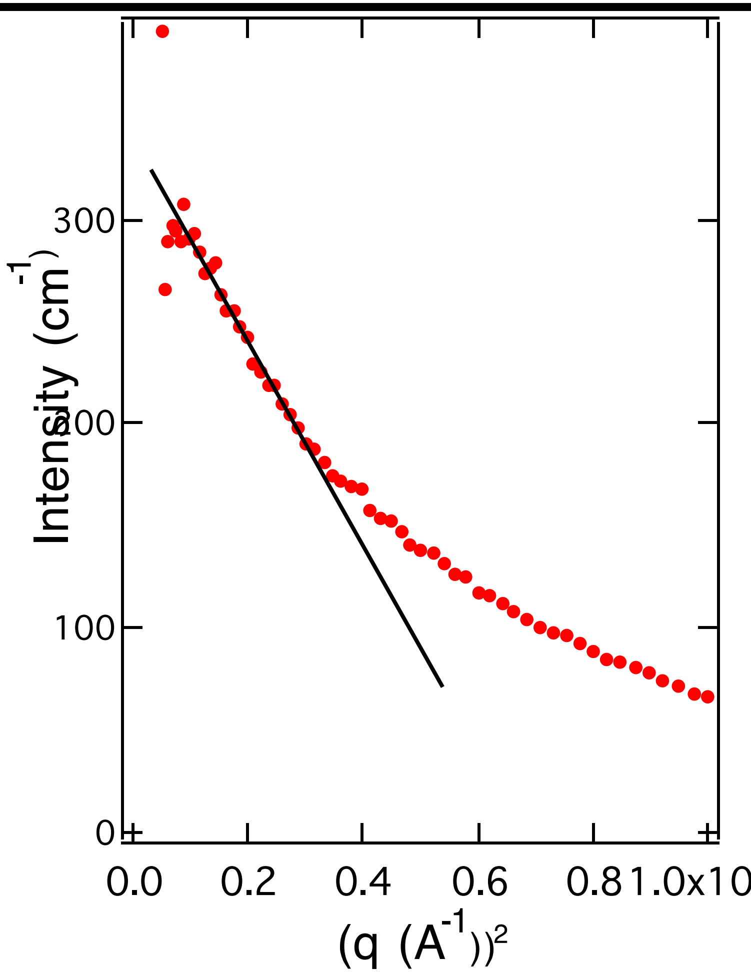
$$I(q) = \left|\mathcal{A}(q)\right|^2 = \Delta\rho^2 v^2 \left[1 - \frac{1}{3} q^2 R_g^2 + \cdots \right]$$

$$R_g^2 = \frac{1}{v} \int r^2 \sigma(\mathbf{r}) d\mathbf{r} \qquad \text{for any shape}$$

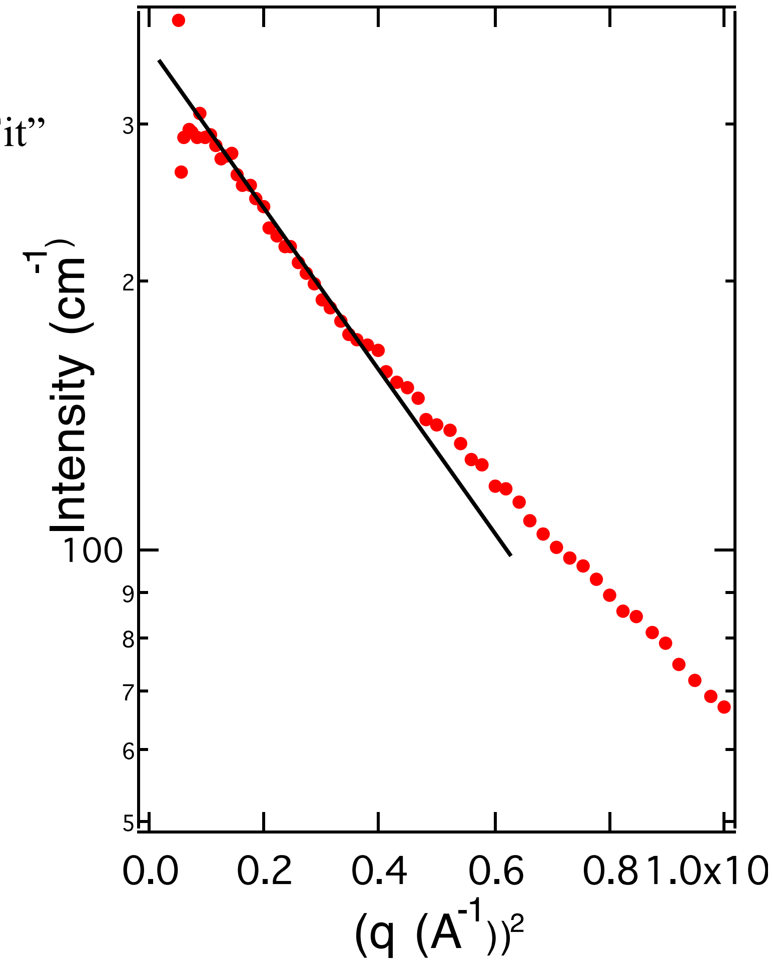
$$\sigma(r) = \left\{ \begin{array}{ll} 1 & r \le R \\ 0 & r > R \end{array} \right\} \text{sphere}$$

$$R_g = \sqrt{\frac{3}{5}} R_{hard}$$

Guinier Fits



Use
“Unified Fit”



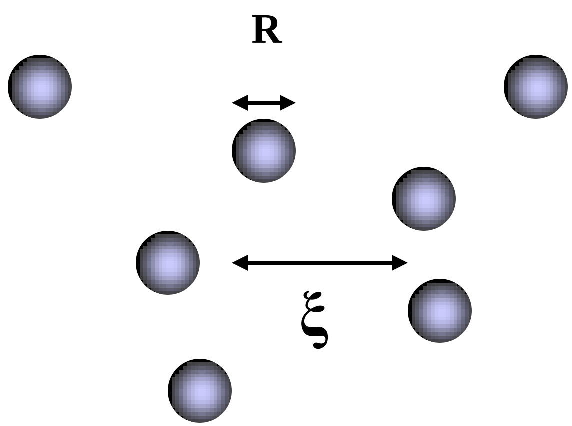
$$I(q) \sim \left[1 - \frac{1}{3}q^2R_G^2 + \cdots\right]$$

