Exploring the Nanoworld: Imaging and Scattering

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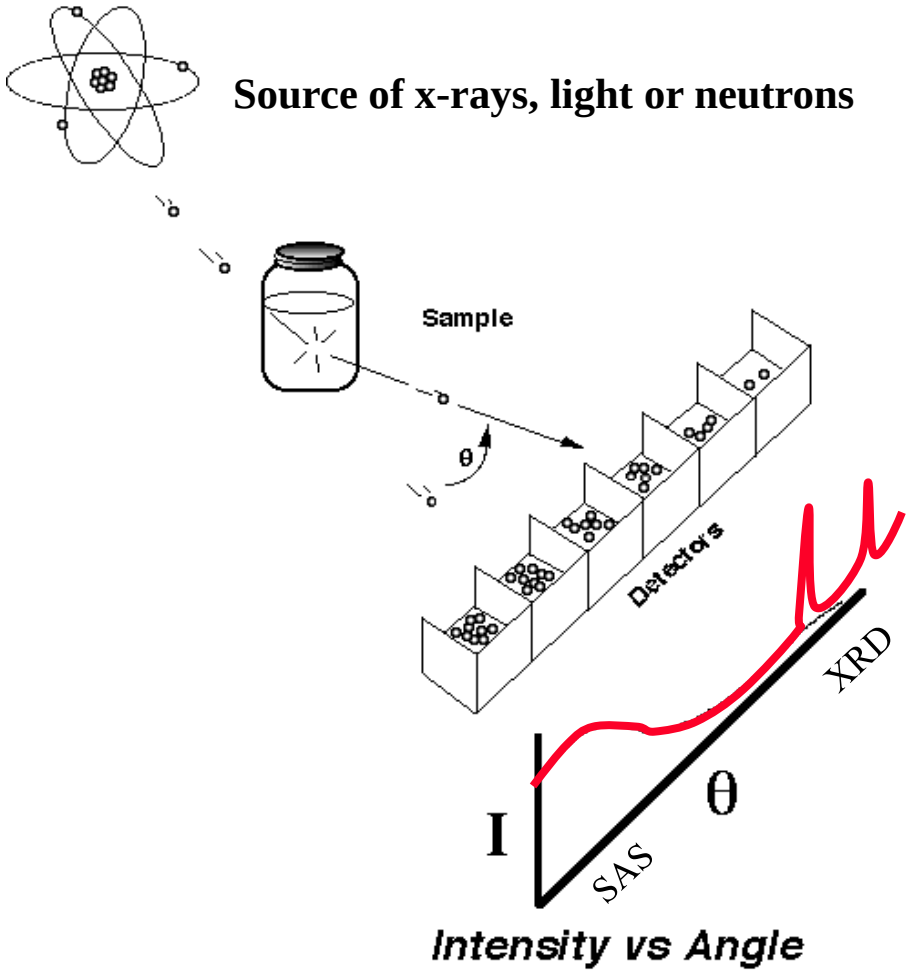
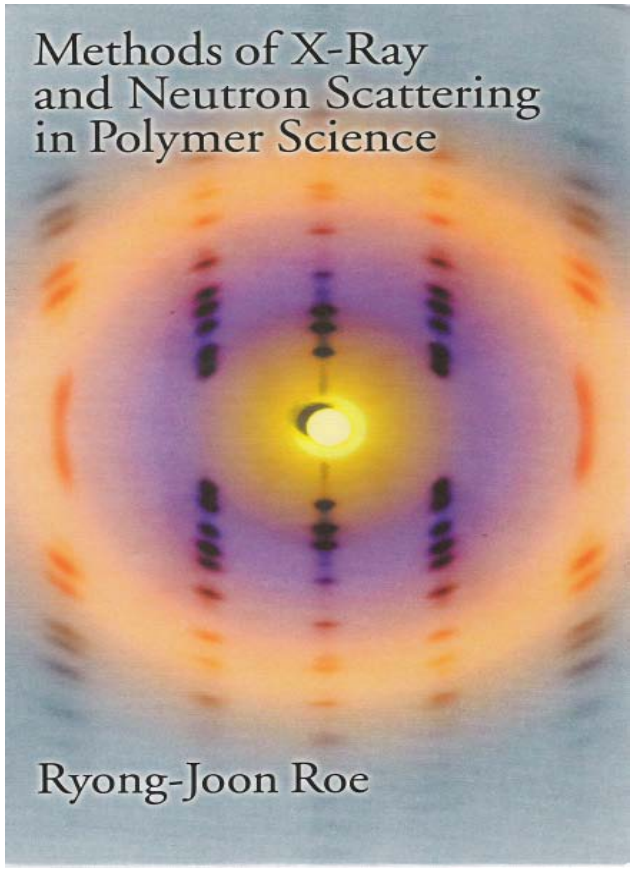
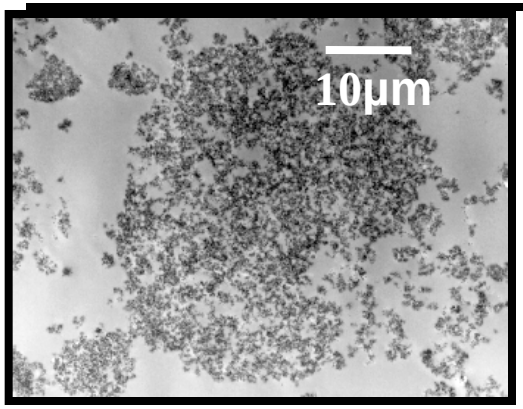




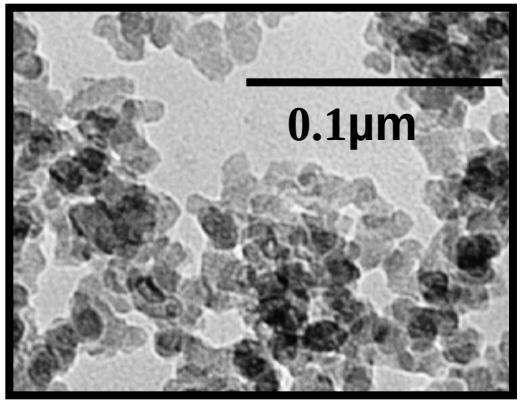
Real Space Imaging



Agglomerates

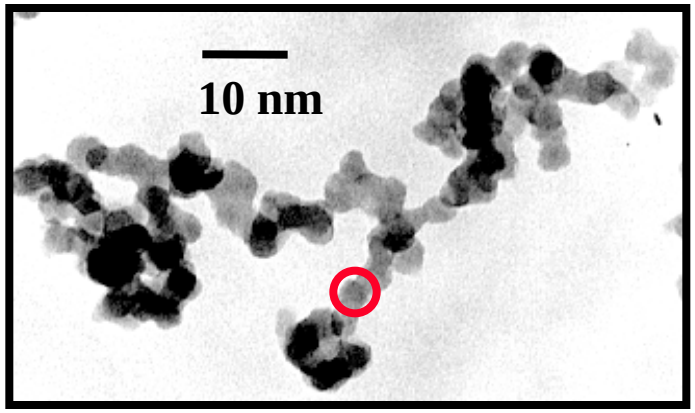
Precipitated Silica

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



Aggregates

Primary Particles

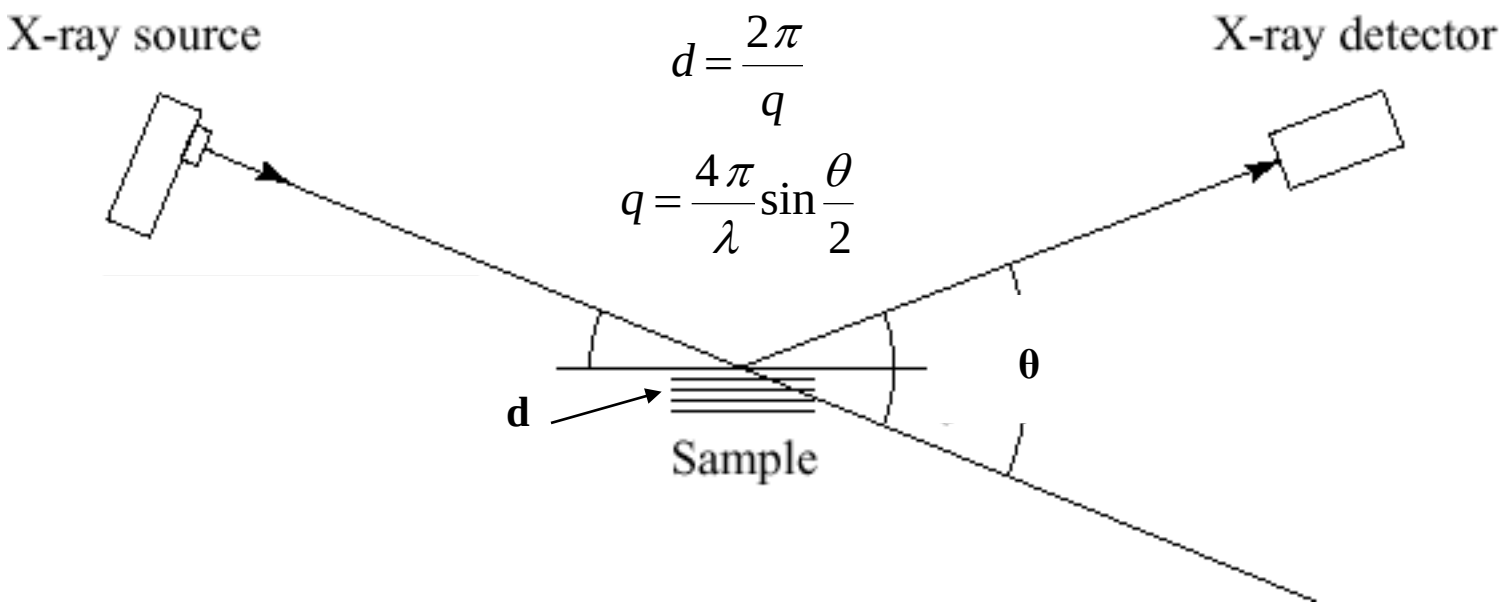


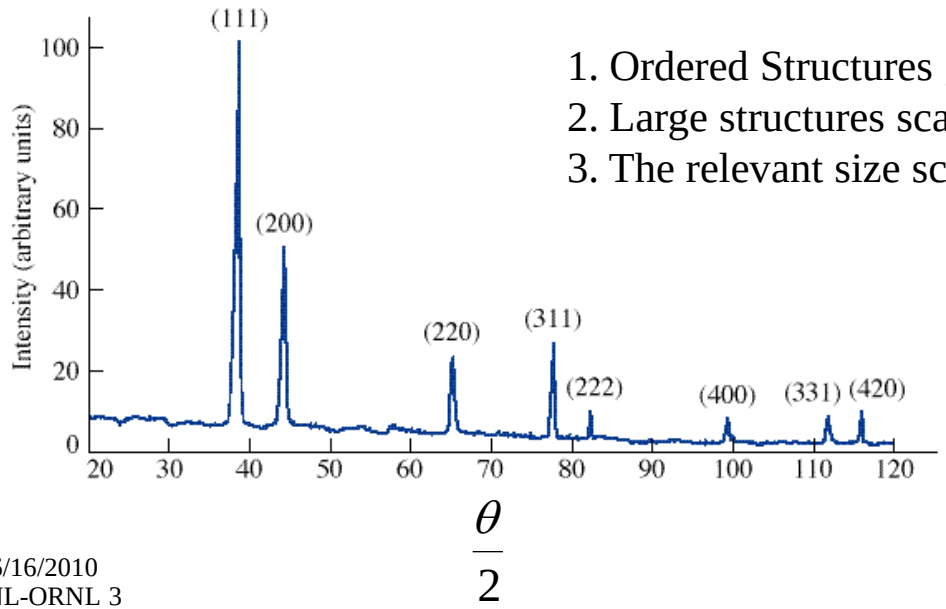
Seven orders of magnitude in length scale.
How can the structure be parameterized?

Bragg's Law and the scattering vector, q

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

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



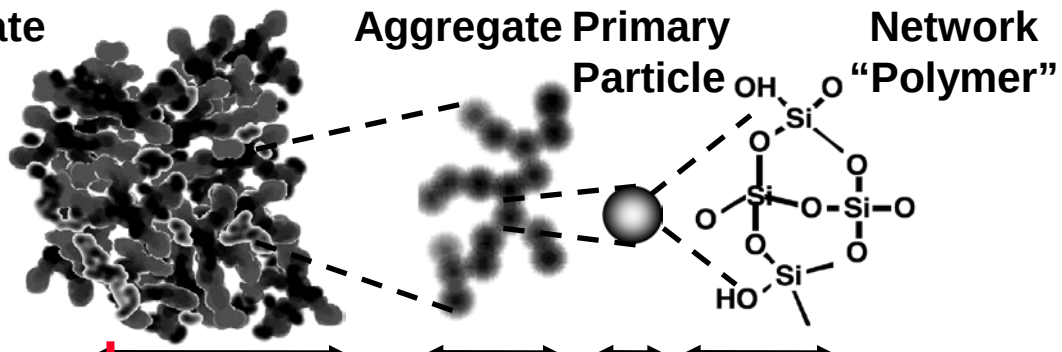


1. Ordered Structures give peaks in "reciprocal" space
2. Large structures scatter at small angles
3. The relevant size scale is determined by $2\pi/q$.

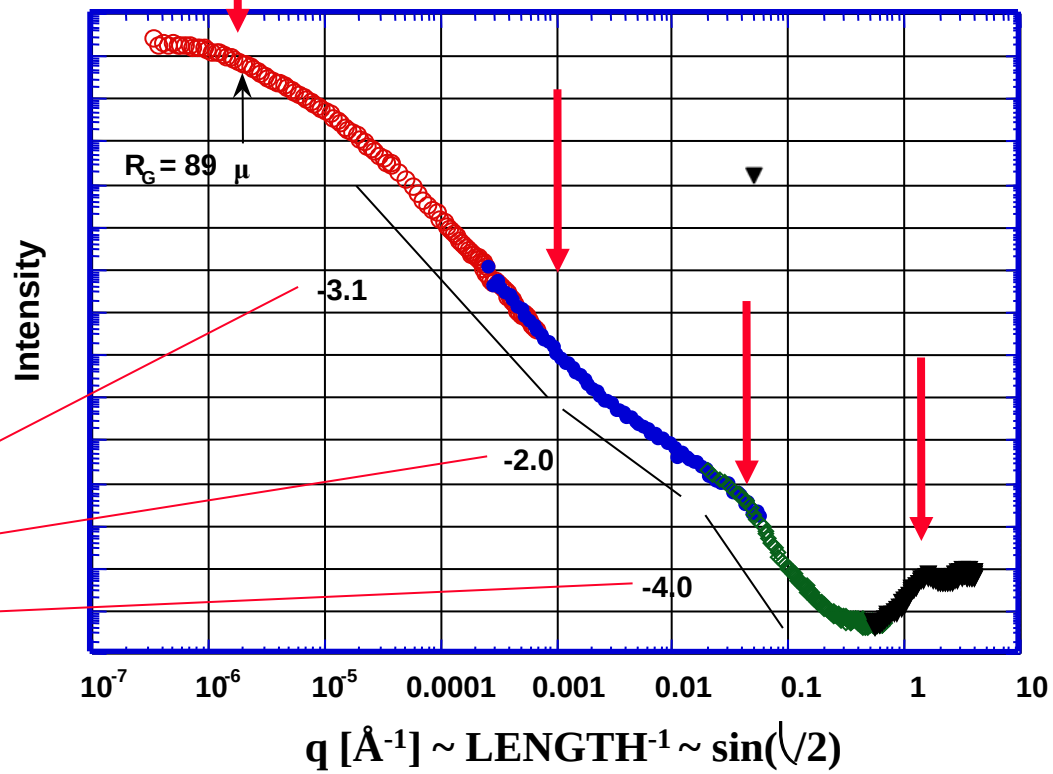
SAXS: θ < 6°

Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes



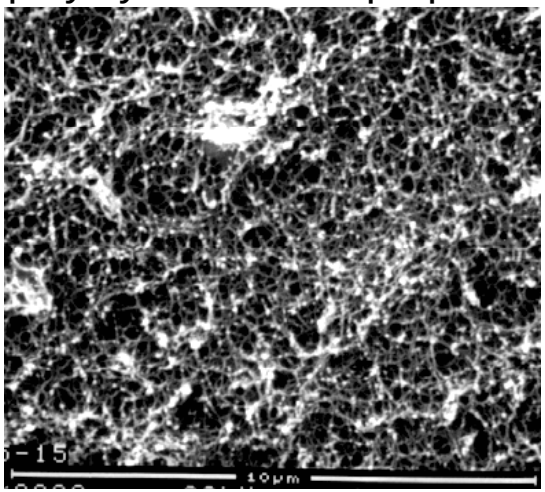
$$q = \frac{2\pi}{d_{bragg}} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

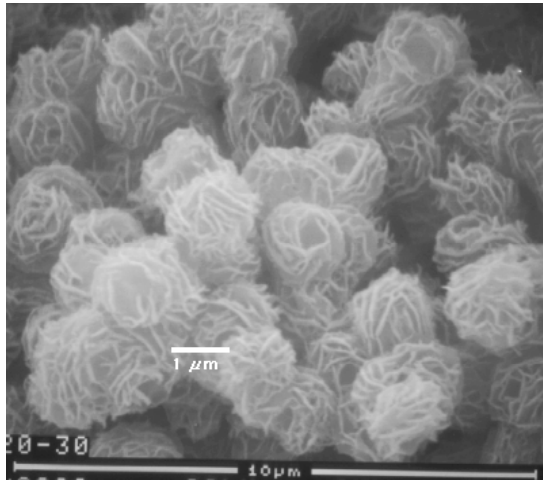


Exponents related to morphogy

Why Reciprocal Space?

