# Exploring the Nanoworld with Small-Angle Scattering

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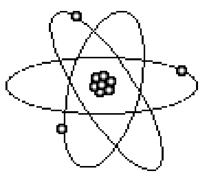
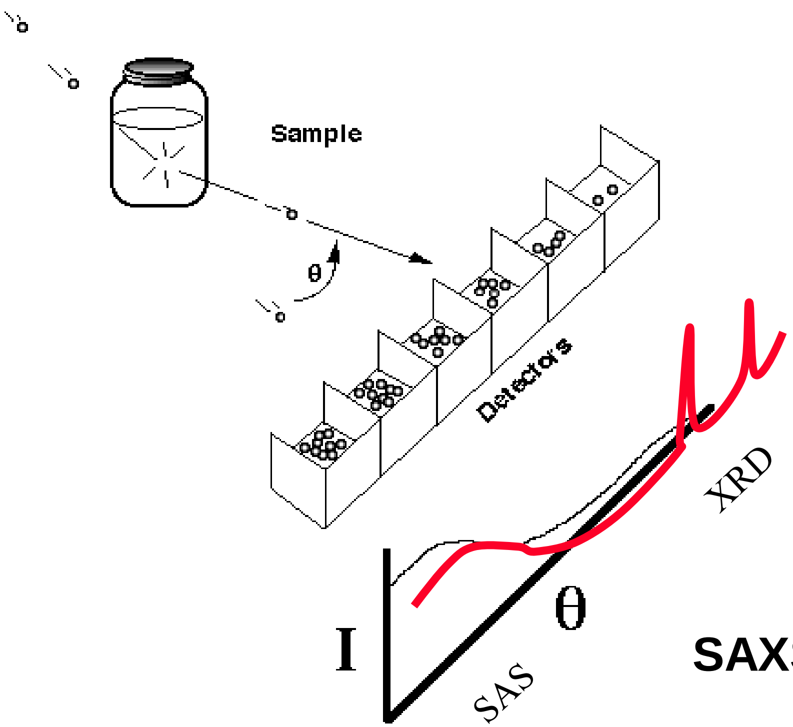
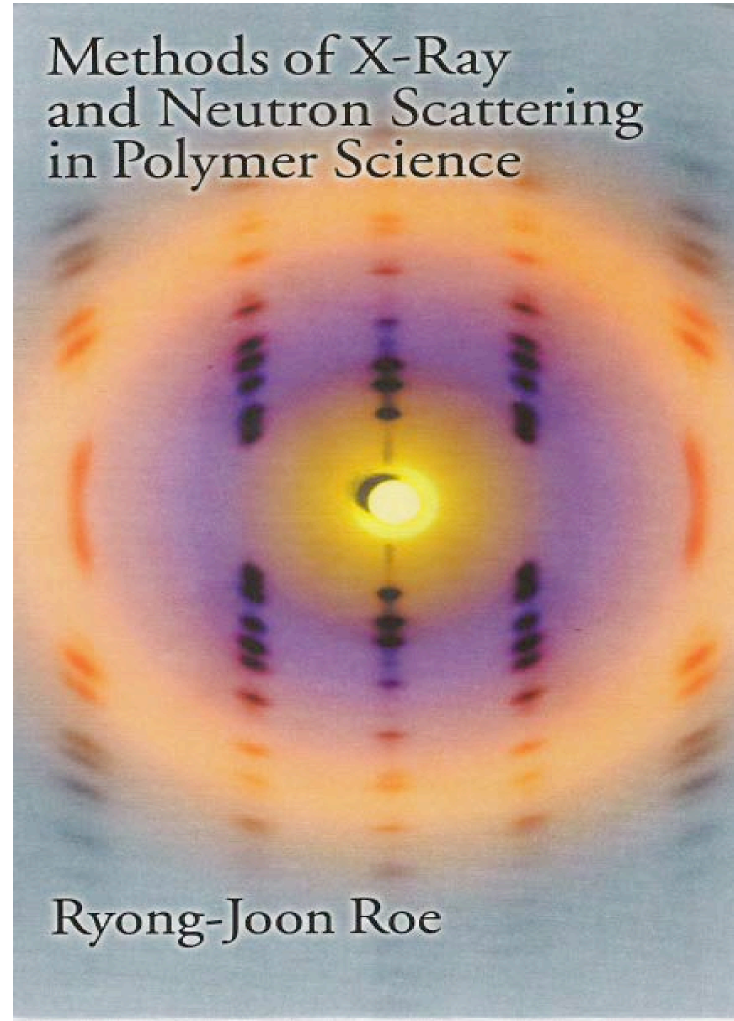


**Source of x-rays, light or neutrons**

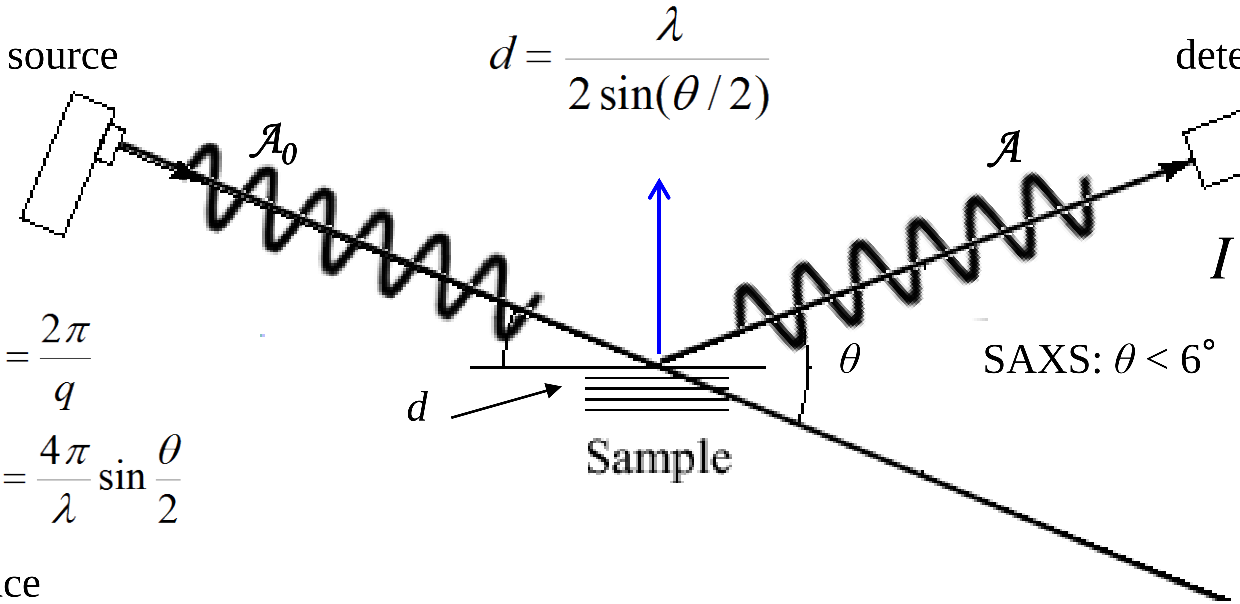



***Intensity vs Angle***

**SAXS & SANS: θ ≤ 6°**



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



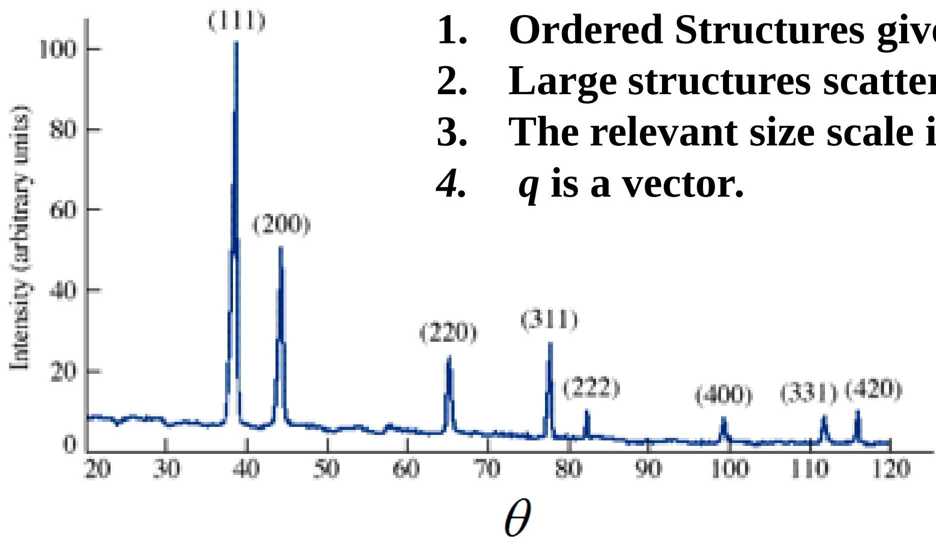

$$d = \frac{\lambda}{2\sin(\theta/2)}$$

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

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

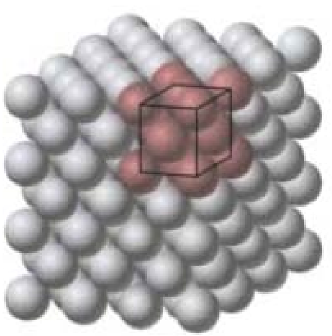
$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

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 2π/*q***
4. ***q* is a vector.**

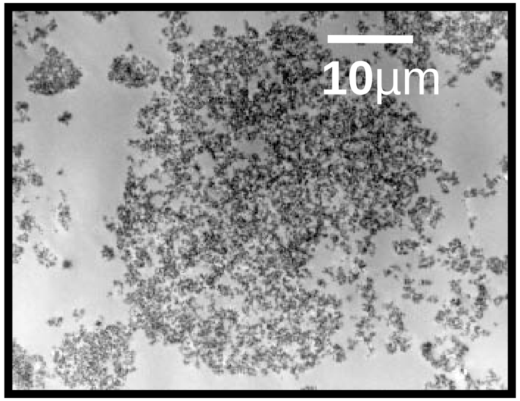
real space



**Problem: Nanomaterials are seldom ordered**

# Disordered Structures in “Real Space”

**Agglomerates**

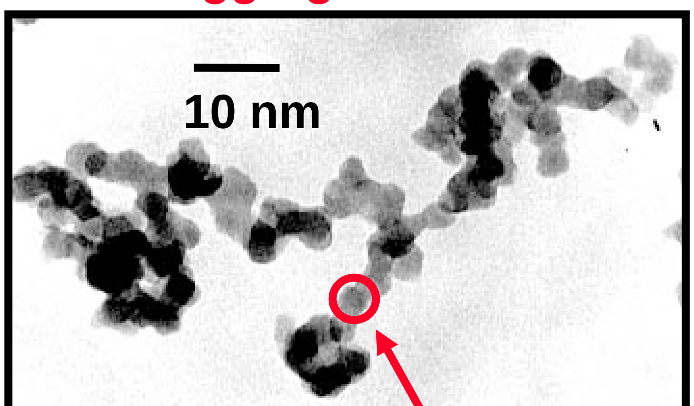



**Precipitated Silica**

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

Water Glass

**Aggregates**




**Primary Particles**

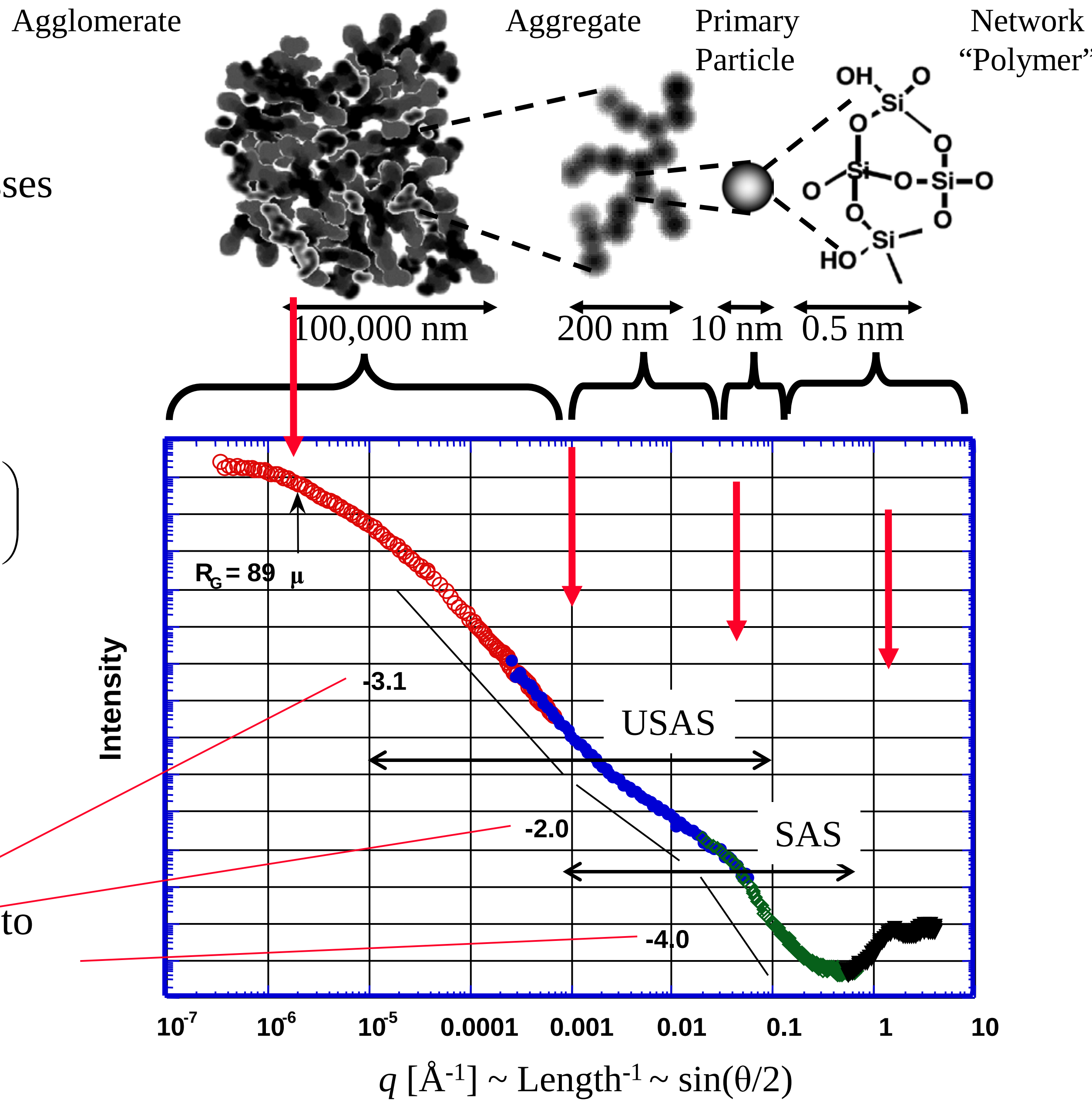
Complex
Hierarchical
Disordered

**Difficult to quantify structure from images.**

# Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

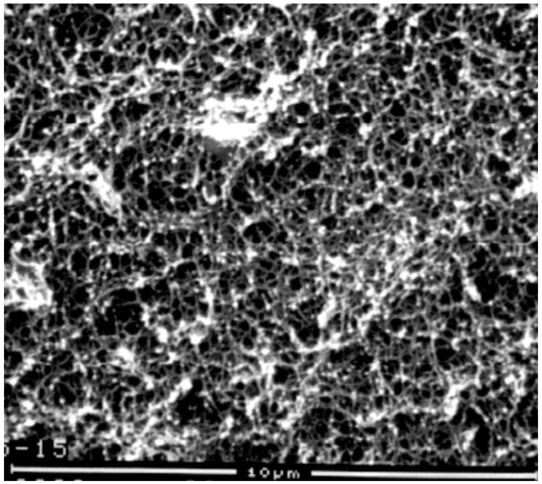
$$q = \frac{2\pi}{d_{Bragg}} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

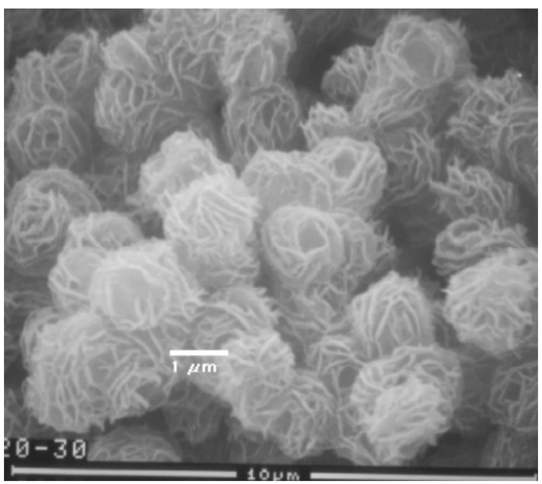



Exponents related to morphology

# Why Reciprocal Space?

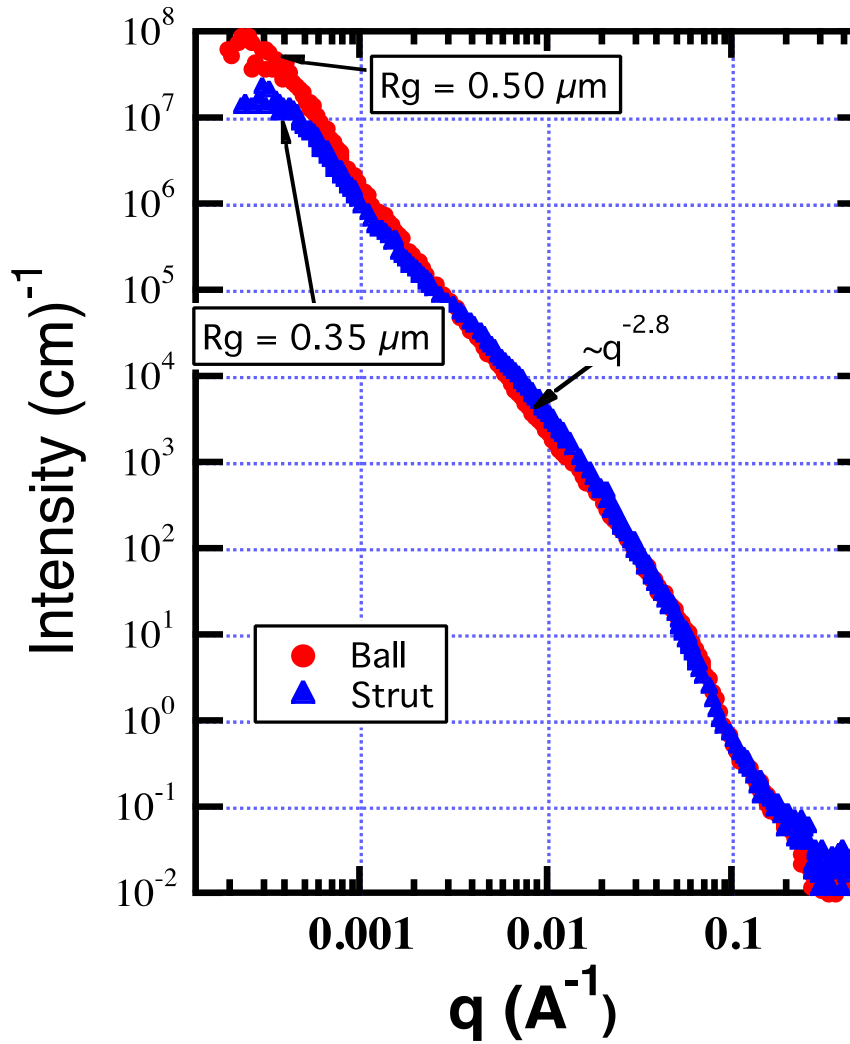
Isotactic polystyrene foams prepared by TIPS




