Light Scattering: In situ characterization of nano-materials

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Materials Characterization

• Carbon nanotubes
• Metal oxide nanoparticles
• Liposomes & micelles
• Homogeneous vs. Heterogeneous Catalysts

Structure Determines Function
Understanding Dynamics

• Precipitation processes
• Gel growth
• Aggregation & sedimentation (or creaming)

Dynamics Reveals Mechanisms & Interactions
Outline

• Methods
  – Dynamic Light Scattering: particle size; growth dynamics
  – Static Light Scattering: aggregate structure

• Selected Projects
  – Control Asphaltene Precipitation & Growth at the Colloidal Scale
  – Identify Homogeneous vs Heterogeneous Catalysis in Water Oxidation
  – Gelation of EPS in Seawater
  – Identify Structure-Function relationship in Carbon Nanotubes

• Additional Projects
Methods
What Can DLS Measure?

- Hydrodynamic Sizes
- Size Distributions
- Aggregation Rates
- Critical Micelle Concentration

DLS reveals Brownian motion of a certain size range

Types of Materials:
- suspensions, emulsions, microemulsions, polymers, micelles
Scattered Light Intensity: $t = 0$

If particles remain fixed, so does intensity at detector

Static scattering reveals structure
Scattered Light Intensity: $t = \Delta t$

Particles have diffused

**If particles move, intensity at detector changes**

Duration of $\Delta t$ before intensity changes gives time scale of motion

Dynamic light scattering reveals ensemble average motion

Detector

$I = I(\Delta t) \neq I_0$
Dynamic Light Scattering: Raw Data

Fluctuations in scattered light arise from diffusive motion

Real-time hardware correlators measure lag time $\Delta t$ at which $I(\Delta t) \neq I_0$

**Diffusion** = $\frac{\text{Length}^2}{\text{Time}}$

Length: $\frac{1}{q}$

Stokes Einstein

$D = \frac{k_B T}{6 \pi \mu a}$
Dynamic Light Scattering: Raw Data

Fluctuations in scattered light arise from diffusive motion

\[ g(\Delta t) \approx \exp\left(-\frac{\Delta t}{\tau}\right) \]

OR extract time scale distribution

\[ g(\Delta t) = \int p(\tau) \exp\left(-\frac{\Delta t}{\tau}\right) \, d\tau \]

Diffusion = \frac{\text{Length}^2}{\text{Time}}

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

Length: \frac{1}{q}

Stokes Einstein

\[ D = \frac{k_B T}{6\pi \mu a} \]
Assessing aggregation

Uniform growth – all particles become incorporated into larger structures

Primary particles grow, but remain; Aggregates form ~2 orders of magnitude larger
Suspension Stability

- Scattered Intensity (magnitude only vs. time)
  - Aggregation/sedimentation over time
  - Addition of salts/surfactants can affect stability

![Graph showing intensity at 90° vs. time]

Methods
- Precipitation Control NP Synthesis Gelation Structure ↔ Function Additional Projects
**Electrophoretic mobility & Zeta Potential**

\[ \mu \equiv \frac{v}{E} \]

Balance electrostatic and hydrodynamic forces:  
\[ \mu \approx \frac{Qe}{6\pi \eta a} \]

Zeta Potential Measurements via Phase Analysis Light Scattering  
Analogous to Doppler shift, but electric field oscillates

**Hückel Theory:**  
\[ \zeta = \frac{3\mu\eta}{2D\varepsilon_0} \]  
For low ionic strengths (apolar) \( \kappa^{-1} >> a \)

**Smoluchowski:**  
\[ \zeta = \frac{\mu\eta}{D\varepsilon_0} \]  
For high ionic strength (aqueous) \( \kappa^{-1} << a \)
Static Light Scattering

- Fractal dimension of aggregates; $qR > 1$

$I \approx q^{-D_f}$

$D_f \sim 1$

$D_f \sim 3$
Stabilizing Asphaltene Precipitation

Sara Hashmi
Kathy Zhong, Leah Quintiliano
Abbas Firoozabadi
Asphaltene precipitation

Soluble in aromatic solvents (*solvents*)
Insoluble in light alkanes (*precipitants*)

Highly aromatic crude components

π-stack even when stable

Colloid growth & aggregation

Liquid-liquid separation

Sedimentation & deposition

Asphaltene Precipitation

- Mix oil with precipitant (heptane)
- Assess sedimentation, aggregation
- Precipitate in heptane with dispersant