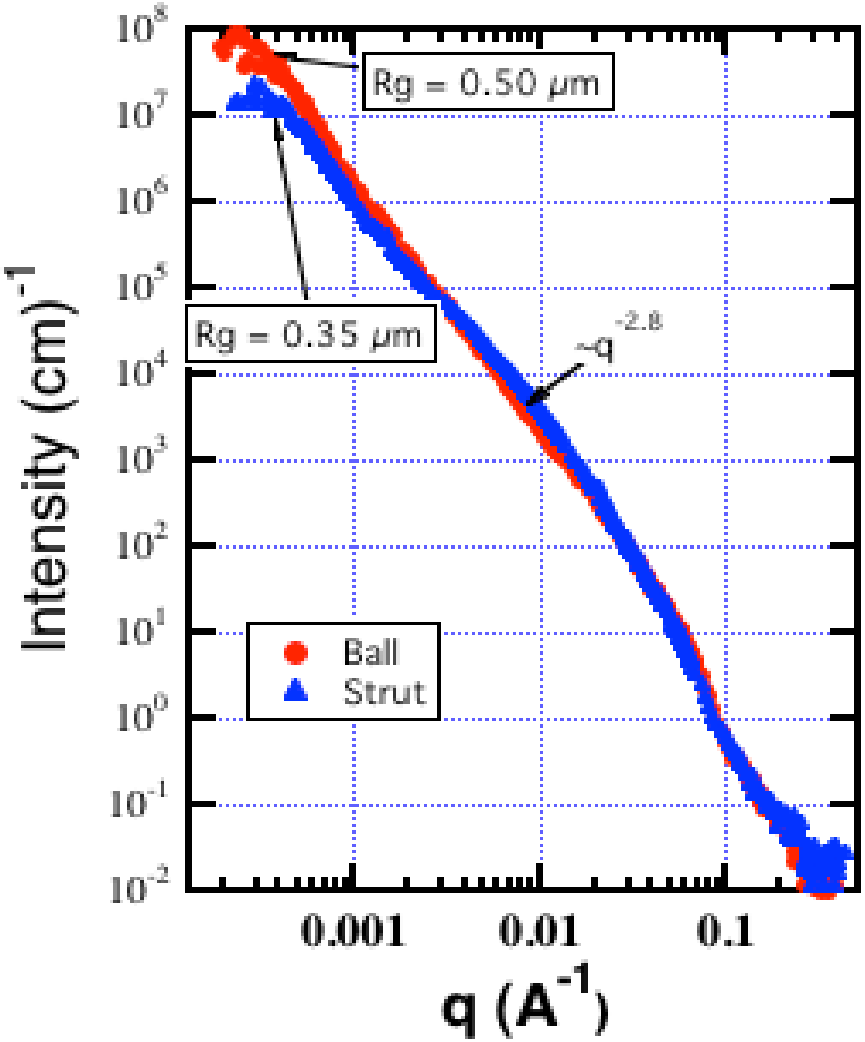
Isotactic polystyrene foams prepared by TIPS





10 μm

Jim Aubert, SNL



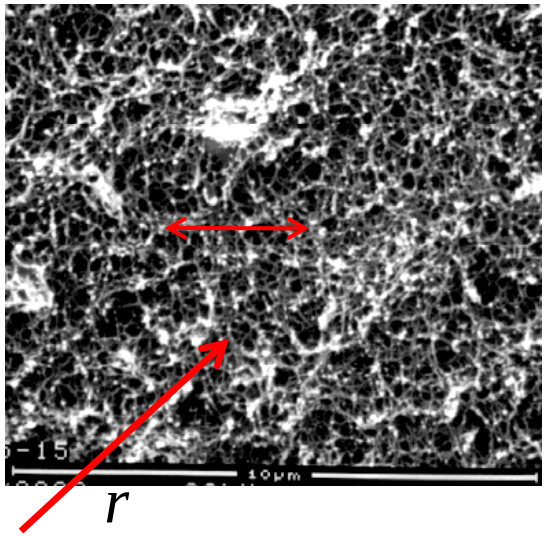
Images miss similarity

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

Characterizing Disorder in Real Space

Electron Density Distribution

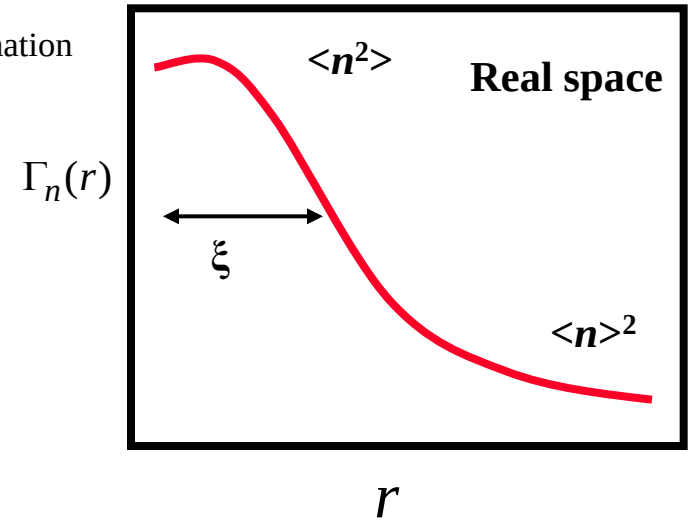
$$n(r)$$



Throw out phase information

Correlation Function of the Electron Density Distribution

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



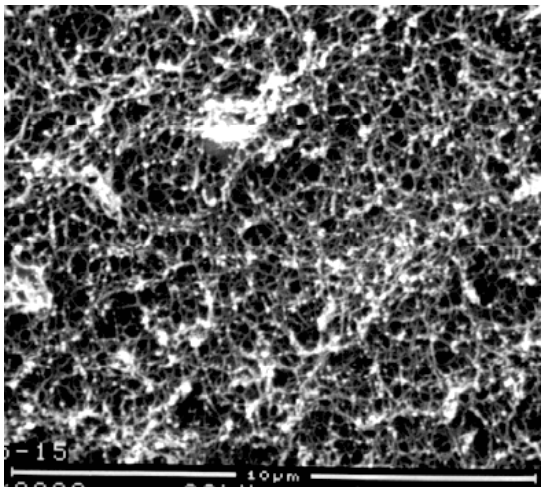
Depends on latitude and longitude.
Too much information to be useful.

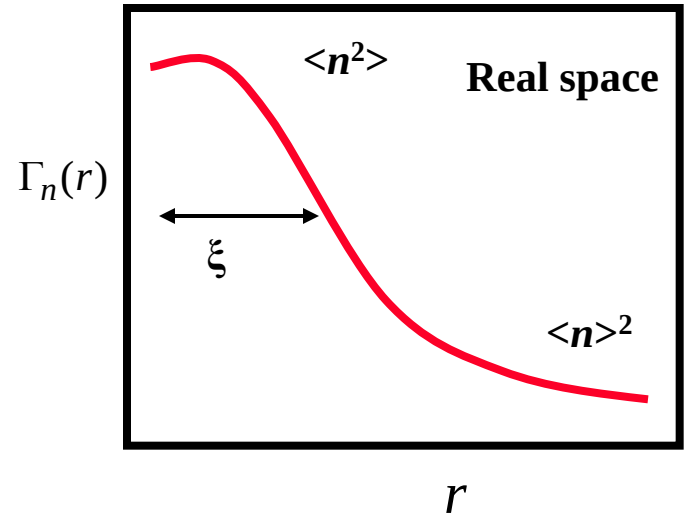
Depends on separation distance.
Retains statistically significant info.

Resolution problems at small *r*
Opacity problems for large *r*

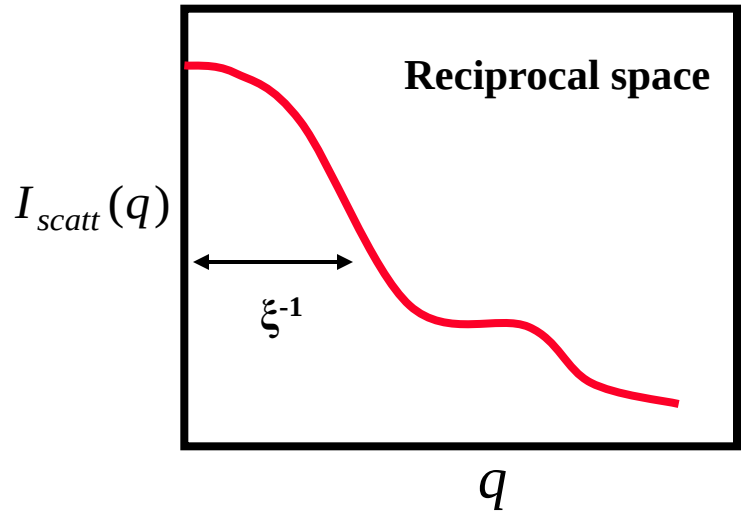
Imaging vs Scattering

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



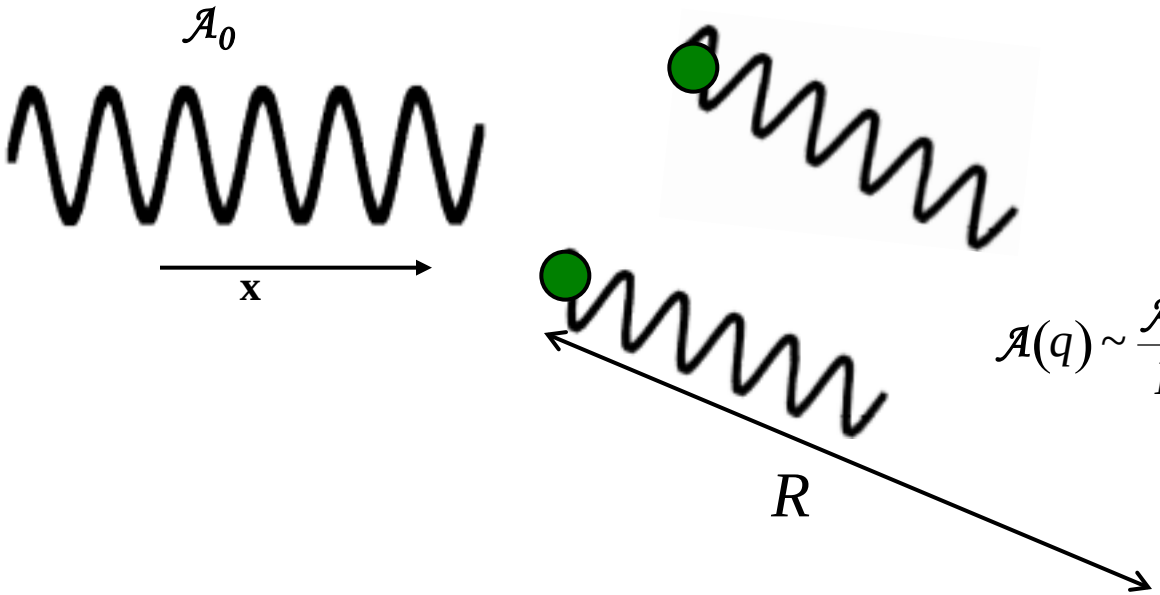


$$I_{scatt} \equiv \int \Gamma_n(\mathrm{r})\ e^{-iqr} d\mathrm{r}$$



Generalized Bragg's Law

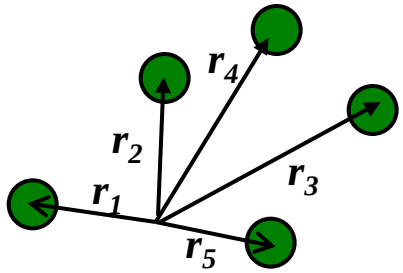
Scattering from 2 electrons



$$\mathcal{A}(q) \sim \frac{\mathcal{A}_o}{R}\left[n(r_1)e^{-i\mathbf{q}\cdot\mathbf{r}_1} + n(r_2)e^{-i\mathbf{q}\cdot\mathbf{r}_2}\right]$$

$n(r) \sim \rho(r) \leftarrow$ scattering length density

multiple electrons



$$\mathcal{A}(\mathbf{q}) = \sum_{j=1}^{N} \rho(r_j) e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

Intensity from Amplitude

$$\sum \rightarrow \int$$

$$\mathcal{A}(q) = \mathcal{A}_o \sum_{j=1}^{N} \rho(r_j) e^{-i\mathbf{q}\cdot\mathbf{r}_j} = \mathcal{A}_0 \int_V \rho(\mathbf{r})\ e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

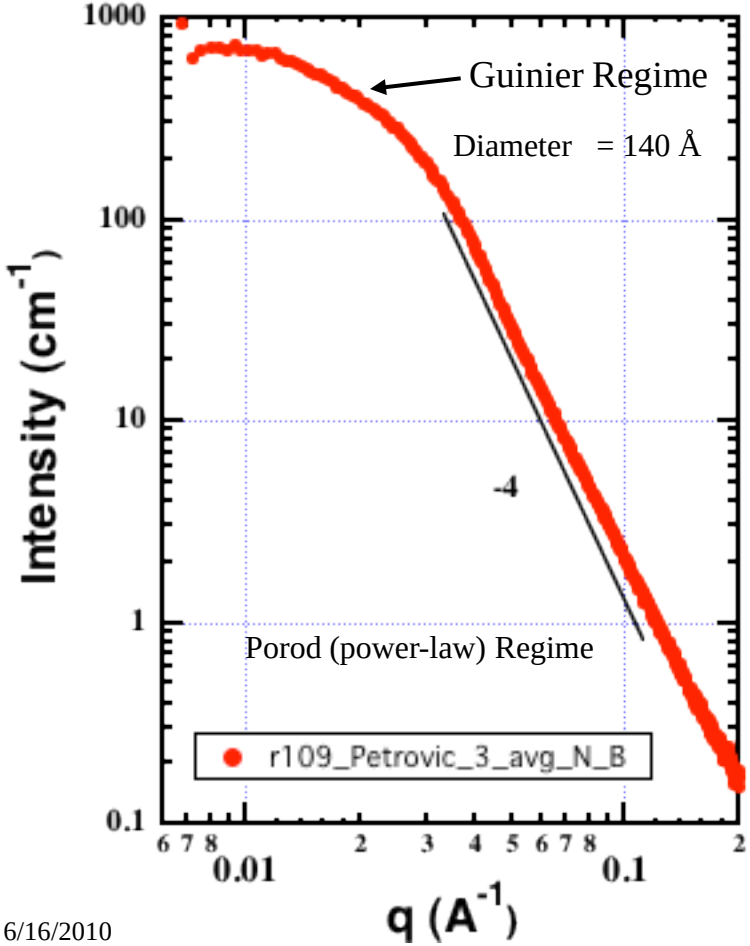
$$I_{scatt} = \left[\frac{\mathcal{A}(q)}{\mathcal{A}_0}\right]^2 = \int_{-\infty}^{\infty} \Gamma_\rho(\mathrm{r})\ e^{-iqr} d\mathrm{r}$$

$$\Gamma_\rho(r) = \int \rho(u)\rho(u+r) du$$

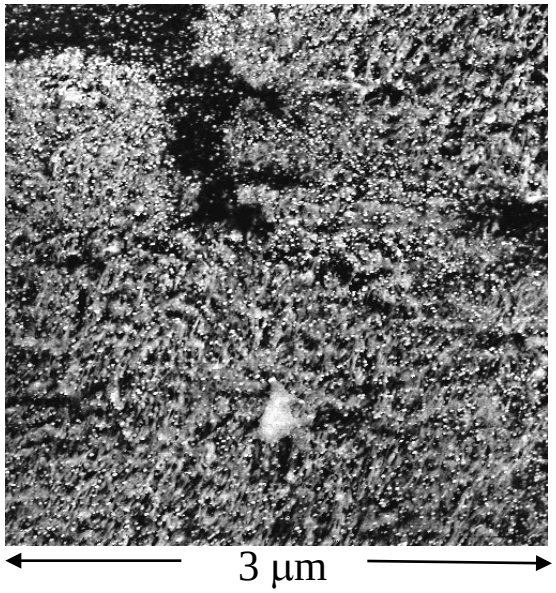
Small-Angle Scattering from Spheres

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

Large object scatter at small angles



Silica in Polyurethane



AFM

Scattering from a Spherical Particle

$$I(\mathrm{q}) = \mathcal{A}^2(q) = \int_V \Gamma_\rho(\mathrm{r})\, e^{-i\mathrm{q}\cdot\mathrm{r}} d\mathrm{r}$$