10 µm

**Jim Aubert, SNL**




**Images miss similarity**

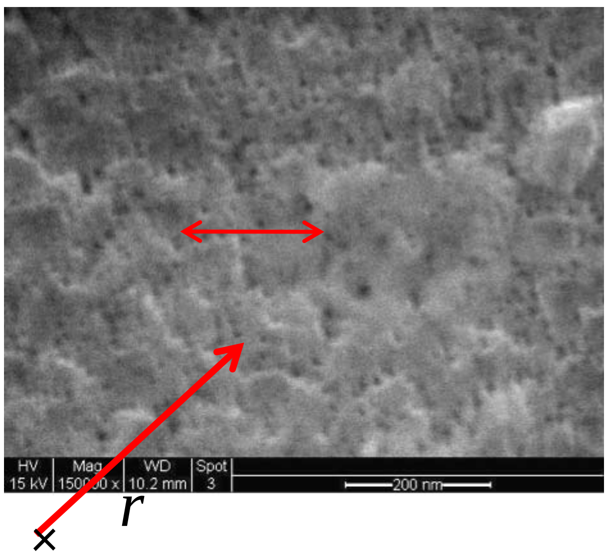


*Ultra-small-angle neutron scattering: a new tool for materials research.* Cur. Opinion Sol. State & Mat Sci, 2004. 8(1): p. 39-47.

# Characterizing Disordered Systems in Real Space

Electron Density Distribution

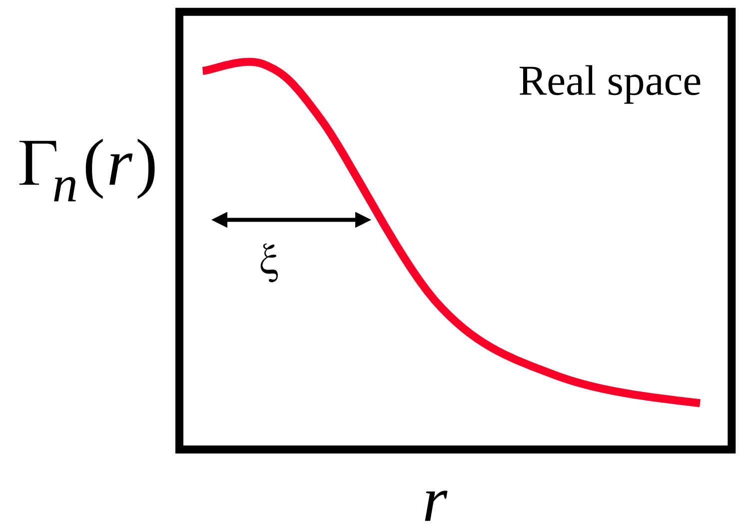
$$n(r)$$




Throw out phase information →

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.

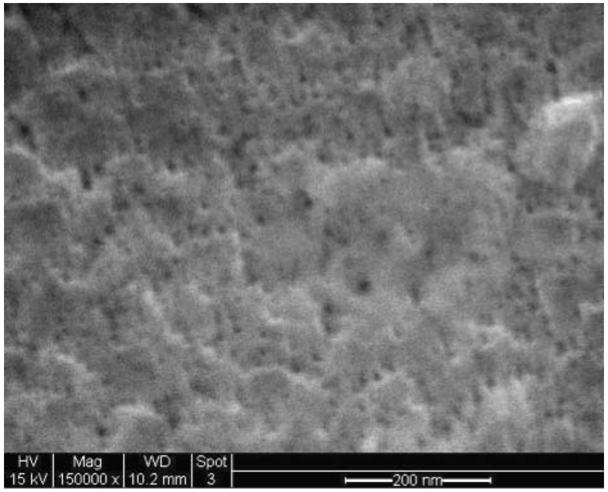
Depends on separation distance.
Retains statistically significant info.

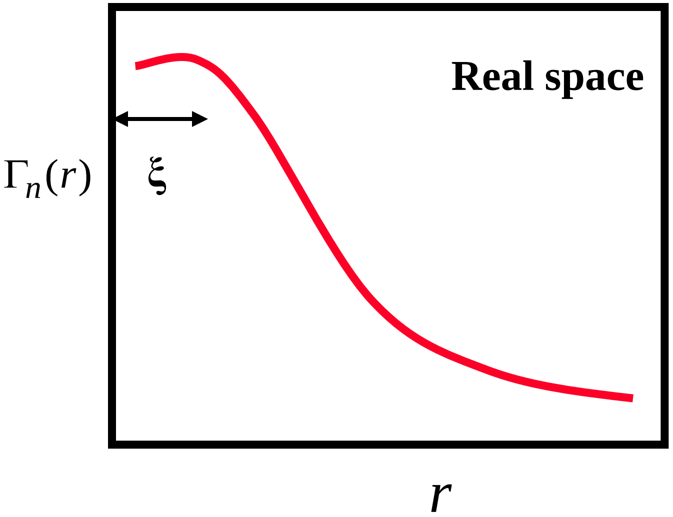
Resolution problems at small $r$
Opacity problems for large $r$
2-dimensional
Operator prejudice

**Problems with real space analysis**

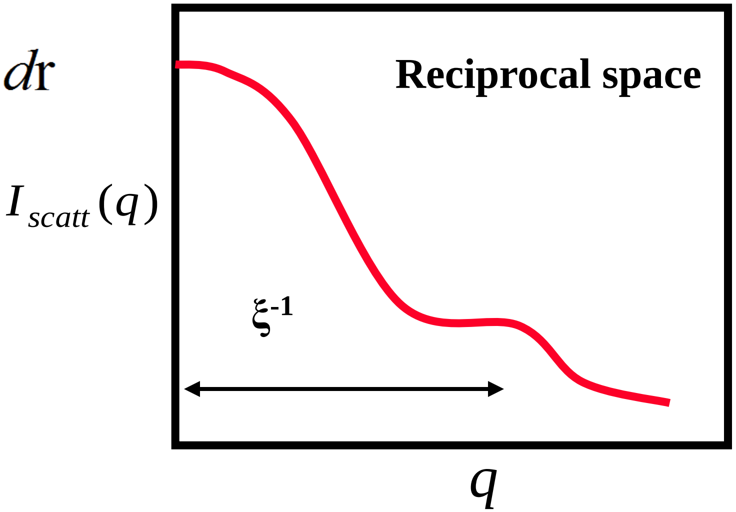
# Imaging vs. Scattering

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



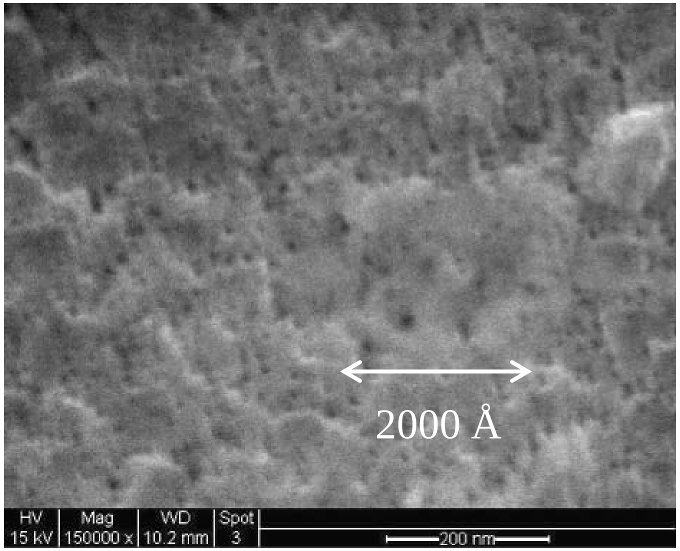

$$I_{scatt} \cong \int \Gamma_n(\mathrm{r})\, e^{-iqr} d\mathrm{r}$$

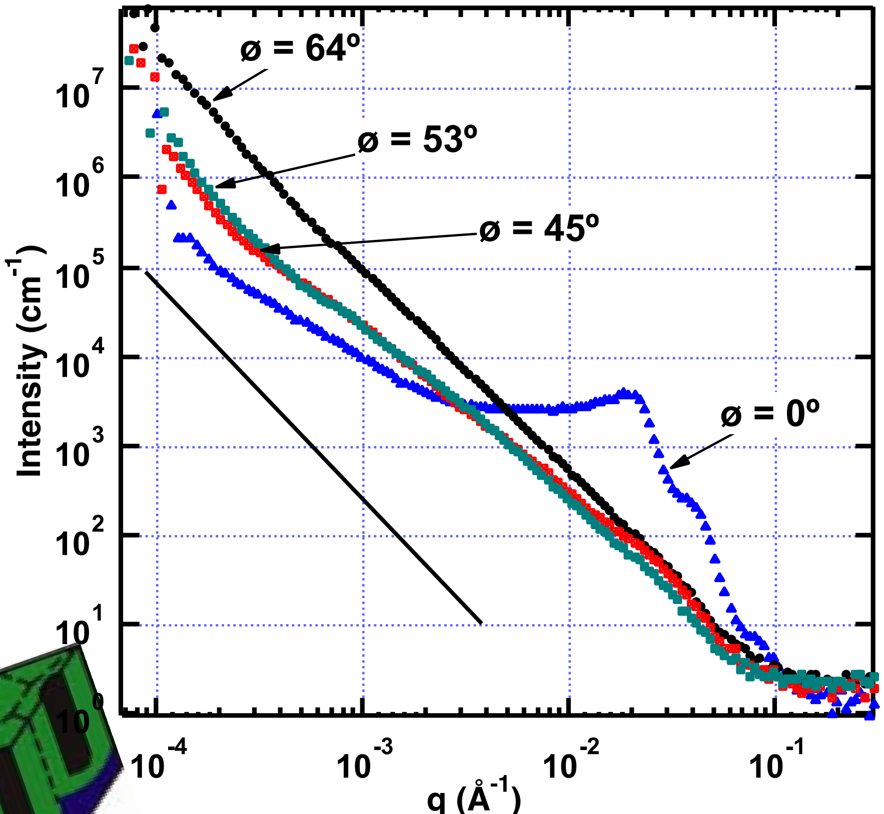


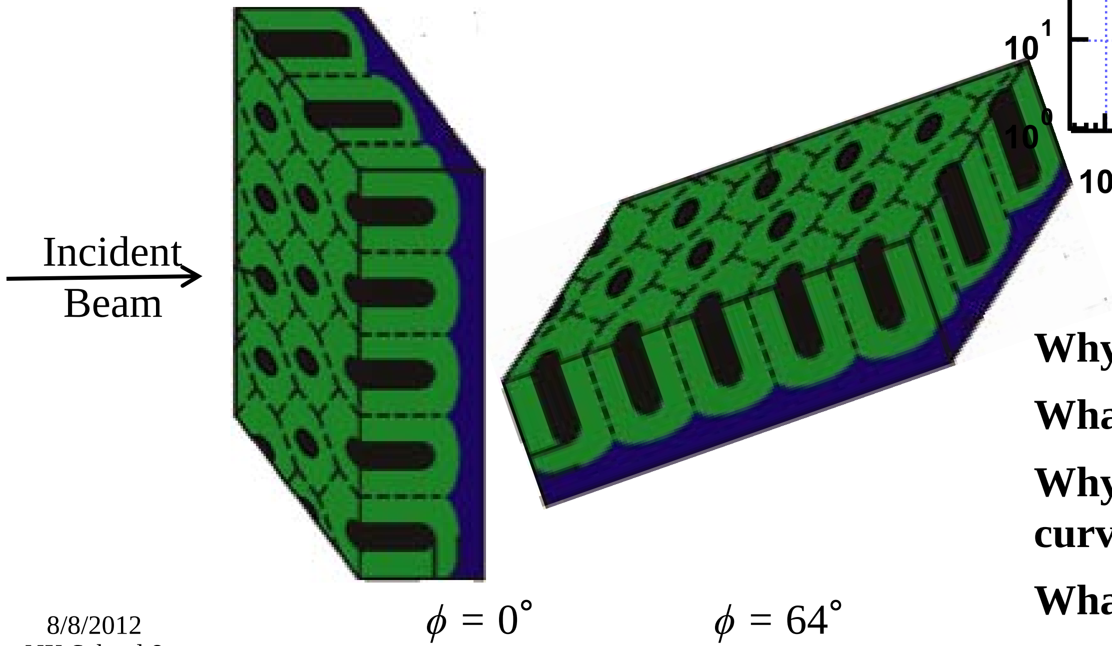

Schaefer, D. W. & Agamalian, M. Ultra-small-angle neutron scattering: a new tool for materials research. *Curr Opin Solid St & Mat Sci* 8, 39-47, (2004).

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

# Anodized Aluminum



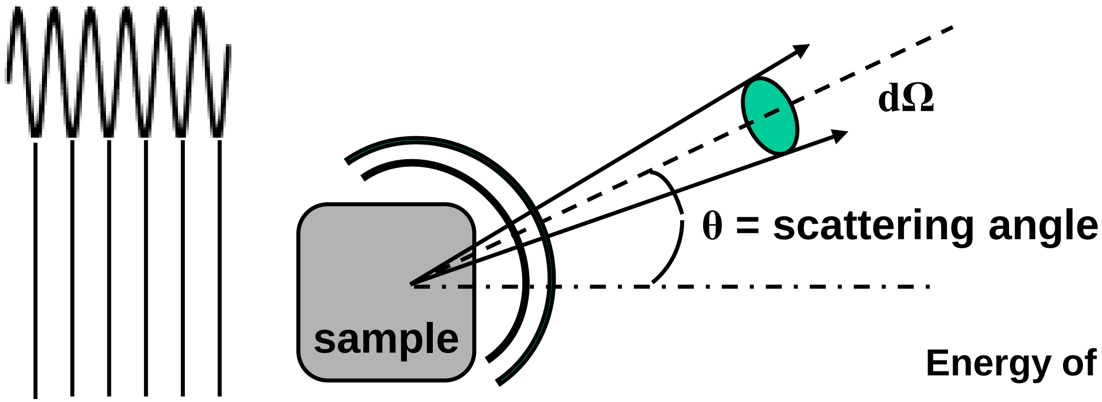

**Why is there a peak?**

**What is the meaning of the peak position?**

**Why did the peak disappear for the 64° curve.**

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

# Intensity and Differential Scattering Cross Section




**Plane wave**
$J_0$

**Spherical wave**
$J_\Omega$

**Energy of a wave ~ Intensity ~ Amplitude² = |$\mathcal{A}$|²**


**Spherical wave:** **Flux $J_\Omega$ = energy/unit solid angle/s or photons/ unit solid angle /s**

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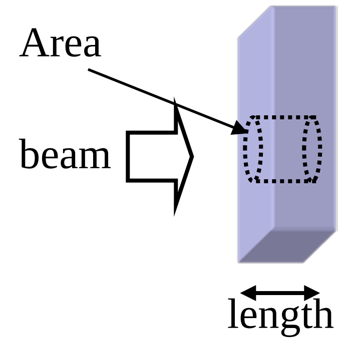
**Plane wave:** **Flux $J_0$ = energy/unit area/s or photons/unit area/s**

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

# What is "Intensity?" What do we really measure?

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

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




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

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

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

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

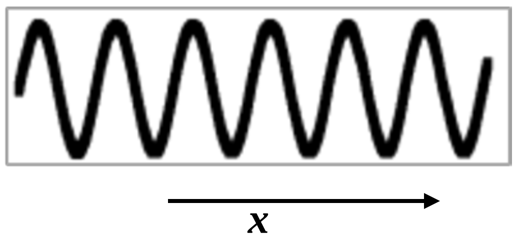
$$\text{Intensity} = \frac{J}{V J_0} = \frac{\mathrm{d}\sigma}{V \mathrm{d}\Omega}\left(\frac{1}{\mathrm{cm}}\right)$$ Experimentalists, Irena, Indra