Dodecyl benzene sulfonic acid

Centrifuge & decant:

| DBSA (ppm) | 50  | 250 | 750 | 2,500 | 7,500 | 10,000 |

Aggregation & Dissolution by Acid

CV $\chi=600$ mL/g; dissolution beyond $c=2500$ ppm

At fixed $\chi$ (mL/g)

stable at $c \approx 100$ ppm

DBSA: dissolution at $c \approx 100$ ppm for SB, QAB; $c \approx 2500$ ppm for CV

Stabilization without dissolution

CV $\chi = 600 \text{ mL/g}$

At fixed $\chi (\text{mL/g})$

Non-ionic dispersant: No dissolution even above 1 wt% dispersant

Particle size with non-ionic dispersant

\[ \chi (\text{mL/g}): \]
- CV: 600
- QAB: 100
- SB: 30

\[ \langle q \rangle (\text{nm}) \]

\[ c (\text{ppm}) \]

aggregation

stable suspensions
no dissolution

fixed \( \Phi \sim 10^{-4} \)

cmc of dispersant in heptane

Increasing mobility with dispersant

Stabilization by adsorption

- Adsorption isotherms corroborate particle characterization
- Non-ionic dispersant: cmc ~ 10 ppm in heptane
- Stabilizes asphaltenes below cmc

Dispersant micelles not required for charge stabilization; isolated dispersant molecules can cover negative charges.

Water Oxidation Catalysis: Homogeneous or Heterogeneous?

Ulrich Hintermair, Staff Sheehan, Julie Thomsen
Crabtree & Brudvig Labs
Yale Chemistry
Water Oxidation

Goal: \(2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2\) Water Splitting

Two Half Reactions:

- Reduction (lower activation barrier): \(4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\)
- Oxidation (higher activation barrier): \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-\)

Oxidant: CAN ceric ammonium nitrate (high oxidative potential)
NaIO\(_4\) Sodium periodate (lower oxidative potential)

Catalyst: \(\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}\)

\(\text{H}_2\text{O} \rightarrow [\text{Ir}] \rightarrow \text{O}_2\)

\(\text{BDE} = 115\ \text{kcal/mol} \quad 4\ \text{e}^- \text{ox.}\)
Oxidation Catalysis

- Platinum: acid stable; not very active
- Ruthenium: active; not acid stable
- **Iridium: active & active stable**

Iridium Precursors

- \( \text{Cp}^* = \text{pentamethylcyclopentadienyl} \)

- Various ligands: tune properties of molecular materials; tune activity
Iridium Catalysis

• **Blue Solution** develops during oxidation reaction

UV-vis measurements

Reaction Assessed by Oxygen Generation

- Oxygen generated at same time as formation of blue band; oxidant gets consumed

If the ligands are stable against oxidation...

- No light scattering... no particles...

→ Homogeneous catalysis

If the ligands are oxidized...

- Particles!

→ Heterogeneous catalysis

Concentration limits initial growth dynamics

![Graph showing particle formation kinetics with data points for 150 equivalents NaIO₄ in blue and 75 equivalents NaIO₄ in green.](image)

- **150 equivalents NaIO₄**
- **75 equivalents NaIO₄**

Particle Formation
Reaction Kinetics
Metal Oxide Particle Synthesis

- Aggregation is diffusion controlled

\[
R^2 = 0.994
\]

Power law dynamics in aggregate growth
Aggregate Characterization

Feature at ~30 nm: primary particle size

Over time $D_f$ evolves to ~2

Suspension forms

Solution only
“Green” Metal Oxide NP Synthesis

- Aqueous, room temperature
- Simplest precursor (off-the-shelf)

![Chemical formula](image)

**Graphs:**
1. Intensity at 90° vs. time (hours)
2. Particle size vs. time (minutes)

*(in preparation)*
Gelation in Seawater

Edo Bar-Zeev & Marissa Toussley
Elimelech Lab
EPS = extracellular polymeric substances

• Anything secreted by bacteria, microorganisms
  – Polysaccharides, proteins, lipids, may contain DNA
• Important in formation of biofilms, pathogenesis
  – Participate in quorum sensing
• Naturally occurring in fresh and seawater

Hydrogel kinetics will be dependent mainly by:

- Concentration,
- Polymer chain size
- Charge density
- Topology (linear, branched)

Abiotic Gel Formation

Methods Precipitation Control NP Synthesis Gelation Structure ↔ Function Additional Projects

Nanogels interpenetrate through axial diffusion

* Low activation energy (<50 kJ mol⁻¹)