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

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

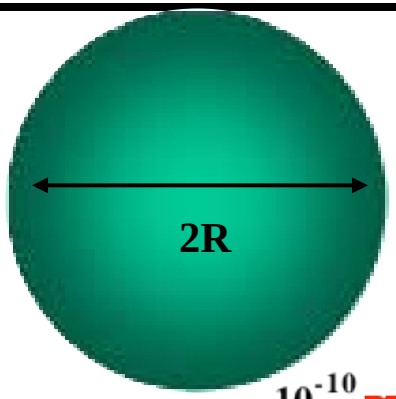
$$= \frac{\rho_0 4\pi}{q} \int_0^R r \sin(qr) dr$$

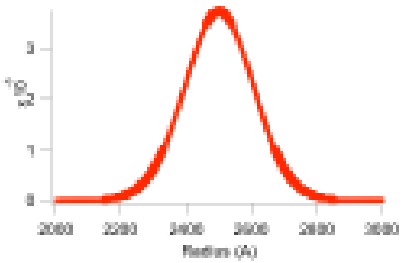
$$= \rho_0 4\pi R^3 \frac{(\sin qR - qR\cos qR)}{(qR)^3}$$

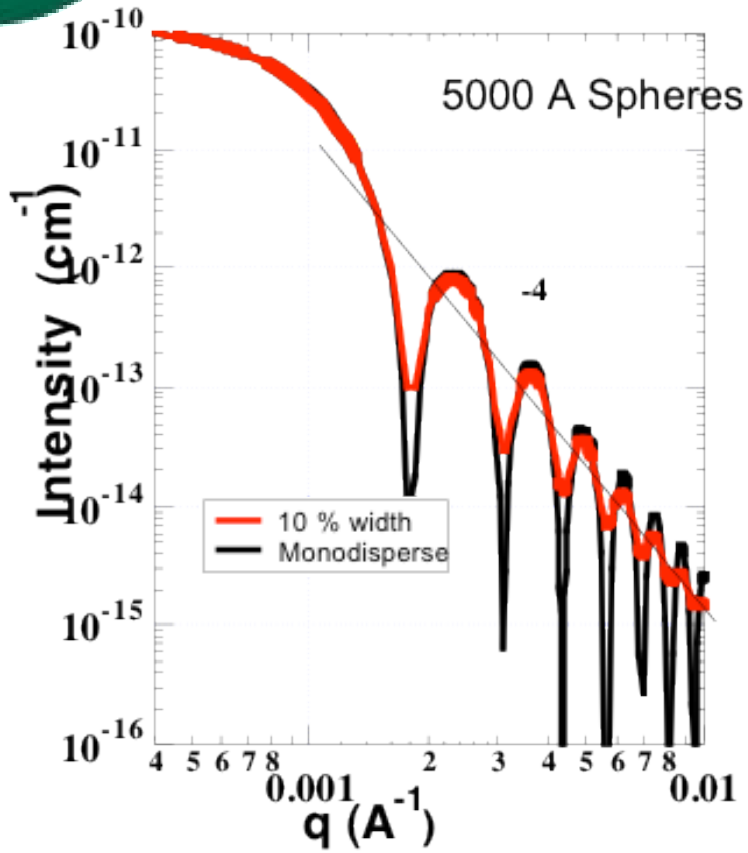
$$= \rho_0 \frac{4\pi R^3}{3} \frac{3(\sin qR - qR\cos qR)}{(qR)^3}$$

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

***v* = particle volume**

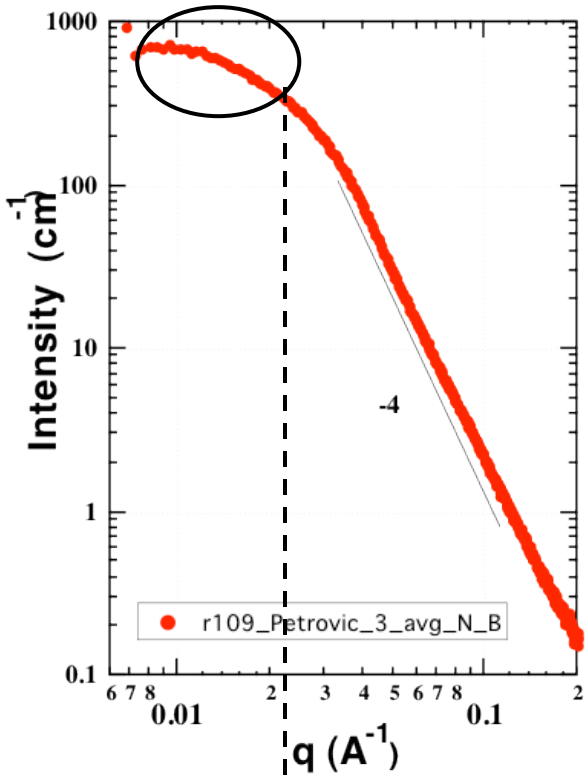






Guinier Radius

Initial curvature is a measure of length



Rg ~ 1/q

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

Derived in 5.2.4.1

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

$$I(q) = |\mathcal{A}(q)|^2 = \rho_0^2 v^2 \left[1 - \frac{1}{3} q^2 R_g^2 + \mathsf{L}\right]$$

$$R_g^2 = \frac{1}{v}\int r^2 \sigma(r) d\mathbf{r}$$

$$\sigma(r) = \begin{cases} 1 & r \le R \\ 0 & r > R \end{cases}$$

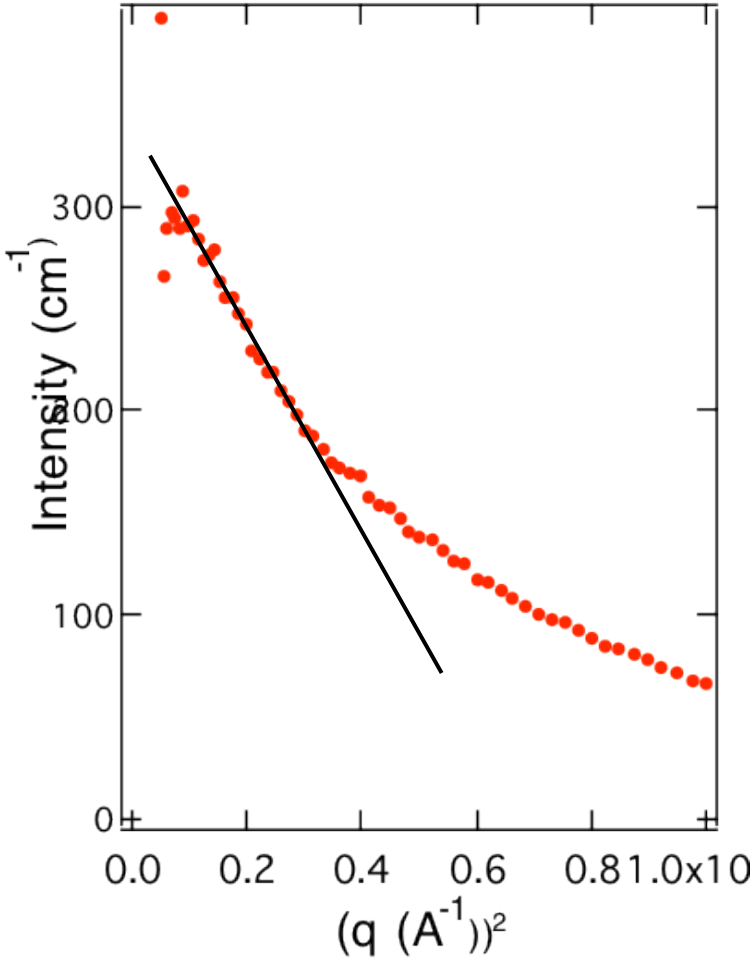
$$R_g = \sqrt{\frac{3}{5}} R_{hard}$$

homework

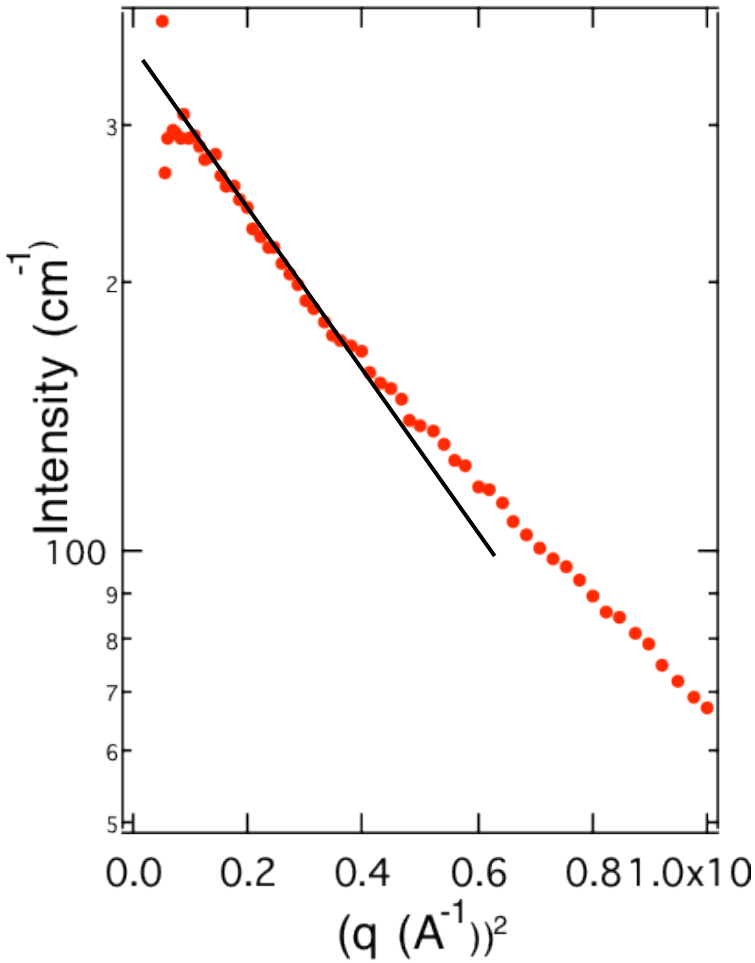
Rg of a sphere

$$\rho_0 4\pi R^3 \frac{(\sin qR - qR\cos qR)}{(qR)^3} = C_1\left[1 - C_2 (qR)^2 + \mathsf{L}\right]$$

Guinier Fits (PS 13)



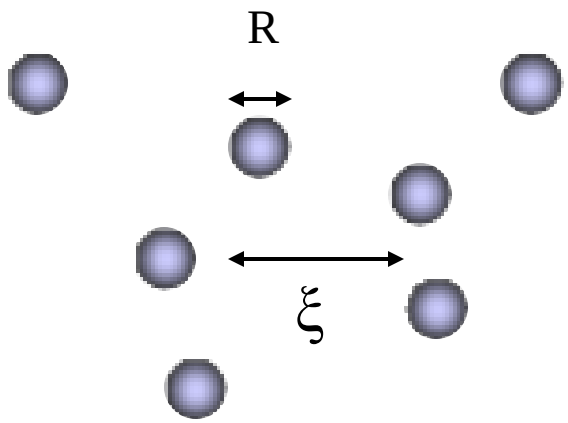
$$I(q) \sim \left[1 - \frac{1}{3} q^2 R_G^2 + \mathrm{L} \right]$$



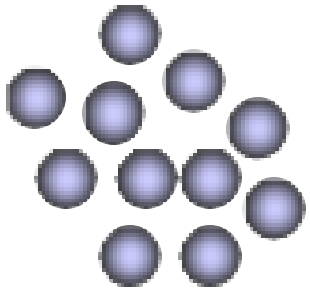
$$I(q) \sim \exp\left[-\frac{1}{3} q^2 R_G^2 + \mathrm{L} \right]$$

$$R_G \xrightarrow{dilute} R_g$$

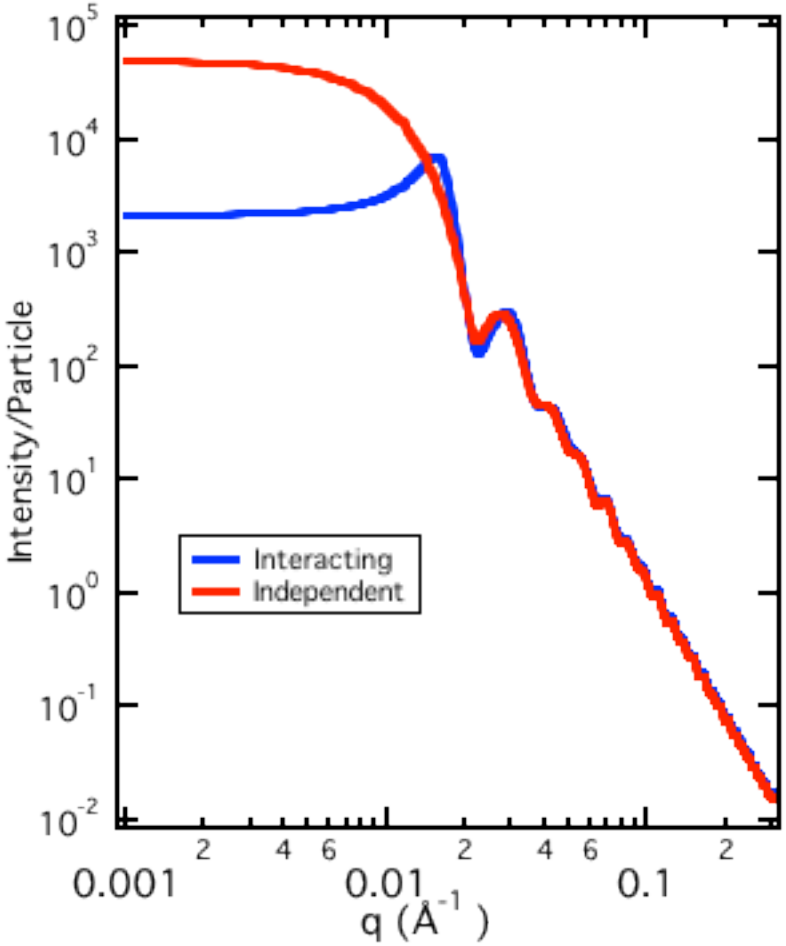
Correlated Particles



Packing Factor = 8 φ



Packing Factor ~ 6



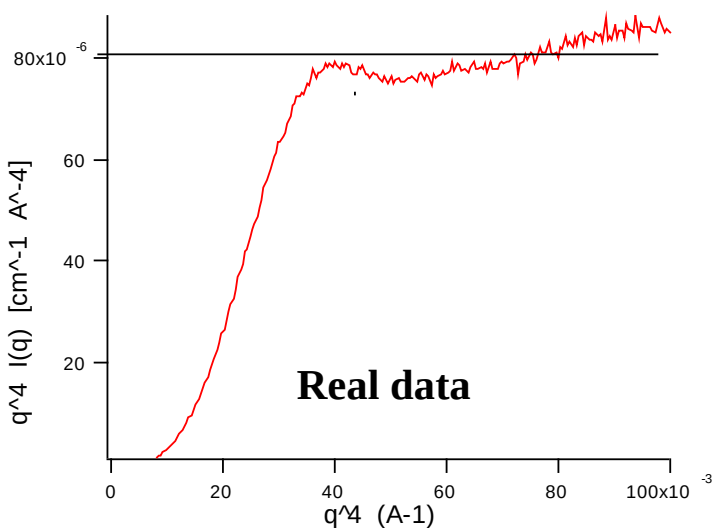
Porod's Law for N Spheres (qR>>1)