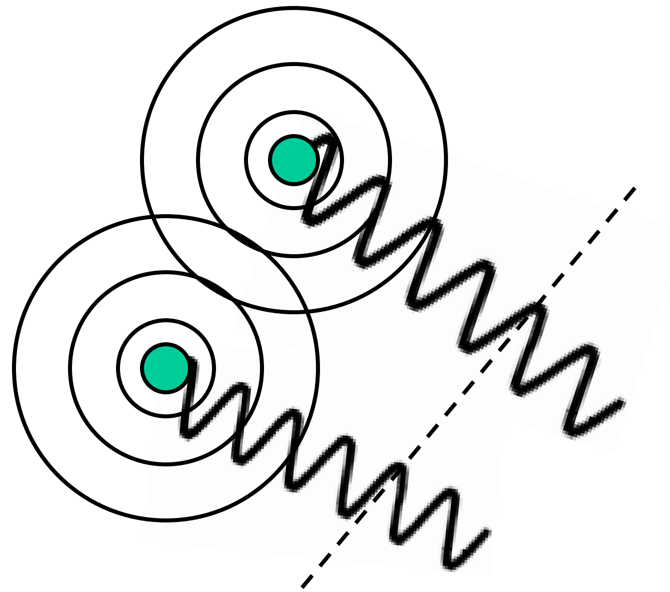
$$\text{Intensity} = (\text{arbitrary constant}) \times J$$ Common Usage

# Generalized Bragg's Law for Disordered System

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

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

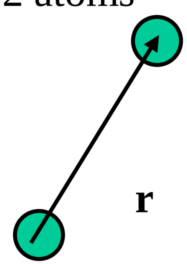


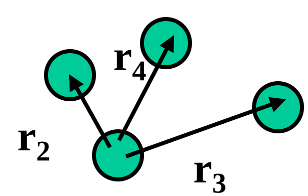
**Scattering from 2 atoms**

**dΩ**

2 atoms

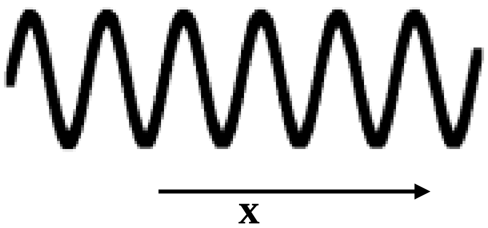


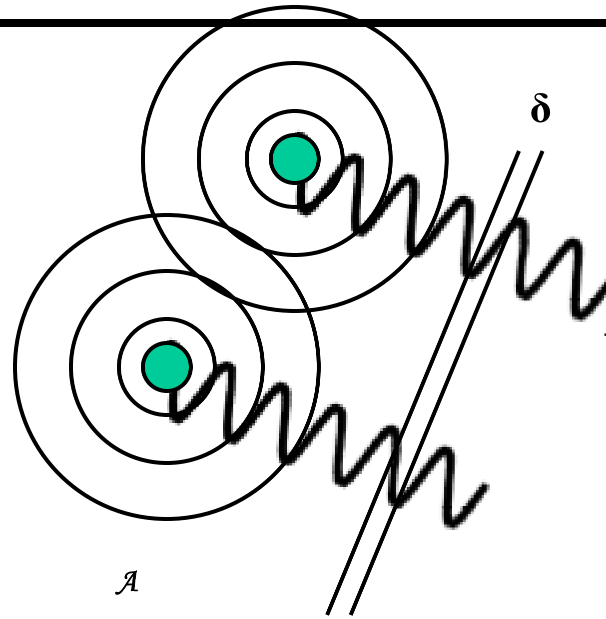

many atoms



# Scattering from two atoms

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




Difference in path length

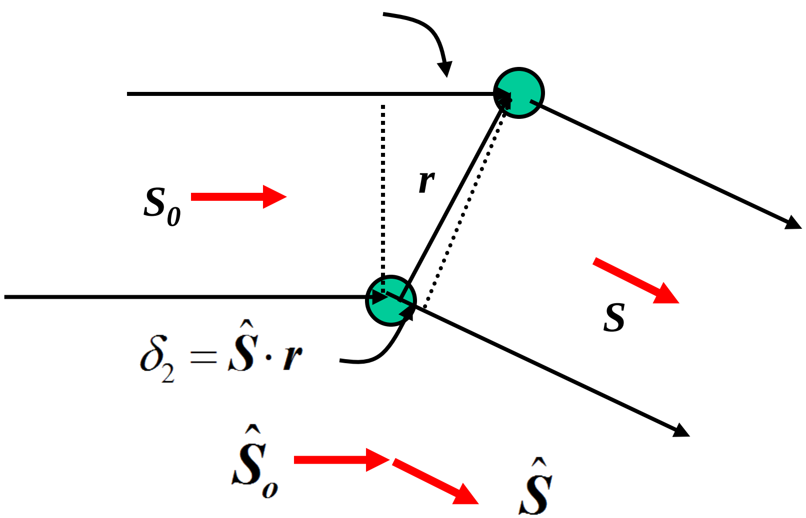
$$\frac{const \times \mathcal{A}_o}{r} e^{i2\pi(\upsilon t-(x+\delta)/\lambda)}$$

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

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

unit vector

$$\delta_1 = \hat{S}_0 \cdot r$$




$$\delta_2 = \hat{S} \cdot r$$

What are the units of const?

Instrument ($q$)

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

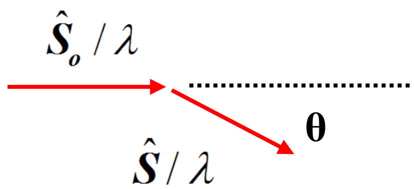
Sample ($r$)

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

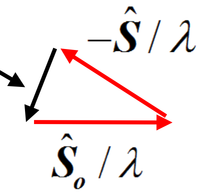
# Scattering vectors *s* and *q*

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

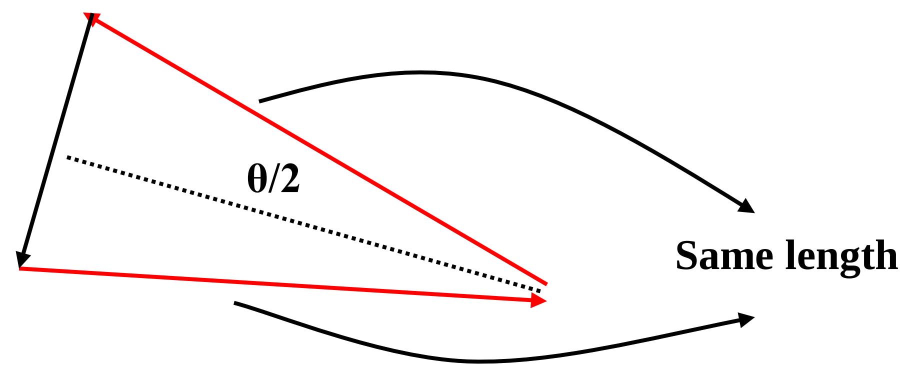
$$\boldsymbol{s} = \frac{\hat{\boldsymbol{S}} - \hat{\boldsymbol{S}}_0}{\lambda}$$ Called the scattering vector




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




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

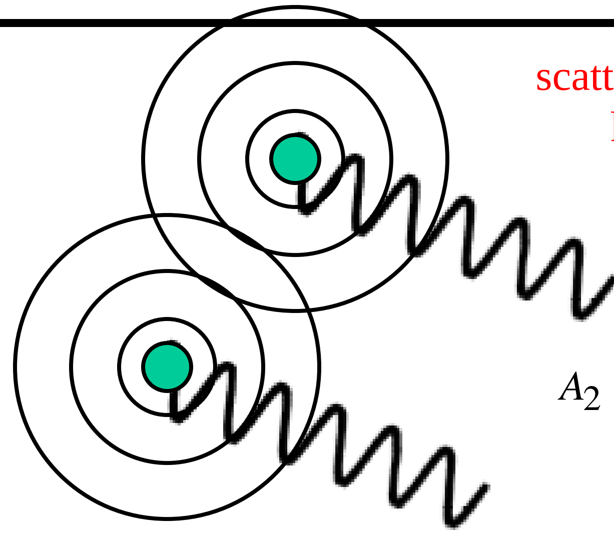



SAXS

- $\boldsymbol{q} = 2\pi \boldsymbol{s}$ Also called the scattering vector
- $$q = 2\pi s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

# 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

$$\Delta\varphi$$

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

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

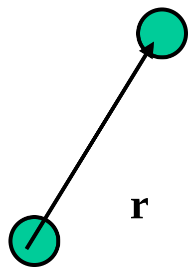
**Total Scattered Wave**

$$A = A_1 + A_2 = \frac{b}{R}\mathcal{A}_0 e^{i2\pi(\upsilon t - x/\lambda)} + \frac{b}{R}\mathcal{A}_0 e^{i2\pi(\upsilon t - x/\lambda) - i2\pi s\cdot r}$$

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

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

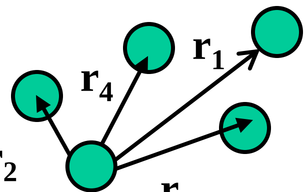
# Adding up the Phases




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

*x* and *t* terms suppressed

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




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

$\sum \to \int$

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

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

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

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

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

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

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

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

# Scattering Length Density (SLD) Distribution

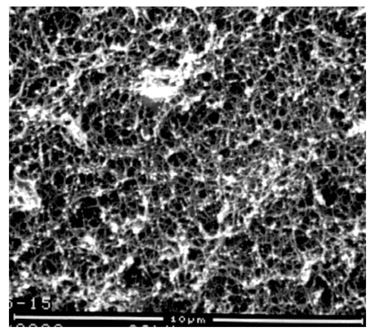
Fourier transform of the scattering length density distribution

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

**Can't be measured**

$\rho(\boldsymbol{r})$ = SLD distribution

= atomic density distribution x atomic scattering length, *b*.



$\rho(\boldsymbol{r})$

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

**Can't be inverted**

What we measure:

Square of the Fourier transform of the SLD distribution

# Scattering from Spherical Particle(s)

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

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

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

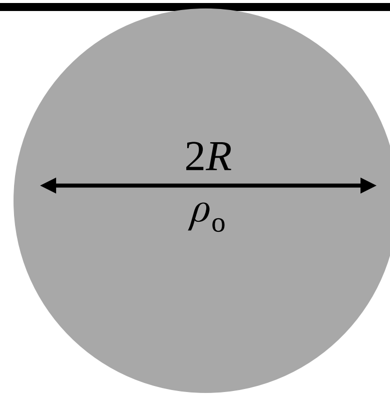
$$= \rho_0 4\pi R^3 \frac{(\sin qR - qR\cos qR)}{(qR)^3}$$

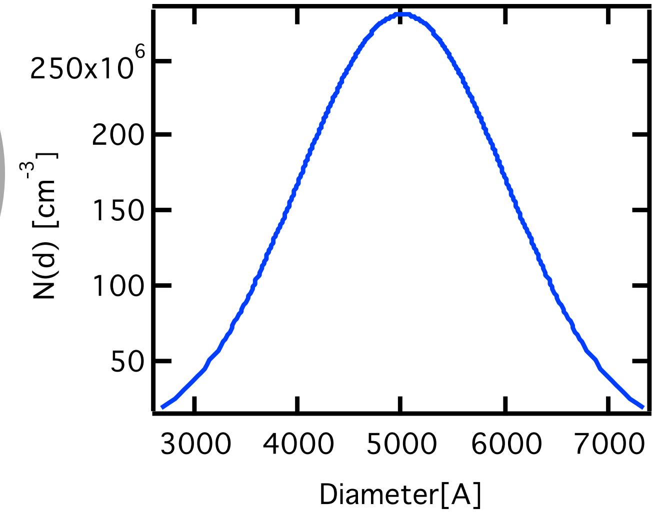
$v$ = particle volume

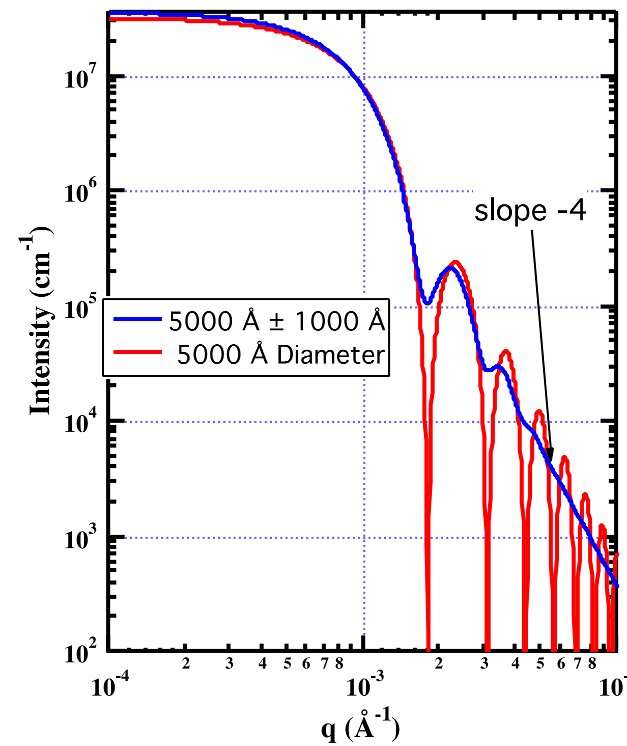
$$= \rho_0 \overbrace{\frac{4\pi R^3}{3}}^{v} \frac{3(\sin qR - qR\cos qR)}{(qR)^3}$$

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

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



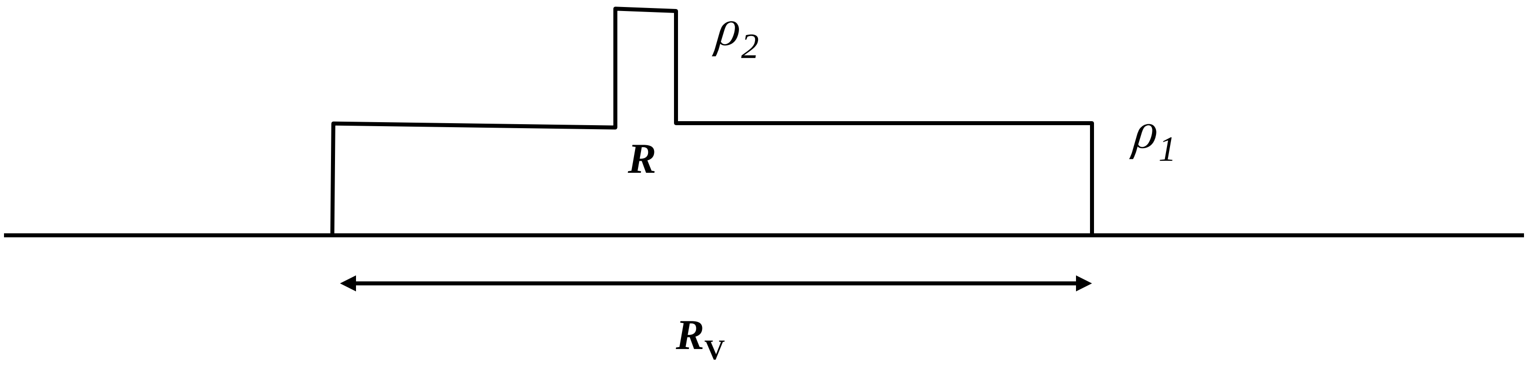




$I(q) \sim N(\rho - \rho_o)^2 v^2 P(q)$ ← Form Factor

↑ solvent SLD

# Particle in Dilute Solution



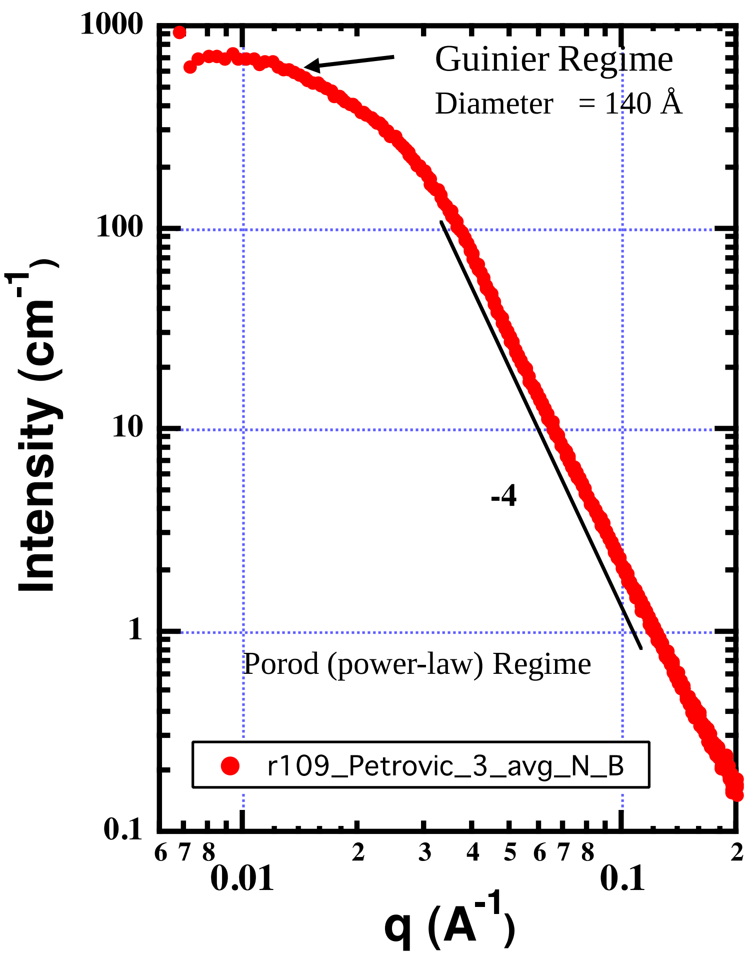

$$\mathcal{A}(q) = \frac{4\pi}{q}(\rho_2 - \rho_1)\int_0^R r\sin(qr)\,dr + \rho_1\int_0^{R_V} r\sin(qr)\,dr$$