* Ca²⁺ cross-link COOH groups in neighboring TEP

Abiotic Gel Formation

Abiotic Hydrogel Formation

TEP precursors

Nanogels

TEP micro

TEP macro

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

Ca^{2+}

TEP = “transparent exopolymer particles”

>>Assembly

Disassembly<<

>>Anneal

Fracture<<

Nanogel Formation: Kinetics & Size

Scattered Intensity

Increasing scatter indicates *Gel formation* with time

Dynamic Light Scattering

0 - - - **Size** - - - 170 nm

0 - - - **Time** - - - 72 h
Nanogel Structure

Methods Precipitation Control NP Synthesis Gelation Structure ↔ Function Additional Projects

Static Light Scattering (SLS)

Fractal dimension ($D_f$): $I/I_0 = q^{-(D_f)}$

$D_f : 1.7$  Diffusion-limited aggregation: imply on a sticky particles

$D_f : 2.2$  Reaction-limited aggregation: imply on a repulsion barrier

Bar-Zeev et al. in progress
Carbon Nanotubes
Dispersion ↔ Function
Leanne Pasquini, Seyla Azoz
Zimmerman & Pfefferle Labs
Environmental Impacts of CNTs

• Applications & Implications
• Release of CNTs to the environment through (products and manufacturing waste)
• Evidence of negative effects of exposure
Proposed Cytotoxicity Mechanism

- **Chemical Perturbation**
- **Physical Perturbation**

**Reactive Oxygen Species (ROS)**

Oxidative stress can lead to RNA, DNA, and protein damage in the cell.

**In Vivo Cytotoxicity**

*Escherichia Coli* K12 are exposed to CNTs in aqueous suspension.

(Alternate assay: on a membrane)

- 0.9% Saline
- CNT
- *E. coli*
- Incubated 1 h, 37°C
- Constant rotation
- 10-fold Dilutions
- Incubate 37°C overnight

**Methods**
- Precipitation
- Control
- NP
- Synthesis
- Gelation

**Structure**
- Function
- Additional Projects

Functionalized SWNT Cytotoxicity

- Identify specific physicochemical properties that correlate with the cytotoxicity.
- Ultimately leading to future safer design of SWNTs
- Maintain functionality; minimize negative impact

Surface Functional Group

How does functionalization affect stability?

Loss of Cell Viability (%)

Very broad distributions

Compare diffusive time scales (non-spherical)

Quantify Dispersion: Fractal Dimension & Polydispersity
How does functionalization affect stability?

Narrower distributions

Compare diffusive time scales (non-spherical)

Quantify Dispersion: Fractal Dimension & Polydispersity
Cytotoxicity Mechanism

Quantify Dispersion: Fractal Dimension Polydispersity

Surface functional groups

Dispersed aggregate state

SWNT toxicity

Controlling MWNT Dispersions

Nitric Acid Treatment Time (hrs)

**HNO₃** treatment increases surface oxygen (COOH) Facilitates more well-dispersed rod-like structures

**SWNT in water:** Azoz et.al. *(in preparation).*
Additional Projects
Silica NPs/s-SEBS microcapsules

(a) Organic Phase

Capsule from water-oil emulsions
Shell made of nanoparticles and polyelectrolytes

Capsule Shell

Polycation
Silica NPs

Gilad Kaufman, Raphael Sarfati, Osuji Lab
**Liposomes with Magnets & Contrast Agent**

*End goal: protect the body from contrast media during X-Ray Imaging of soft tissue*

EXTRANAL MAGNET to retrieve contrast agents after imaging

Encapsulation of contrast agent to avoid biological interaction

200 nm liposome (PEG)

Trey Turner & Candice Gurbatri, van Tassel Lab
Selenium Remediation via nano-Hematite

Selenium in the Environment

- Selenite (Se(IV))
- Selenate (Se(VI))

Se(VI) more difficult to remediate than Se(IV).

Iron Oxide NPs
- Thermodynamically stable
- Cheap & abundant
- Increased surface area to volume

Hematite (α-Fe₂O₃)
- Iron oxides = nature’s adsorbent
- Thermodynamically stable
- Cheap & abundant

Nano Hematite (nα-Fe₂O₃)
- Increased surface area to volume

Amanda Lounsbury, Zimmerman Lab
Biomimetic Membranes Using Aquaporin

• **Project goal:**
  – Vesicle rupture approach to fabricate a biomimetic membrane for water desalination incorporating the protein water channel aquaporin

• **Intermediate Formulations & Characterization:**
  – Stable, monodisperse vesicles constructed of lipids or block co-polymers

• **People:**
  – Menachem Elimelech (PI)
  – Corey Wilson (co-PI)
  – Jay Werber (graduate student)


Jay Werber, Elimelech Lab
Photoluminescence indicates average band gap $E_g \approx 1.89 \text{ eV}$

Interaction with light can produce singlet oxygen (ROS)

Disinfection Technologies?