$$I(q) \sim \exp\left[-\frac{1}{3}q^2R_G^2 + \cdots\right]$$

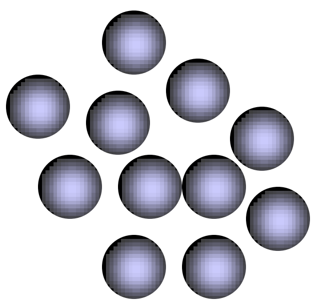
$$R_G \xrightarrow{dilute} R_g$$

Guinier radius   Radius-of-Gyration

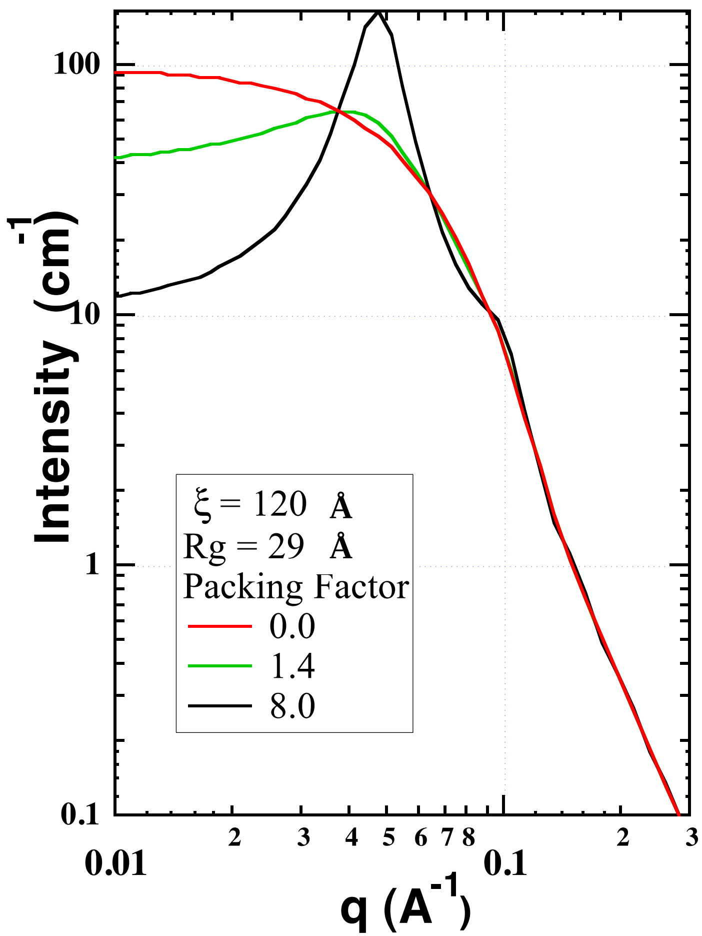
Dense packing: Correlated Particles



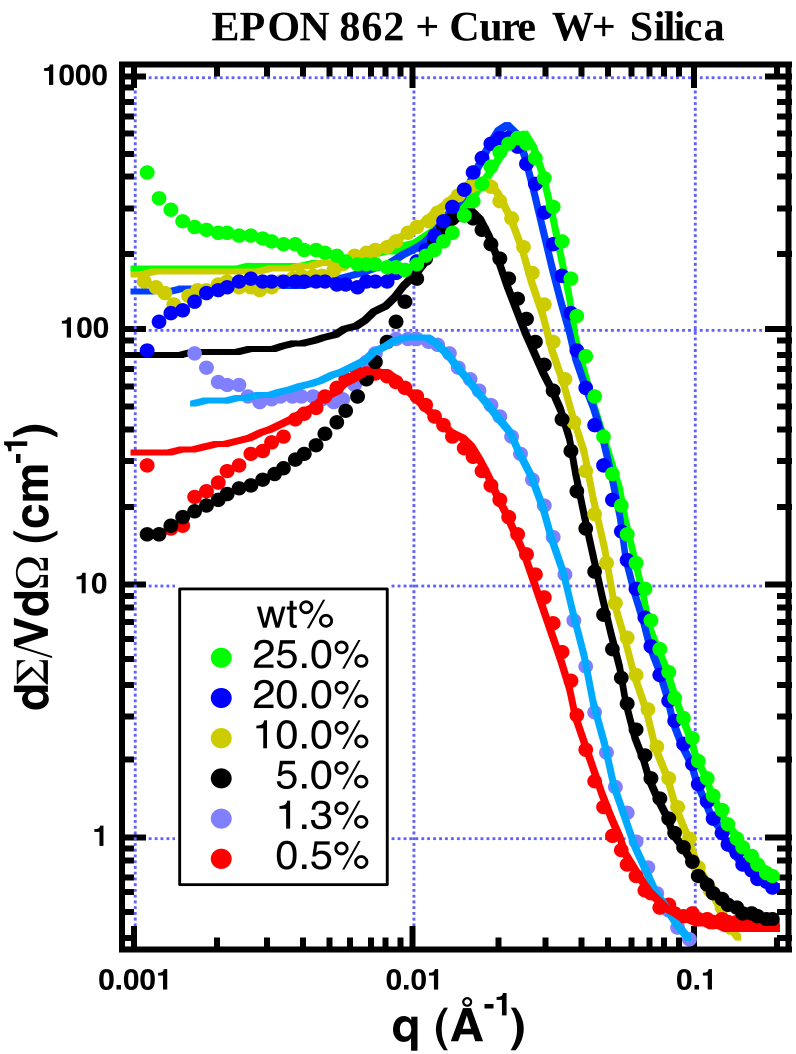
Packing Factor = k = 8 ϕ

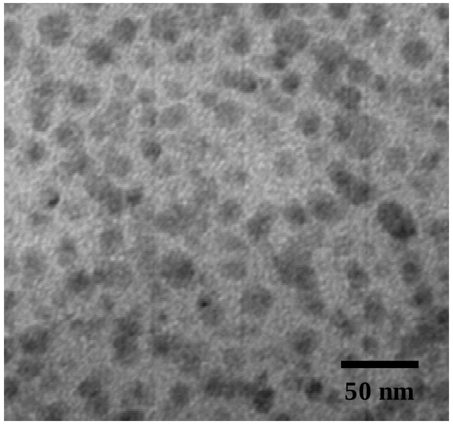


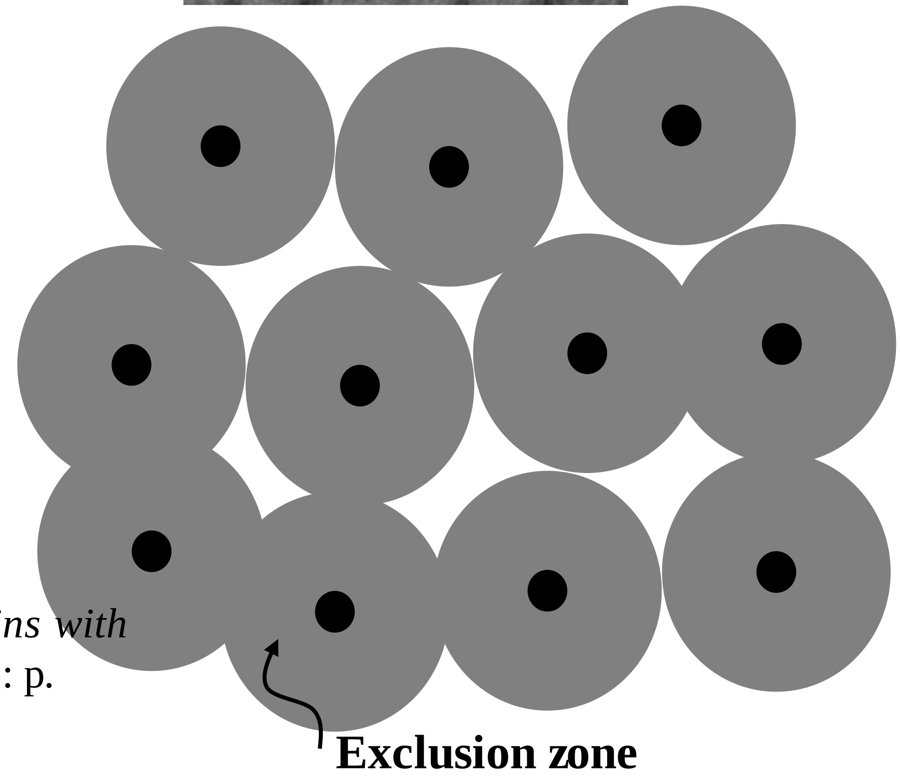
Packing Factor ≅ 6



Colloidal Silica in Epoxy



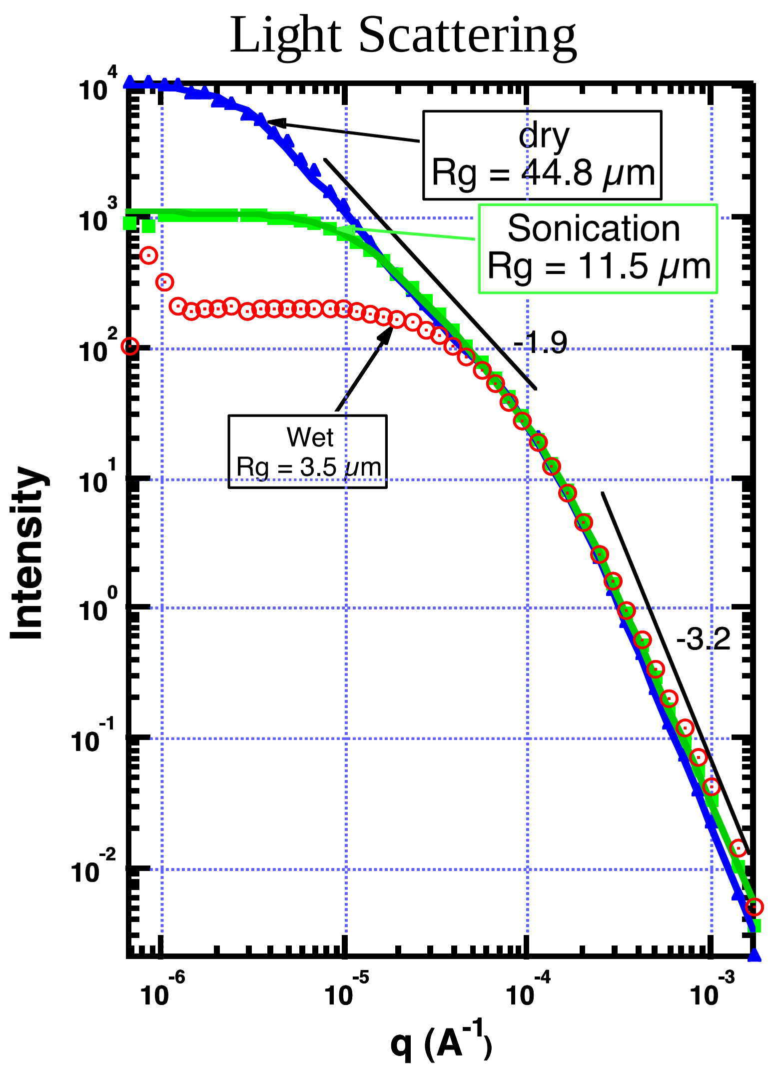


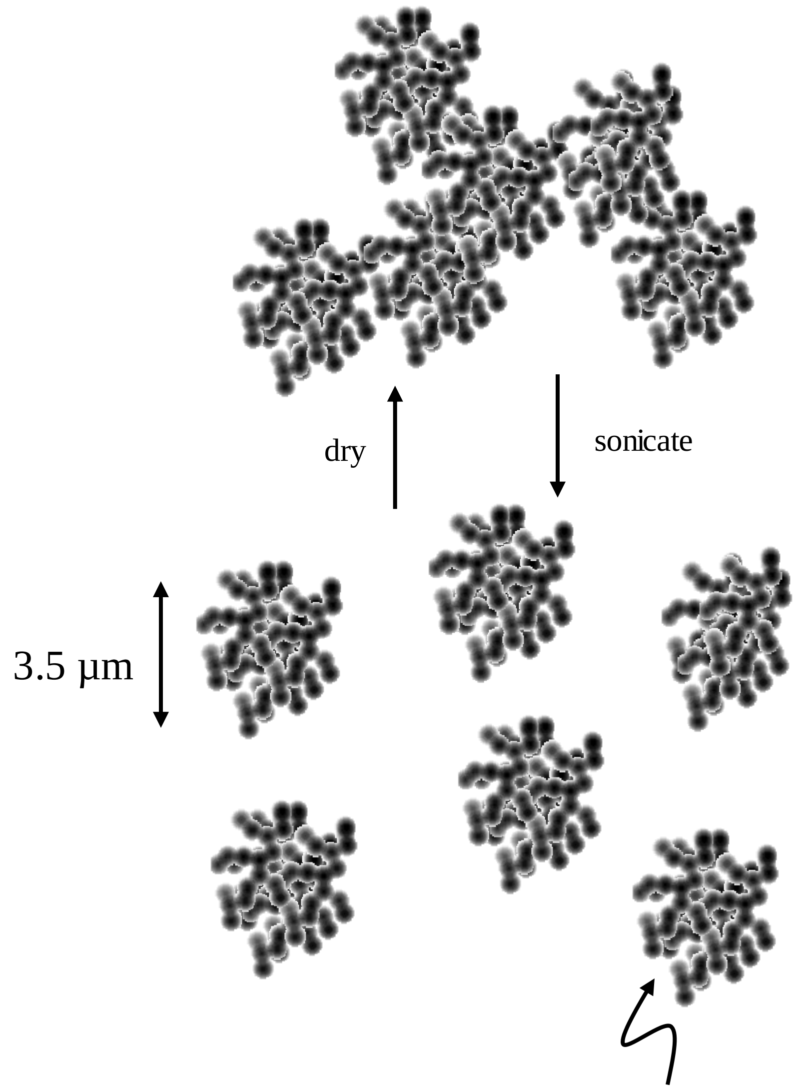


Chen, R.S. et al, *Highly dispersed nanosilica-epoxy resins with enhanced mechanical properties* Polymer, 2008. 49(17): p. 3805-3815.

University of Cincinnati

Using R_G: Agglomerate Dispersion





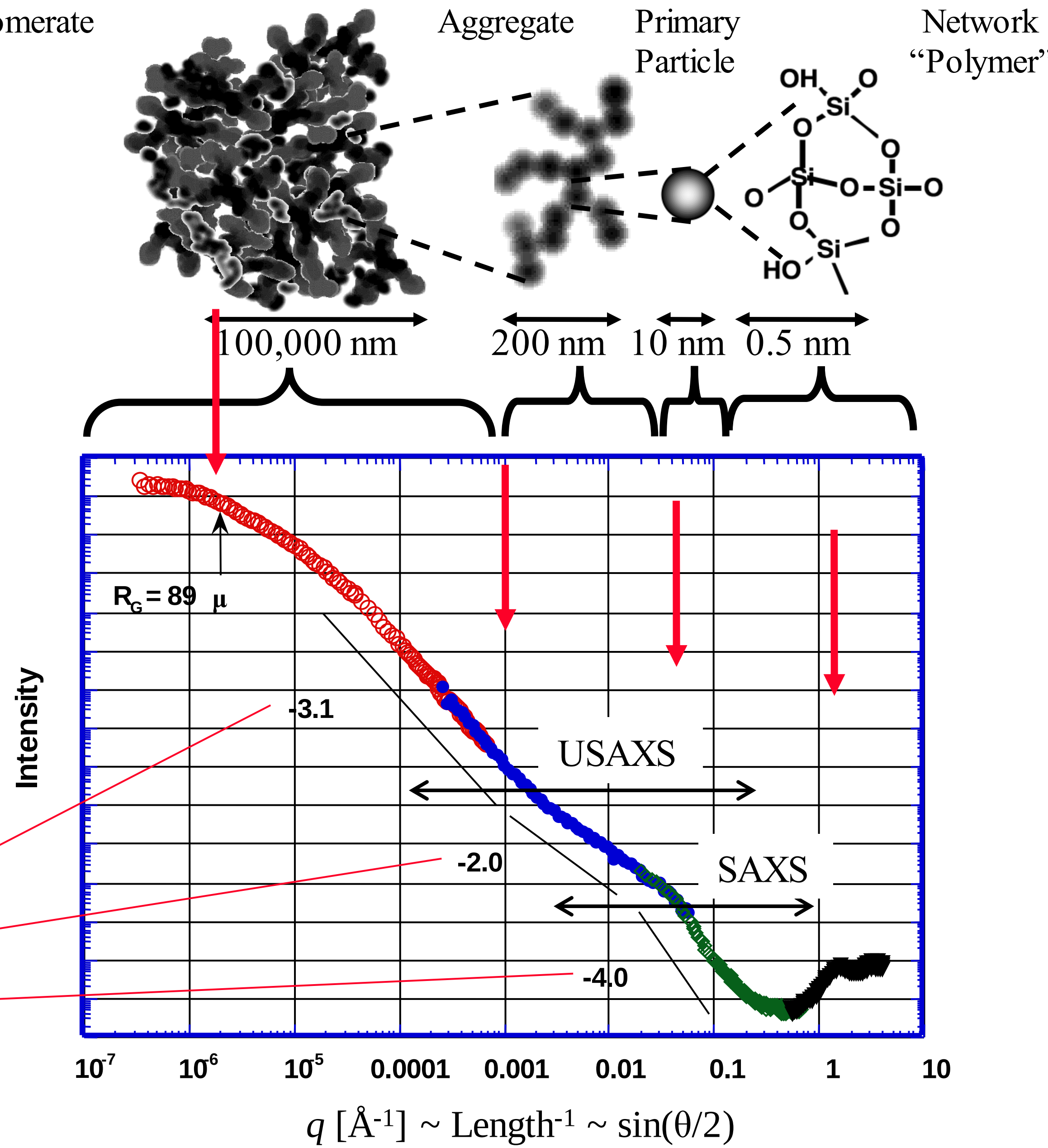
D.W. Schaefer, D. Kohls and E. Feinblum, *Morphology of Highly Dispersing Precipitated Silica: Impact of Drying and Sonication*. J Inorg Organomet Polym, 2012. 22(3): p. 617-623.)

Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

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

Exponents related to morphology

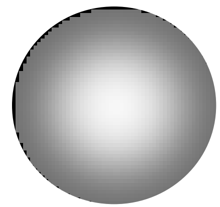


Fractal description of disordered objects

Real Space

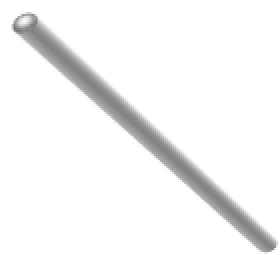
$\boxed{M \sim R^d}$

$M \sim V \sim R^3$

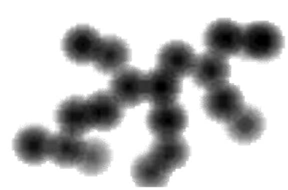


$M \sim V \sim R^2$

$M \sim V \sim R^1$



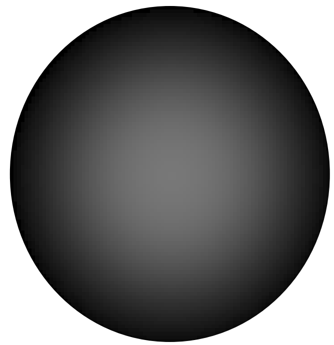
$M \sim V \sim R^{2.2}$



Mass Fractal Dimension = d

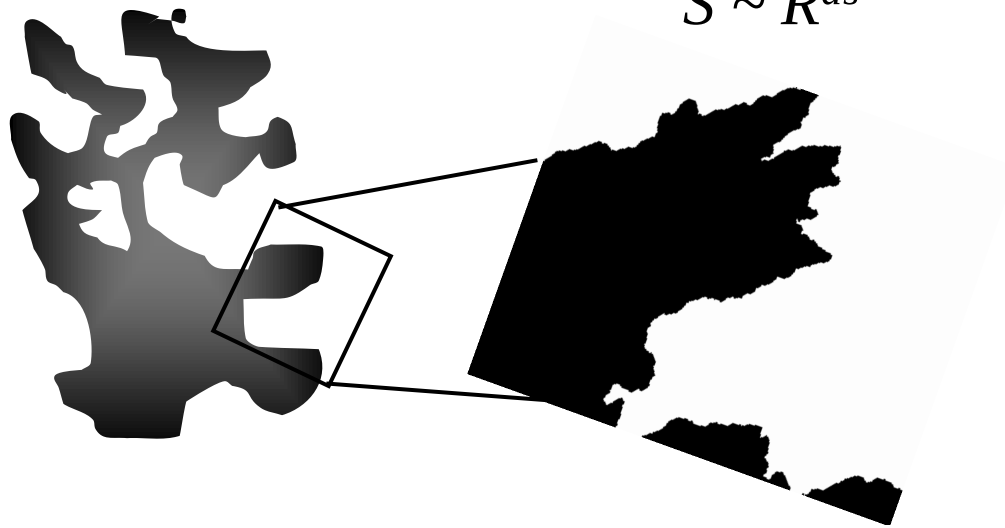
Surface Fractal Dimension

Sharp interface



$S \sim R^2$

$S \sim R^{ds}$



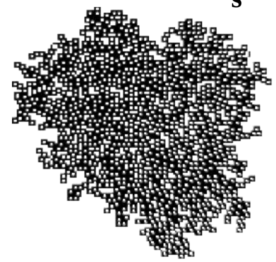
fractal or self-affine surface

Scattering from Fractal Objects: Porod Slopes

d = Mass Fractal Dimension

$M \sim v \sim R^3$ solid particle

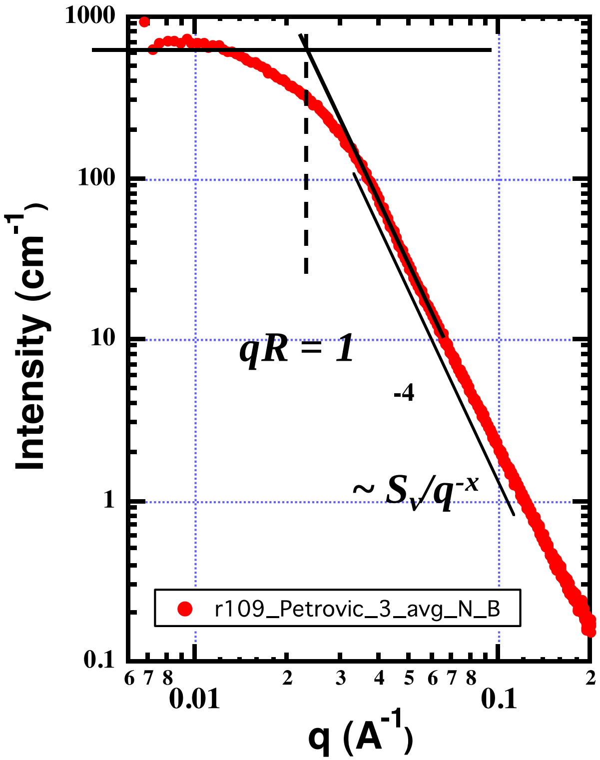
$M \sim v \sim Nv_u \sim R^d v_u$ mass fractal



d_s = Surface Fractal Dimension

$S = R^2$ solid particle

$S \sim R^{d_s}$ surface fractal



Small q

$$I(q=0) \sim v^2 \sim (Nv_u)^2 \sim R^{2d}$$

Large q

$$I_P(qR >> 1) \approx \left(\frac{S_v}{q^x}\right) \sim \frac{R^{d_s}}{q^x} \sim \frac{R^{d_s+x}}{(qR)^x}$$

Match at $qR = 1$

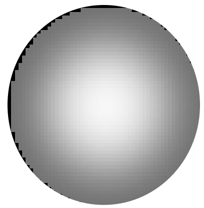
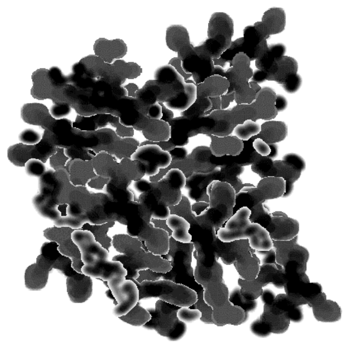
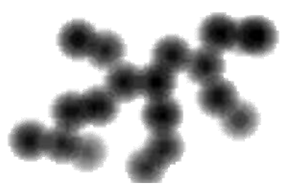
$$R^{d_s+x} \sim R^{2d}$$

$$x = 2d - d_s$$

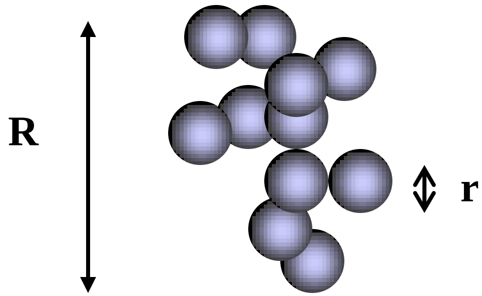
$$\boxed{I(q) \sim q^{-(2d-d_s)}}$$

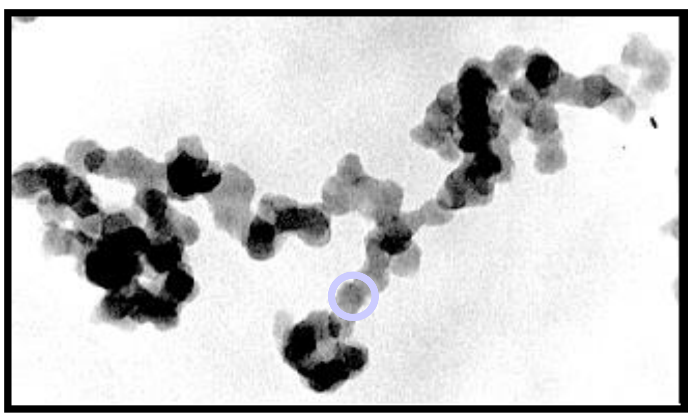
Porod Slope for Fractals

$$I(q)=q^{d_s-2d_m}$$

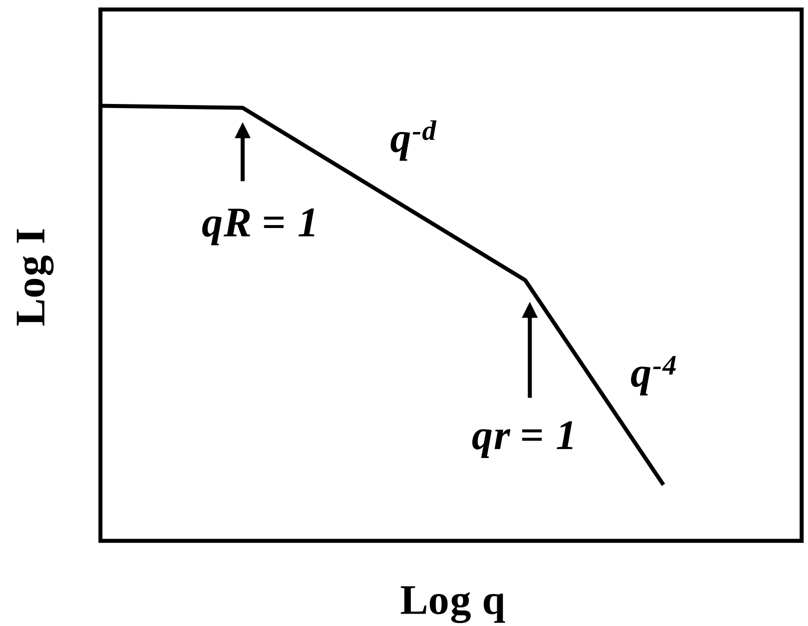
	Structure	Scaling Relation	Porod Slope $= d_s - 2d_m$ $qR >> 1$
Smooth Surface		$d_m = 3$ $d_S = 2$	- 4
Rough Surface		$d_m = 3$ $2 < d_S \leq 3$	$-3 \leq$ Slope ≤ -4
Mass Fractal		$1 \leq d_s = d_m \leq 3$	$-1 \leq$ Slope ≤ -3