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

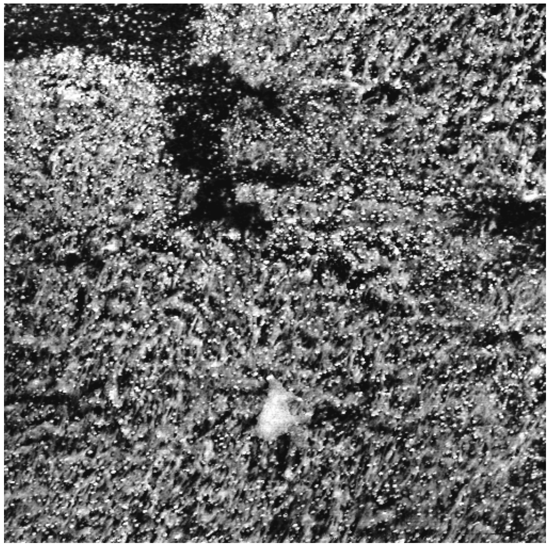
# Small-Angle Scattering from Spheres

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

Large object scatter at small angles




Silica in Polyurethane



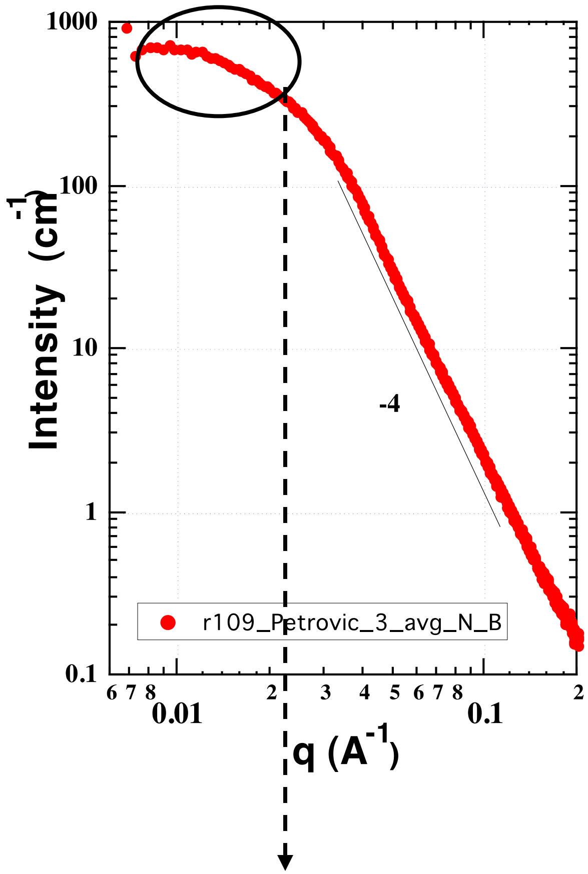
3 µm

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




$R_g \sim 1/q$

$$\mathcal{A}(q) = \frac{\mathrm{A}(q)}{\mathrm{A}_0} = \int \Delta\rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

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

**Derived in 5.2.4.1**

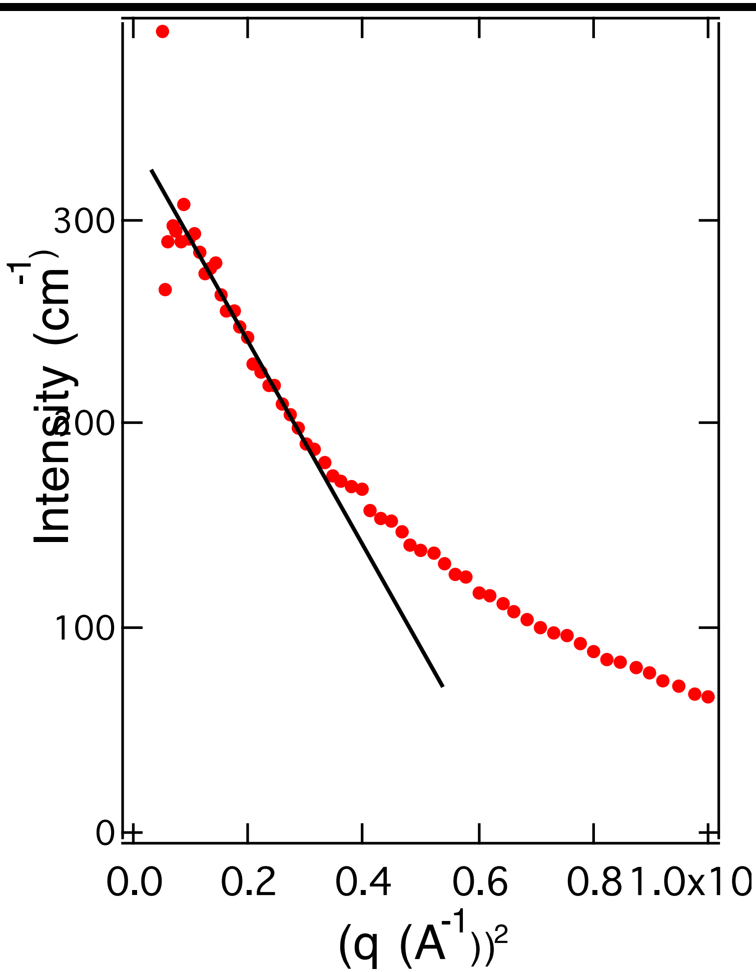
$$R_g^2 = \frac{1}{v} \int r^2 \sigma(\mathbf{r}) d\mathbf{r} \qquad \text{for any shape}$$

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

$$\mathcal{A}_{sphere}(q) = \Delta\rho 4\pi R^3 \frac{(\sin qR - qR\cos qR)}{(qR)^3} = C_1\left[1 - C_2 (qR)^2 + \cdots\right]$$

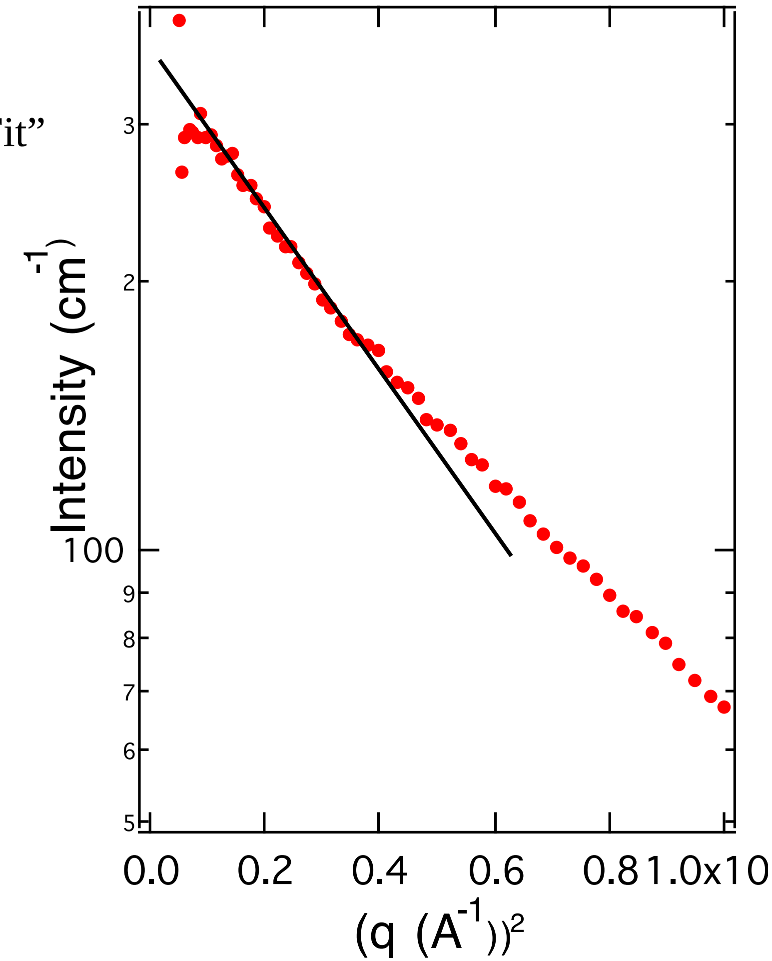
$$R_g = \sqrt{\frac{3}{5}} R$$

# Guinier Fits




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

Use
"Unified Fit"

