Light Scattering: In situ characterization of nano-materials

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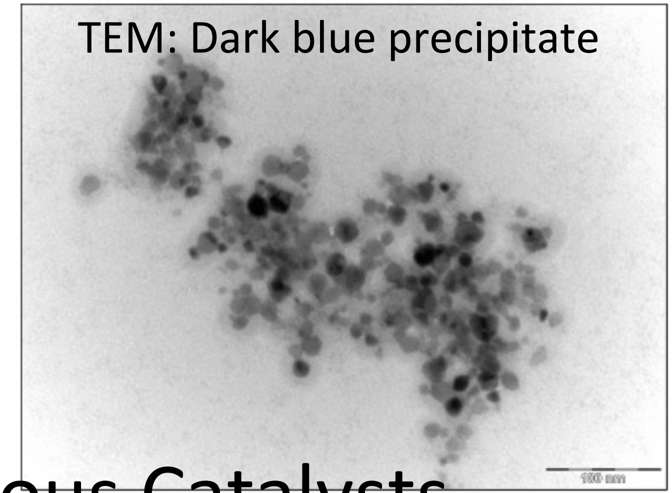
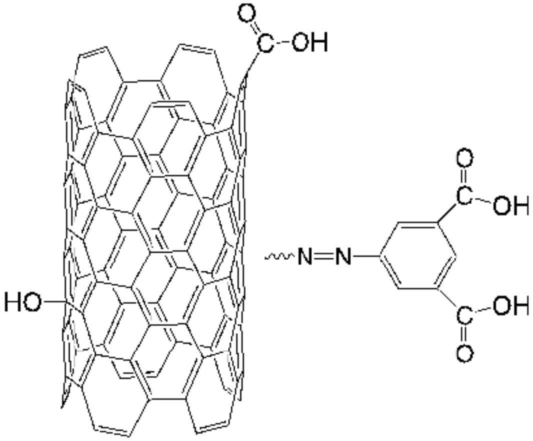
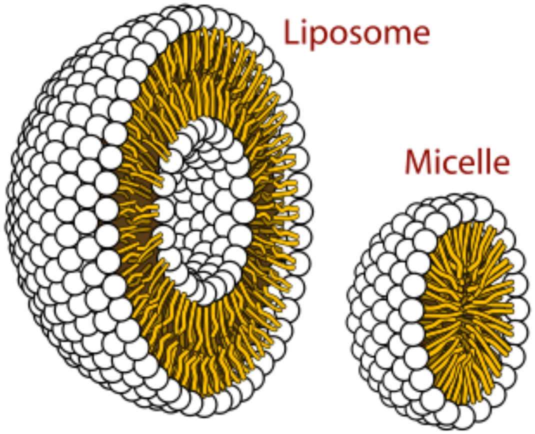
Department of Chemical & Environmental Engineering