Kyle Moor, Ezra Cates, Kim Lab
Fullerene aggregation

Salt reduces magnitude of surface charge; destabilizes suspension

EPM (μm s⁻¹ V cm⁻¹)

(a)

0 mg/L HA

1 mg/L HA

NaCl (mM)

0 100 200 300 400

0.0 0.5 1.0 1.5 2.0

500 mM NaCl + FNPs

Meng, Z. et al. Langmuir
Acknowledgements

• Meny Elimelech: Edo Bar-Zeev, Marissa Toussley, Jay Werber
• Julie Zimmerman: Leanne Gilbertson, Amanda Lounsbury
• Chinedum Osuji: Gilad Kaufman
• Paul van Tassel: Trey Turner, Candice Gurbatri
• Jaehong Kim: Kyle Moor
• Bob Crabtree/Gary Brudvig: Ulrich Hintermair, Julie Thomsen, Staff Sheehan
Thank You!

Questions?
Extra Slides
How Small?

In water; 532 nm; 90°

$g(\Delta t) \approx \exp(-\Delta t / \tau)$

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

$\tau = \frac{1}{2q^2D}$

$D = \frac{k_B T}{6\pi \mu \alpha}$

Particle size measurement: spherical approximation

$10^{-2}$ ms $\rightarrow$ $\sim$ 2 nm
Interconversion

- Molecular species $\rightarrow$ particles (blue) $\rightarrow$ reduction to molecular species (yellow)

Understanding particle size decrease

Dispersant increases surface area; no dissolution: \( \frac{SA}{V} \propto c \)

Spheres: \( \frac{SA}{V} \propto a^{-1} \rightarrow a \propto c^{-1} \)

What if the particles aren’t spherical?

For fractal objects: \( \frac{SA}{V} \propto a^{-(3-D_f)} \) \(\rightarrow a \propto c^{-1/(3-D_f)}\)

Evidence for surface adsorption

\[ a \propto c^{-1/(3-D_f)} \]

Model requires measure of \( D_f \)

By SLS:

\[ D_f = 1.63 \]

\[ \chi (\text{mL/g}): \]

- CV: 600
- QAB: 100
- SB: 30

Model: Slope = -0.73, \( R^2 = 0.96 \)

cmc of dispersant in heptane

Instrument Setup

• ALV 5000 goniometer + Verdi laser (Coherent)
• Instrument parameters: wavelength $\lambda$, scattering angle $\theta$, temperature $T$
• Suspension parameters: index of refraction $n$, viscosity $\mu$
Dynamic Light Scattering: Setup

- Incident light
- Diffusing colloids in a sample
- Unscattered light
- Light scatters in all directions
- Fluctuating scattered light intensity
- Detector

Fluctuations in scattered light arise from diffusion
Size Distributions: non-monodisperse

CONTIN: Provencher (1982)

Distinct decays indicate distinct particle populations

\[ g(\Delta t) = \int p(\tau) \exp(-\Delta t / \tau) d\tau \]

\[ p(\tau) \rightarrow p(\alpha) \]

Freely available; implemented in Fortran, C; data handling can be done in Matlab
DLS Measurements Over Time

BAB: $\chi = 20$ mL/g; $c = 0$ ppm

Indicates much longer diffusive time scale: *aggregates*
CONTIN Analysis

$g(\Delta t) = \int p(\tau) \exp\left(-\frac{\Delta t}{\tau}\right) d\tau$

$\langle \tau \rangle = \frac{\int \tau p(\tau) d\tau}{\int p(\tau) d\tau}$

SB: $\chi = 30 \text{ mL/g}; c = 0 \text{ ppm}$
Composition Dependent Growth

Adding dispersant $\rightarrow$ delays, suppresses aggregation

Application to Carbon Nanotubes

- DLS measures Diffusion constant $D \rightarrow$
  - Can be used to obtain Diameter:Length ratio