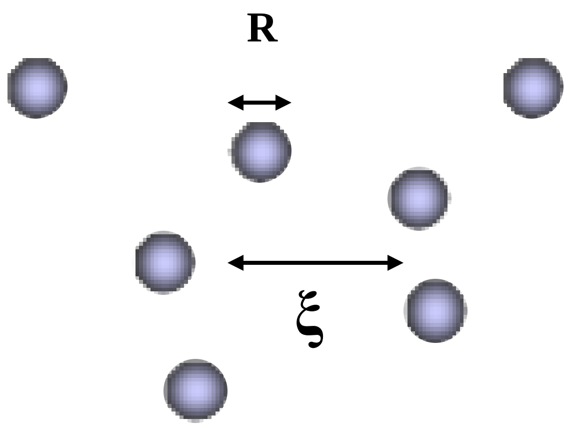



$$I(q) \sim \exp\left[-\frac{1}{3} q^2 R_G^2 + \cdots\right]$$

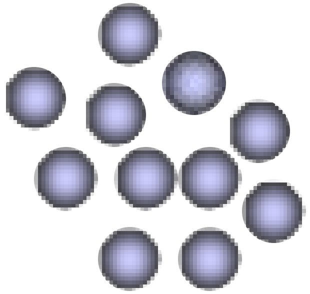
$$R_G \xrightarrow{dilute} R_g$$

Guinier radius Radius-of-Gyration

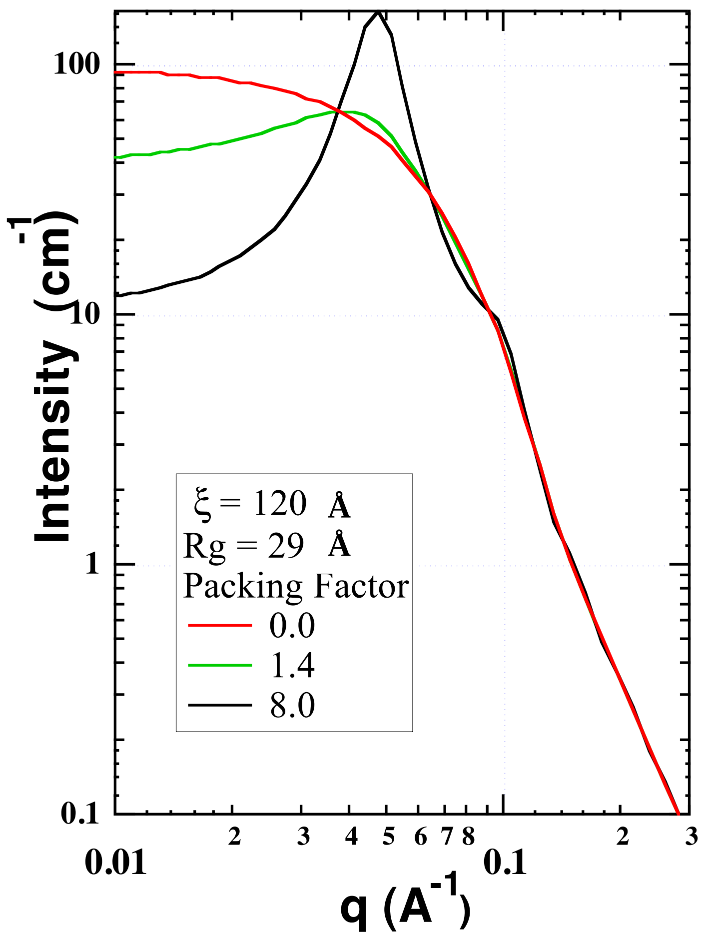
# Dense packing: Correlated Particles



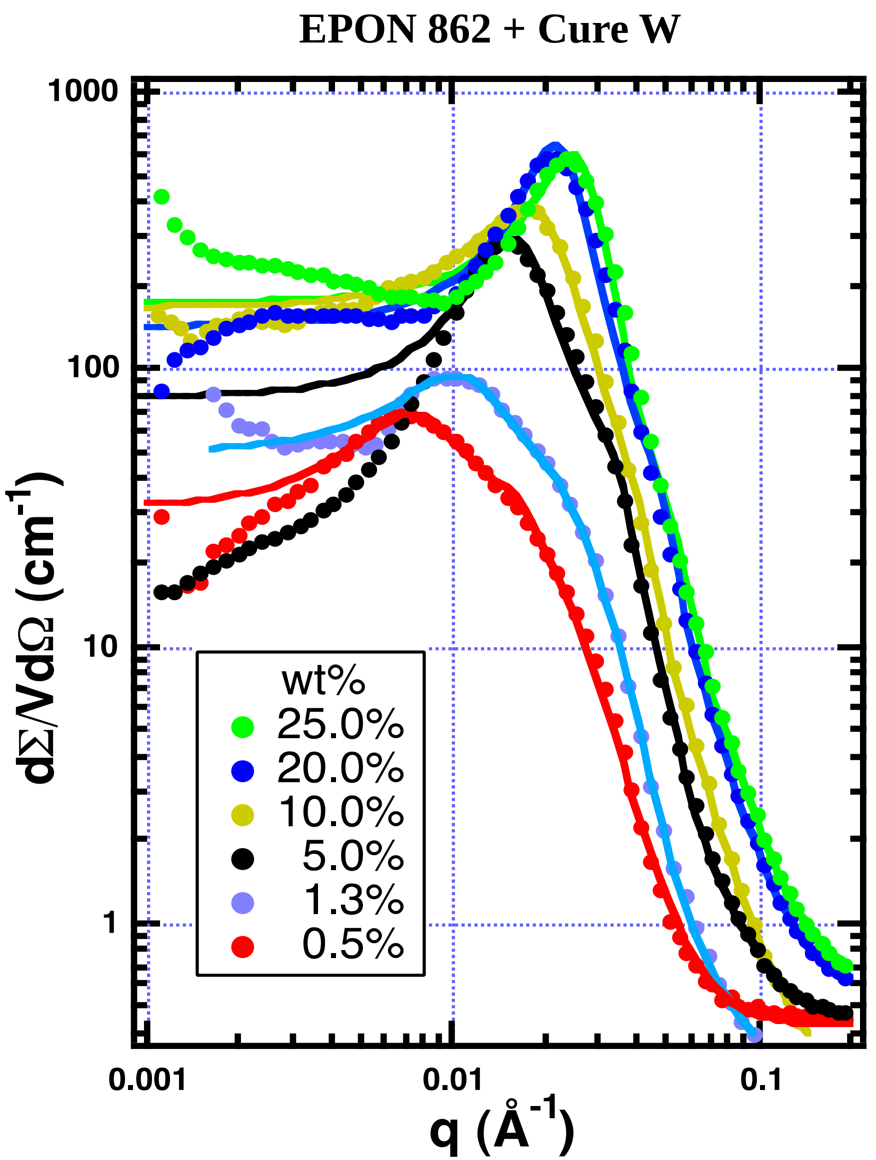

Packing Factor = k = 8 $\phi$

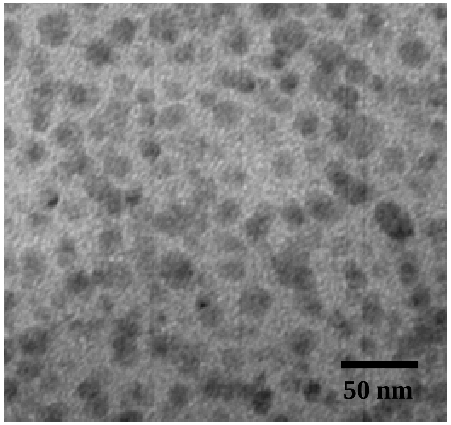


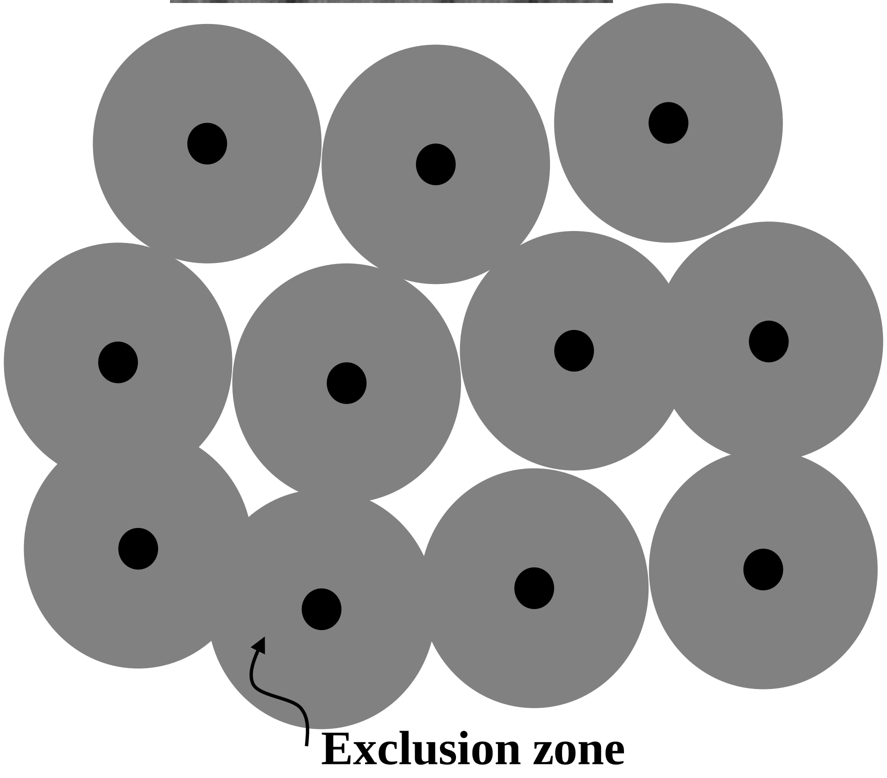
Packing Factor ≅ 6



# Colloidal Silica in Epoxy

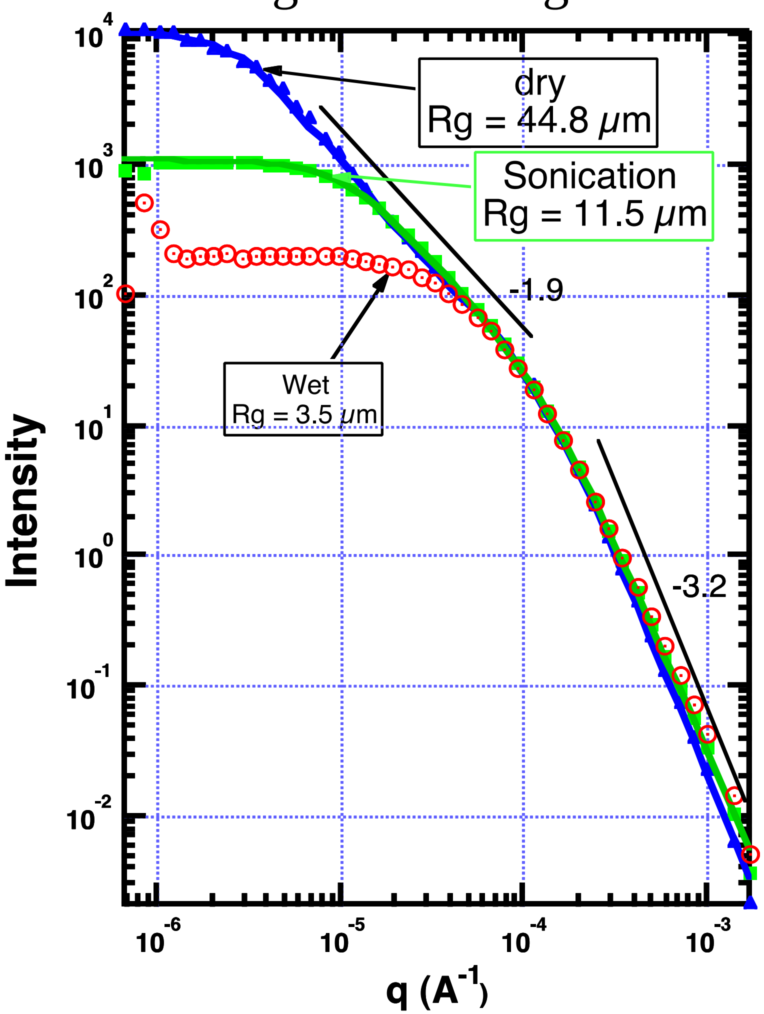


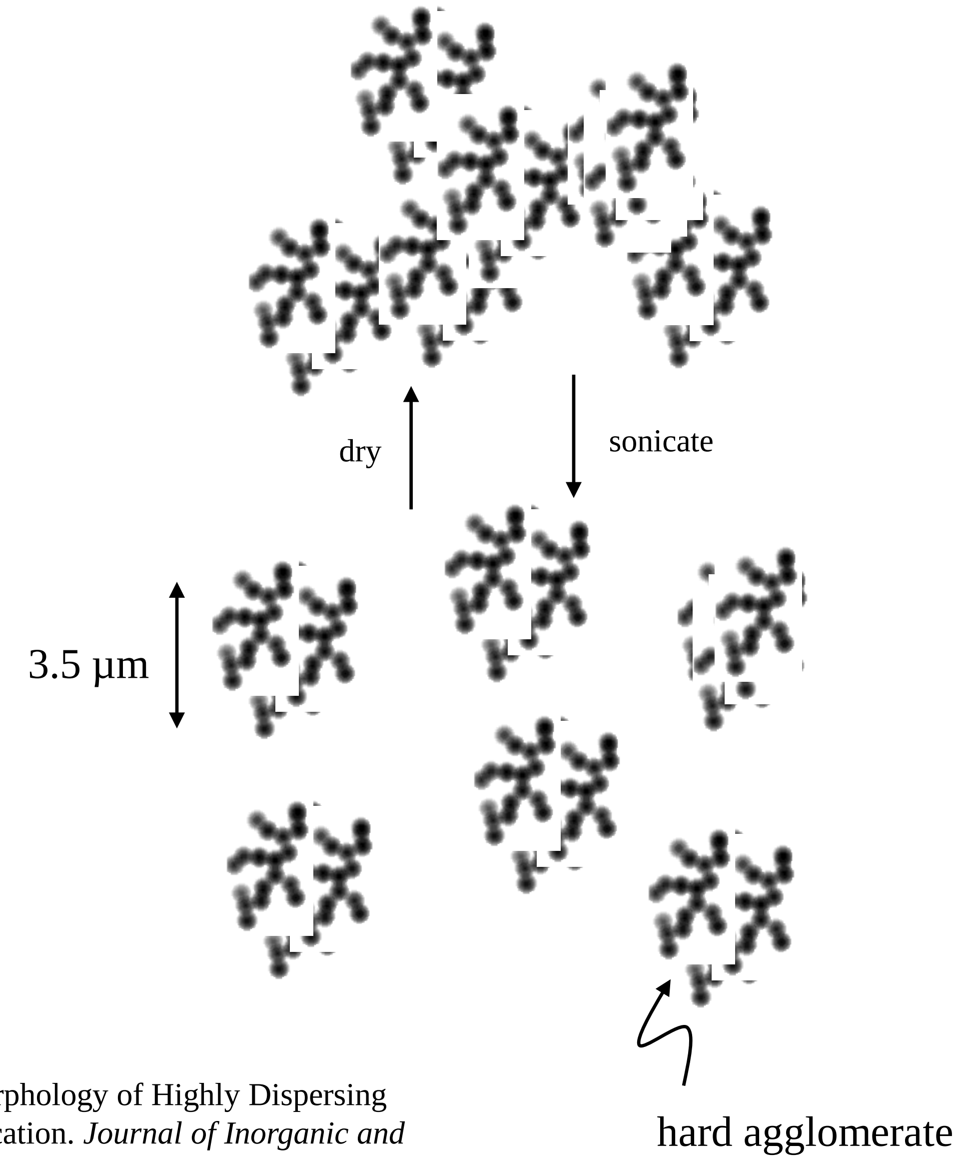



# Using $R_g$: Agglomerate Dispersion

Light Scattering



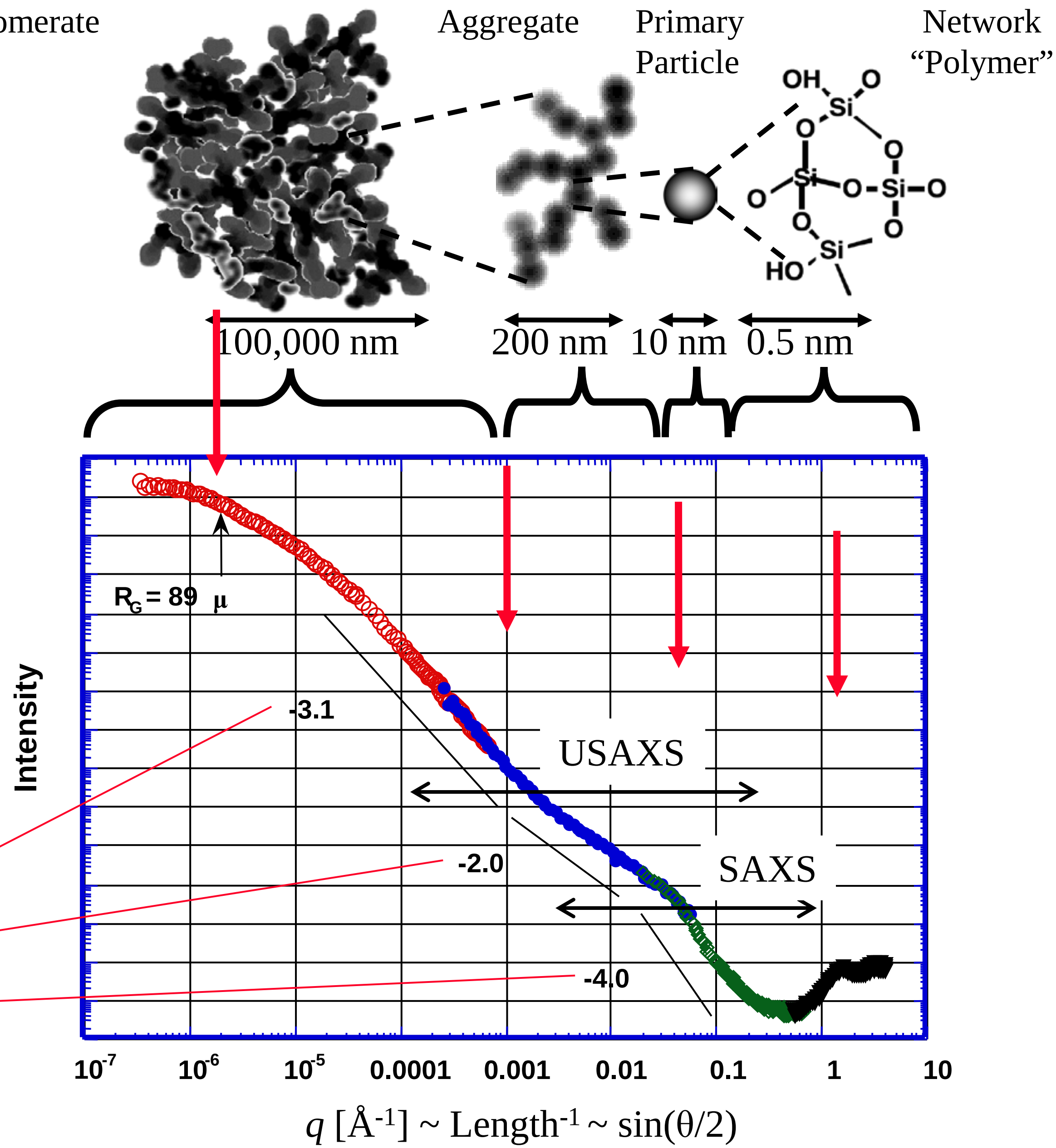




Schaefer, D. W., Kohls, D. & Feinblum, E. Morphology of Highly Dispersing Precipitated Silica: Impact of Drying and Sonication. *Journal of Inorganic and Organometallic Polymers and Materials* DOI: 10.1007/s10904-011-9643-y, (2011)

# Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

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



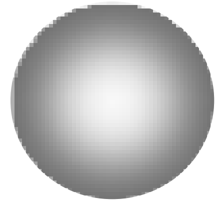

Exponents related to morphology

# Fractal description of disordered objects

**Real Space**

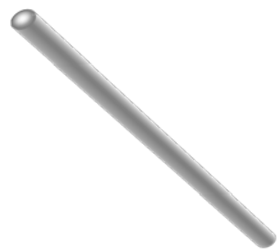
$M \sim R^d$

$M \sim V \sim R^3$

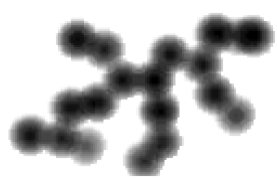


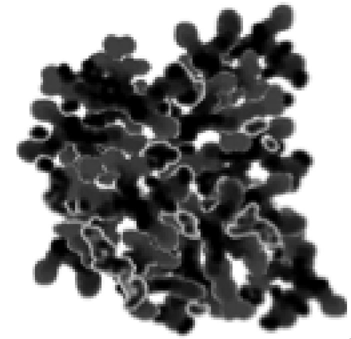
$M \sim V \sim R^2$

$M \sim V \sim R^1$



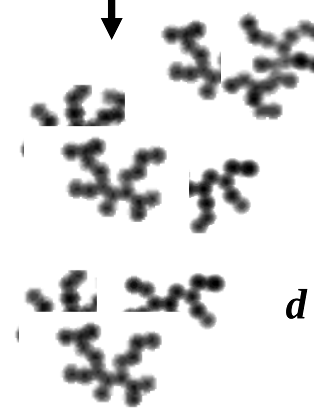
$M \sim V \sim R^{2.2}$





***d* = 3**

**Dispersion of colloidal fillers.**

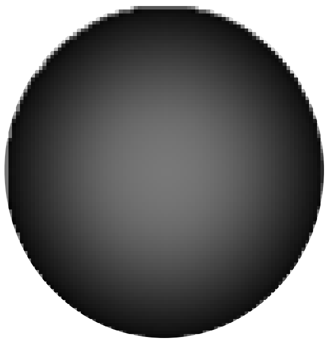


***d* = 2**

Mass Fractal Dimension = *d*

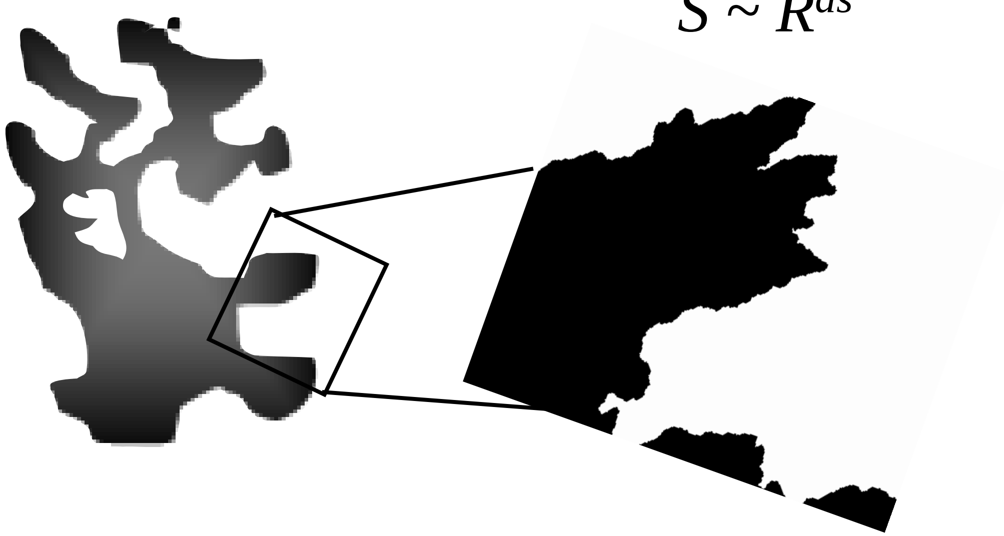
# Surface Fractal Dimension

**Sharp interface**



$S \sim R^2$

$S \sim R^{ds}$



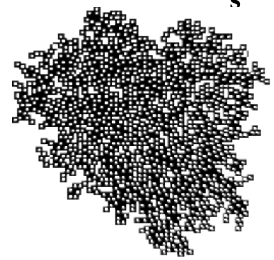
fractal or self-affine surface

# Scattering from Fractal Objects: Porod Slopes

**$d$ = Mass Fractal Dimension**

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

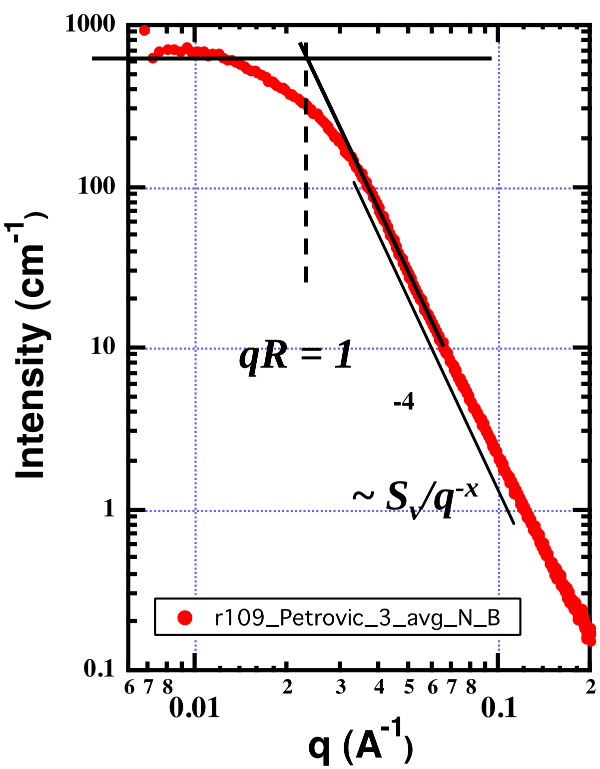
$M \sim v \sim N v_u \sim R^d v_u$ mass fractal