Materials Characterization



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

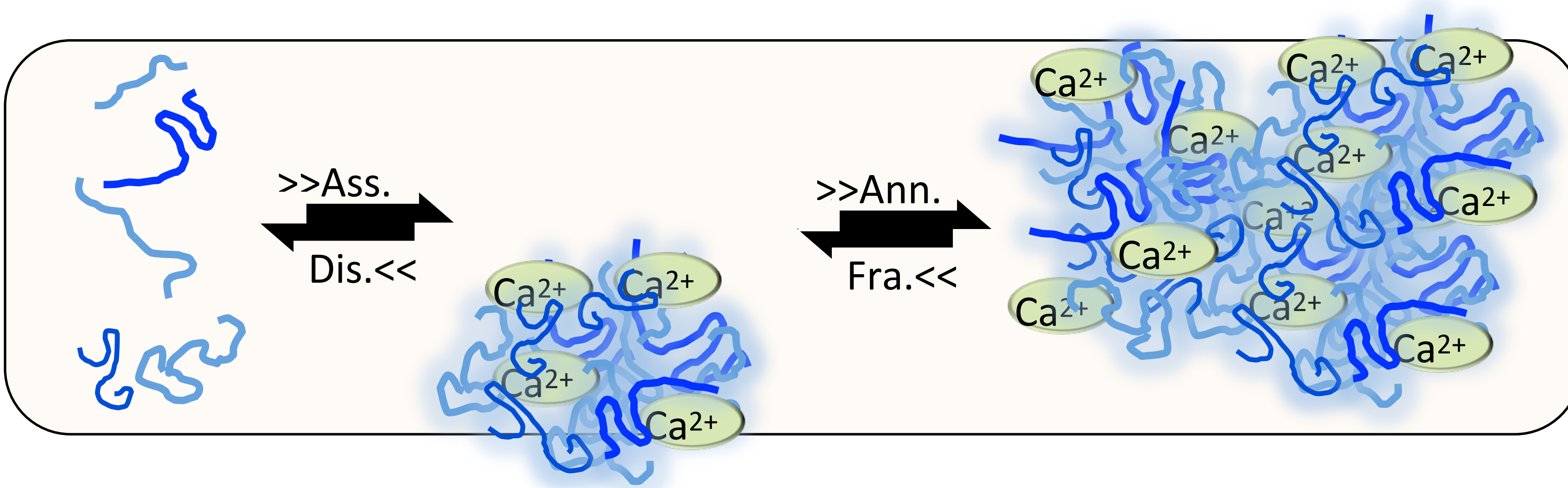




Structure Determines Function

Understanding Dynamics

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



Dynamics Reveals Mechanisms & Interactions

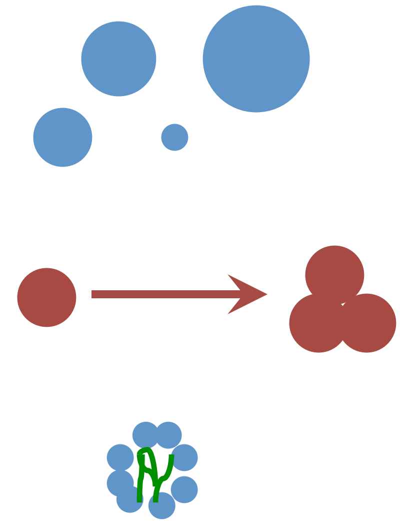
Outline

- 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

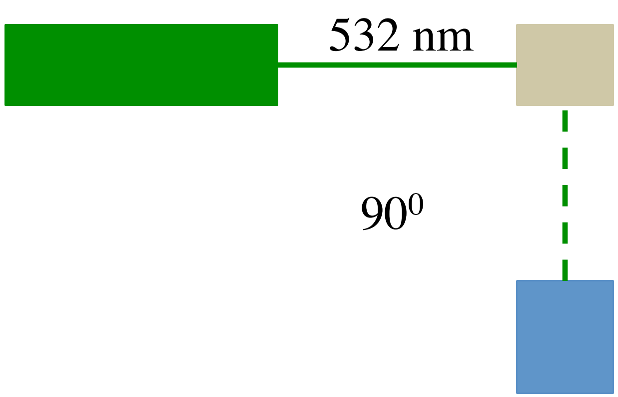
Methods

What Can DLS Measure?

