Exploring the Nanoworld: Imaging and Scattering

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Source of x-rays, light or neutrons

Methods of X-Ray and Neutron Scattering in Polymer Science

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Intensity vs Angle
Seven orders of magnitude in length scale. How can the structure be parameterized?
Bragg’s Law and the scattering vector, $q$

\begin{align*}
  d &= \frac{2\pi}{q} \\
  q &= \frac{4\pi}{\lambda} \sin \frac{\theta}{2}
\end{align*}

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: $\theta < 6^\circ$
Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

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

Exponents related to morphology

\[ \text{Intensity} \]

\[ q \, [\text{Å}^{-1}] \sim \text{LENGTH}^{-1} \sim \sin\left(\frac{\sqrt{2}}{2}\right) \]
Why Reciprocal Space?

Isotactic polystyrene foams prepared by TIPS

Characterizing Disorder in Real Space

Electron Density Distribution
\[ n(r) \]

Correlation Function of the Electron Density Distribution
\[ \Gamma_n(r) = \int n(u)n(u + r)du \]

- Throw out phase information
- Real space
- \( \xi \)
- \( \langle n^2 \rangle \)
- \( \langle n \rangle^2 \)
- \( r \)

- 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

\[ \Gamma_n(r) = \int n(u)n(u + r)du \]

\[ I_{scatt}(q) \equiv \int \Gamma_n(r) \, e^{-iqr} \, dr \]

Real space

Reciprocal space
Generalized Bragg’s Law

Scattering from 2 electrons

\[ A(q) \sim \frac{A_0}{R} \left[ n(r_1) e^{-i \cdot q \cdot r_1} + n(r_2) e^{-i \cdot q \cdot r_2} \right] \]

\[ n(r) \sim \rho(r) \leftarrow \text{scattering length density} \]

\[ A(q) = \sum_{j=1}^{N} \rho(r_j) e^{-i \cdot q \cdot r_j} \]
Intensity from Amplitude

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

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

\[ \Gamma_{\rho}(r) = \int \rho(u) \rho(u + r) du \]
Small-Angle Scattering from Spheres

\[ \sin \theta = \frac{\lambda}{2d} \quad \text{d} \gg \lambda \rightarrow \theta \]

Large object scatter at small angles

Guinier Regime

Diameter = 140 Å

Porod (power-law) Regime

Silica in Polyurethane

AFM
Scattering from a Spherical Particle

\[ I(q) = A^2(q) = \int_V \Gamma \rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r} \]

\[ A(q) = \frac{A(q)}{A_0} = \int \rho(r)e^{-i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r} \]

\[ = \int_0^\infty \rho(r) 4\pi r^2 \frac{\sin qr}{qr} \, dr \]

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

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

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

\[ = \rho_0 \frac{3\sin qR - qR \cos qR}{(qR)^3} \]

\[ \nu = \text{particle volume} \]

5000 Å Spheres
Guinier Radius

Initial curvature is a measure of length

\[ I(q) = \int_V \Gamma \rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r} \]

\[ A(q) = \frac{A(q)}{A_0} = \int \rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r} \]

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

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

\[ \sigma(r) = \begin{cases} 
1 & r \leq R \\
0 & r > R 
\end{cases} \]

\[ R_g = \sqrt{\frac{3}{5} R_{\text{hard}}} \]

Homework

Rg of a sphere

\[ \rho_0 4 \pi R^3 \frac{(\sin qR - qR \cos qR)}{(qR)^3} = C_1 \left[ 1 - C_2 (qR)^2 + L \right] \]
Guinier Fits (PS 13)

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

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

\[ R_G \xrightarrow{\text{dilute}} R_g \]
Correlated Particles

Packing Factor $= 8 \varphi$

Packing Factor $\sim 6$
Porod’s Law for N Spheres (qR >> 1)

\[
\frac{I(q)}{V} \bigg|_{cm^{-1}} = \frac{N}{V} <\Delta\rho>^2 v^2 \frac{9(sinqR-qRcosqR)^2}{(qR)^6} \quad qR >> 1 \rightarrow \equiv B \frac{q^4}{q^4}
\]

Surface Area/Unit Volume = \(S_v\)

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

Real data
Fractal description of disordered objects

Real Space

\[ M \sim V \sim R^d \]

\[ d = 3 \]

\[ M \sim V \sim R^3 \]

\[ d = 2 \]

\[ M \sim V \sim R^2 \]

\[ M \sim V \sim R^{2.2} \]

\[ M \sim V \sim R^1 \]

Dispersion

Mass Fractal Dimension = d
Rough and Diffuse Interfaces

Sharp interface

\[ S \sim R^2 \]

Diffuse Interface

\[ S \sim R^{d_s} \]

fractal or self-affine surface

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ANL-ORNL 17
Scattering from Fractal Objects