**$d_s$ = Surface Fractal Dimension**

$S = R^2$ solid particle

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




**Small *q***

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

**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**

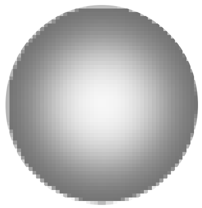
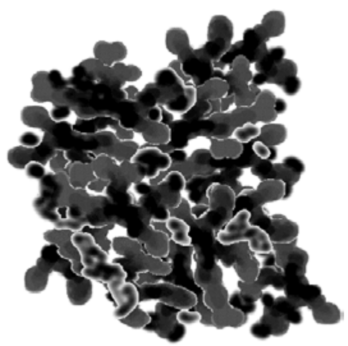
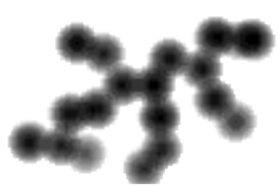
$$R^{d_s+x} \sim R^{2d}$$

$$x = 2d - d_s$$

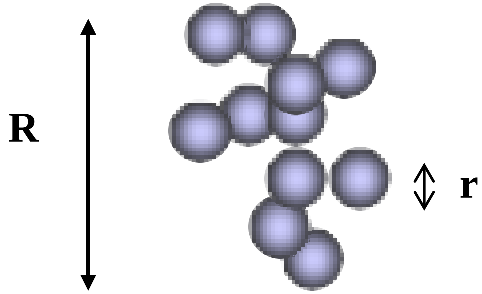
$$I(q) \sim q^{-(2d-d_s)}$$

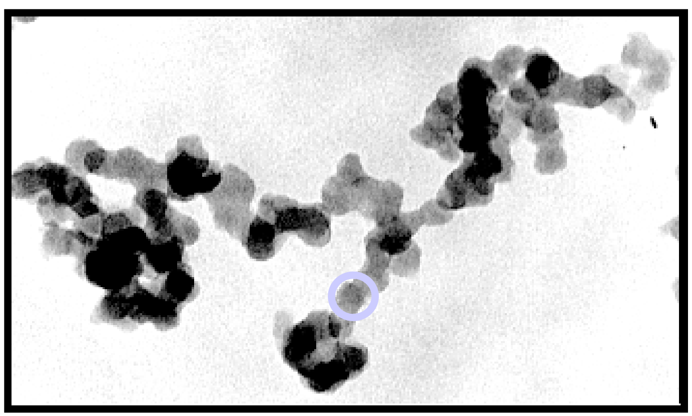
# Porod Slope for Fractals

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

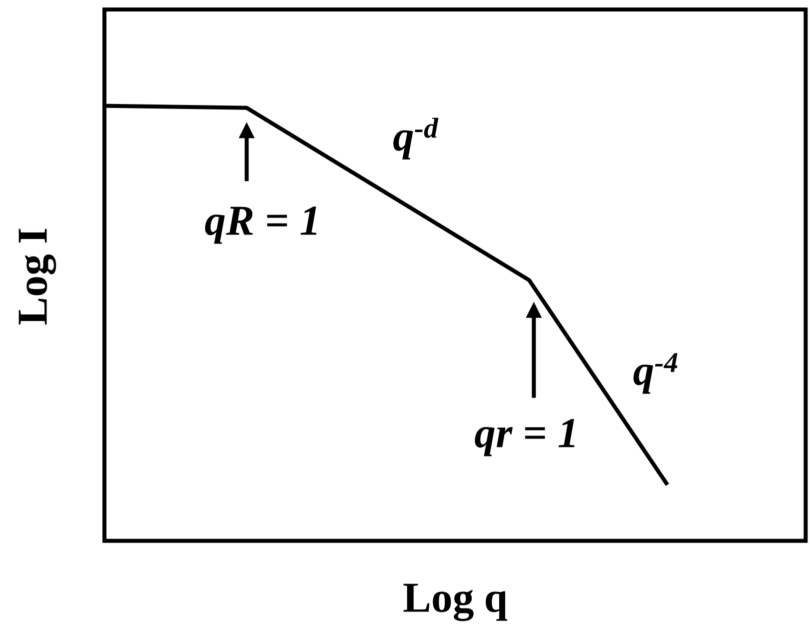
| | Structure | Scaling Relation | Porod Slope $= d_s - 2d_m$<br>$qR >> 1$ |
|---|---|---|---|
| Smooth Surface |  | $d_m = 3$<br>$d_S = 2$ | $-4$ |
| Rough Surface |  | $d_m = 3$<br>$2 < d_S \leq 3$ | $-3 \leq$ Slope $\leq -4$ |
| Mass Fractal |  | $1 \leq d_s = d_m \leq 3$ | $-1 \leq$ Slope $\leq -3$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

# Scattering from colloidal aggregates



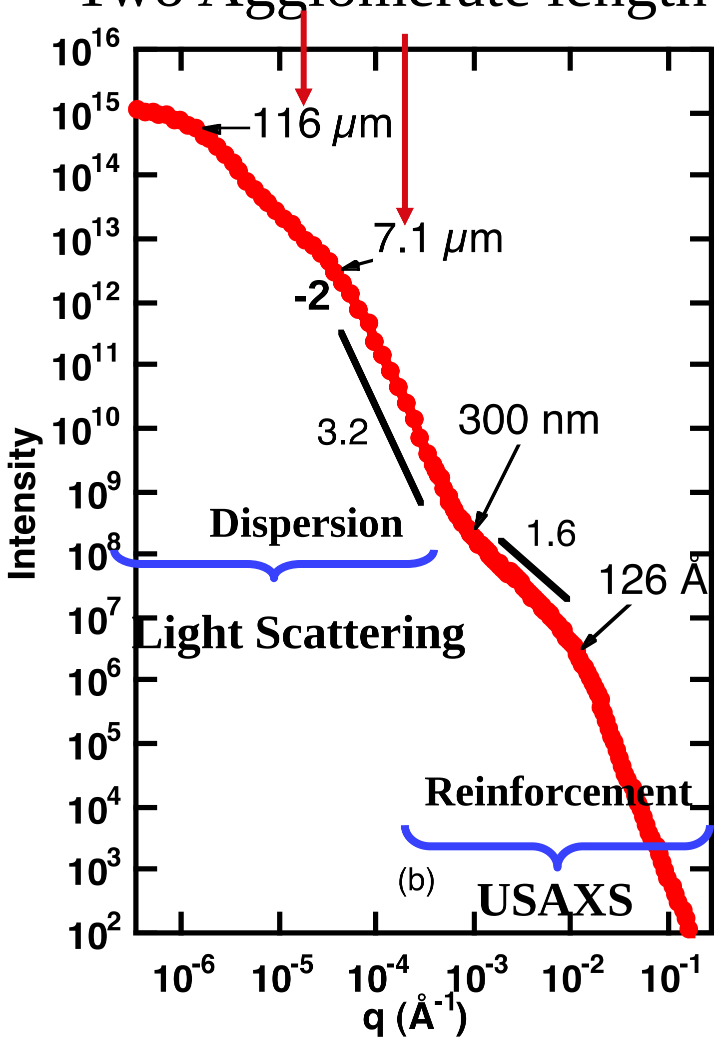



**Precipitated Silica**



# Morphology of Dimosil® Tire-Tread Silica

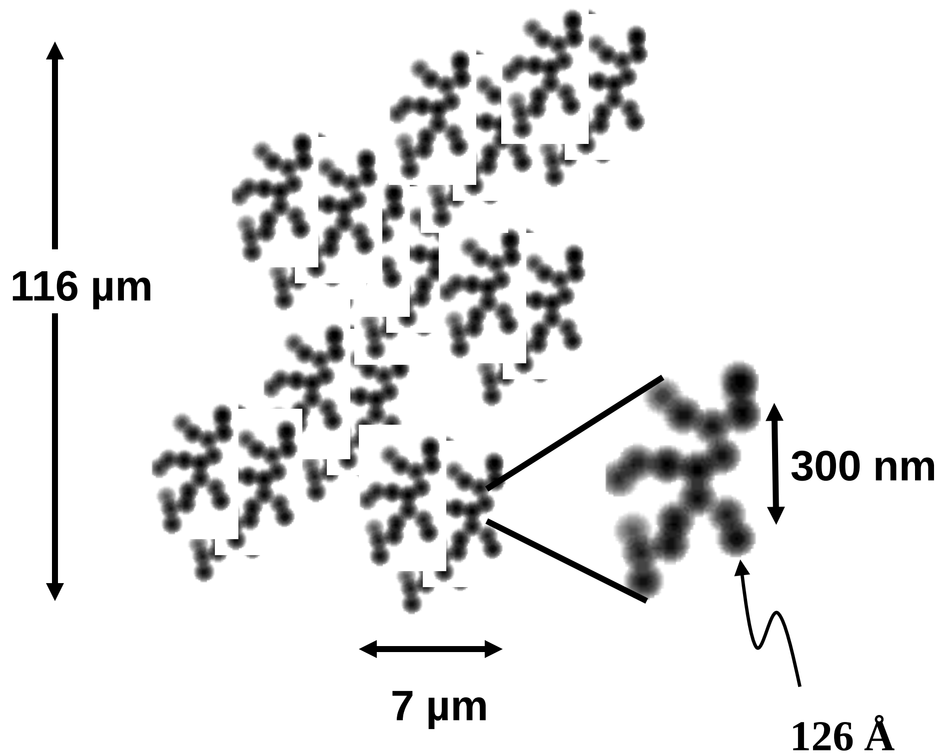
## Two Agglomerate length Scales



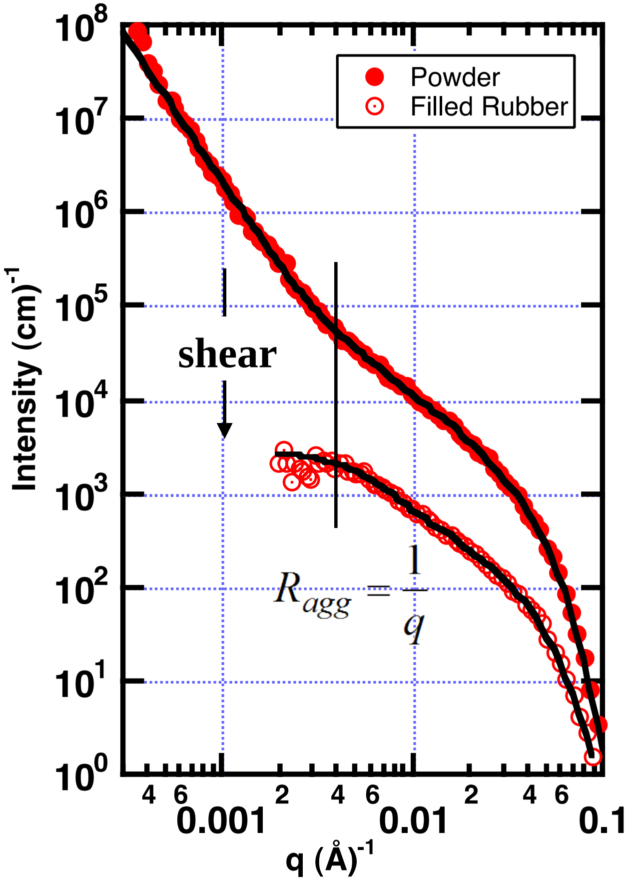

-4

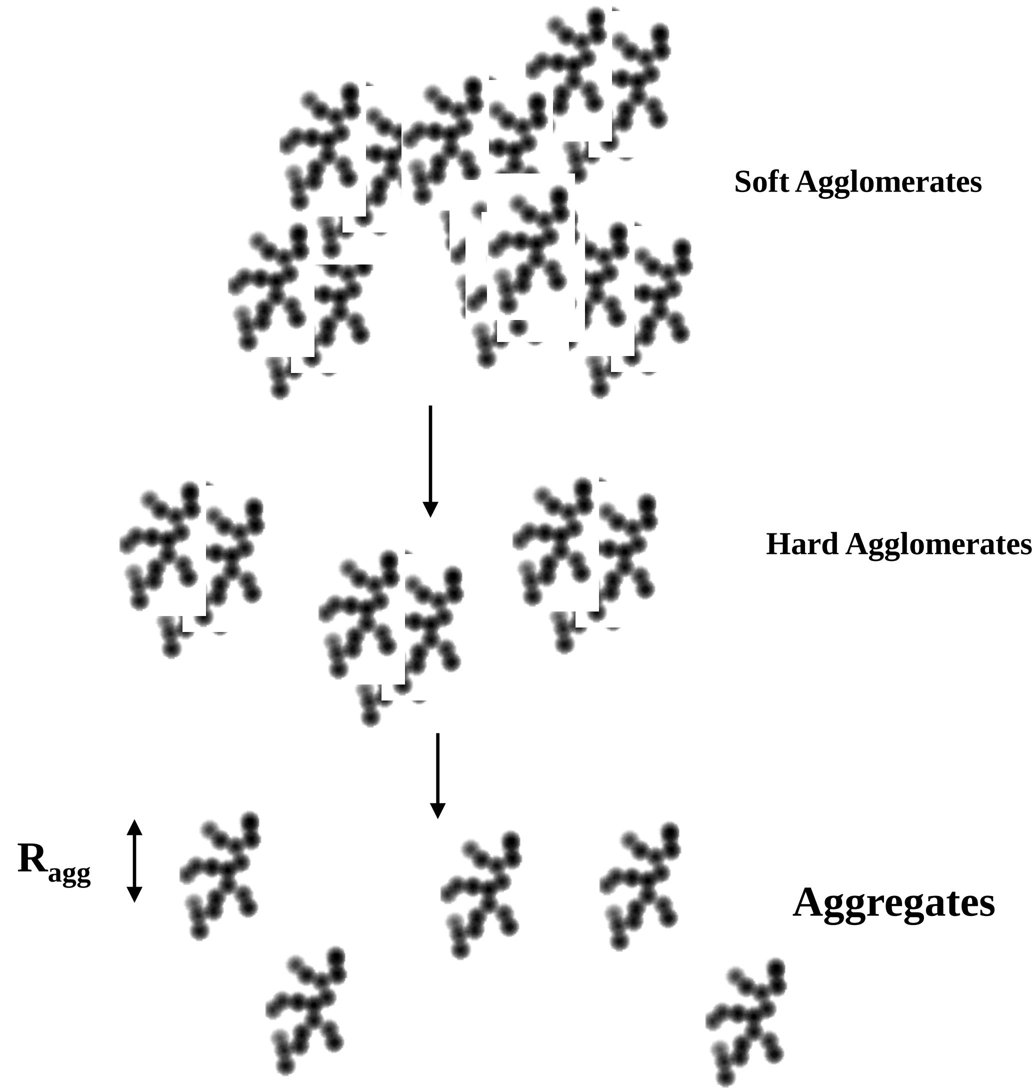
Soft = Chemically Bonded

Hard = Physically Bonded



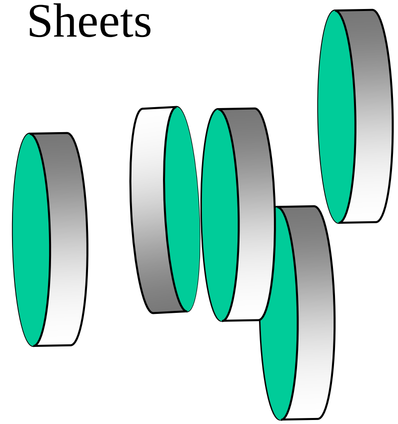
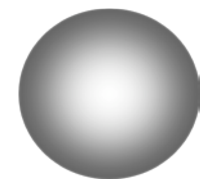
# Aggregates are robust




**What is the ideal aggregate size?**

# Exploring the Nanoworld

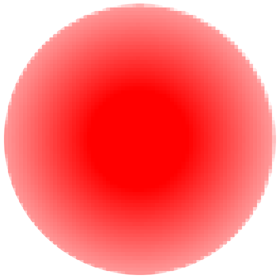
| *1-d* | *2-d* | *3-d* |
|---|---|---|
| Tubes | Sheets | Spheres |
|  |  |  |
| Carbon Nanotubes | Layered Silicates | Colloidal Silica |

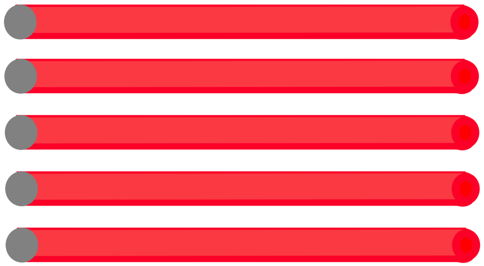
How valid are the cartoons?
What are the implications of morphology for material properties?

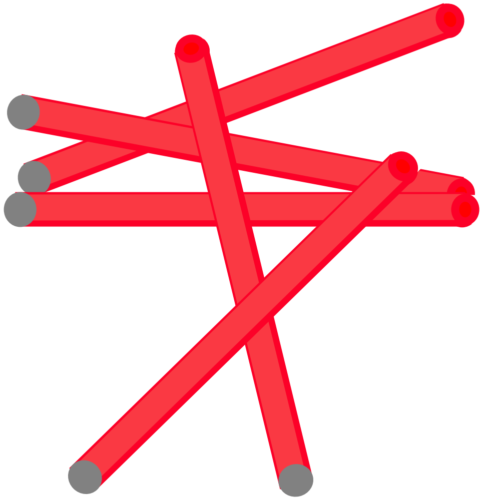
## Answers come from Small-Angle Scattering.