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

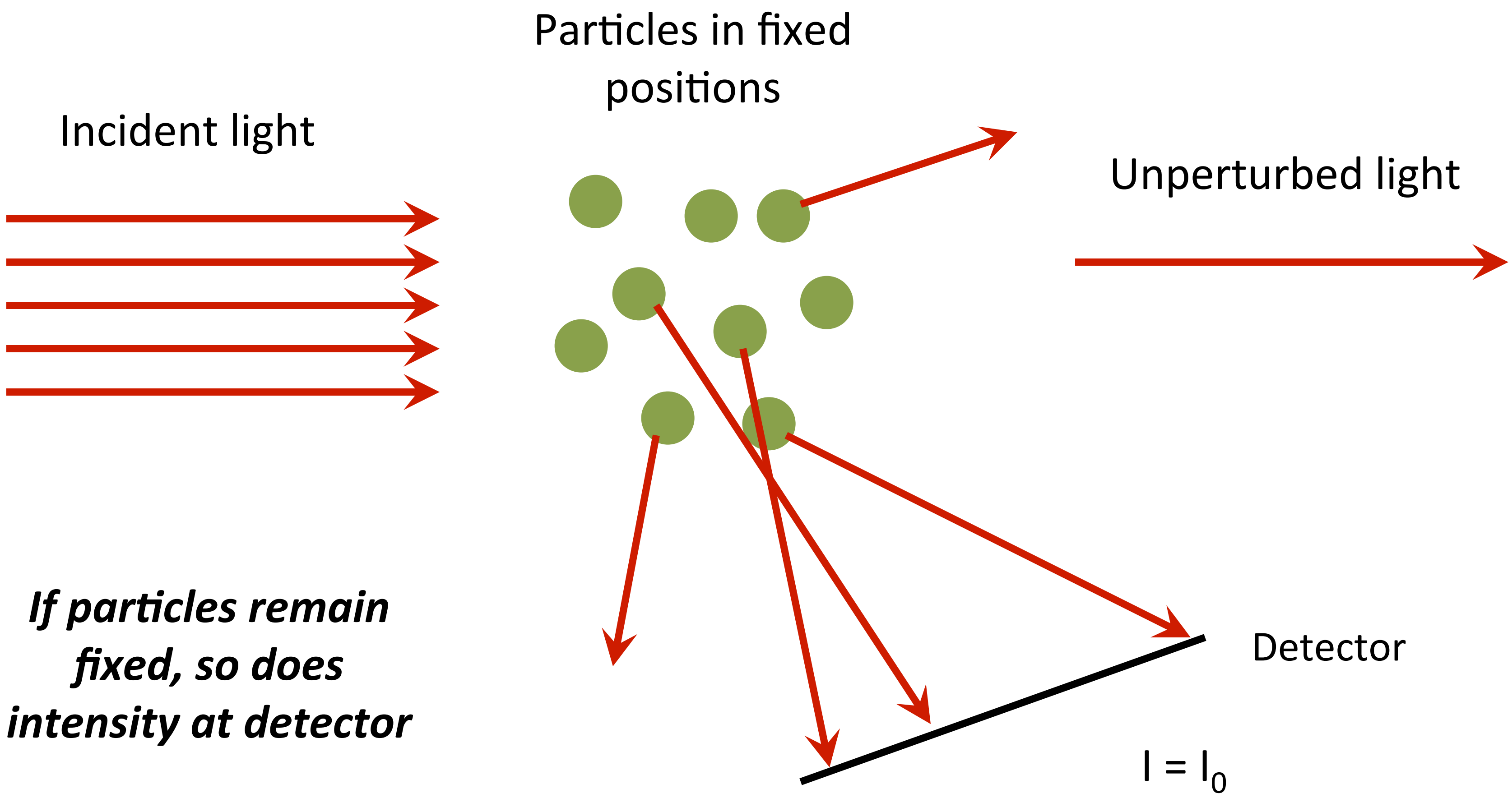


DLS reveals* Brownian motion *of a certain size range



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

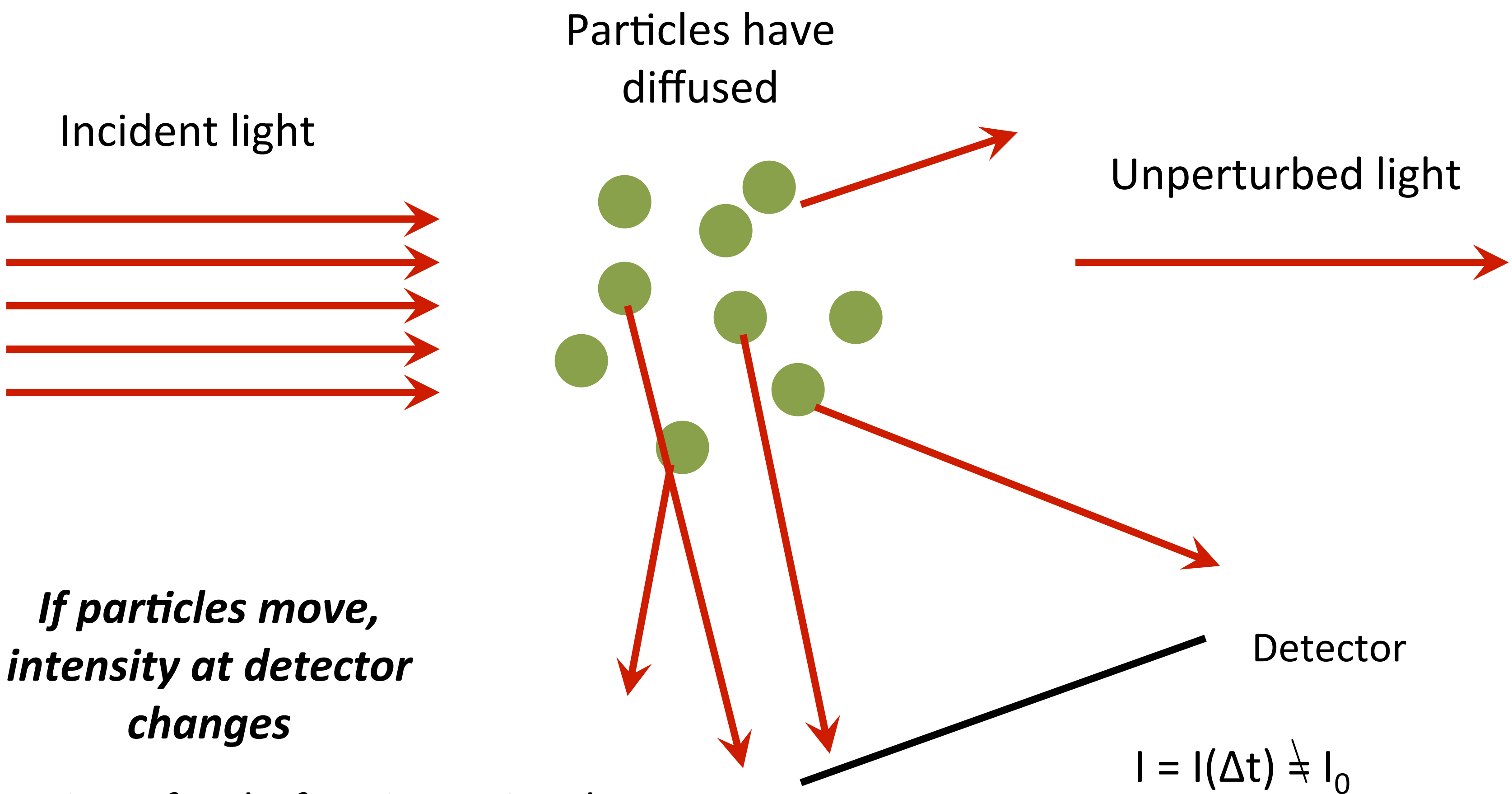
Scattered Light Intensity: t = 0



If particles remain fixed, so does intensity at detector