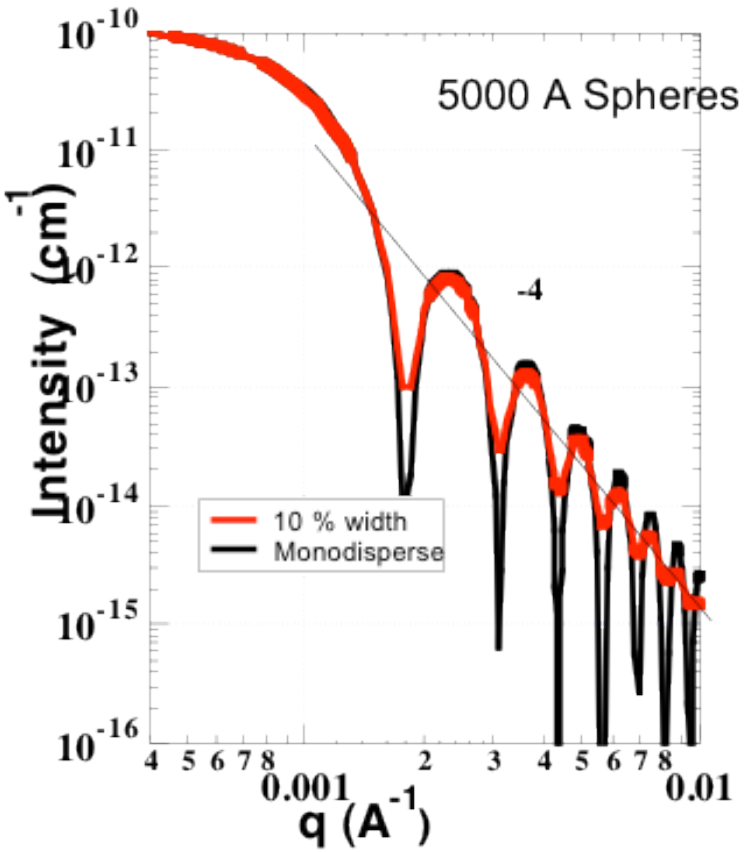
$$\frac{I(q)}{V}\left[cm^{-1}\right] = \frac{N}{V} < \Delta\rho >^2 \; v^2 \frac{9(\sin qR - qR\cos qR)^2}{(qR)^6} \xrightarrow{qR>>1} \equiv \frac{B}{q^4}$$

See (5.72)

Surface Area/Unit Volume = S_v

$$B\left[cm^{-1}A^{-4}\right] = 2\pi < \Delta\rho >^2 \; S_v = \text{Porod Constant}$$





Fractal description of disordered objects

Real Space

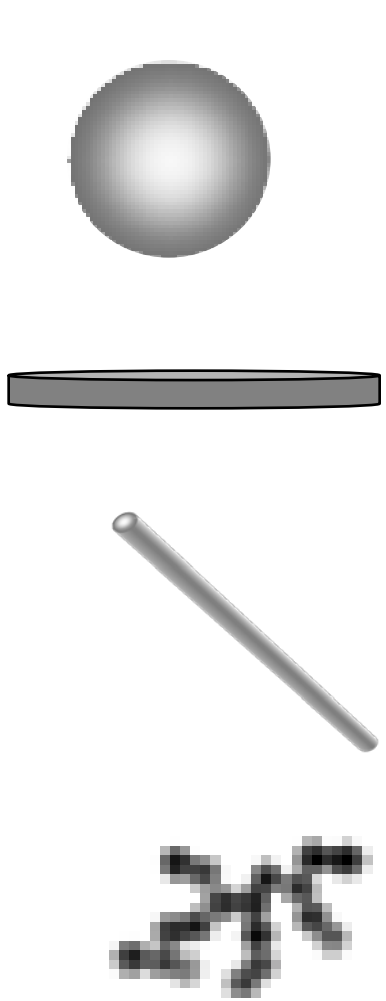
$M \sim V \sim R^3$

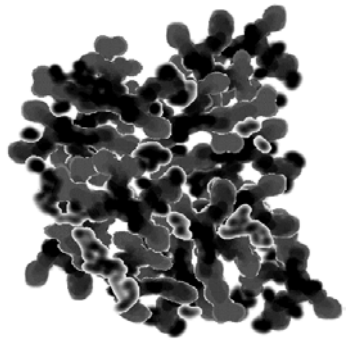
$M \sim V \sim R^2$

$M \sim R^d$

$M \sim V \sim R^1$

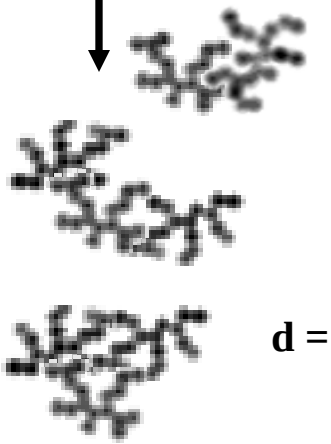
$M \sim V \sim R^{2.2}$





d = 3

Dispersion

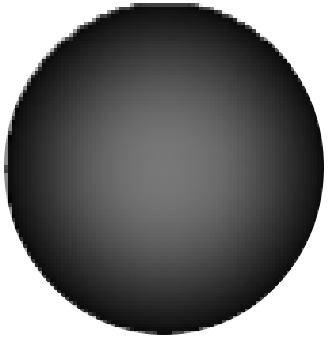


d = 2

Mass Fractal Dimension = d

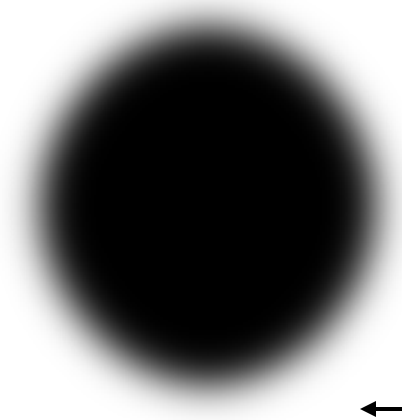
Rough and Diffuse Interfaces

Sharp interface



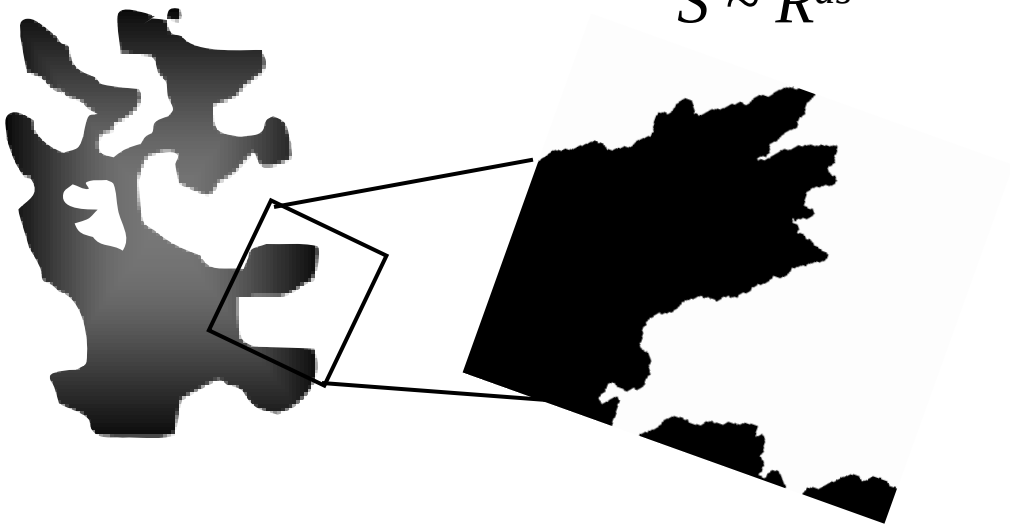
$S \sim R^2$

Diffuse Interface



σ

$S \sim R^{ds}$



fractal or self-affine surface

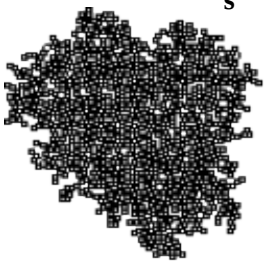
Scattering from Fractal Objects

d = Mass Fractal Dimension

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

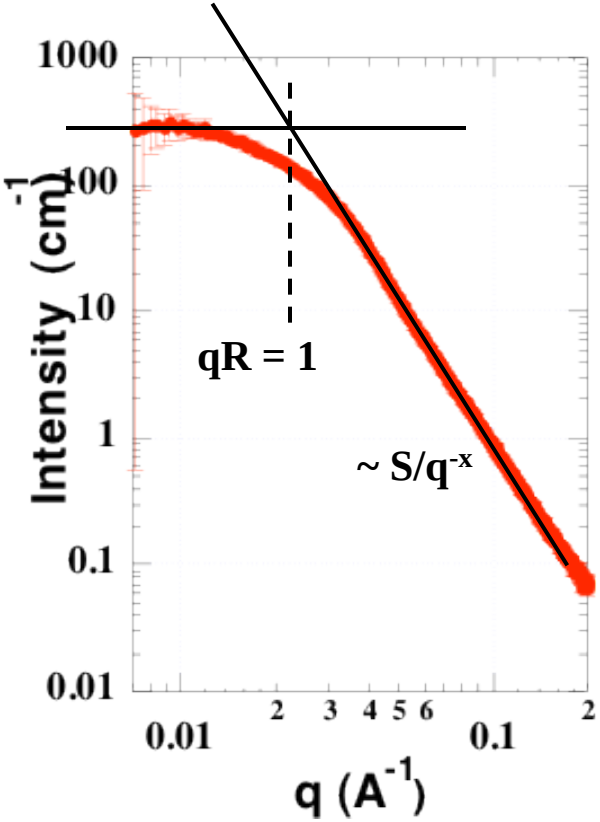
$M \sim v \sim N v_u \sim R^d v_u$ mass fractal

d_s = Surface Fractal Dimension



$S = R^2$ solid particle

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



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

Assume a power law for large q

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

Match at qR = 1

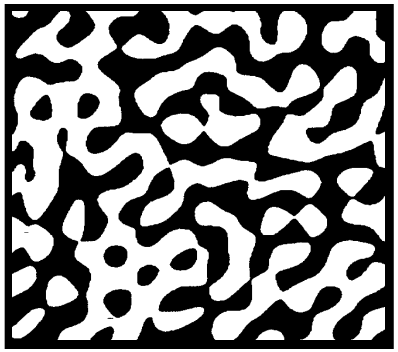
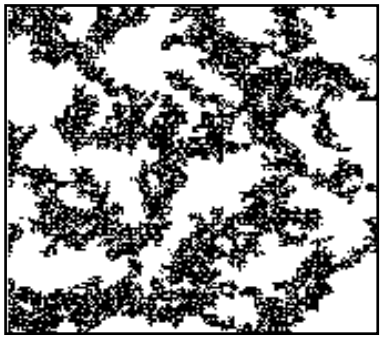
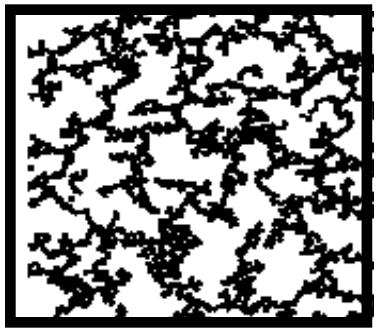
$$R^{d_s+x} \sim R^{2d}$$

$$x = 2d - d_s$$

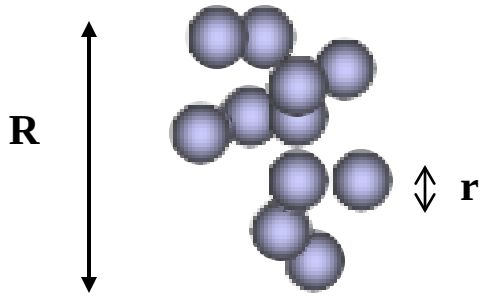
$$\boxed{I(q) \sim q^{-(2d-d_s)}}$$

Porod Slope for Fractals

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

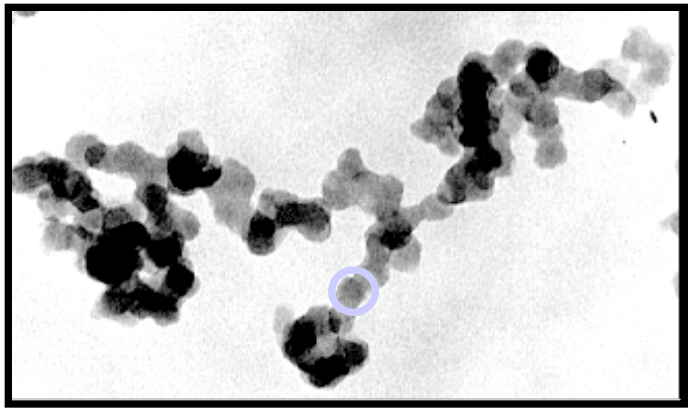
	Structure	Scaling Relation	Porod Slope = $d_s - 2d$
Smooth Surface		$d_m = 3$ $d_S = 2$	**- 4**
Rough Surface		$d_m = 3$ $2 < d_S \leq 3$	**- 3 ≤ SLOPE ≤ - 4**
Mass Fractal		$1 \leq d_S = d_m \leq 3$	**- 1 ≤ SLOPE ≤ - 3**