\( d = \) Mass Fractal Dimension

\( \mathcal{M} \sim v \sim R^3 \quad \) solid particle

\( M \sim v \sim N v_u \sim R^d v_u \quad \) mass fractal

\( d_s = \) Surface Fractal Dimension

\( S = R^2 \quad \) solid particle

\( S \sim R^{d_s} \quad \) surface fractal

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

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

Assume a power law for large \( q \)

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

Match at \( qR = 1 \)

\[
R^{d_s + x} \sim R^{2d}
\]

\[
x = 2d - d_s
\]
## Porod Slope for Fractals

<table>
<thead>
<tr>
<th>Structure</th>
<th>Scaling Relation</th>
<th>Porod Slope = $d_s - 2d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth Surface</td>
<td>$d_m = 3$</td>
<td>- 4</td>
</tr>
<tr>
<td></td>
<td>$d_S = 2$</td>
<td></td>
</tr>
<tr>
<td>Rough Surface</td>
<td>$d_m = 3$</td>
<td>- 3 ≤ SLOPE ≤ - 4</td>
</tr>
<tr>
<td></td>
<td>$2 &lt; d_S ≤ 3$</td>
<td></td>
</tr>
<tr>
<td>Mass Fractal</td>
<td>$1 ≤ d_S = d_m ≤ 3$</td>
<td>- 1 ≤ SLOPE ≤ - 3</td>
</tr>
</tbody>
</table>
Scattering from colloidal aggregates

\[ M \sim r^d \]
\[ S \sim M \sim r^d \quad d = d_s \]

\[ I(q) \sim q^{-2d-d_s} = q^{-d} \]
Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

Agglomeration
Aggregate
Primary
Network
Particle
“Polymer”

100,000 nm
200 nm
10 nm
0.5 nm

Intensity

$\theta$

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

$R_g = 89 \, \mu$

-4.0
-3.1
-2.0

Exponents related to fractal dimensions

Light LS230
SAXS BH (UNM)
SAXS PH (UNM)
Diffraction

Light LS230
SAXS BH (UNM)
SAXS PH (UNM)
Diffraction

$q [\text{Å}^{-1}] \sim \text{LENGTH}^{-1} \sim \sin(2\theta/2)$
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)
Mechanical Properties are “normal”

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

- Guth-Gold
- Lewis-Nielsen No Slip
- Lewis-Nielsen Slip
- Smallwood

Interface modification effect
The Promise of Nanotube Reinforcement

\[ E_\delta = \frac{E_{\text{composite}}}{E_{\text{matrix}}} \]

\[ E_\delta = 1 + 2.5\phi \]

\[ = 1 + 2\alpha\phi \cong 1 + 2000\phi \]

\[ = 1 + 0.4\alpha\phi \cong 1 + 400\phi \]

\[ \alpha = \text{aspect ratio} \]
0.01% Loading CNTs in Bismaleimide Resin

\[ \frac{d\Sigma}{d\Omega} (\text{cm}^{-1}) \]

\[ q (\text{Å}^{-1}) \]

Length | Diameter | Surface | Local Structure

Intensity

\[ \text{Intensity} \]

\[ q (\text{Å}^{-1}) \]

Length: \(-1\)
Diameter: \(-4\)
Surface: \(-4\)
Local Structure: PD

\[ r_0 = 450 \, \text{Å} \]
\[ L = 1 \times 10^6 \, \text{Å} \]
\[ T = 100 \, \text{Å} \]

[Image: Electron microscopy micrograph of CNTs]
0.05% Carbon in Bismaleimide Resin

Worm-like branched cluster

\[ \alpha = \frac{L_p}{r} = 4.5 \]

\[ \text{Tube} \quad r = 450 \text{ Å} \]
\[ T = 100 \text{ Å} \]
\[ L_p = 2000 \text{ Å} \]
\[ \sigma_m = 2.85 \]
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

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

\[ \approx 1 + 2\phi \]

No better than spheres
CNTs in Epoxy

Assumes no connectivity

Layered Silicates

Idealized

\[ I(q) \]

\[ q \]

\[ I(q) \]

\[ q \]
USAXS NaMMT in Water

< 100 Å = Sheet-like

No evidence of interparticle correlation

Exfoliated
Flexible Sheet Model

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

\[ g(r) \approx \frac{1}{r^D} \]
Simplified Disk Model

Radius, $R$

Thickness, $H$

Intensity (cm$^{-1}$)

$q$ (Å$^{-1}$)

Contrast = $1.02 \times 10^{-5}$ Å$^{-2}$
Radius = 10000 Å
Thickness = 100 Å
Vol. Fract. = 0.5
Crumpled Surfaces and the Flexible Sheet Model

Hartmut Fischer

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

H = 9 Å
R_p = 80 Å
Rcluster = 3301 Å
D = 2.65

0.1% NaMMT in Water
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.


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