Static scattering reveals structure

Scattered Light Intensity: $t = \Delta t$



If particles move, intensity at detector changes

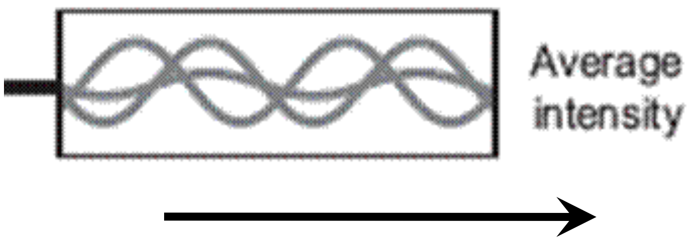
Duration of Δt before intensity changes gives time scale of motion

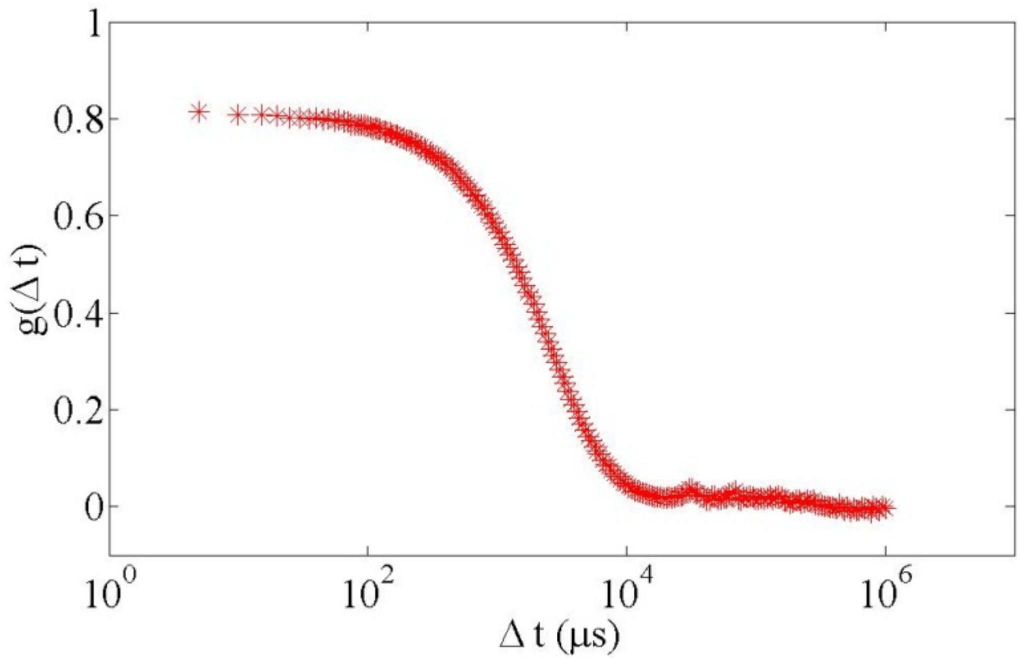
Dynamic light scattering reveals ensemble average motion