Scattering from colloidal aggregates

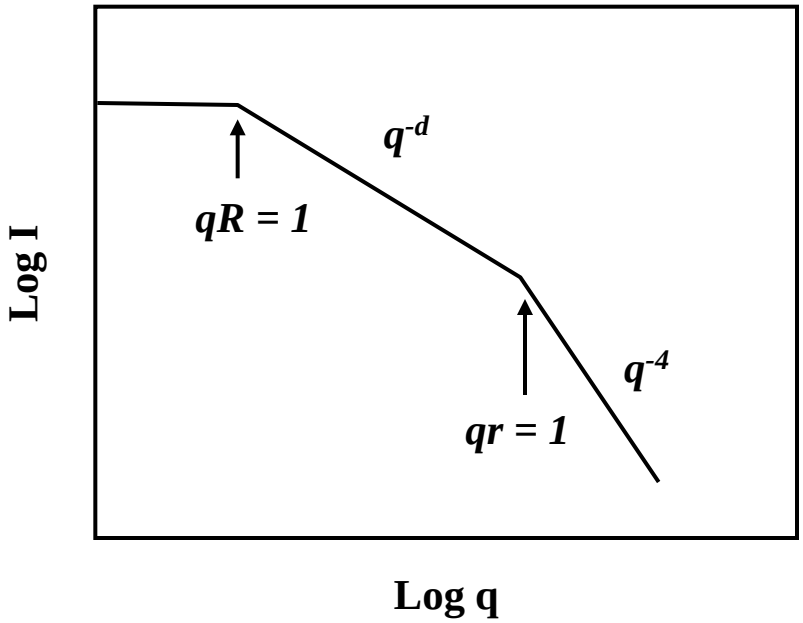


$$M \sim r^d$$
$$S \sim M \sim r^d \qquad d = d_s$$

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

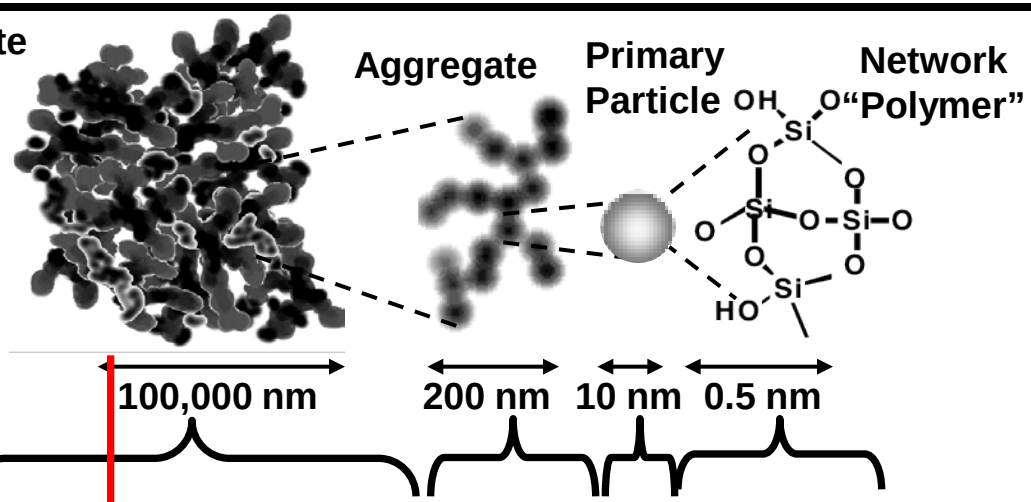


Precipitated Silica

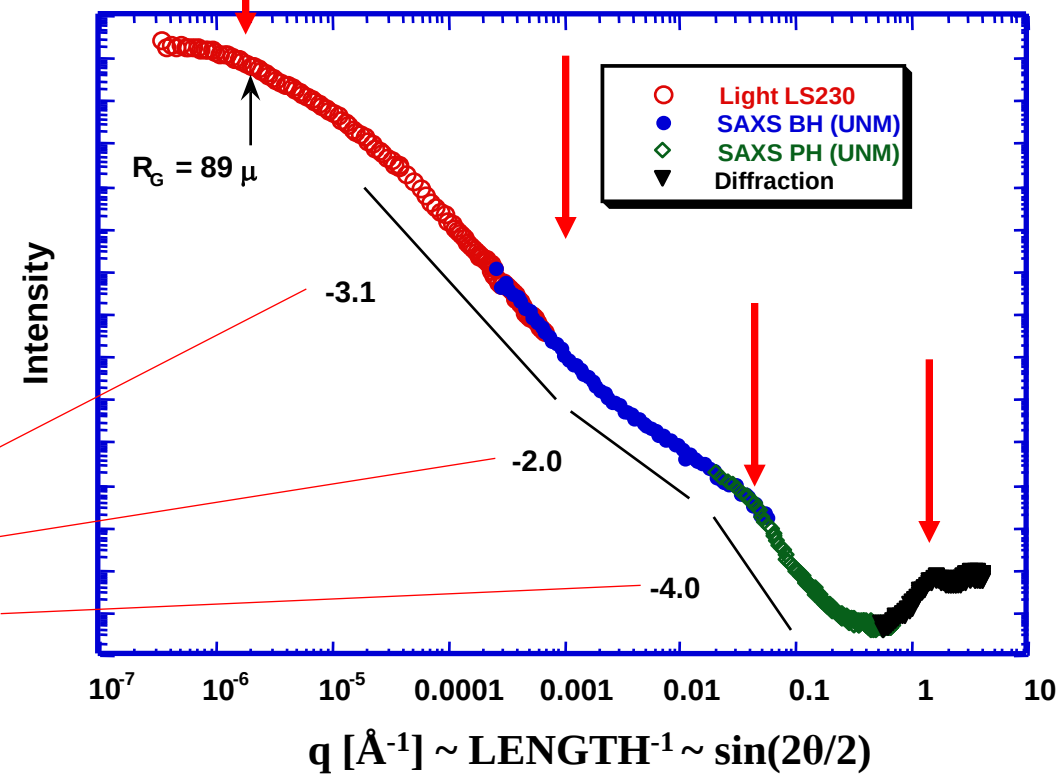


Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes



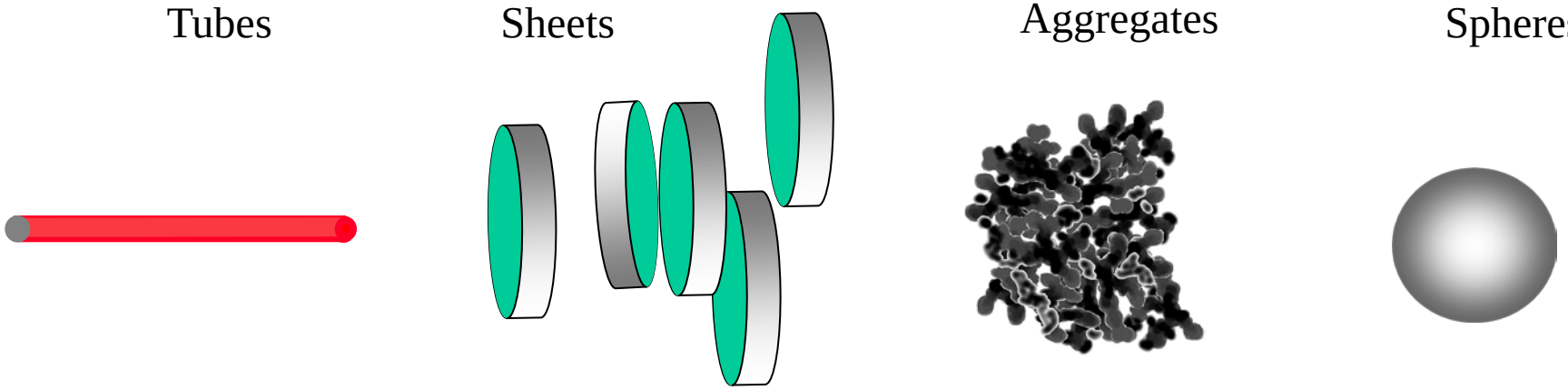
$$q = \frac{2\pi}{d_{bragg}} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$



Exponents related to fractal dimensions

Nanoscale Reinforcing Fillers for Nanocomposites

1-d	*2-d*	*2.5-d*	*3-d*
Tubes	Sheets	Aggregates	Spheres



Carbon Nanotubes	Layered Silicates	Precipitated Silica	Colloidal Silica

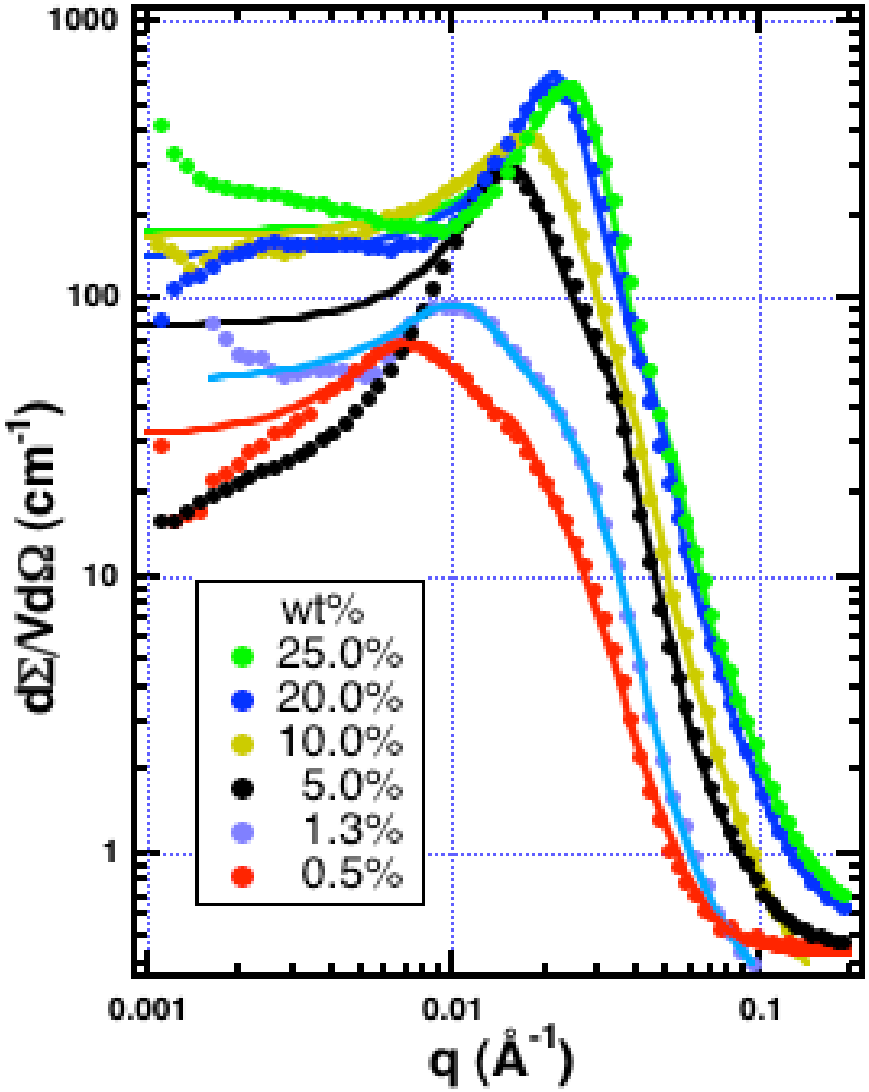
+ Polymer Matrix

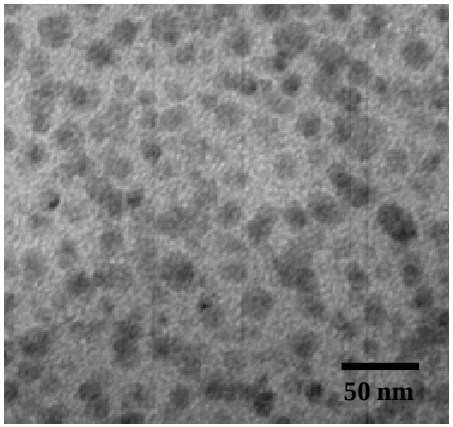
How valid are the cartoons?
What are the implications of morphology for reinforcement?

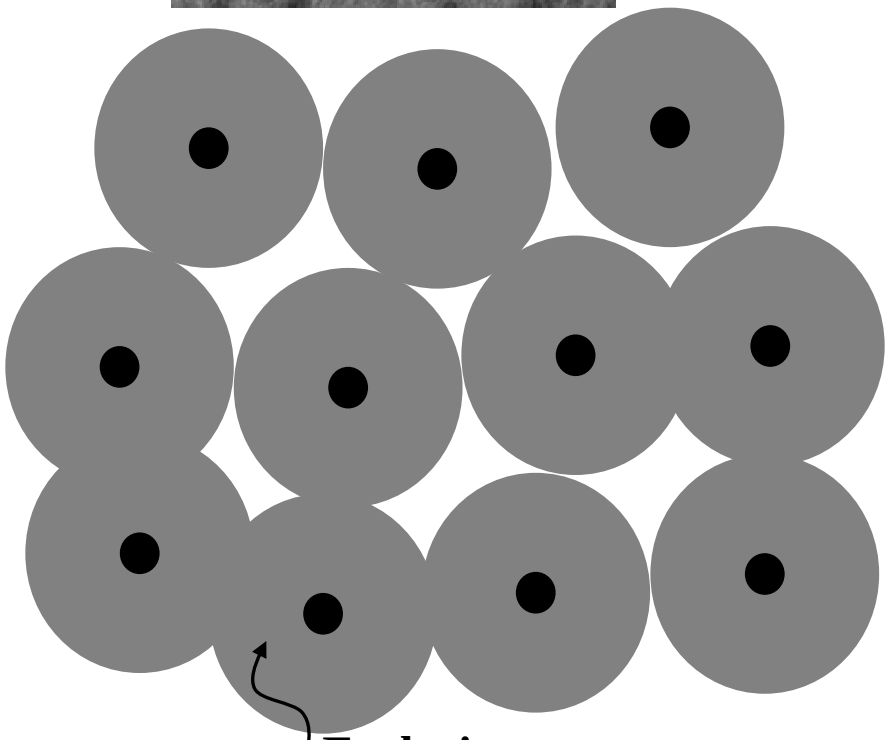
3-d Colloidal Silica in epoxy
2.5-d Precipitated silica in rubber
1-d Carbon nanofibers in epoxy and PU thermoplastic elastomer
2-d Layered Silicates (Clays)

Colloidal Silica in Epoxy

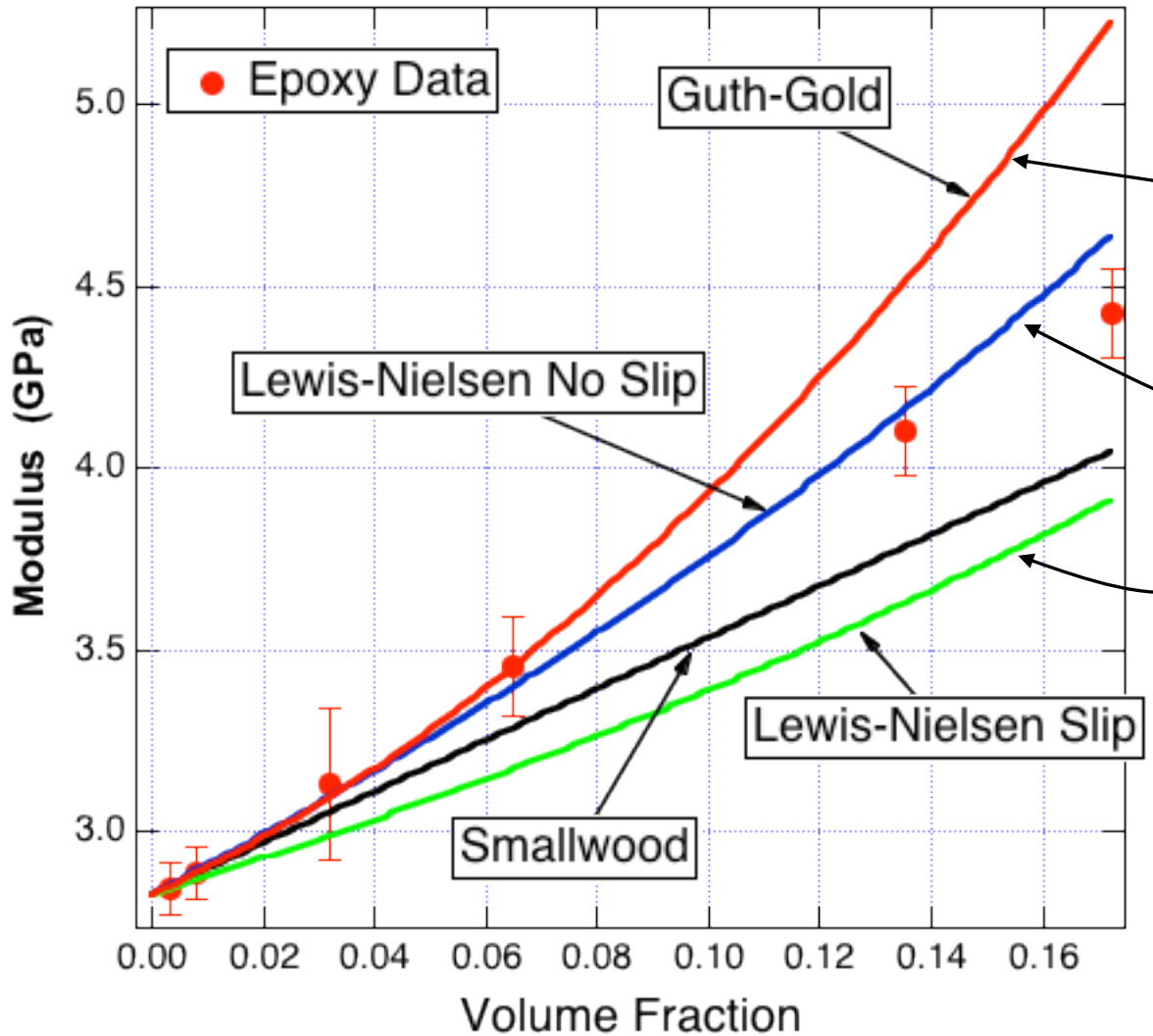
EPON 862 + Cure W







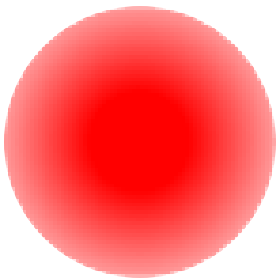
Mechanical Properties are “normal”

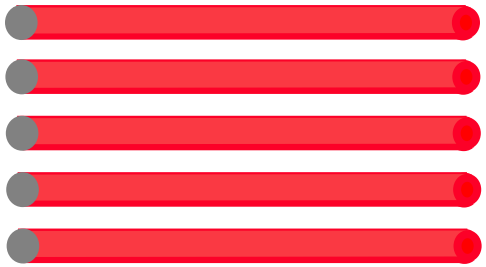


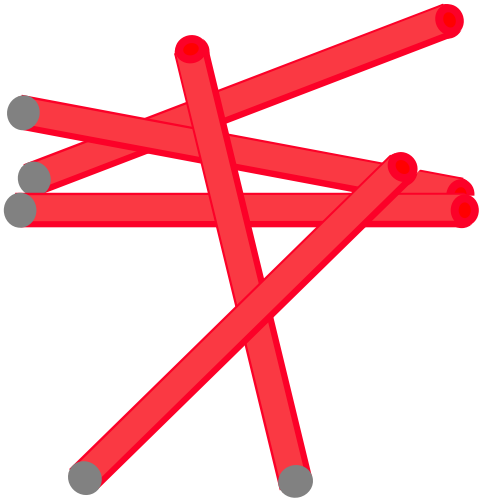
$$E = E_{matrix}(1 + 2.5\phi + 14.1\phi^2)$$