Scattering from colloidal aggregates



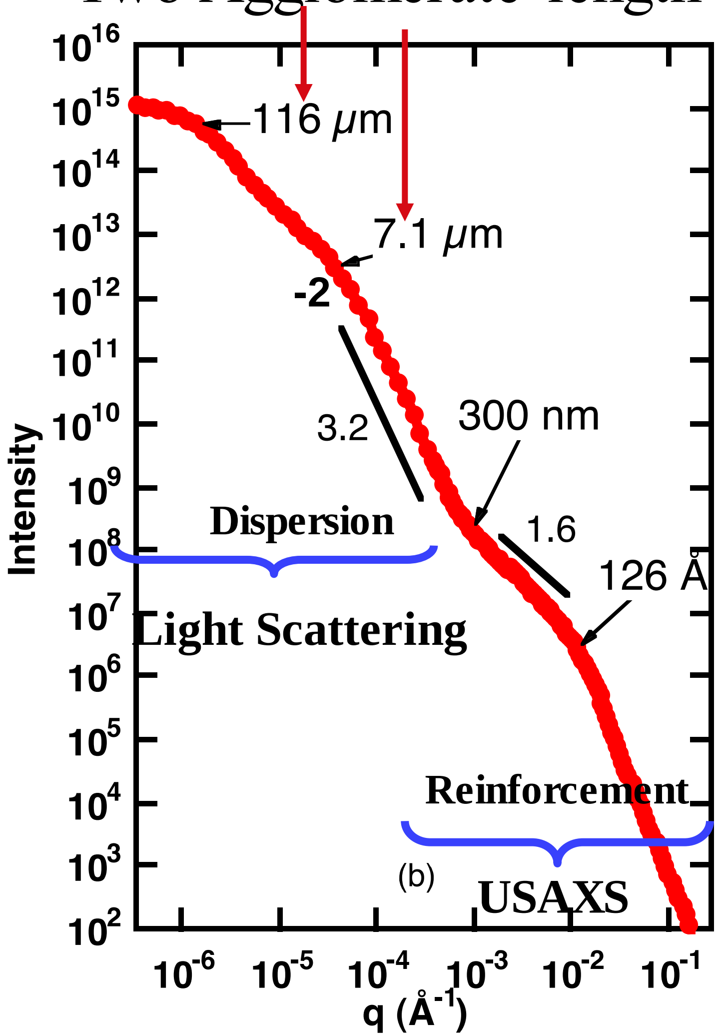


Precipitated Silica



Morphology of Dimosil® Tire-Tread Silica

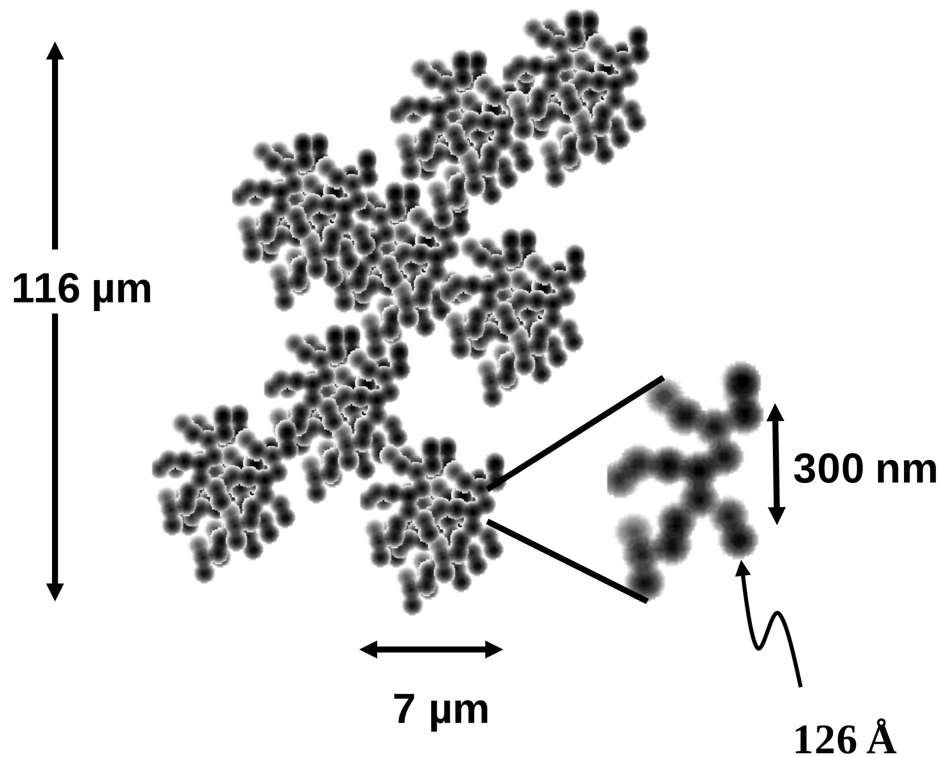
Two Agglomerate length Scales



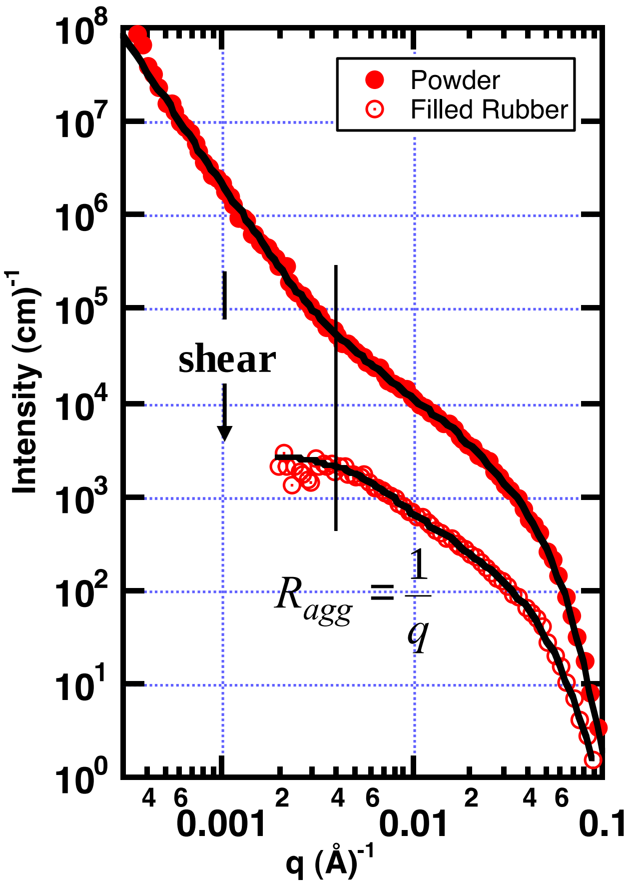
Soft = Chemically Bonded

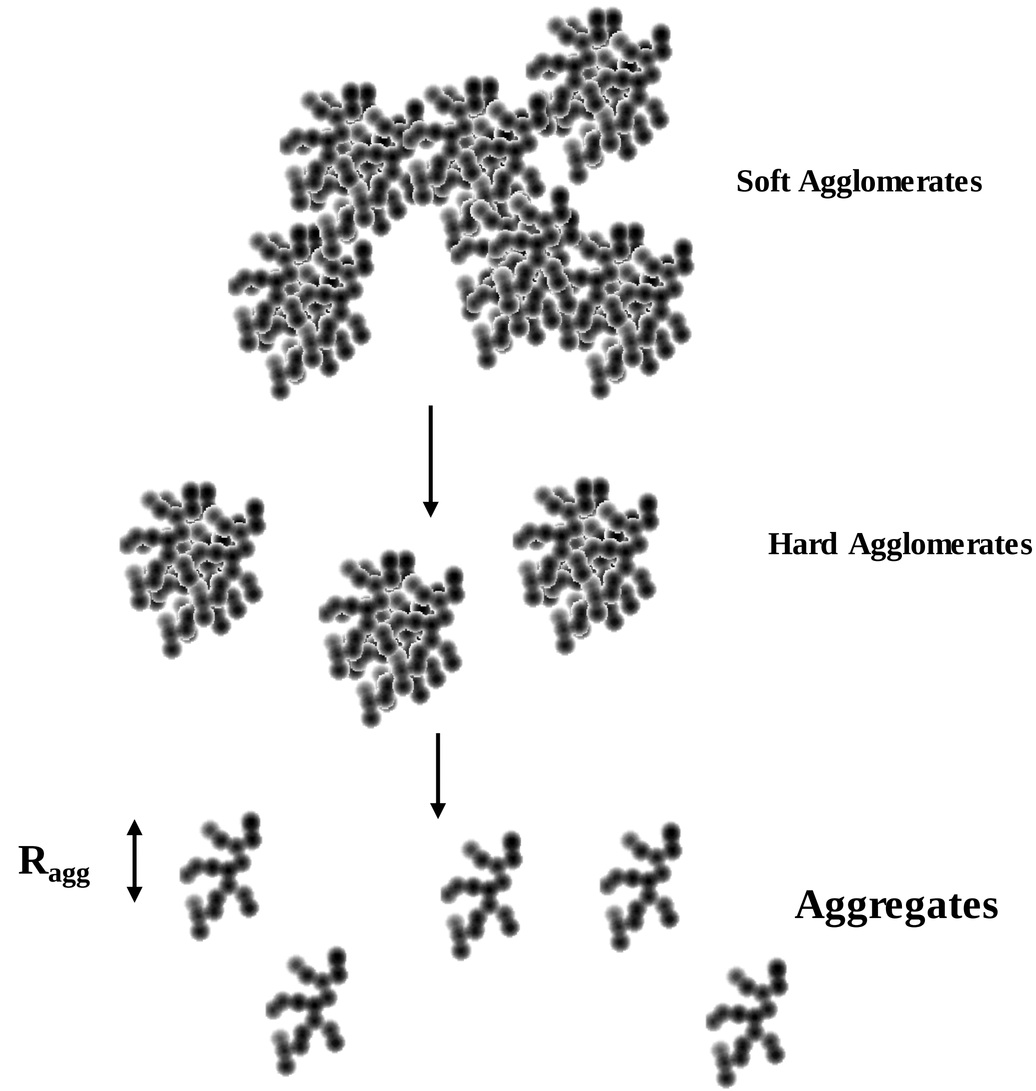
Hard = Physically Bonded

-4



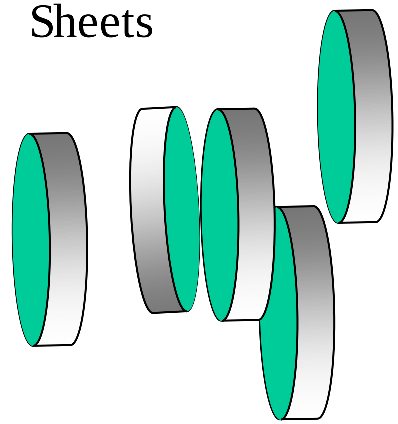
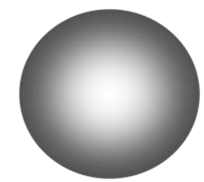
Aggregates are robust





What is the ideal aggregate size?