Dynamic Light Scattering: Raw Data

Fluctuations in scattered light arise from diffusive motion

Detector





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

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

Length: $1/q$

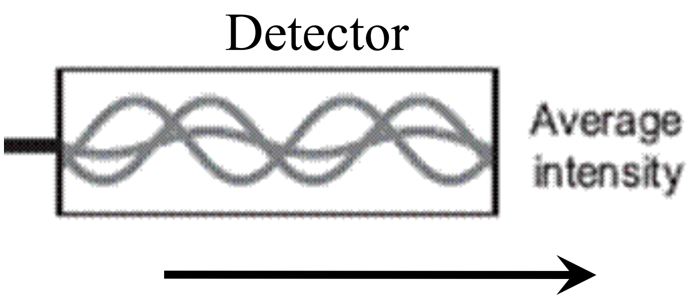
$$q = 4\pi n \sin\left(\theta/2\right)/\lambda$$

Stokes Einstein

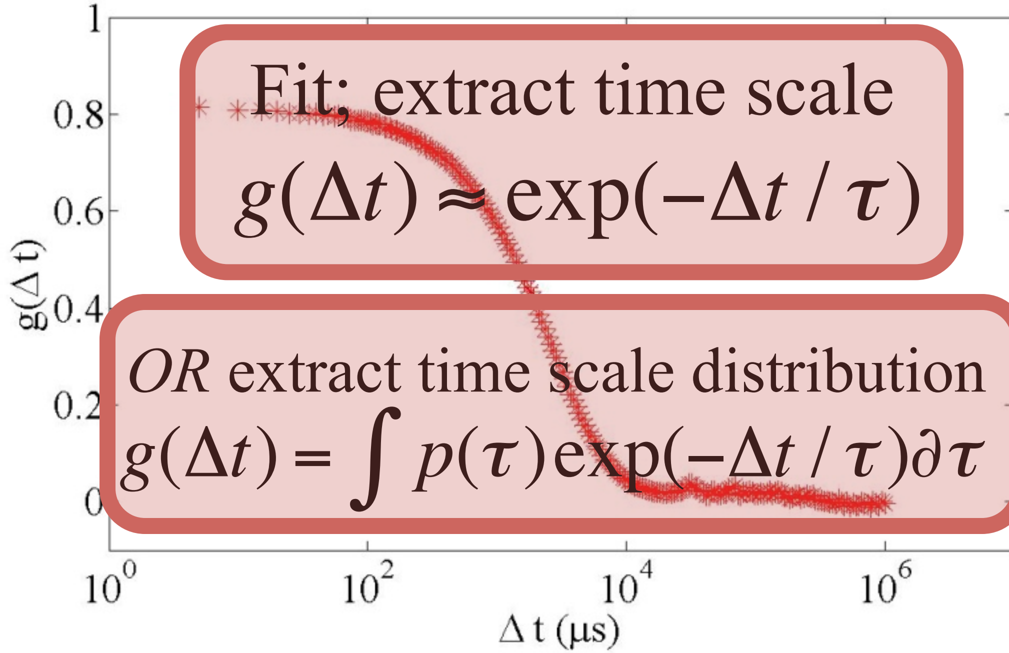
$$D = k_B T / 6\pi\mu a$$

Dynamic Light Scattering: Raw Data

Fluctuations in scattered light arise from diffusive motion



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



Fit; extract time scale

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

OR extract time scale distribution

$$g(\Delta t) = \int p(\tau)\exp(-\Delta t / \tau)\partial\tau$$

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

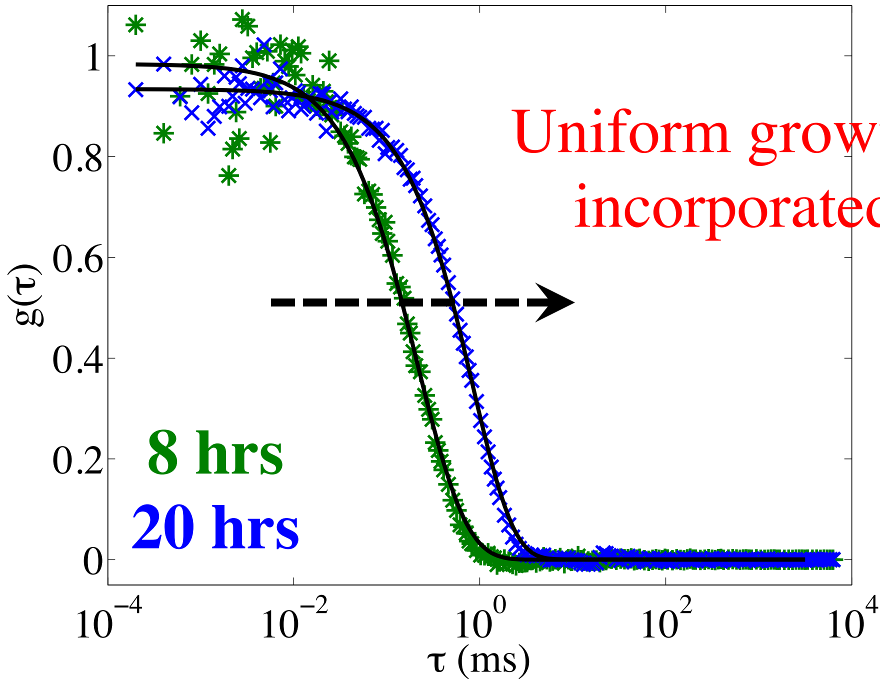
Length: $1/q$

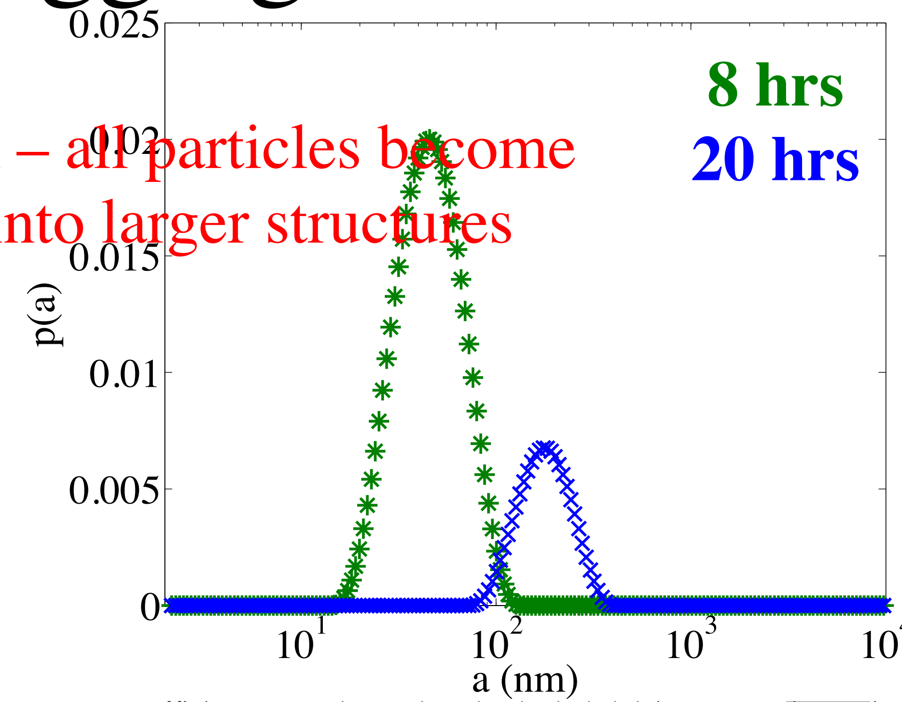
$$q = 4\pi n \sin\left(\theta/2\right)/\lambda$$