Interface modification effect

The Promise of Nanotube Reinforcement







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

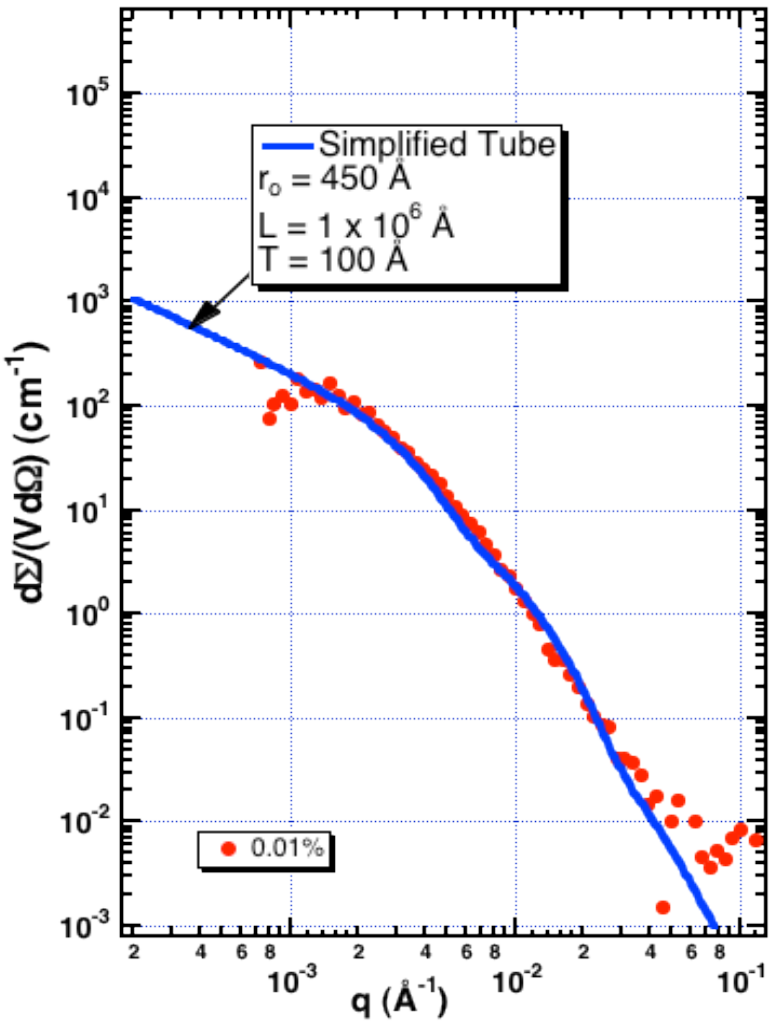
$$E_\delta = 1 + 2.5\phi$$

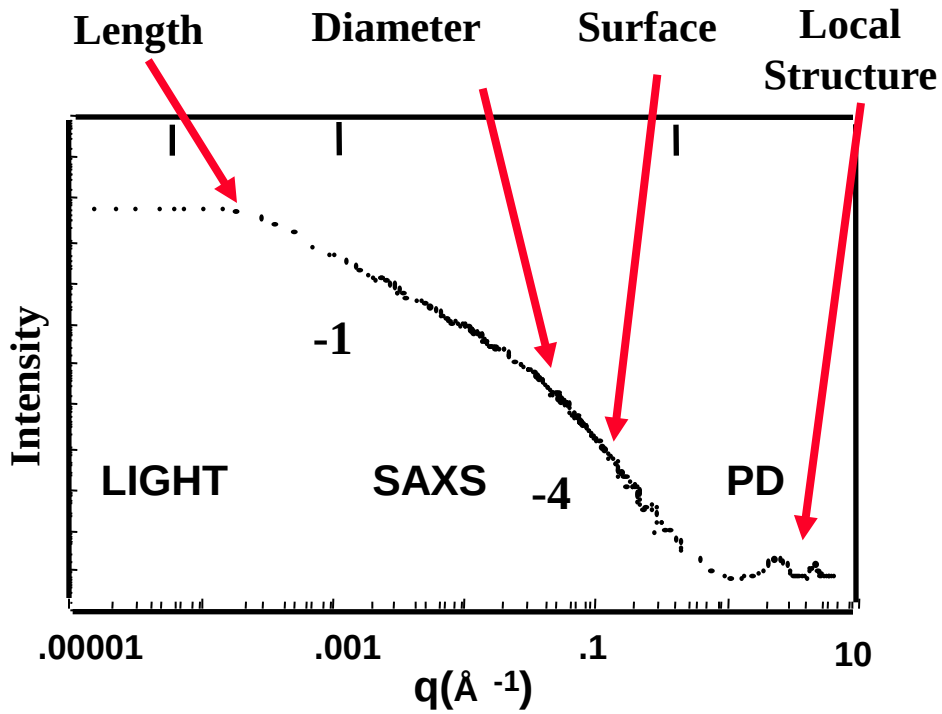
$$= 1 + 2\alpha\phi \cong 1 + 2000\phi$$

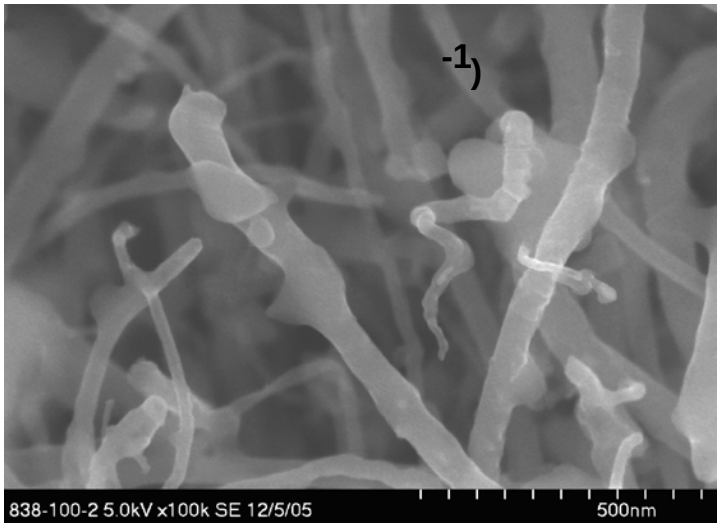
$$= 1 + \underline{0.4\alpha\phi} \cong 1 + 400\phi$$

α = aspect ratio

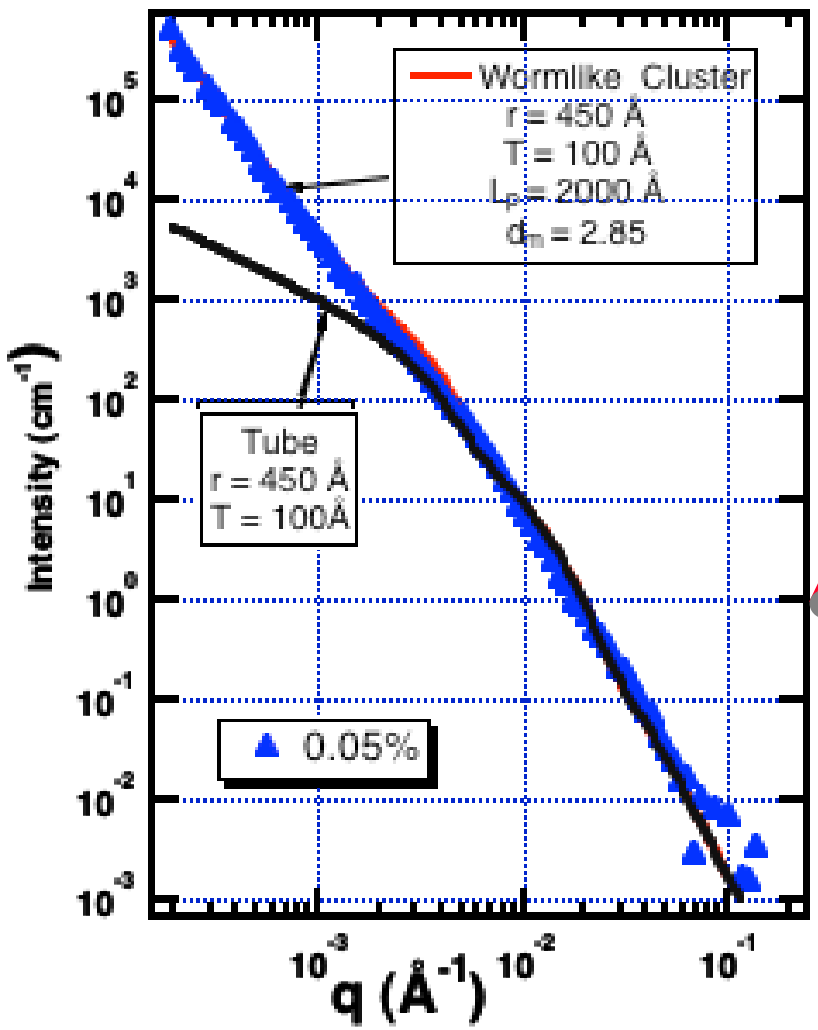
0.01% Loading CNTs in Bismaleimide Resin



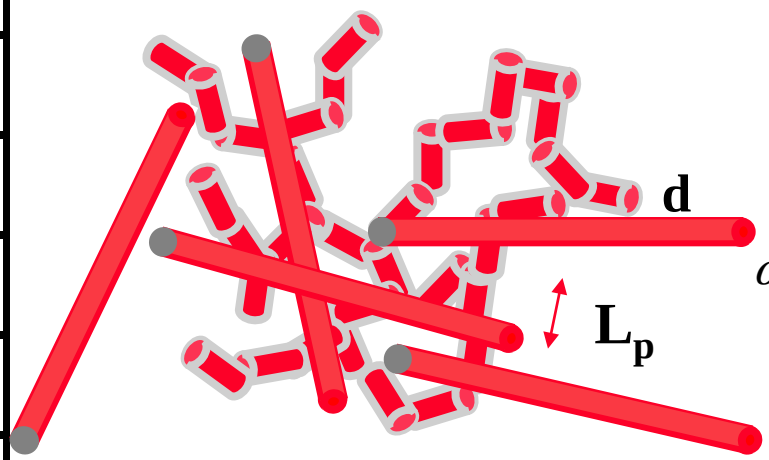




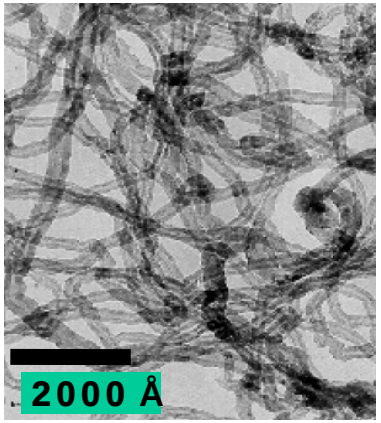
0.05% Carbon in Bismaleimide Resin



Worm-like branched cluster

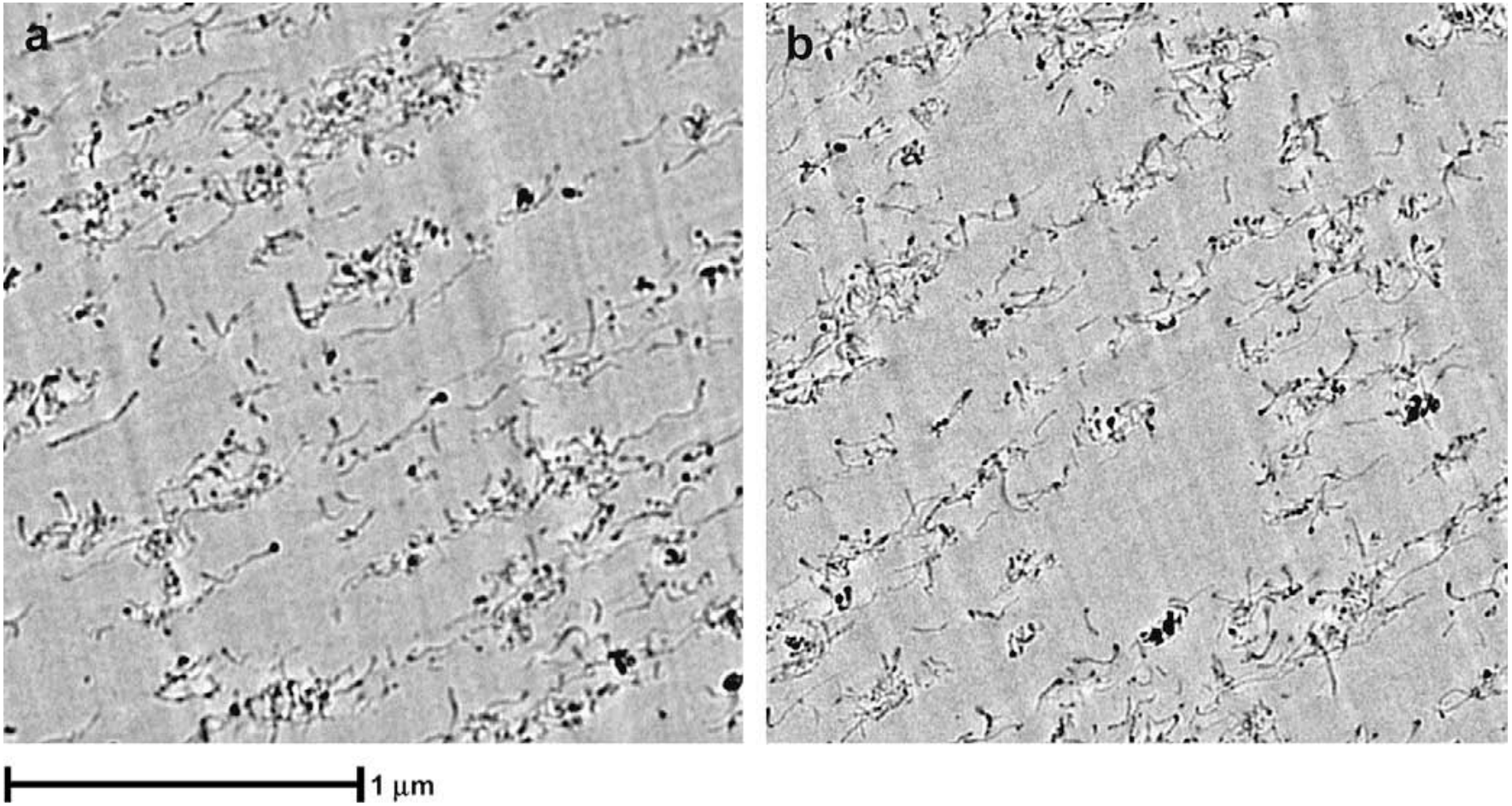


$$\alpha = \frac{L_p}{r} = 4.5$$



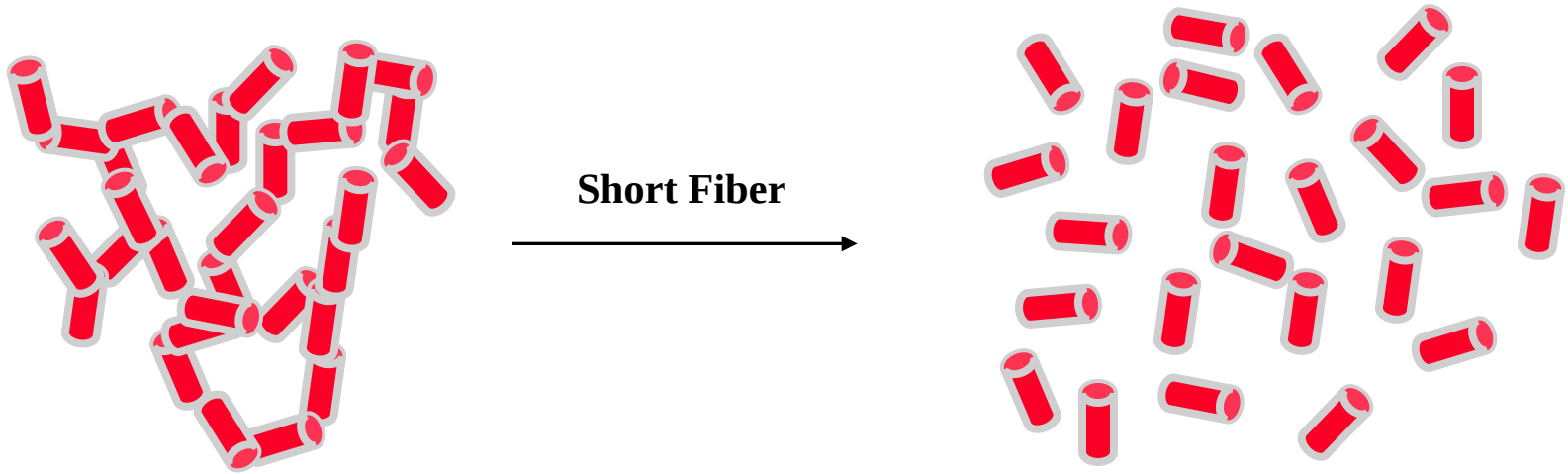
TEM of Nanocomposites

Hyperion MWNT in Polycarbonate



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

Morphology and Mechanical Properties



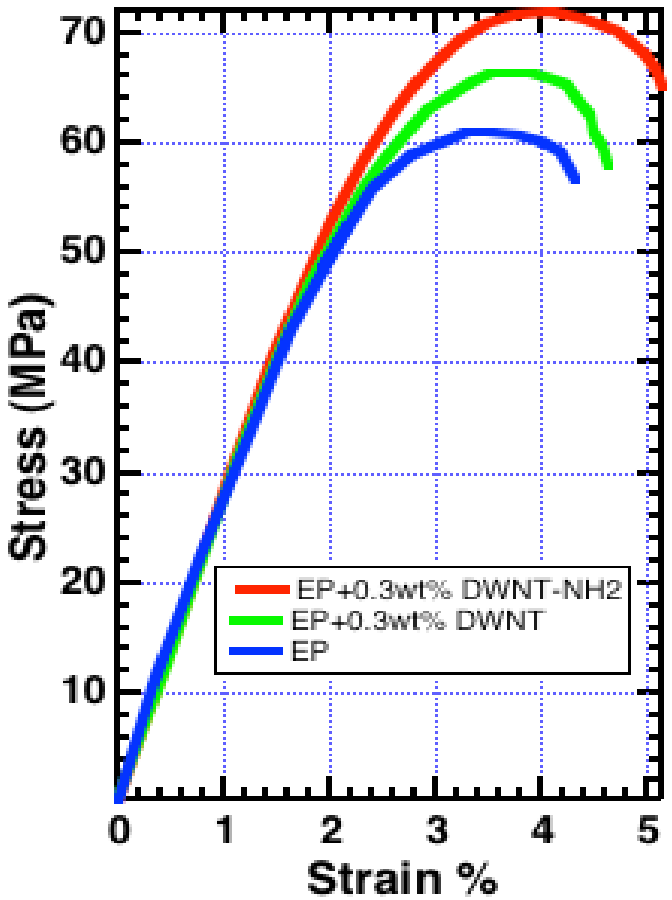
Halpin-Tsai, random, short, rigid fiber limit