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

# The Promise of Nanotube Reinforcement







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

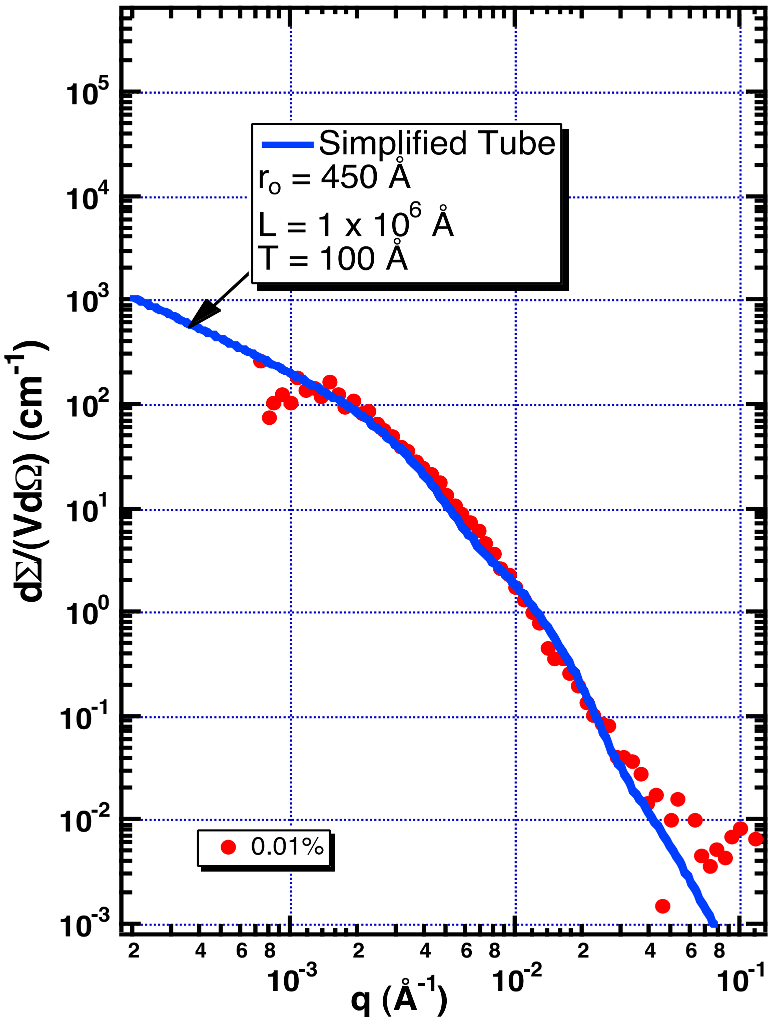
$$E_\delta = 1 + 2.5\phi$$

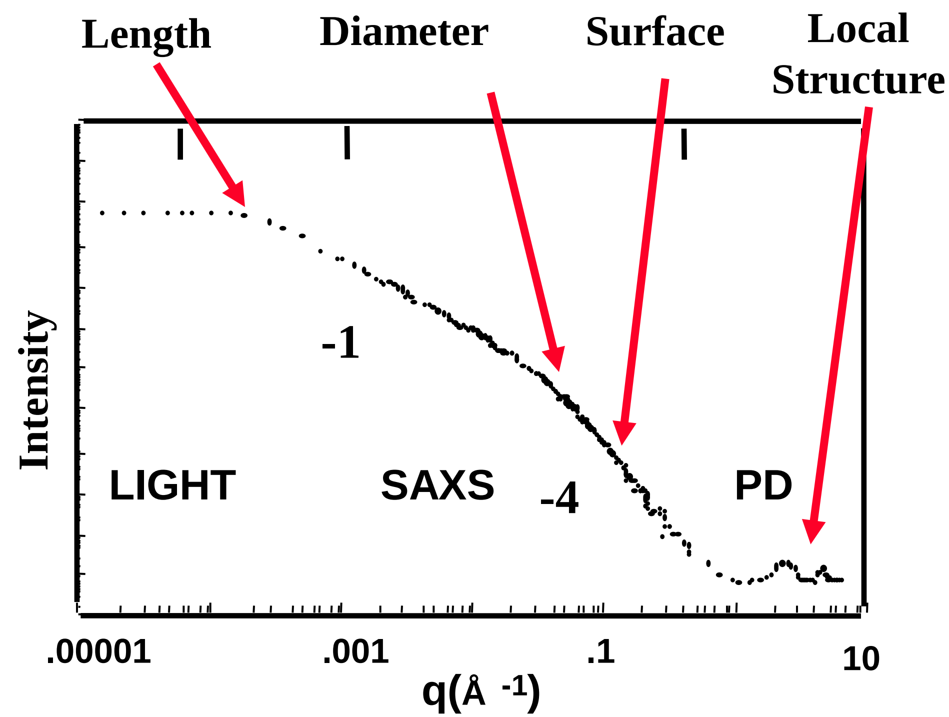
$$= 1 + 2\alpha\phi \cong 1 + 2000\phi$$

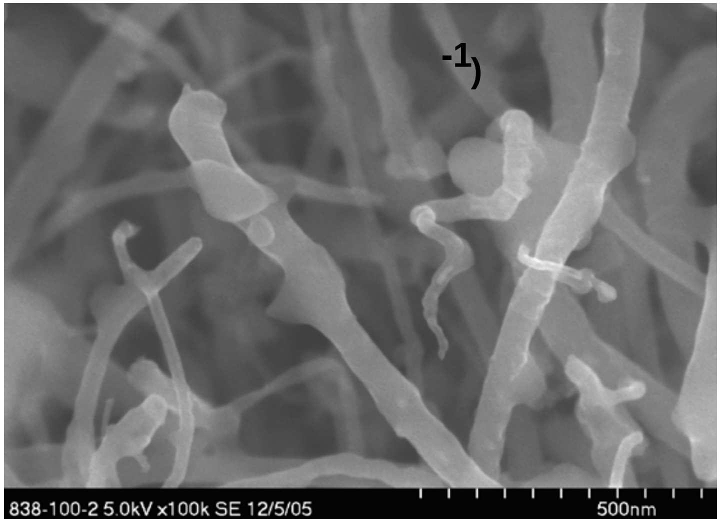
$$= 1 + \underline{0.4\alpha\phi} \cong 1 + 400\phi$$

α = aspect ratio

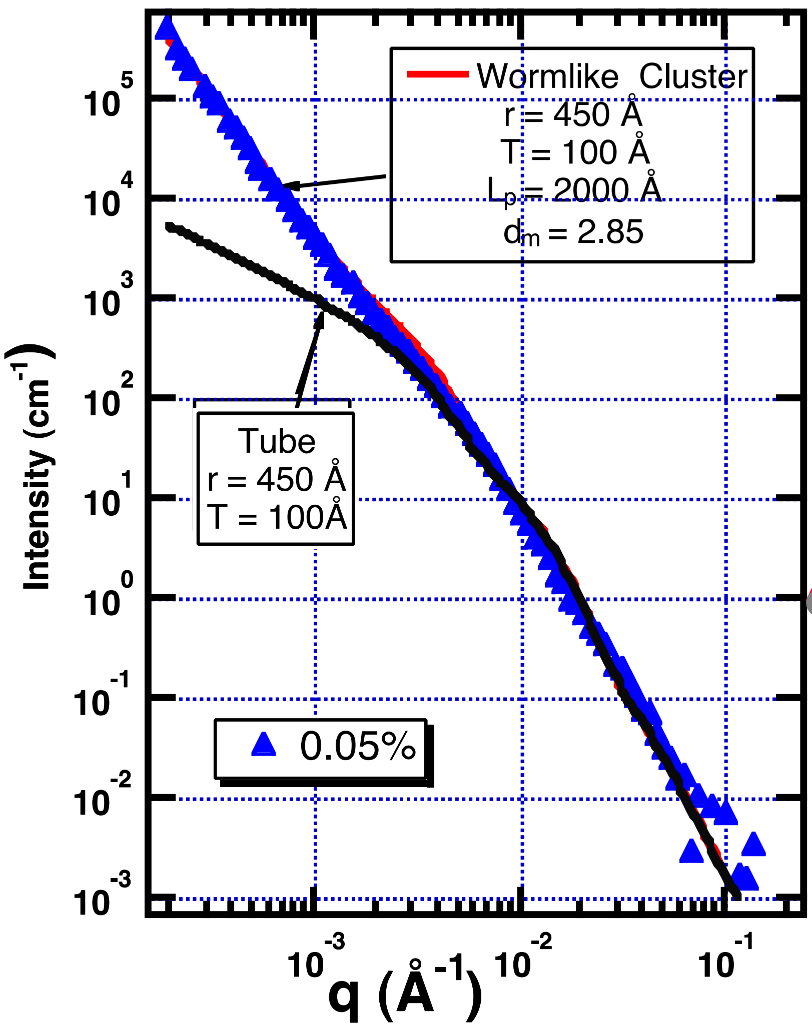
# 0.01% Loading CNTs in Bismaleimide Resin



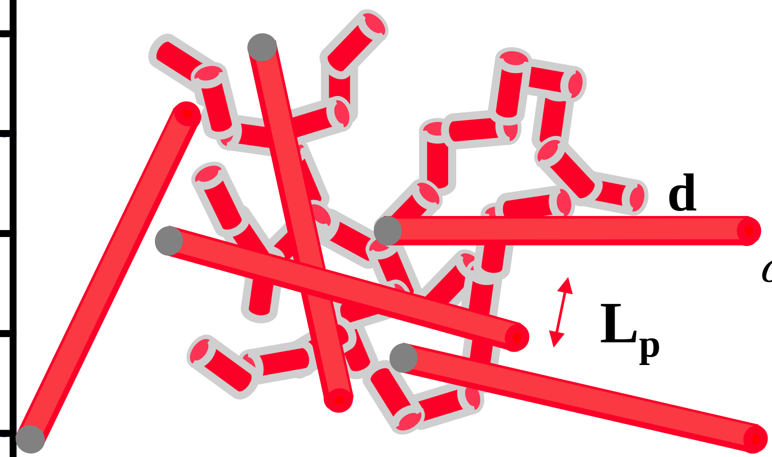



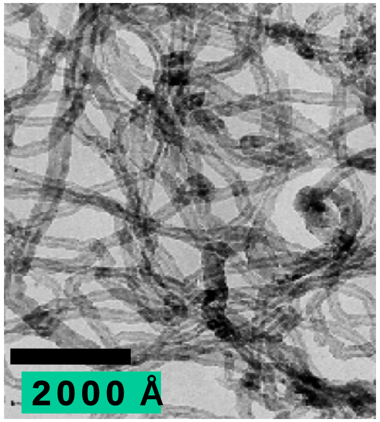
# 0.05% Carbon in Bismaleimide Resin




**Worm-like branched cluster**

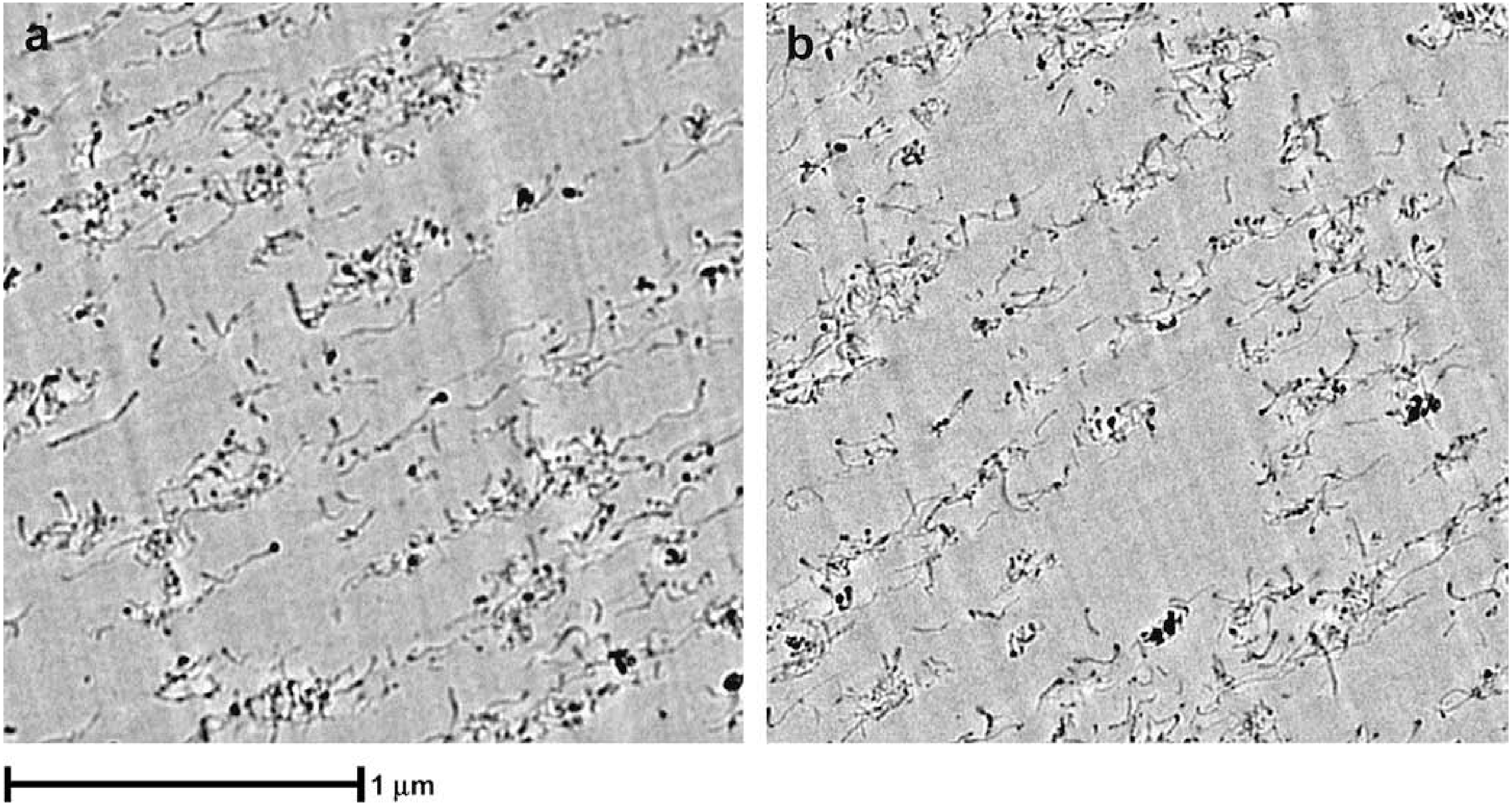



$$\alpha = \frac{L_p}{r} = 4.5$$



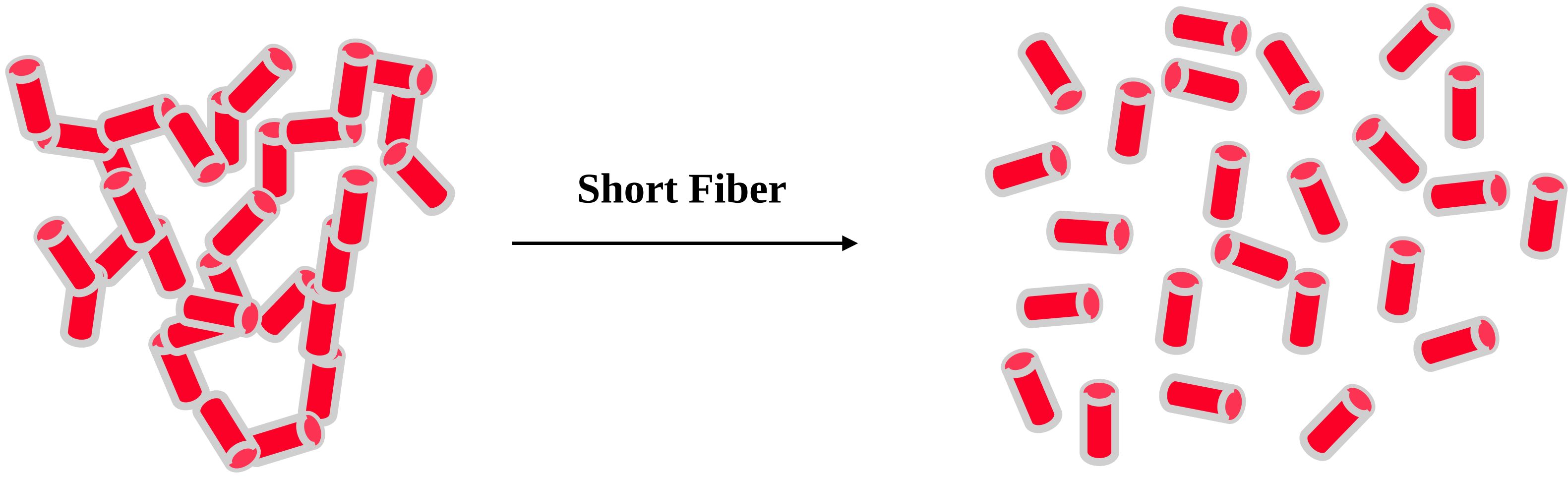
# TEM of Nanocomposites

**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

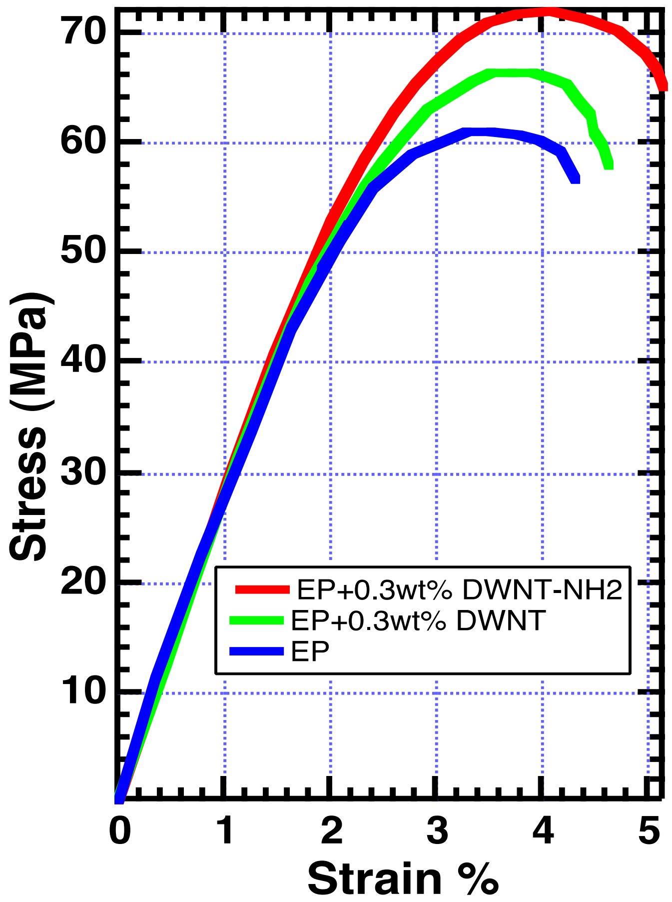
$$E_\delta = \frac{E_c}{E_m} = 1 + 0.4\alpha\phi \qquad \alpha = 4.5$$

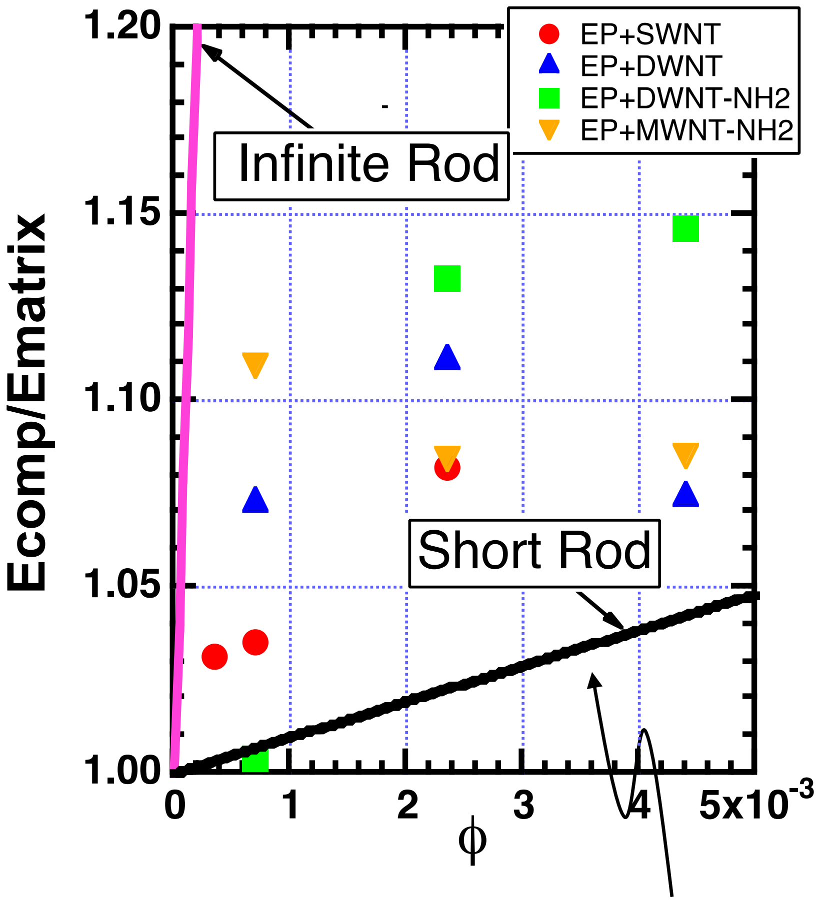
$$\cong 1 + 2\phi$$

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**

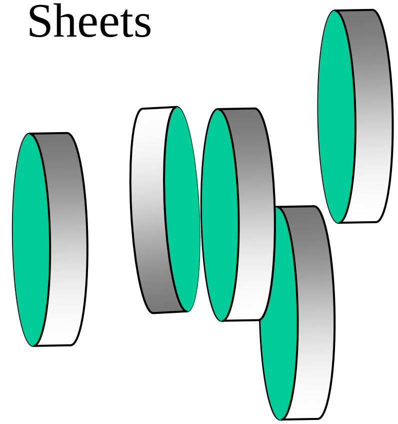
$\alpha = 4.5$

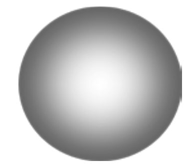
Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Comp. Sci. & Tech.* 2005, 65, (15-16), 2300-2313.