Stokes Einstein

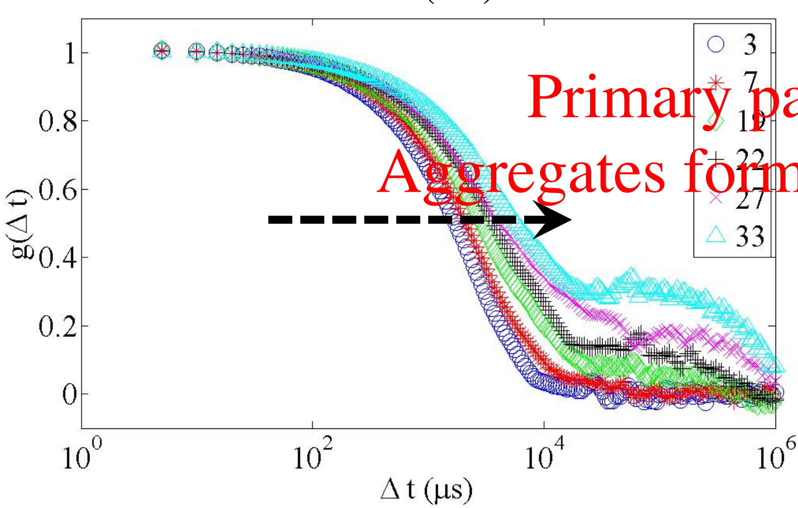
$$D = k_B T / 6\pi\mu a$$

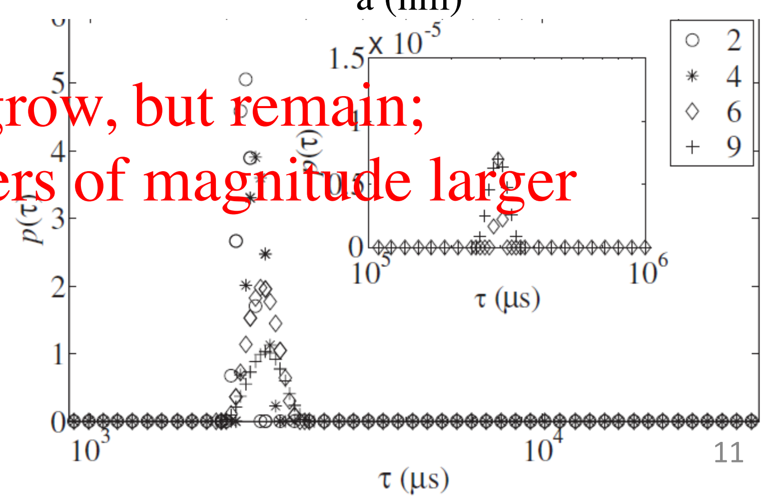
Assessing aggregation





Uniform growth – all particles become incorporated into larger structures

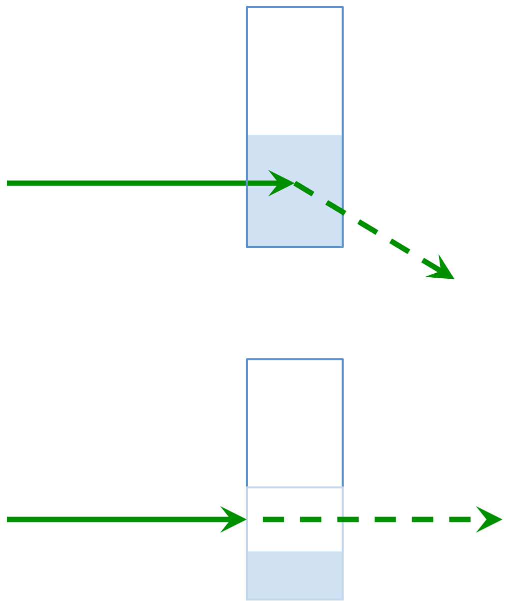


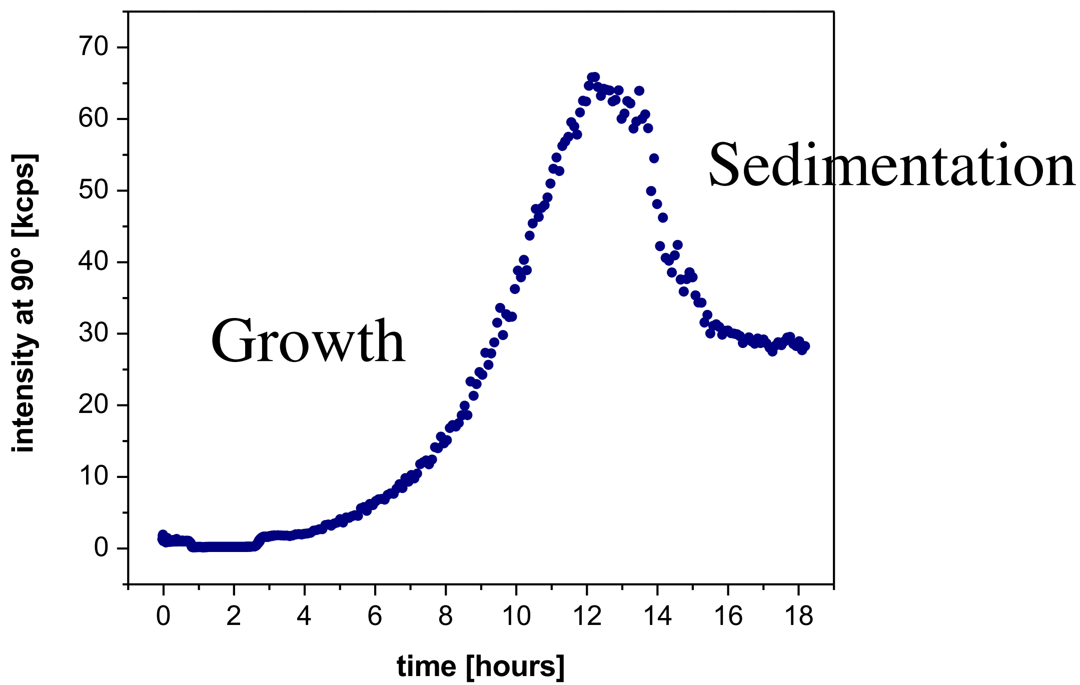


Primary particles grow, but remain;
Aggregates form ~2 orders of magnitude larger

Suspension Stability

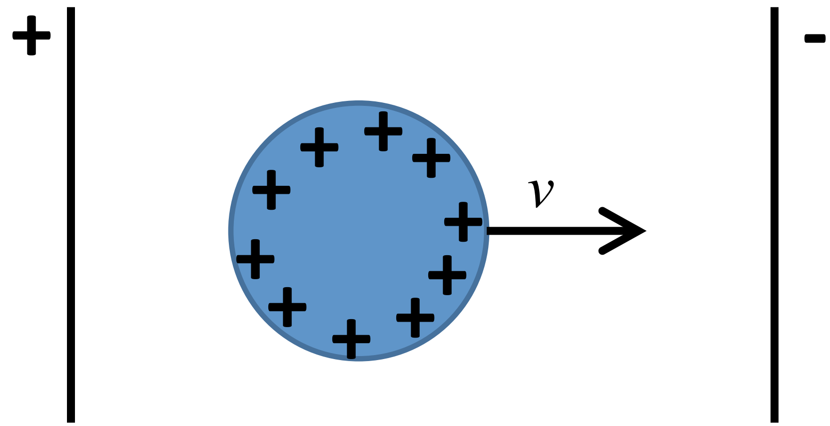
- Scattered Intensity (magnitude only vs. time)
  - Aggregation/sedimentation over time
  - Addition of salts/surfactants can affect stability





Electrophoretic mobility & Zeta Potential

$$\mu \equiv \frac{v}{E}$$



Balance electrostatic and hydrodynamic forces: $\mu \approx \dfrac{Qe}{6\pi\eta a}$