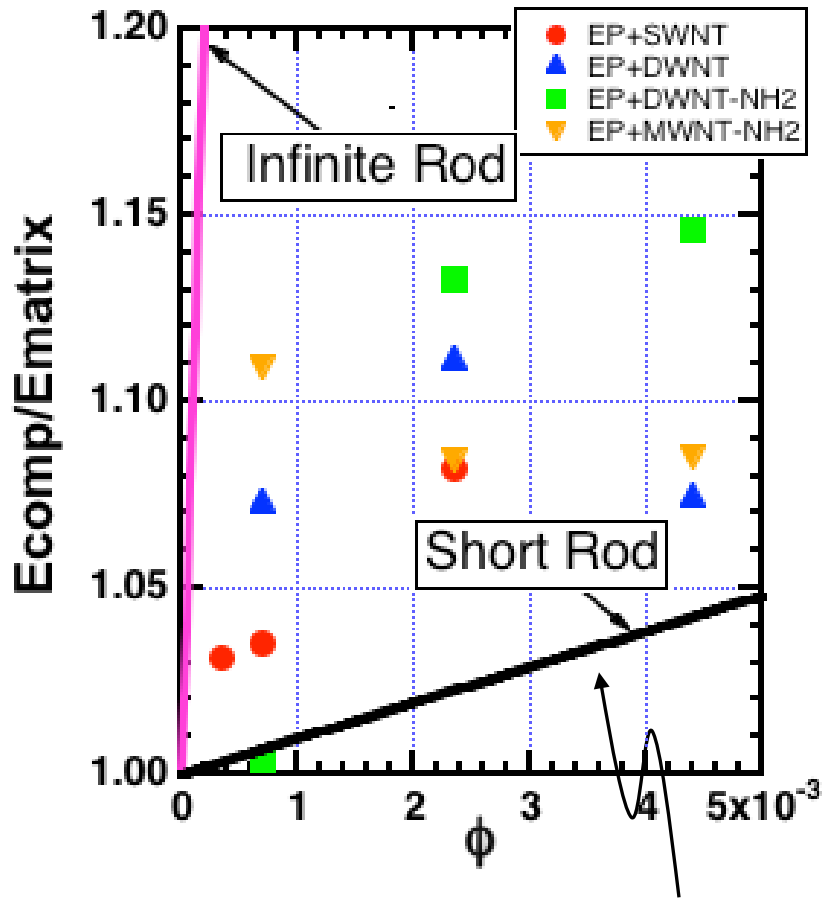
$$E_\delta = \frac{E_c}{E_m} = 1 + 0.4\alpha\phi$$

$$\cong 1 + 2\phi$$

No better than spheres

CNTs in Epoxy



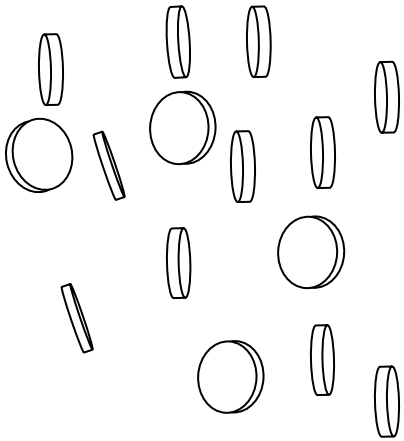


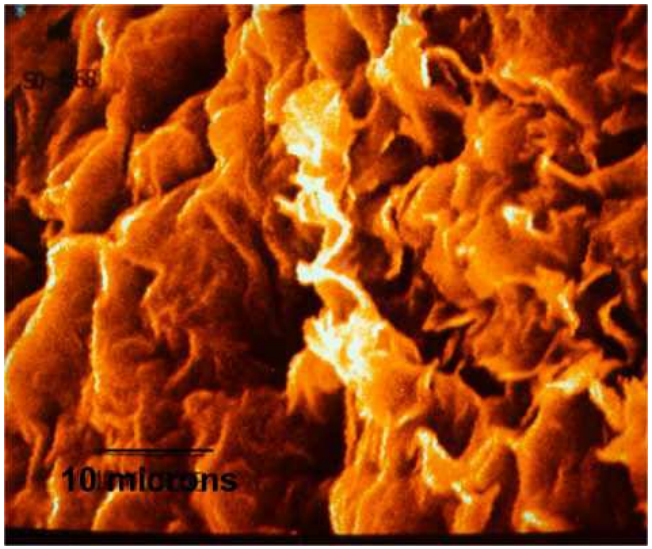
Assumes no connectivity

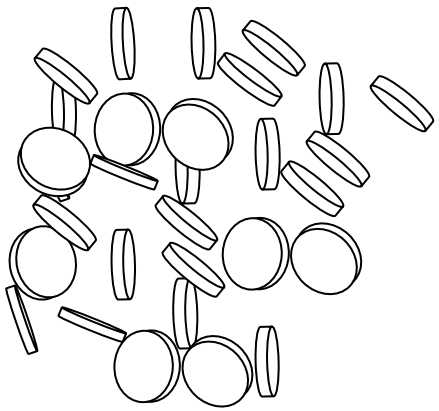
Gojny, F. H.; Wichmann, M. H. G.; Fiedler, B.; Schulte, K. *Comp. Sci. & Tech.* 2005, 65, (15-16), 2300-2313.