Exploring the Nanoworld

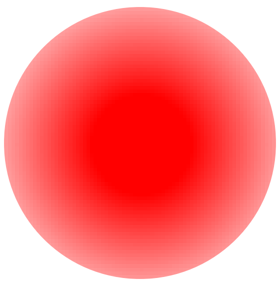
1-d	*2-d*	*3-d*
Tubes	Sheets	Spheres
		
Carbon Nanotubes	Layered Silicates	Colloidal Silica

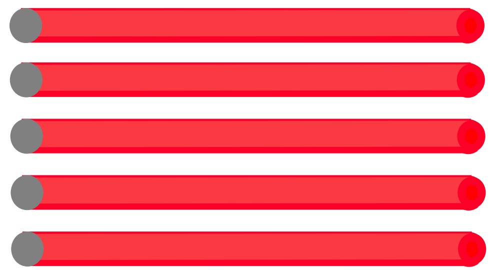
How valid are the cartoons?
What are the implications of morphology for material properties?

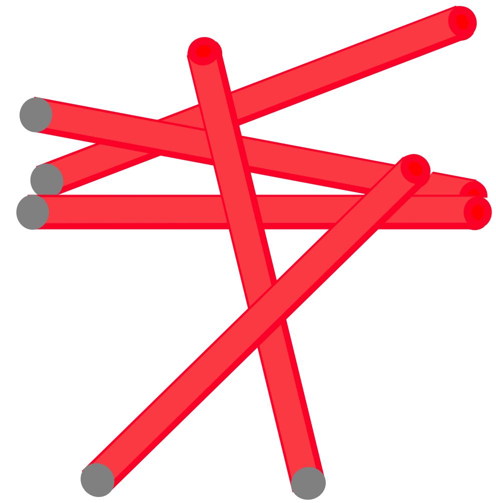
Answers come from Small-Angle Scattering.

Schaefer, D.W. and R.S. Justice, *How nano are nanocomposites?* Macromolecules, 2007. 40(24): p. 8501-8517.

The Promise of Nanotube Reinforcement







$$E_\delta = \frac{E_{\text{composite}}}{E_{\text{matrix}}}$$

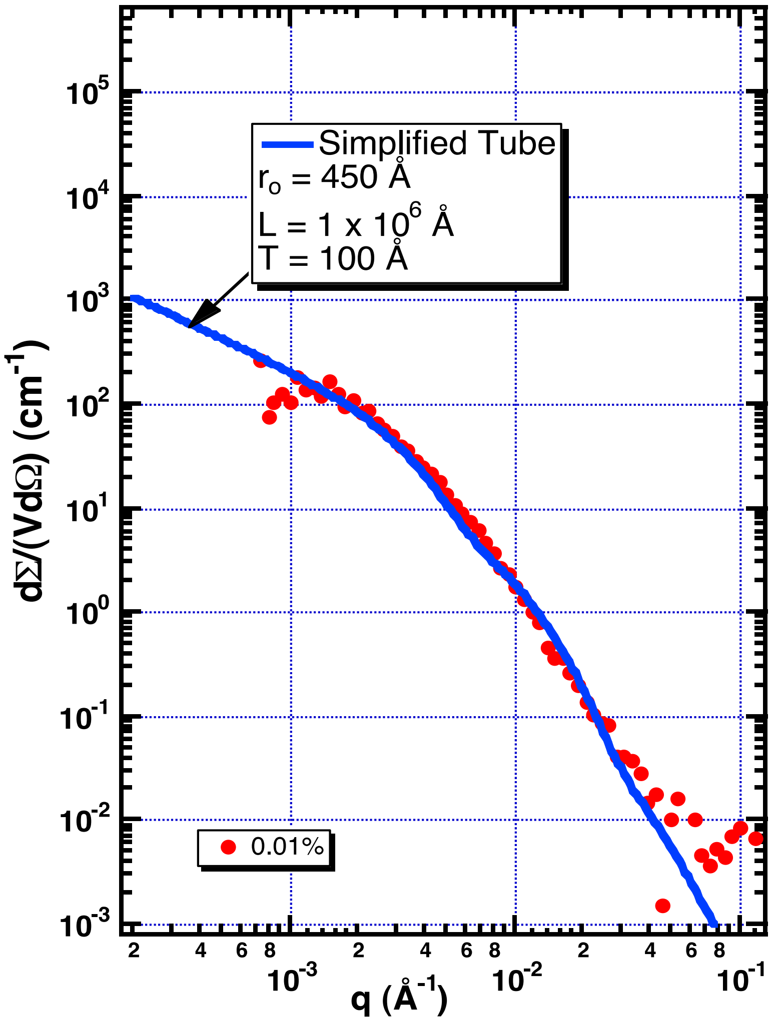
$E_\delta = 1 + 2.5\phi$

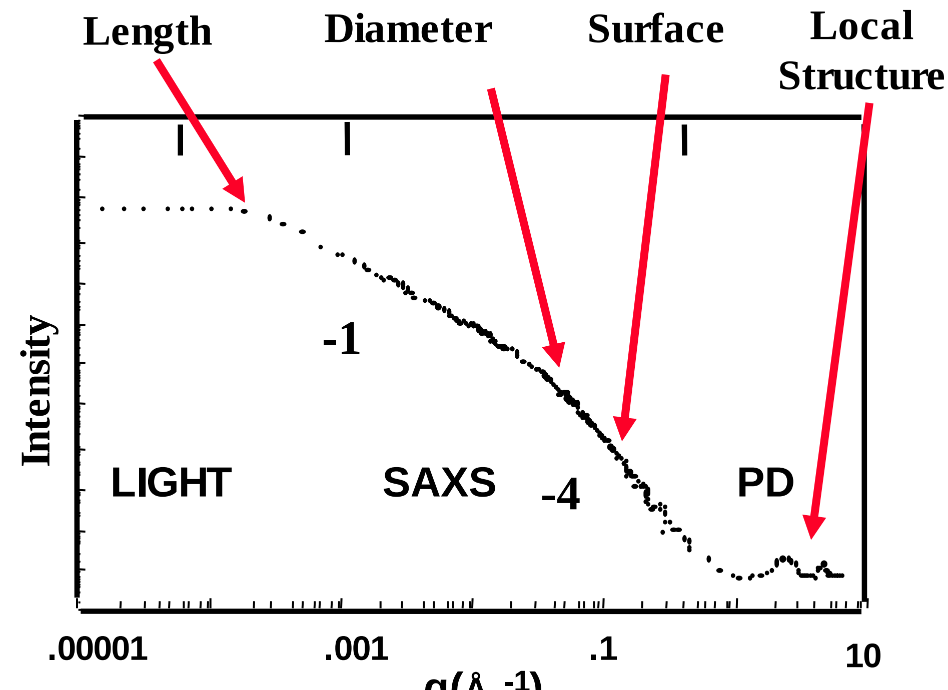
$= 1 + 2\alpha\phi \cong 1 + 2000\phi$

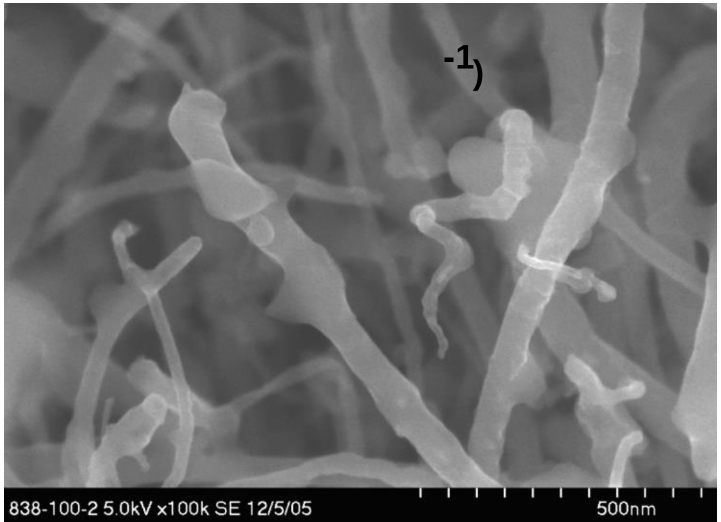
$= 1 + \underline{0.4\alpha\phi} \cong 1 + 400\phi$

α = aspect ratio

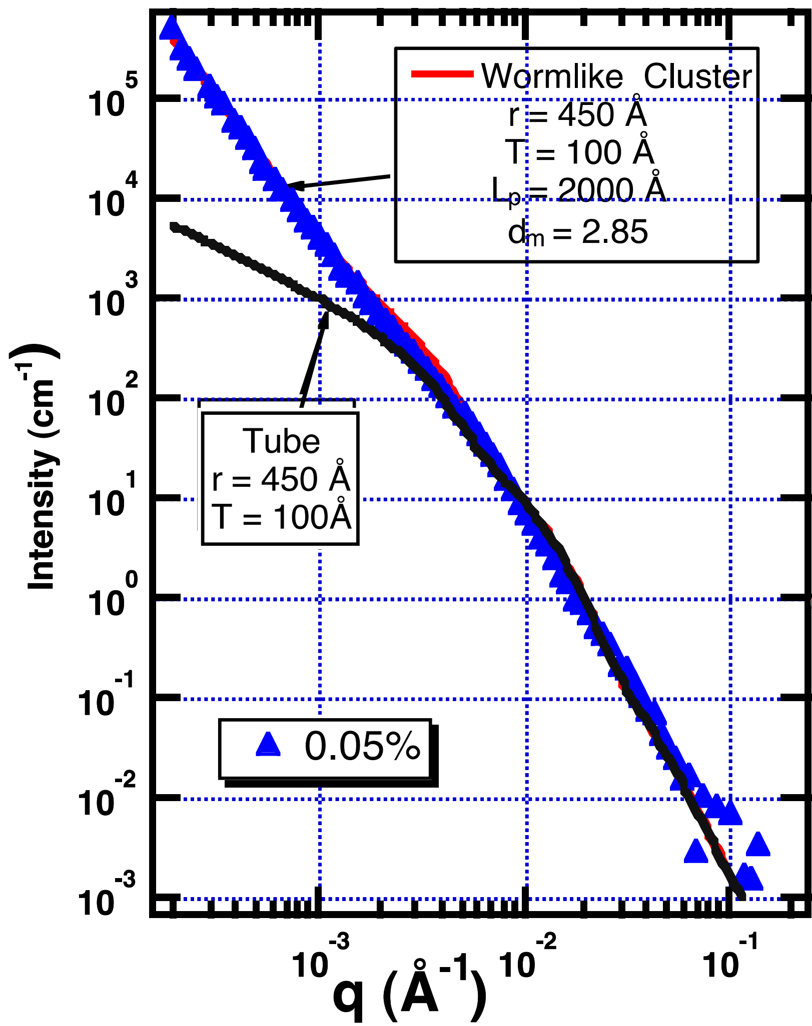
0.01% Loading CNTs in Bismaleimide Resin