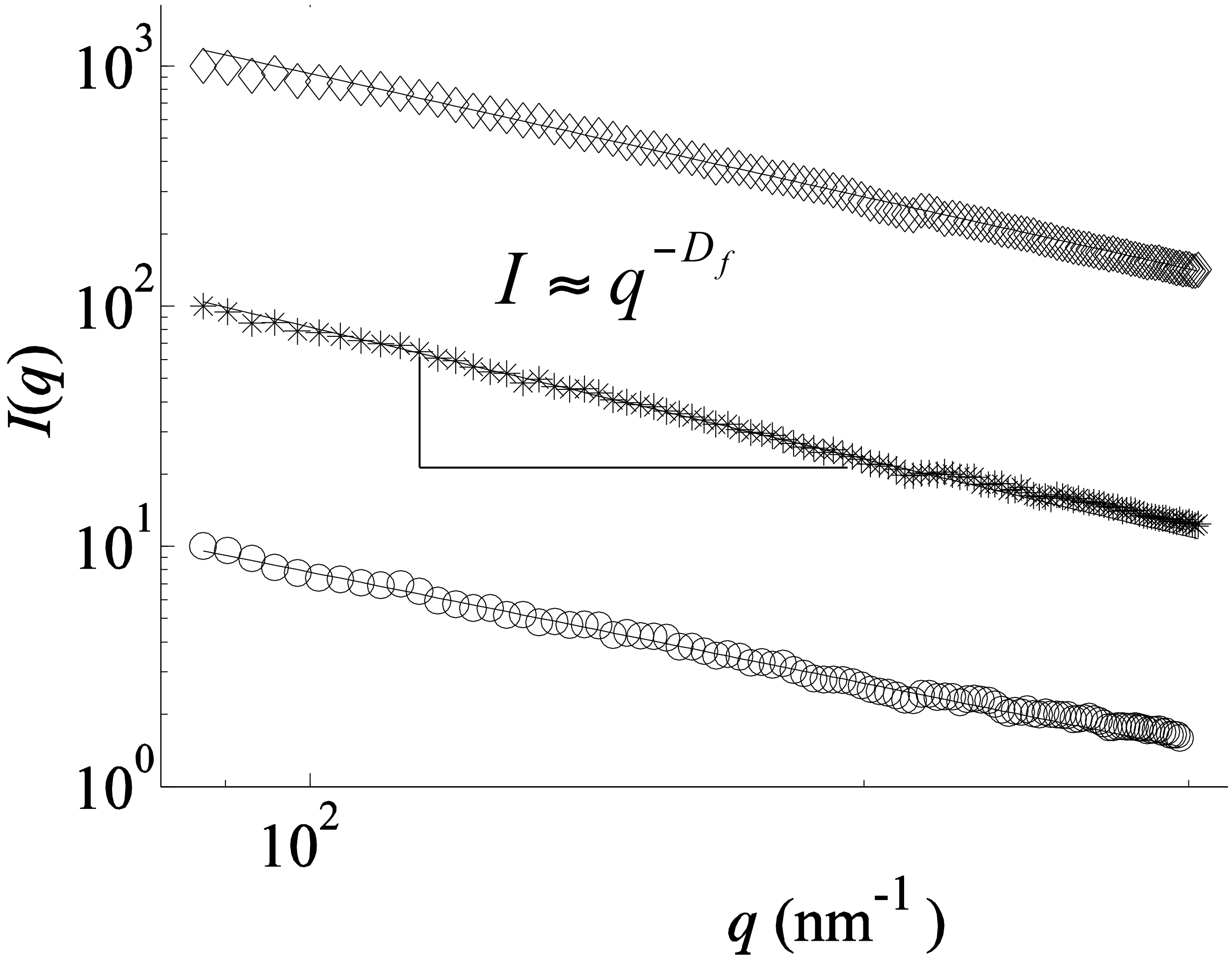
Zeta Potential Measurements via Phase Analysis Light Scattering
Analogous to Doppler shift, but electric field oscillates

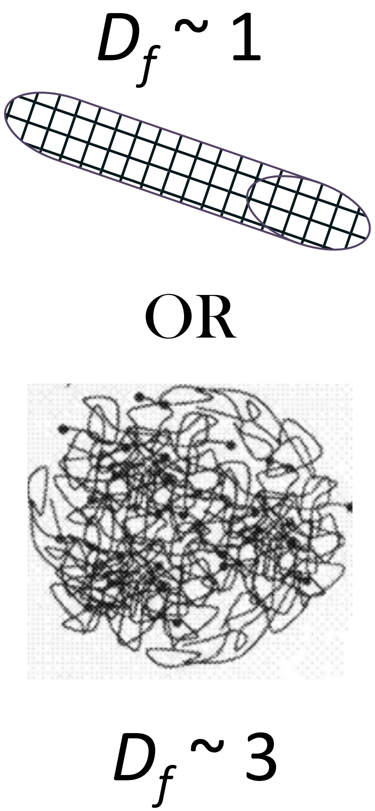
Hückel Theory: $\zeta = \dfrac{3\mu\eta}{2D\varepsilon_0}$ For low ionic strengths (apolar) $\kappa^{-1} >> a$

Smoluchowski: $\zeta = \dfrac{\mu\eta}{D\varepsilon_0}$ For high ionic strength (aqueous) $\kappa^{-1} << a$