# Don’t Believe the Cartoons

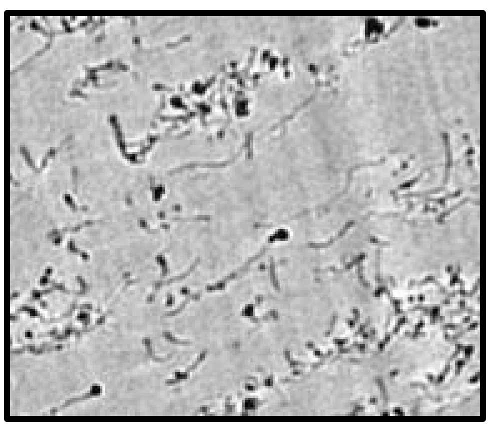
*1-d* | *2-d* | *3-d*

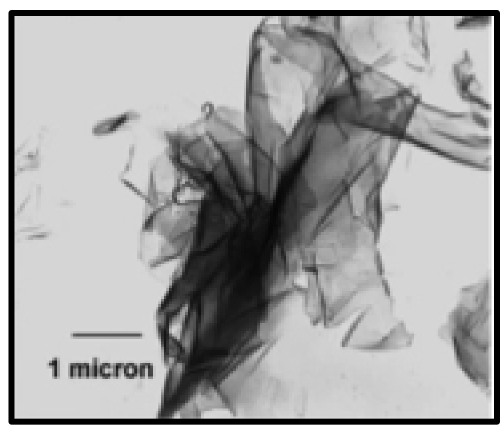
Tubes | Sheets | Spheres

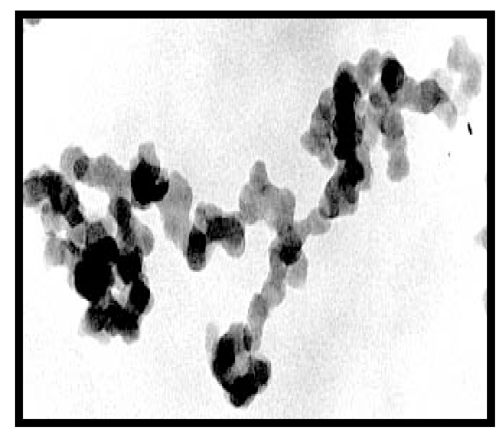




Carbon Nanotubes | Layered Silicates | Colloidal Silica





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

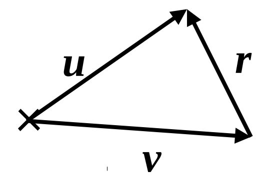
depends on absolute position of atoms

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

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

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

Ensemble Average < >




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

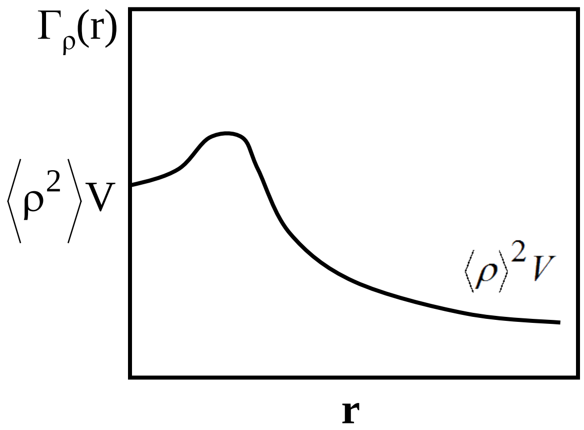
**Problem!**
**Must know sample geometry**

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

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

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

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



# Extending to infinite integrals

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

$$= \int_{-\infty}^{\infty} \left[\Gamma_\rho(\mathrm{r}) - \langle\rho\rangle^2 V\right] e^{-i\mathrm{q}\cdot\mathrm{r}}\, d\mathrm{r} + \langle\rho\rangle^2 V \iint \int_{-\infty}^{\infty} e^{-i\mathrm{q}\cdot\mathrm{r}}\, d\mathrm{r}$$

$$\equiv \int_{-\infty}^{\infty} \Gamma_\eta(\mathrm{r}) e^{-i\mathrm{qr}}\, d\mathrm{r} \qquad q \neq 0$$

$$\eta(\mathrm{r}) = \rho(\mathrm{r}) - \langle\rho\rangle$$

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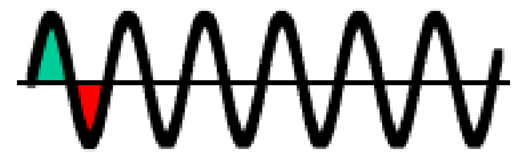
$$e^{iqr} = \cos qr + i \sin qr$$



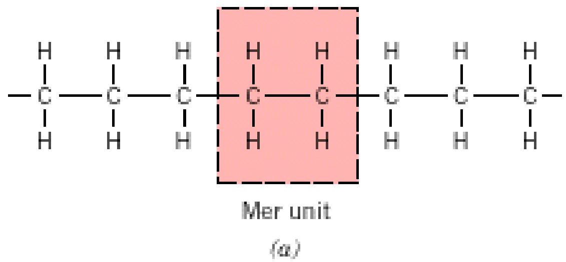
$\Gamma_\eta$ = Autocorrelation of the fluctuation of the scattering length density.

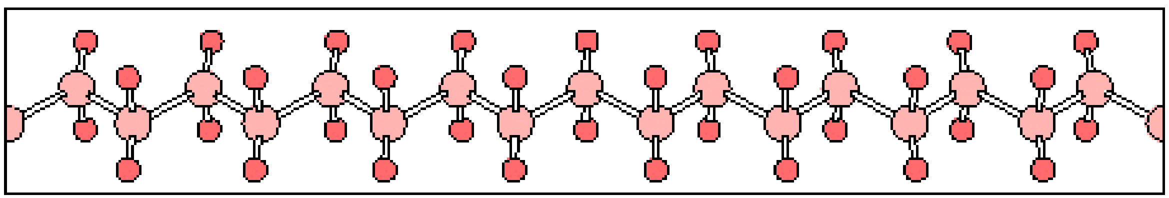
$$\delta(\mathrm{q}) = \int e^{-i\mathrm{qx}} d\mathrm{x}$$

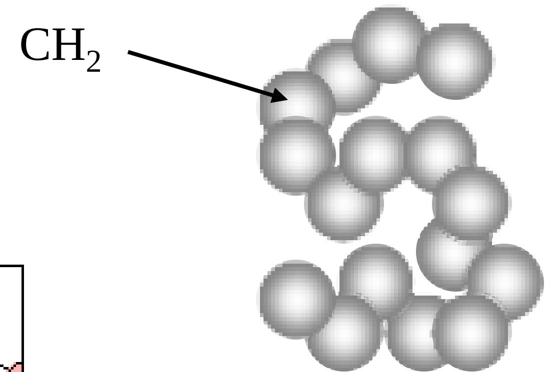
Scattering is determined by fluctuations of the density from the average

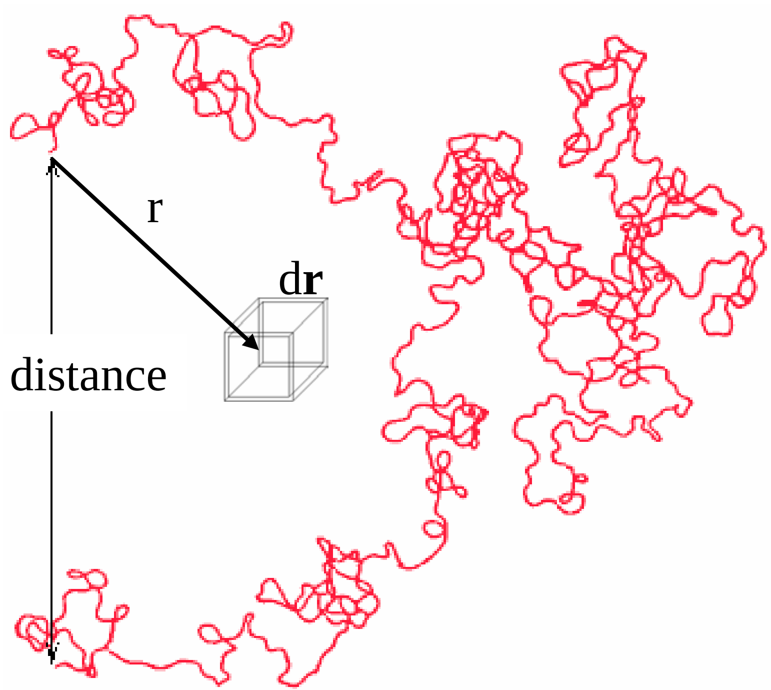
A dilute gas does not “diffract” (scatter coherently).

# SAXS from Polymers



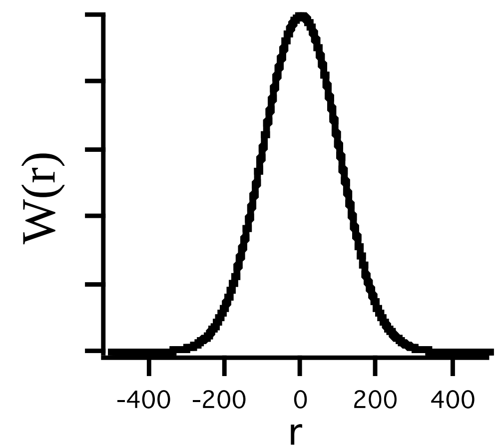


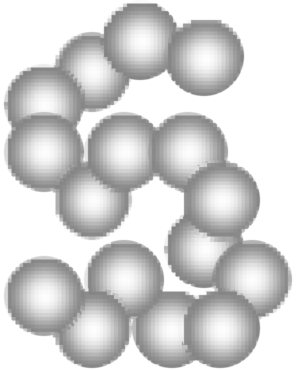

End-to-end distance

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

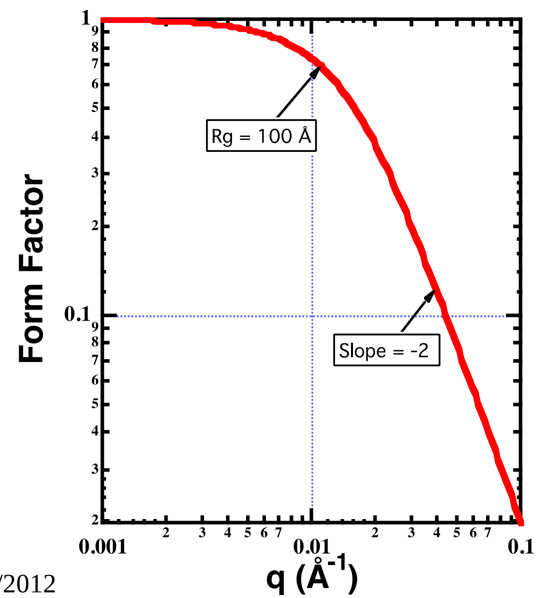


N bonds of length $l$, N+1 beads of volume $v_u$
scattering length of one bead = $\rho_0 v_u$

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

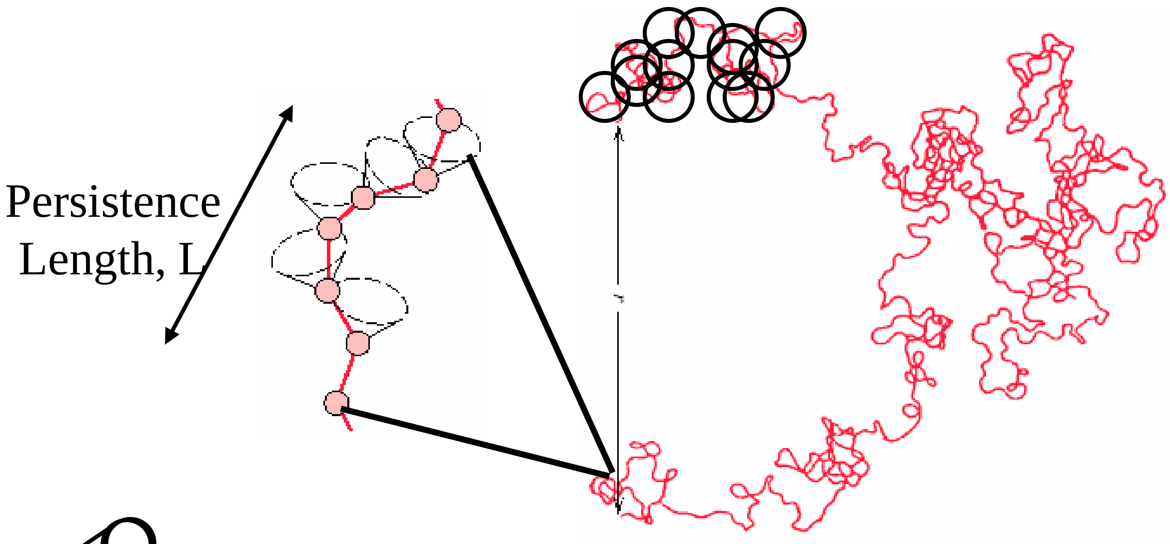
$$P(r) = 2\underbrace{\sum_{K=0}^{n}\left(N+1-K\right)}_{\text{Number of walks of K steps}}\underbrace{\left(\frac{3}{2\pi K l^2}\right)^{3/2}\exp\left(\frac{3r^2}{2Kl^2}\right)}_{\text{e-e distribution for a walk of K steps}}$$

$l$ = bond length



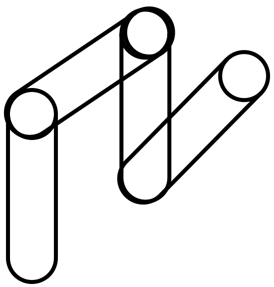

$$I(q) = \left(\rho_o v_u\right)^2 \underbrace{\frac{2(e^{-x} + x - 1)}{x^2}}_{\text{Debye form factor}}; \quad x = \frac{q^2 N l^2}{6} = q^2 \langle R_g \rangle^2$$

# Worm-like Chain

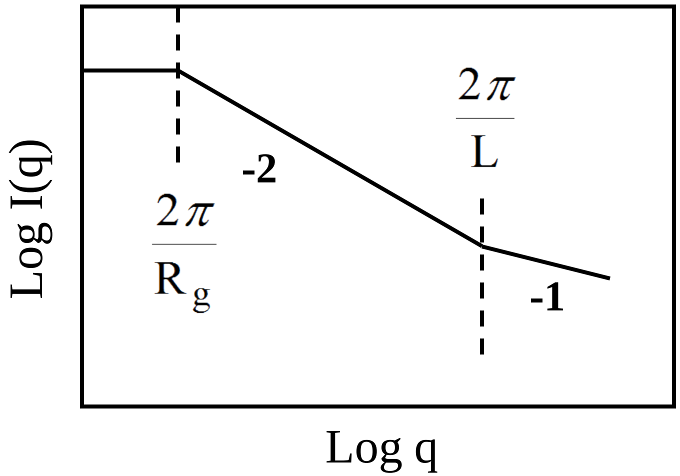



**Gaussian on large length scales**

**d = 2**



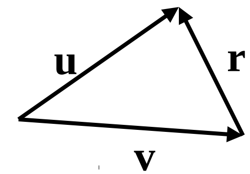
Rod like on short length scales **d = 1**



# Correlation Functions

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

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

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

$$I(\mathbf{q}) \equiv \int \Gamma_\rho(\mathbf{r})\ e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

$$\Gamma_\rho(\mathrm{r}) = \left\langle \int_{V_{sample}} \rho(\mathbf{u})\rho(\mathbf{u}+\mathbf{r}) d\mathbf{u} \right\rangle$$

$\Gamma_\rho(\mathrm{r})$ 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)**