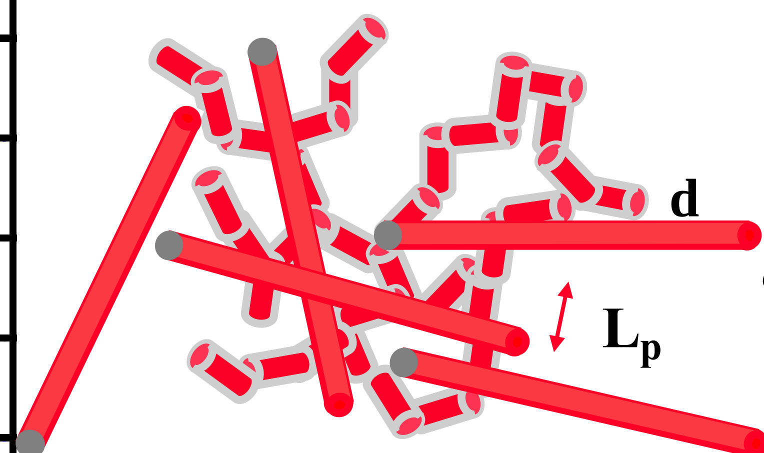




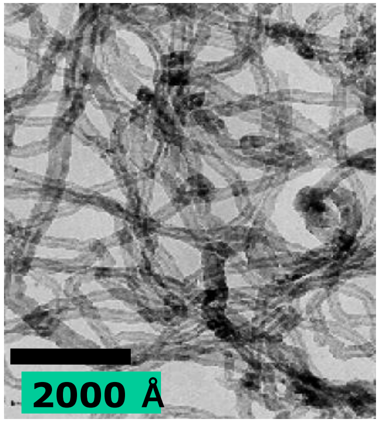
0.05% Carbon in Bismaleimide Resin



Worm-like branched cluster

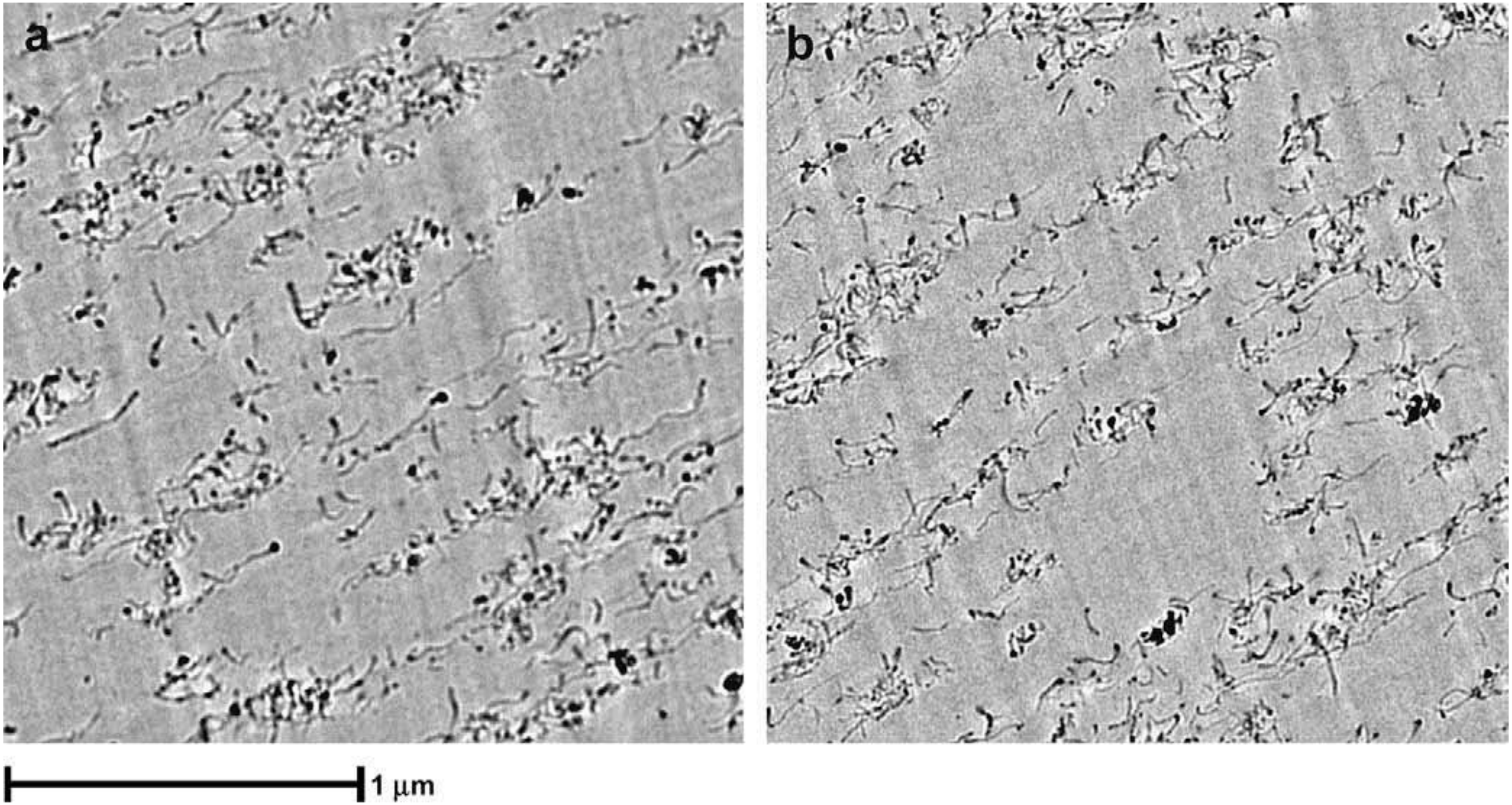


$$\alpha = \frac{L_p}{r} = 4.5$$



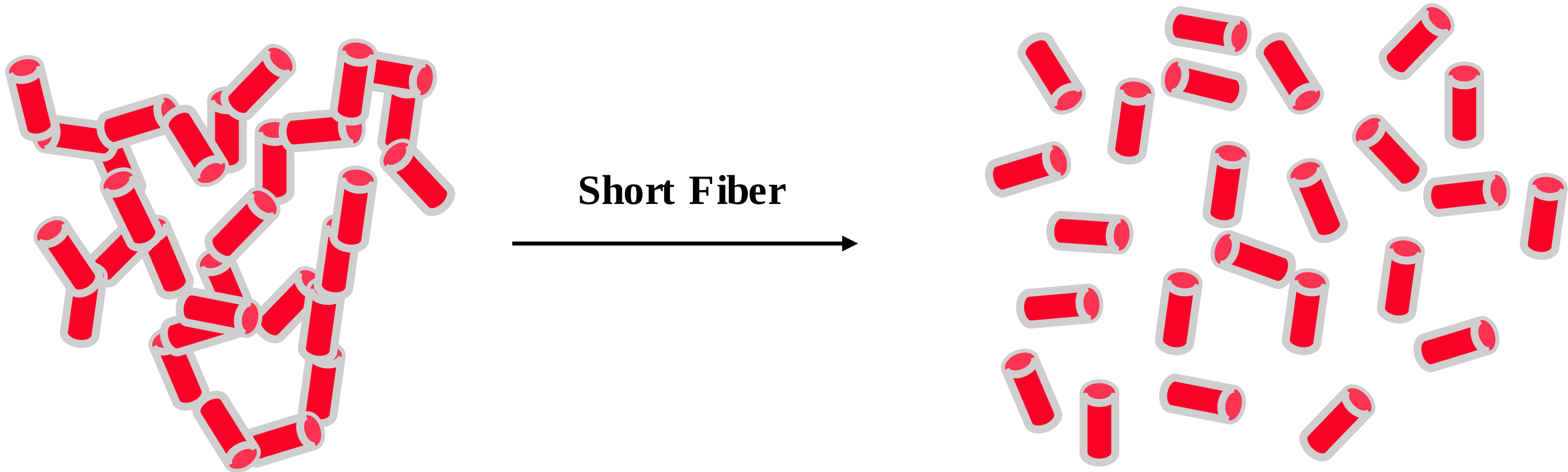
TEM of Nanocomposites

Hyperion MWNT in Polycarbonate



Pegel et al. Polymer (2009) vol. 50 (9) pp. 2123-2132

Morphology and Mechanical Properties



Halpin-Tsai, random, short, rigid fiber limit

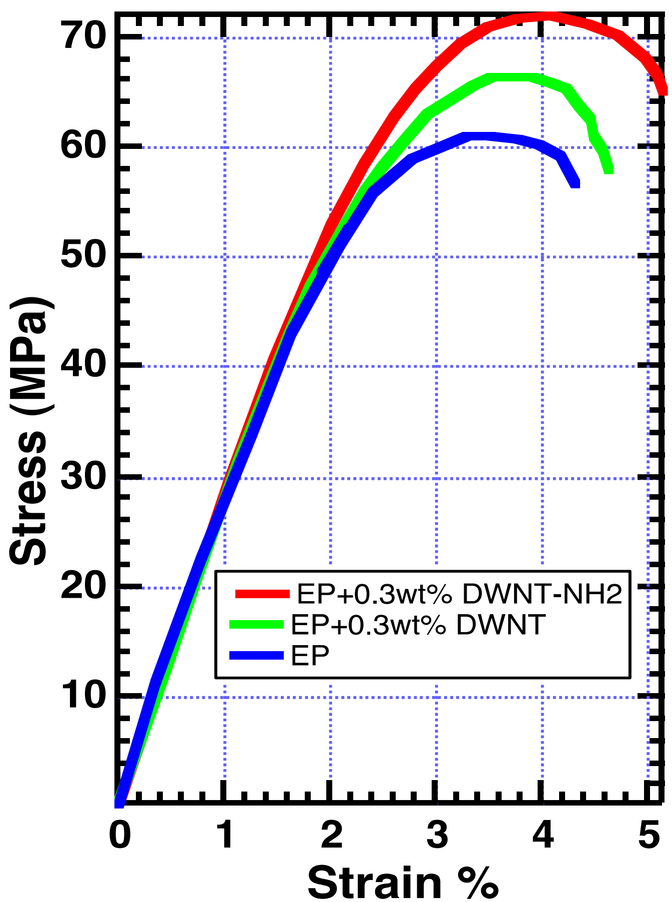
$$E_d = \frac{E_c}{E_m} = 1 + 0.4af \qquad a = 4.5$$

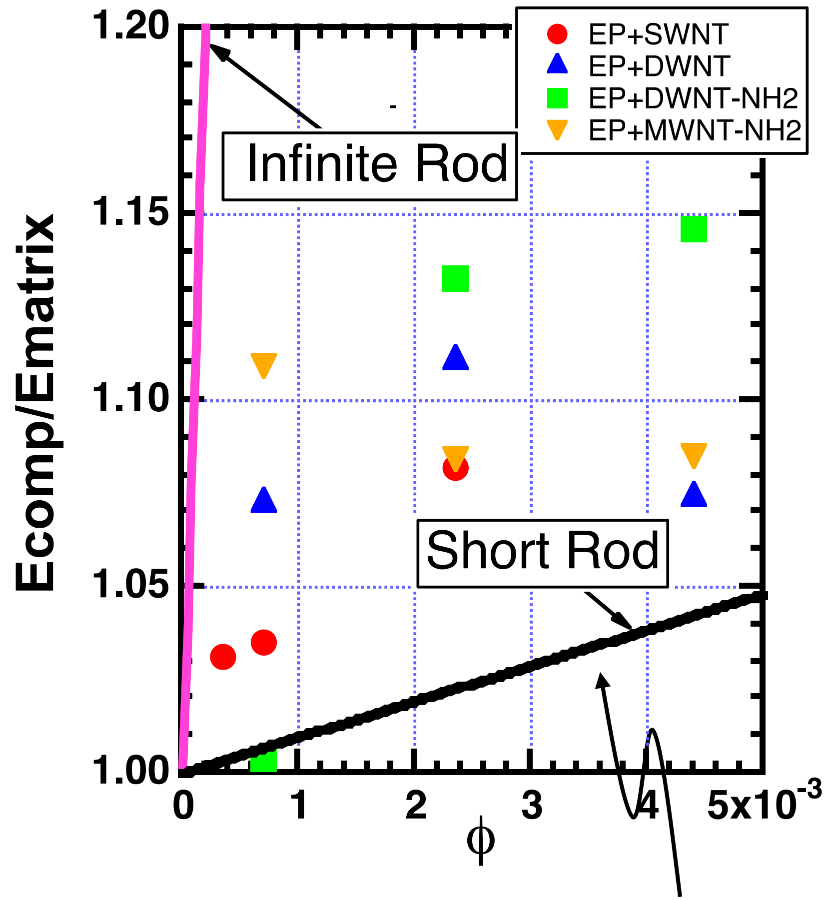
$$\cong 1 + 2f$$

No better than spheres

Schaefer, D.W. and R.S. Justice, *How nano are nanocomposites?* Macromolecules, 2007. 40(24): p. 8501-8517.