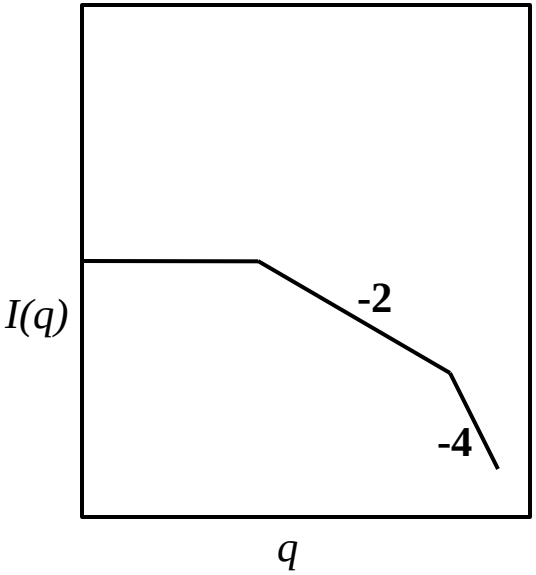
Layered Silicates

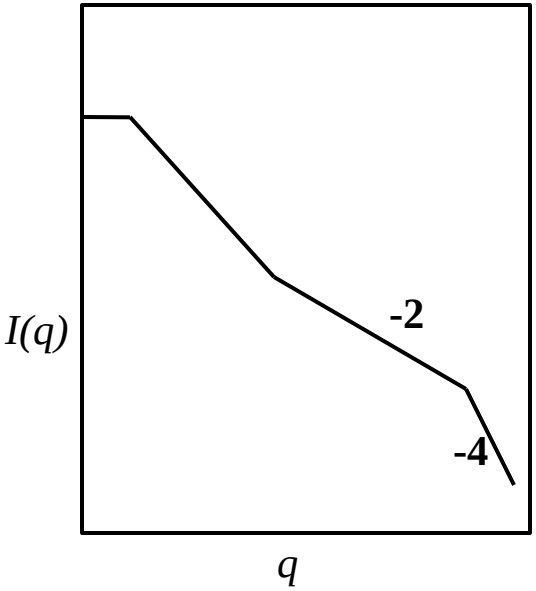
Idealized



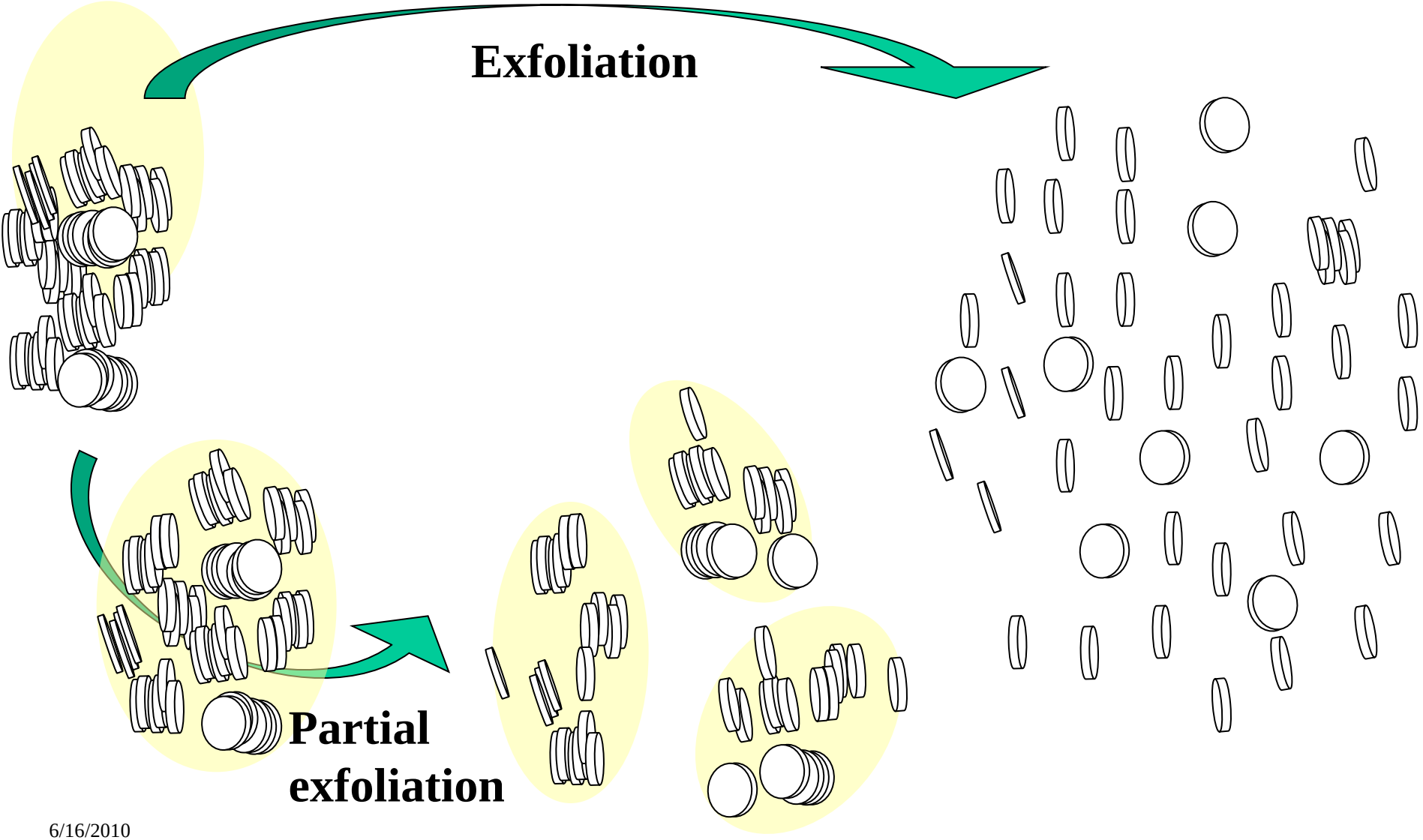




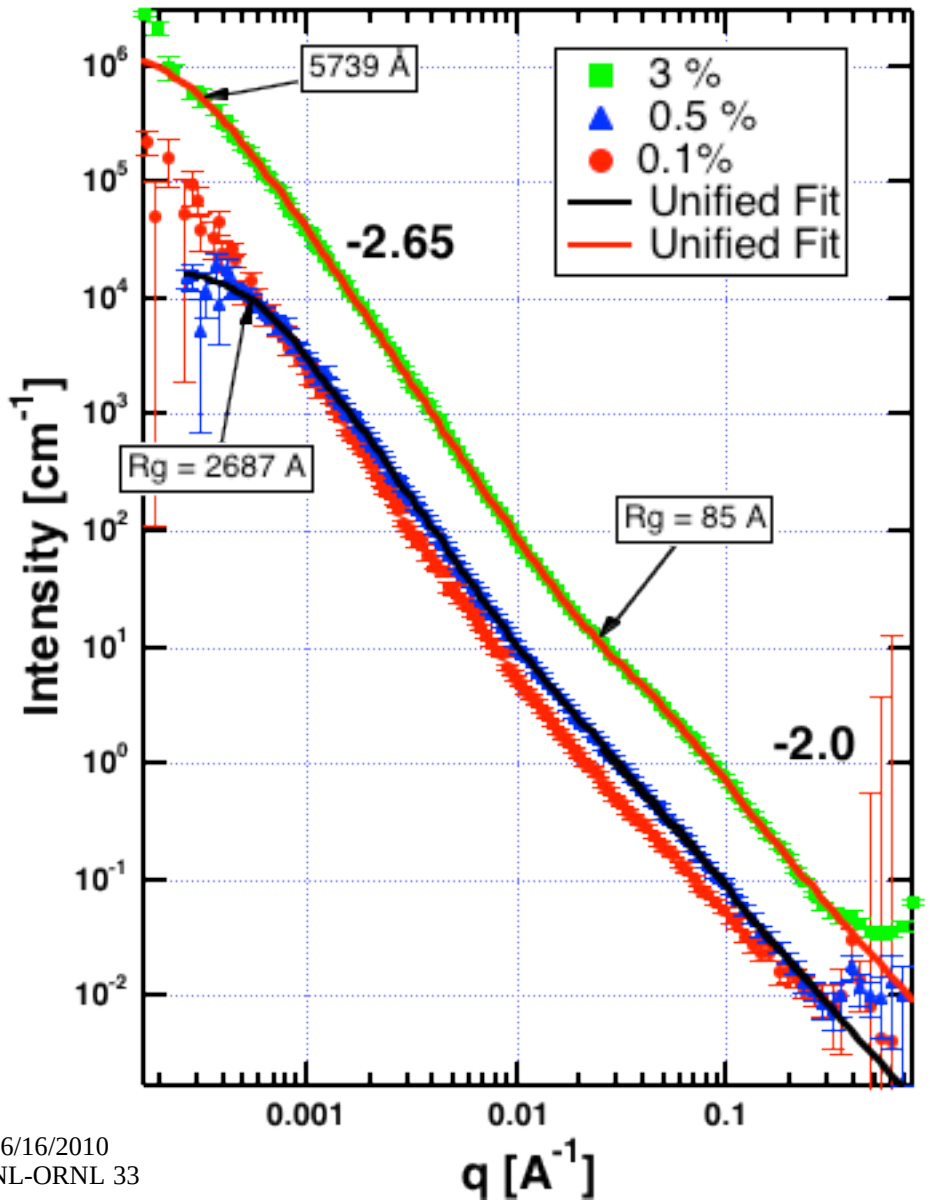




Dispersion



USAXS NaMMT in Water

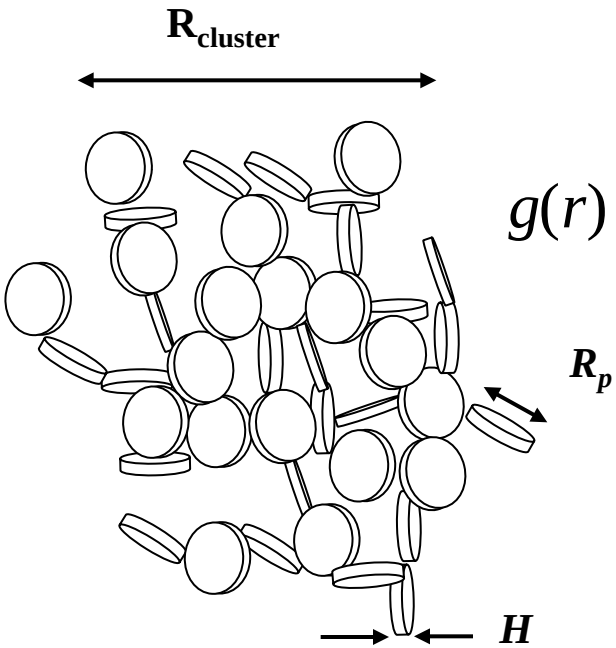


< 100 Å = Sheet-like

No evidence of interparticle correlation

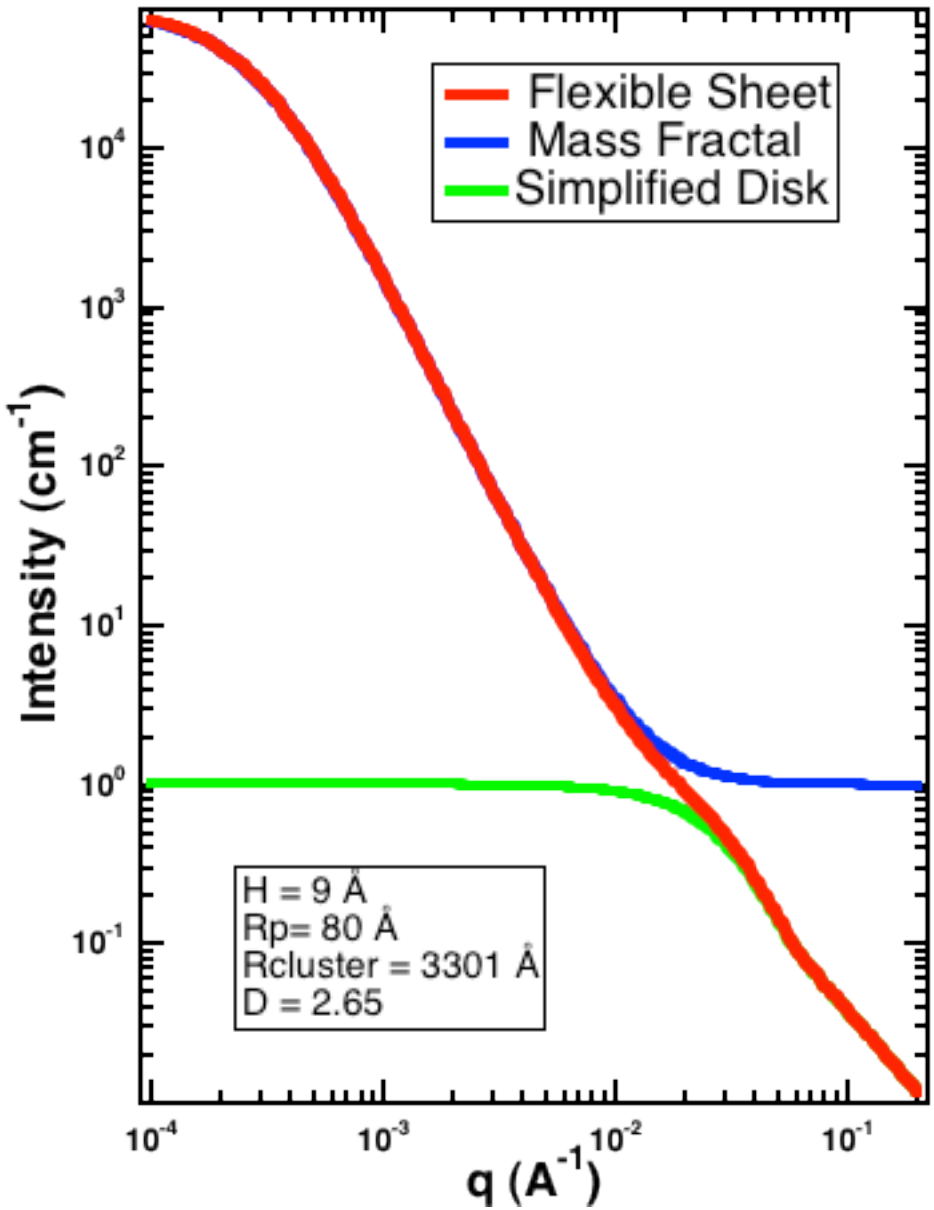
Exfoliated

Flexible Sheet Model

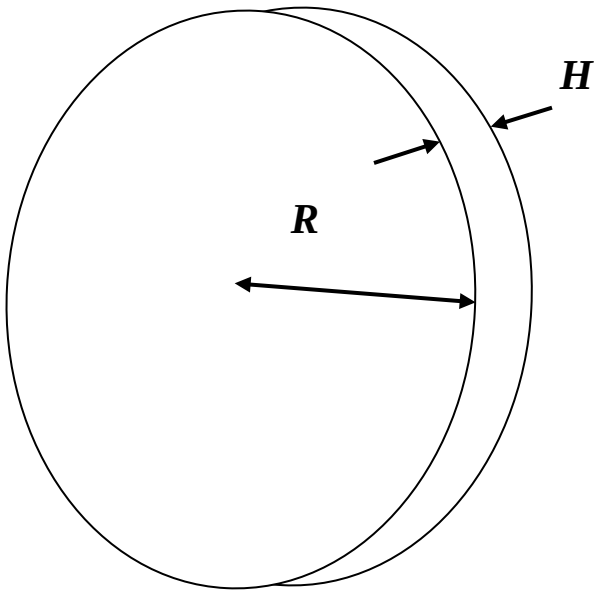


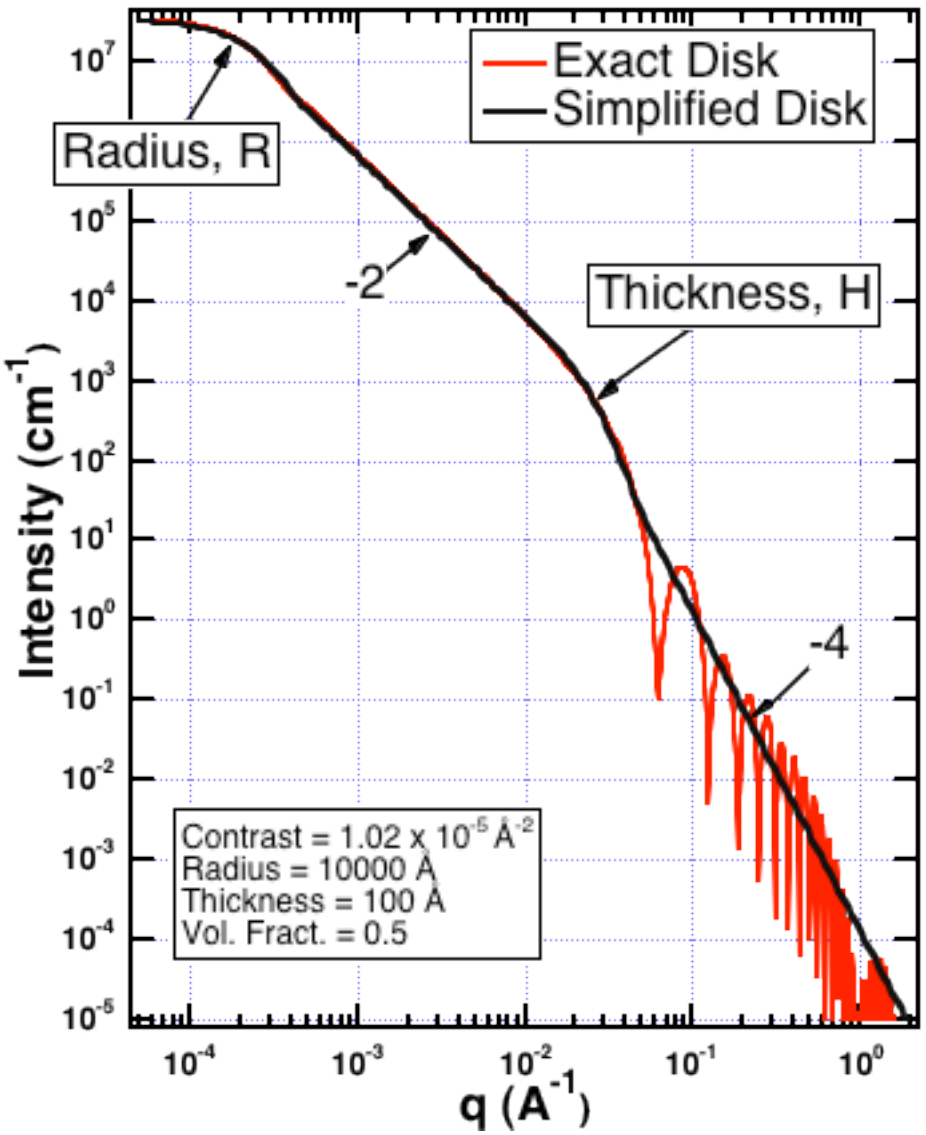
$$g(r) \approx \frac{1}{r^D}$$

Short-scale = Simplified Disk
Large-scale = Mass Fractal

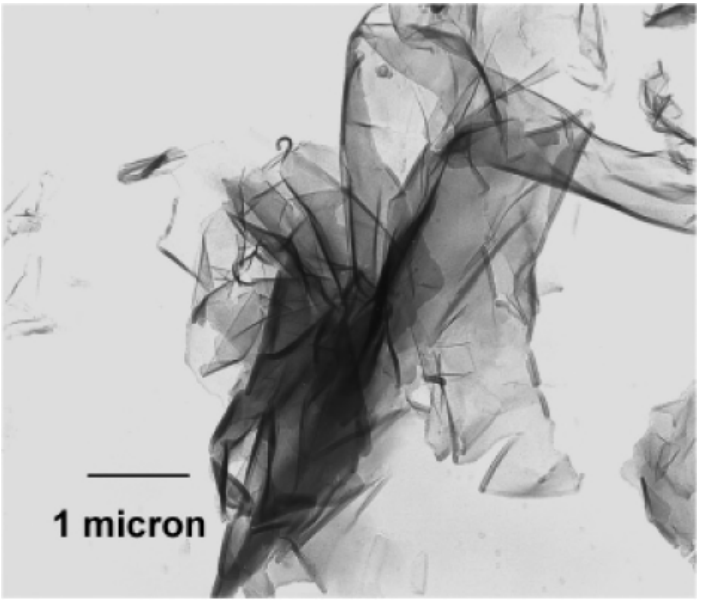


Simplified Disk Model

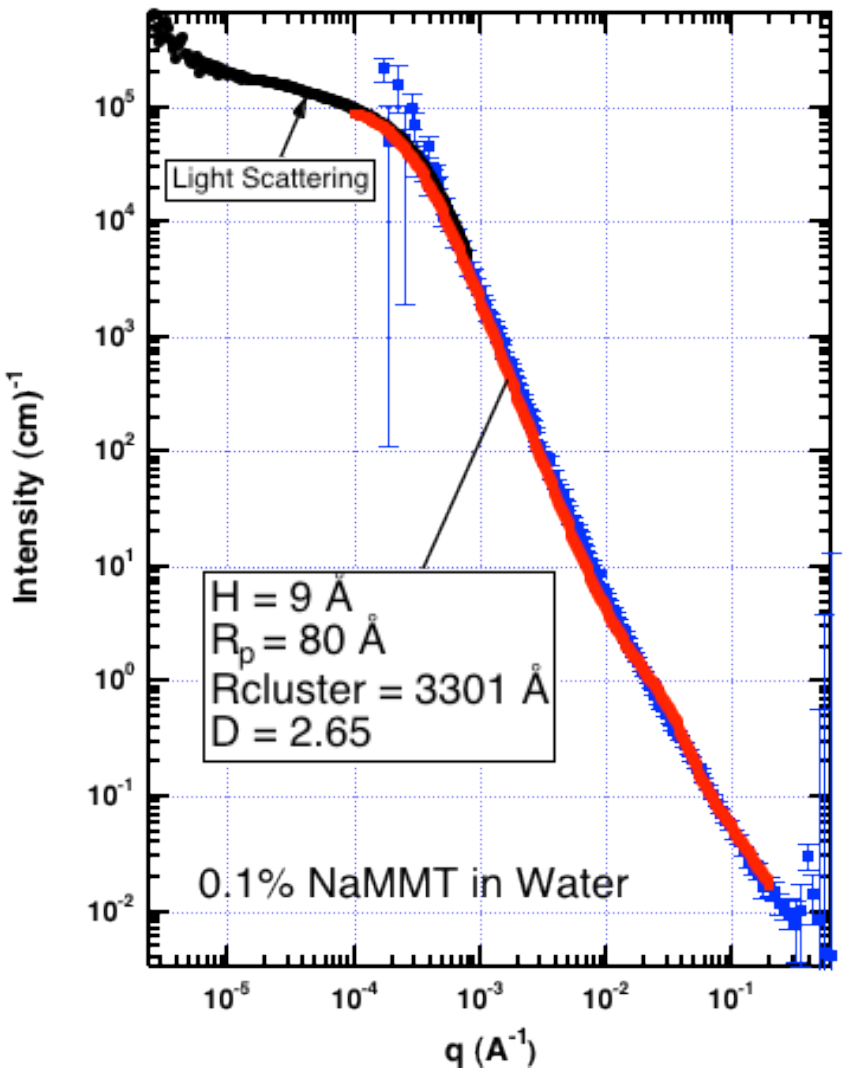




Crumpled Surfaces and the Flexible Sheet Model



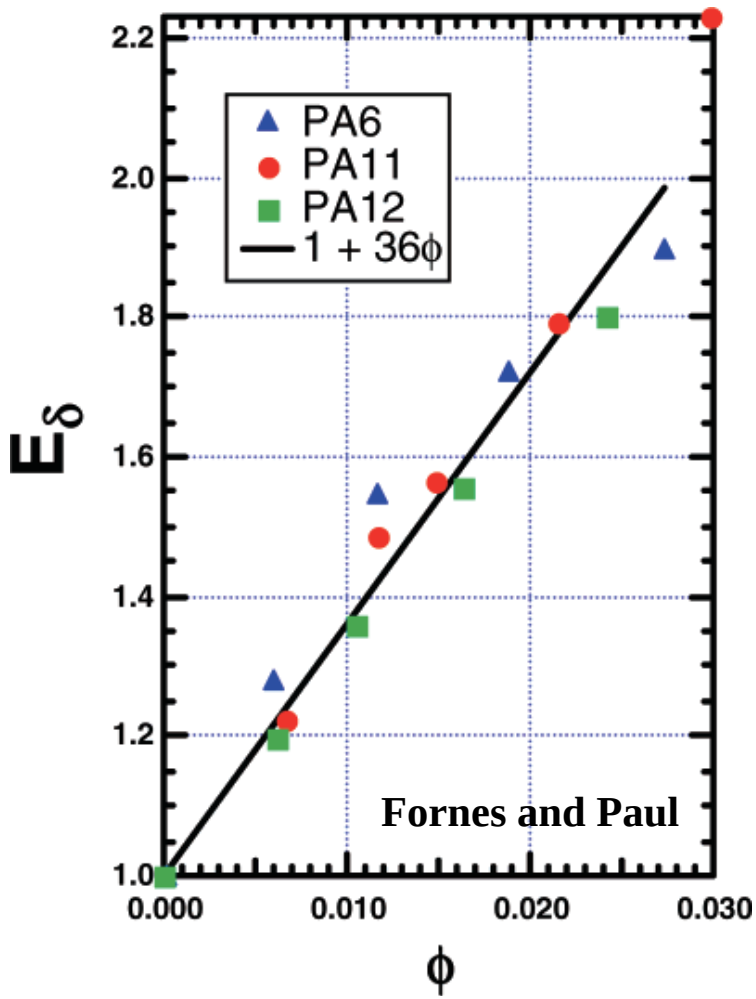
Hartmut Fischer



$$\alpha = \frac{2R_p}{H} = \frac{180\text{Å}}{9\text{Å}} = 20$$

Flexible Sheet Model

$$E_\delta = 1 + \alpha\varphi = 1 + 20\varphi$$



Conclusions

1. Aggregation is ubiquitous in nanocomposites.
2. Large aggregates don't reinforce hard materials.
3. Large enhancements are due to impact of filler on matrix.
4. Abusive dispersion may be counterproductive.
5. Skipping research in favor of "breakthrough materials" is wasteful.

1. Schaefer, D.W., J. Zhao, H. Dowty, M. Alexander, and E.B. Orler, *Nanofibre Reinforcement of Soft Materials.* Soft Matter, 2008. 4(10): p. 2071 - 2079.

2. Kohls, D.J., D.W. Schaefer, R. Kosso, and E. Feinblum, *Silica Fillers for Elastomer Reinforcement*, in *Current Topics in Elastomers Research*, A.K. Bhowmick, Editor. 2008, CRC Press: Boca Raton, FL. p. 505-517.

3. Chen, C., R.S. Justice, D.W. Schaefer, and J.W. Baur, *Highly dispersed nanosilica-epoxy resins with enhanced mechanical properties* Polymer, 2008. 49(17): p. 3805-3815.

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

Acknowledgements

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