**spheres**

$$D = \frac{k_B T}{6\pi \mu a}$$

**rods**

$$D = \frac{k_B T}{3\pi \mu L} \left[ \ln \left( \frac{L}{D} \right) + 0.316 + 0.5825 \left( \frac{D}{L} \right) + 0.050 \left( \frac{D}{L} \right)^2 \right]$$

Dependence on Aspect Ratio

\[ p = \frac{D}{L}; \quad D = \frac{k_B T}{3\pi \mu L} \left[ \ln\left( \frac{1}{p} \right) + 0.316 + 0.5825p + 0.050p^2 \right] \]

Legend indicates values of \( L \) (nm)

Both bundling & length increase \( \tau \)
Practical Considerations

• Sample Preparation
  – Absorption at $\lambda$
    • Confirm/check with UV-vis spectroscopy
  – Concentration
    • Need ‘enough’ particles; avoid multiple scattering
    • Other methods can accommodate multiple scattering (back-scattering, DWS)

– Particle size
  • Estimate given system/sample parameters
Understanding dynamics: Ir NP’s

Power law growth – diffusion limited aggregation
Exponential growth – reaction limited aggregation
What Can SLS Measure?

• Radius of gyration
• Molar mass
• Second virial coefficient
• Fractal dimension

• Types of Materials: suspensions, emulsions, microemulsions, polymers, micelles, proteins

SLS reveals structure over a certain size range
Size Estimates

\[ D = \frac{k_B T}{6\pi \mu a} \]
\[ a = \frac{2q^2\tau k_B T}{6\pi \mu} \]

Parameters (water)

\[ \lambda = 532 \text{ nm} \]
\[ \theta = \pi / 2 \text{ Radians} \]
\[ n = 1.333 \]
\[ \mu = 0.001 \text{ Pa.s} \]
\[ T = 298 \text{ K} \]

\[ k_B = 1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \]

\[ q = \frac{4\pi n \sin \left( \frac{\theta}{2} \right)}{\lambda} = 0.0315 \text{ nm}^{-1} \]

\[ \tau \approx 10^{-4} \text{ s} \]

\[ a \approx 40 \text{ nm} \]
Size Distributions: Monodisperse

\[ g(\Delta t) \approx \exp\left(-\frac{\Delta t}{\tau}\right) \]

Instrument assumes Gaussian distribution

\[ p(\tau) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{1}{\tau} - \Gamma\right)^2\right] \]

Average \( \Gamma = 1/\langle \tau \rangle \)  
Variance \( \sigma^2 \)

First Order Cumulant  \( g(\Delta t) = \exp(-\Delta t \Gamma) \)

Second Order Cumulant  \( g(\Delta t) = \exp(-\Delta t \Gamma + \sigma^2 (\Delta t)^2 / 2) \)

Third Order Cumulant  \( g(\Delta t) = \exp(-\Delta t \Gamma + \sigma^2 (\Delta t)^2 / 2 - \omega^3 (\Delta t)^3 / 6) \)

When 2\textsuperscript{nd} order \( \Gamma \sim 3\textsuperscript{rd} \) order \( \Gamma \); Gaussian is good approximation
**Electrophoretic mobility**

\[ \mu = \frac{v}{E} \]

Balance electrostatic and hydrodynamic forces: \( \mu \approx \frac{Qe}{6\pi\eta a} \)

Hückel Theory: \( \zeta = \frac{3\mu\eta}{2D\varepsilon_0} \) \quad \text{Valid for low ionic strengths:} \quad \kappa^{-1} > a \\

Mobility measurements respond to *particle velocity* 

Instrument resolution \( \sim 3 \times 10^{-10} \text{ m}^2/\text{Vs} \)
Controlling Precipitation

- Mix oil with precipitant (heptane)
- Filter to Isolate asphaltenes
- Dissolve in toluene → ‘model oil’
- Reprecipitate in heptane; add dispersants

Dodecyl benzene sulfonic acid

Mix:

Centrifuge & decant:

DBSA: 50 250 750 2,500 7,500 10,000 ppm

Controlling MWNT Dispersions

Nitric Acid Treatment Time

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<thead>
<tr>
<th>MWNT 1</th>
<th>MWNT 3</th>
<th>MWNT 5</th>
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<tbody>
<tr>
<td>MWNT 2</td>
<td>MWNT 4</td>
<td>MWNT 6</td>
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Tube Diameter

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<tr>
<th>MWNT 13</th>
<th>MWNT 4</th>
<th>MWNT 14</th>
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Fractal Dimension

HNO$_3$ treatment increases surface oxygen (COOH)