CNTs in Epoxy



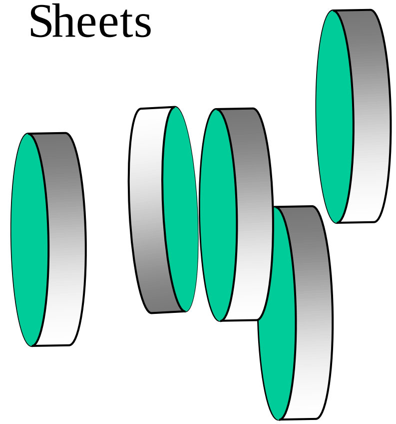


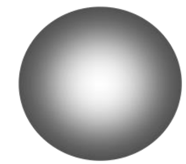
Assumes no connectivity
$\alpha = 4.5$

Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Comp. Sci. & Tech*. 2005, 65, (15-16), 2300-2313.

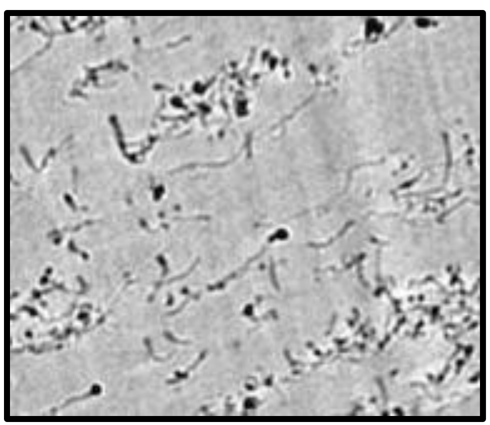
Don't Believe the Cartoons

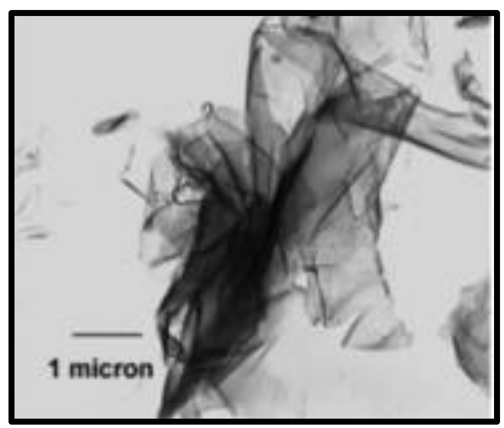
1-d	*2-d*	*3-d*
Tubes	Sheets	Spheres

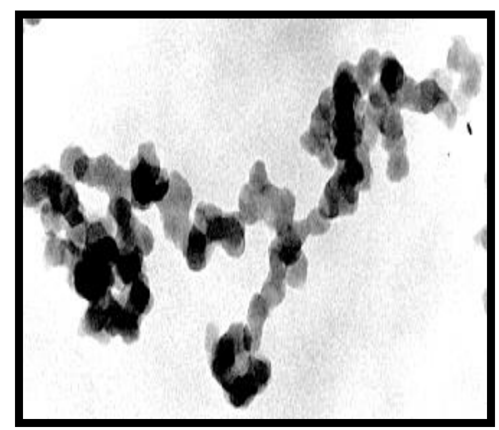




Carbon Nanotubes	Layered Silicates	Colloidal Silica







Schaefer, D.W. and R.S. Justice, *How nano are nanocomposites?* Macromolecules, 2007. 40(24): p. 8501-8517.

Conclusion

If you want to determine the morphology of a disordered material

use small-angle scattering.

Extras

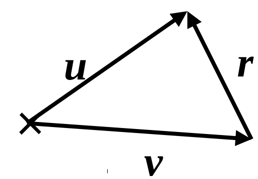
Correlation Functions

depends on absolute position of atoms

Ensemble Average < >

$$I(\boldsymbol{q}) = \left\langle \left| \mathcal{A}(\boldsymbol{q}) \right| \right\rangle^2 = \left\langle \left| \int \rho(\boldsymbol{r})\, e^{-i\mathrm{q}\cdot\mathrm{r}}\, d\boldsymbol{r} \right|^2 \right\rangle$$

$$= \left\langle \left[\int \rho(\boldsymbol{u})\, e^{-i\mathrm{q}\cdot\mathrm{u}}\, d\boldsymbol{u} \right] \left[\int \rho(\boldsymbol{v})\, e^{i\mathrm{q}\cdot\mathrm{v}}\, d\boldsymbol{v} \right] \right\rangle$$



$$\boldsymbol{r} = \boldsymbol{u} - \boldsymbol{v}$$

new **r** is independent of origin

problem

$$= \int_{volume} \left\langle \left[\int \rho(\boldsymbol{u})\rho(\boldsymbol{u}+\boldsymbol{r})\, d\boldsymbol{u} \right] \right\rangle e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, d\boldsymbol{r}$$

depends on relative position of atoms

$$I(\boldsymbol{q}) \equiv \int \Gamma_{\Delta\rho}(\boldsymbol{r})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, d\boldsymbol{r} \qquad \Gamma_{\Delta\rho}(\boldsymbol{r}) = \left\langle \int_{\infty} \Delta\rho(\boldsymbol{u})\Delta\rho(\boldsymbol{u}+\boldsymbol{r})\, d\mathbf{u} \right\rangle \qquad \Delta\rho = \rho - \langle \rho \rangle$$

$\Gamma_{\Delta\rho}(\boldsymbol{r})$ is the autocorrelation function of the fluctuation of scattering length density = Patterson function

Scattering cross section is the Fourier transform of the ensemble average of the correlation function of the fluctuation of scattering length density.

Not really a Fourier Transform

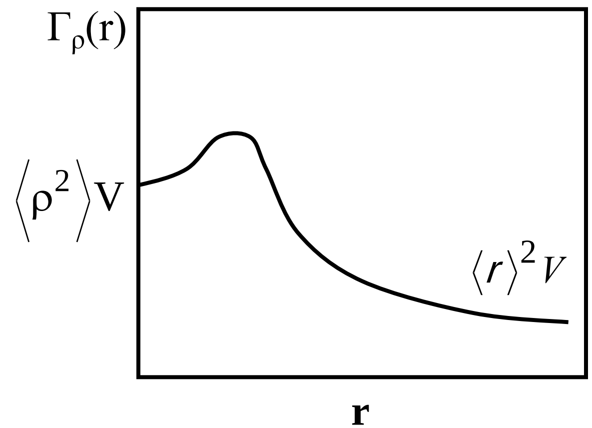
Problem!
Must know sample geometry

$$I(\mathrm{q}) = \int_V \Gamma_\rho(\mathrm{r})\ e^{-i\mathrm{q}\cdot\mathrm{r}} d\mathrm{r} \neq \int_{-\infty}^{\infty} \Gamma_\rho(\mathrm{r})\ e^{-i\mathrm{q}\cdot\mathrm{r}} d\mathrm{r}$$

$$\Gamma_\rho(0) = \left\langle \int \rho(\mathbf{v})\ \rho(\mathbf{v}) d\mathbf{v} \right\rangle = \left\langle \rho^2 \right\rangle V$$

$$\Gamma_\rho(\infty) = \left\langle \int \rho(\mathbf{v})\ \rho(\mathbf{v}+\infty) d\mathbf{v} \right\rangle = \langle \rho \rangle \langle \rho \rangle V = \langle \rho \rangle^2 V$$

$$I(\boldsymbol{q}) = \int_{-\infty}^{\infty} \Gamma_\rho(\boldsymbol{r})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, d\boldsymbol{r} = \infty$$



Extending to infinite integrals

$$I(q) = \int_V \Gamma_\rho(r)\, e^{-iq\cdot r}\, dr = \int_V \left[\Gamma_\rho(r) - \langle\rho\rangle^2 V + \langle\rho\rangle^2 V\right] e^{-iq\cdot r}\, dr$$

$$= \int_{-\infty}^{\infty} \left[\Gamma_\rho(r) - \langle\rho\rangle^2 V\right] e^{-iq\cdot r}\, dr + \langle\rho\rangle^2 V \iiint_{-\infty}^{\infty} e^{-iq\cdot r}\, dr$$

$$\equiv \int_{-\infty}^{\infty} \Gamma_\eta(r) e^{-iqr}\, dr \qquad q \neq 0$$

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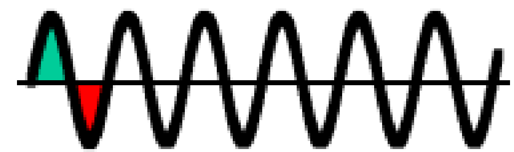
$$e^{iqr} = \cos qr + i \sin qr$$



$$\eta(r) = \rho(r) - \langle\rho\rangle$$

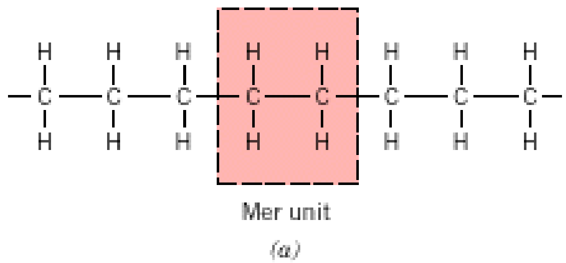
Γ_η = Autocorrelation of the fluctuation of the scattering length density.

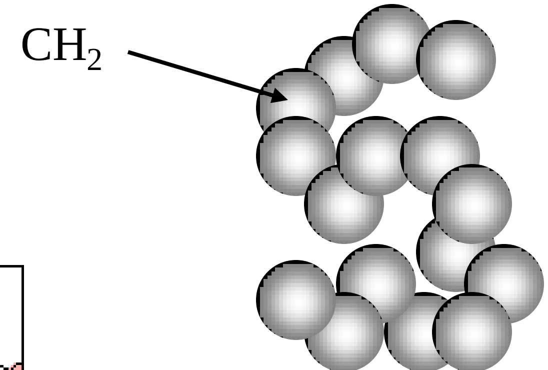
$$\boxed{\delta(q) = \int e^{-iqx}\, dx}$$

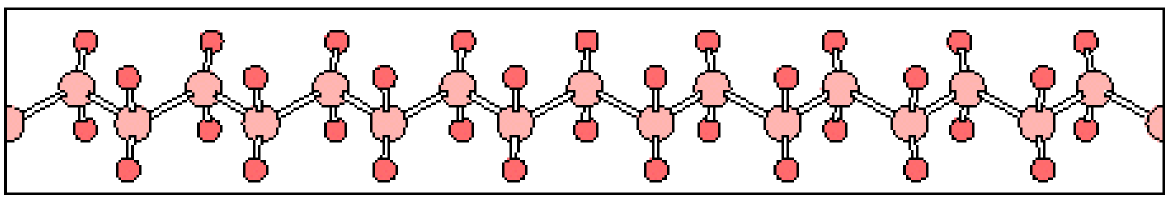
Scattering is determined by fluctuations of the density from the average

A dilute gas does not “diffract” (scatter coherently).

SAXS from Polymers

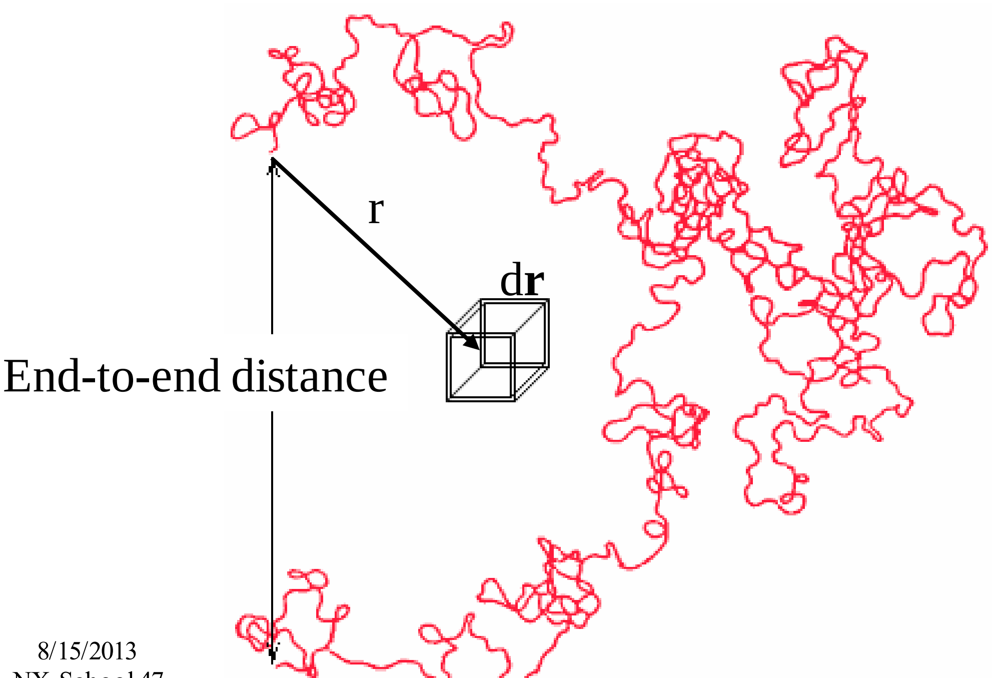


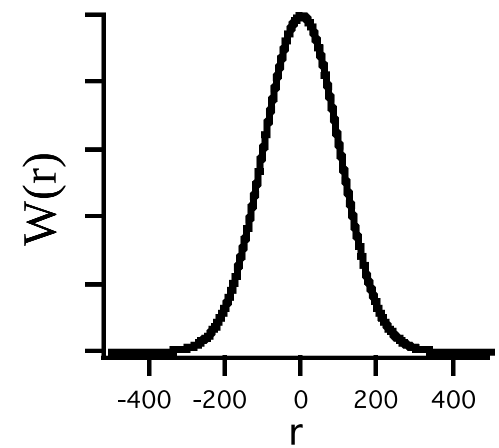




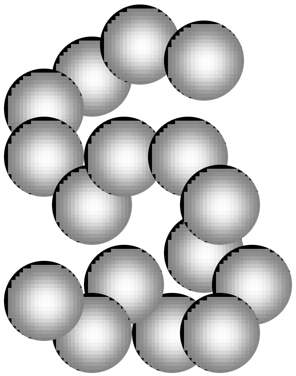
Gaussian probability distribution

$$w(N,r)d\mathbf{r} = \left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left(\frac{3r^2}{2Nl^2}\right) d\mathbf{r}$$





Scattering from Polymer Coils

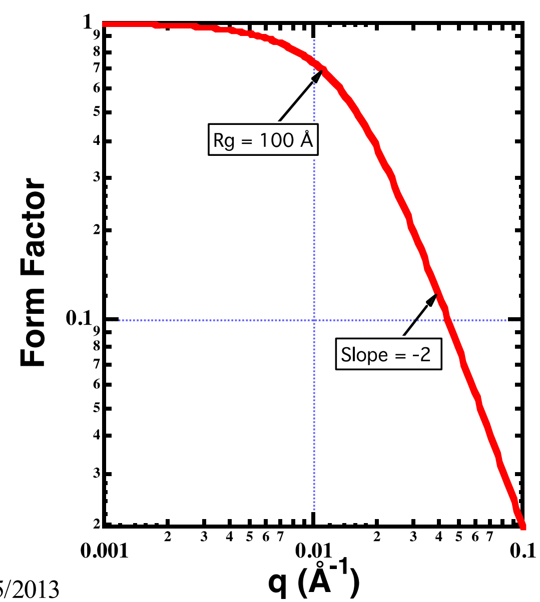


N bonds of length l, N+1 beads of volume v_u
scattering length of one bead = $\rho_0 v_u$

$$I(\mathbf{q}) = \left(\rho_o v_u\right)^2 \sum_{j=0}^{N+1}\sum_{k=0}^{N+1} e^{-i\mathbf{q}\cdot\mathbf{r}_{jk}} = \left(\rho_o v_u\right)^2 \int P(r) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$P(r) = 2\underbrace{\sum_{K=0}^{n}\left(N+1-K\right)}_{\text{Number of walks of K steps}}\underbrace{\left(\frac{3}{2\pi K l^2}\right)^{3/2}\exp\left(\frac{3r^2}{2Kl^2}\right)}_{\text{e-e distribution for a walk of K steps}}$$

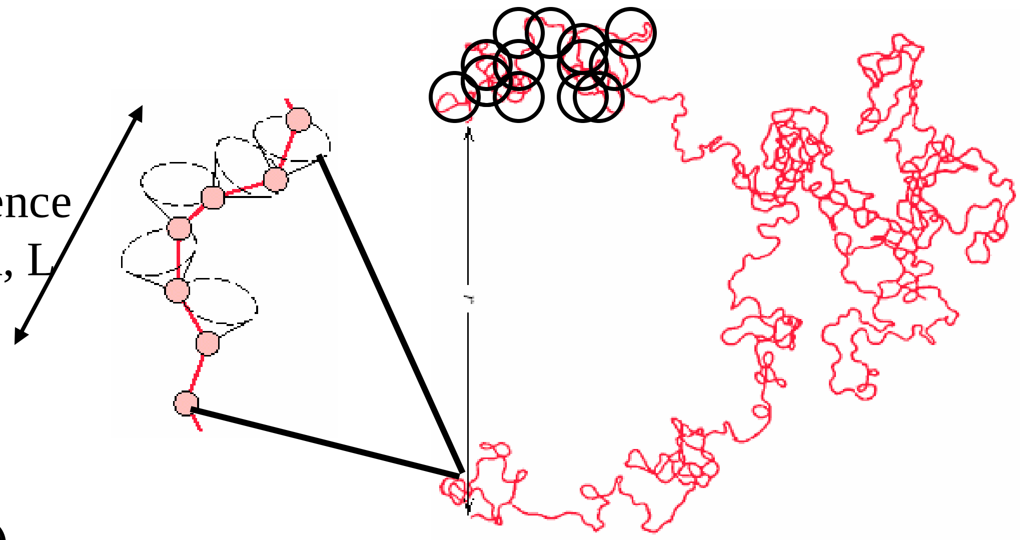
l = bond length



$$I(q) = \left(r_o v_u\right)^2 \underbrace{\frac{2(e^{-x}+x-1)}{x^2}}_{\text{Debye form factor}}; \quad x = \frac{q^2 N l^2}{6} = q^2\left\langle R_g\right\rangle^2$$

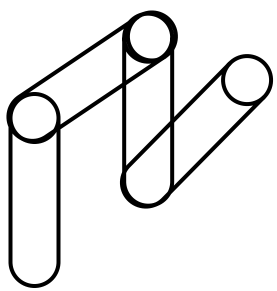
Worm-like Chain

Persistence Length, L

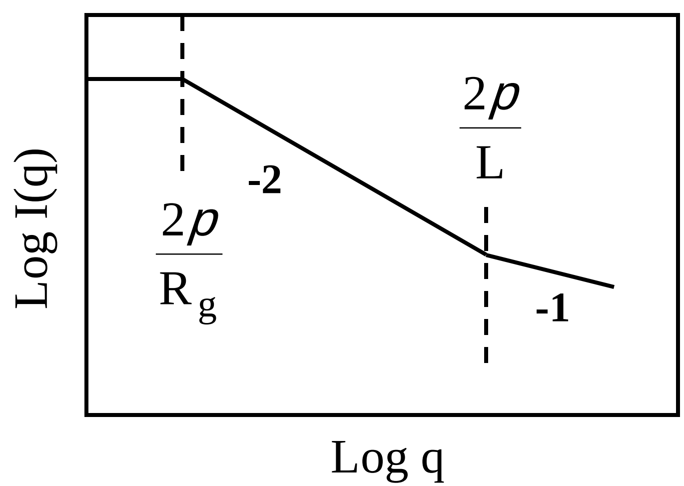


Gaussian on large length scales

d = 2



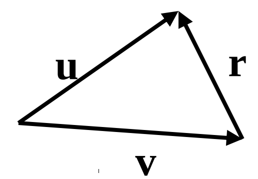
Rod like on short length scales **d = 1**



Correlation Functions

$$\frac{d\sigma}{d\Omega} = I_{scatt}(\mathbf{q}) = \frac{J(\mathbf{q})}{J_0} = \left\langle \left|\mathcal{A}(\mathbf{q})\right| \right\rangle^{\mathbf{2}} = \left\langle \left| \int \rho(\mathbf{r})\ e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2 \right\rangle$$

Ensemble Average < >



$$I(\mathbf{q}) = \left\langle \left[\int \rho(\mathbf{u})\ e^{-i\mathbf{q}\cdot\mathbf{u}} d\mathbf{u} \right] \left[\int \rho(\mathbf{v})\ e^{i\mathbf{q}\cdot\mathbf{v}} d\mathbf{v} \right] \right\rangle$$

$$\mathbf{r} = \mathbf{u} - \mathbf{v}$$

new **r** is independent of origin

$$I(\mathbf{q}) = \int \left\langle \left[\int \rho(\mathbf{u}) \rho(\mathbf{u}+\mathbf{r}) d\mathbf{u} \right] \right\rangle e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$\boxed{\begin{aligned} I(\mathbf{q}) &\equiv \int \Gamma_\rho(\mathbf{r})\ e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \\ \Gamma_\rho(\mathrm{r}) &= \left\langle \int_{V_{sample}} \rho(\mathbf{u}) \rho(\mathbf{u}+\mathbf{r}) d\mathbf{u} \right\rangle \end{aligned}}$$

Γ_ρ(r) is the autocorrelation function of the scattering length density

Scattering Cross section is the Fourier Transform of the ensemble average of the correlation function of the scattering length density (Patterson Function)