Static Light Scattering

- Fractal dimension of aggregates; $qR>1$





Stabilizing Asphaltene Precipitation

Sara Hashmi

Kathy Zhong, Leah Quintiliano

Abbas Firoozabadi

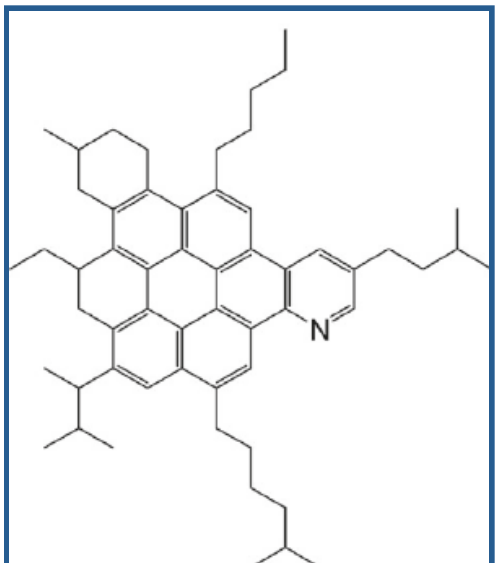
R E R I

Reservoir Engineering Research Institute

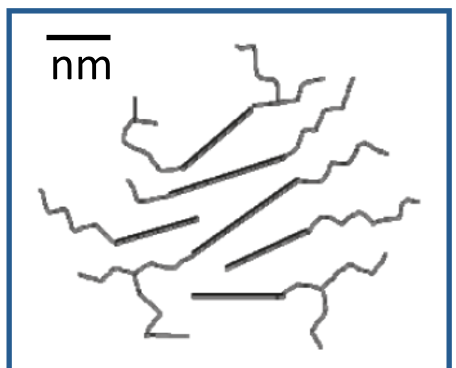
Asphaltene precipitation

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

Highly aromatic crude components

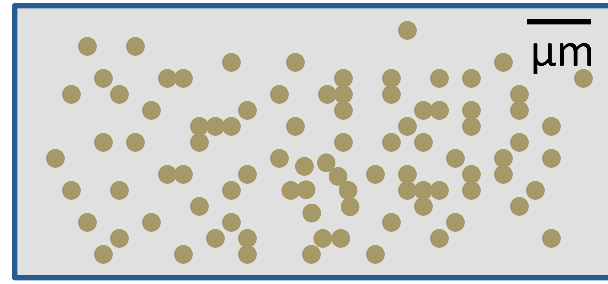


Liquid-liquid separation



π-stack even when stable

Colloid growth & aggregation

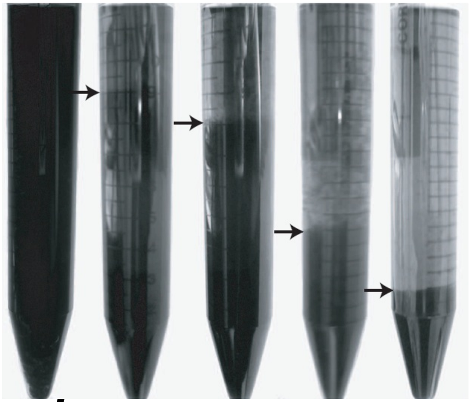


Sedimentation & deposition

Mullins, O. C. *Energy & Fuels* **24** 2179 (2010).

Asphaltene Precipitation

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



- Precipitate in heptane *with dispersant*

Dodecyl benzene sulfonic acid

Centrifuge & decant:

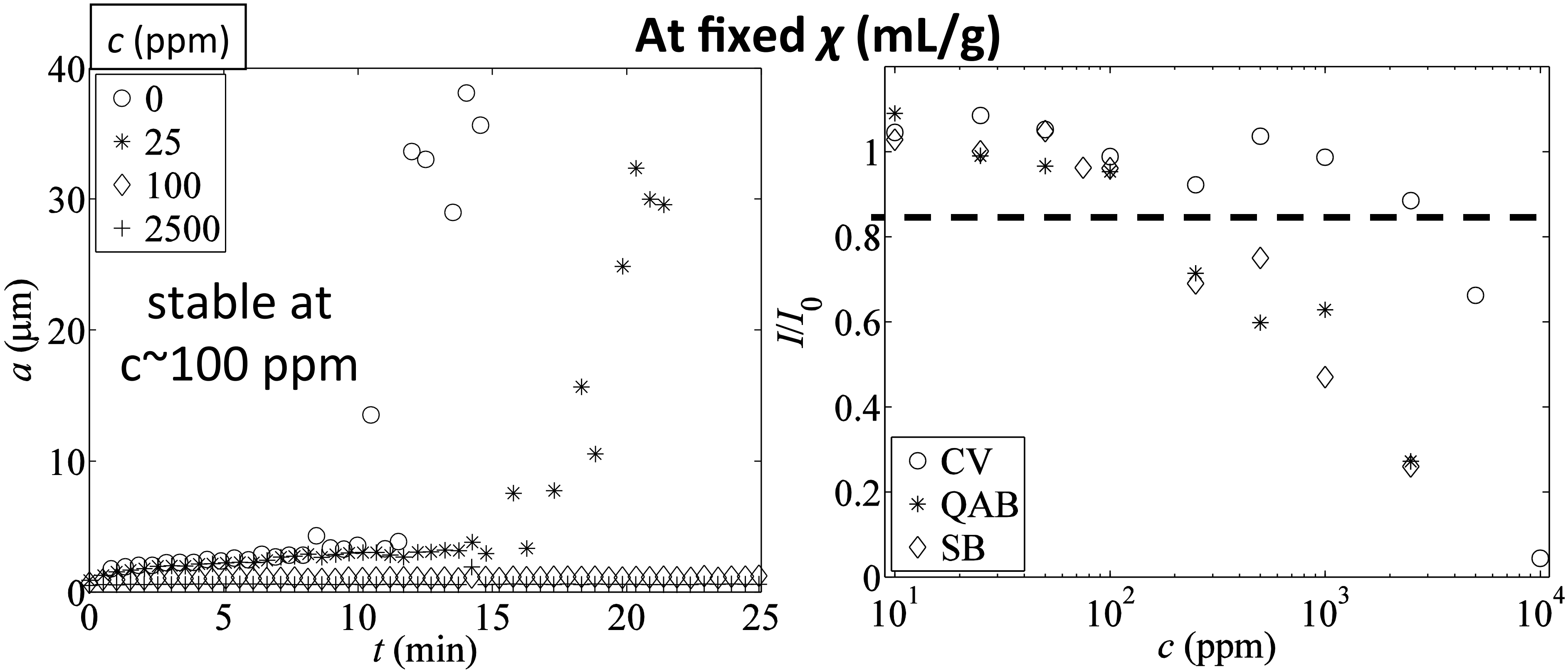
DBSA: 50 250 750 2,500 7,500 10,000 ppm

Hashmi, et. al. *Soft Matter* **8** 8778 (2012).

Hashmi, et. al. *Langmuir* **8** 8778 (2010).

Aggregation & Dissolution by Acid

CV χ=600 mL/g; dissolution beyond c=2500 ppm



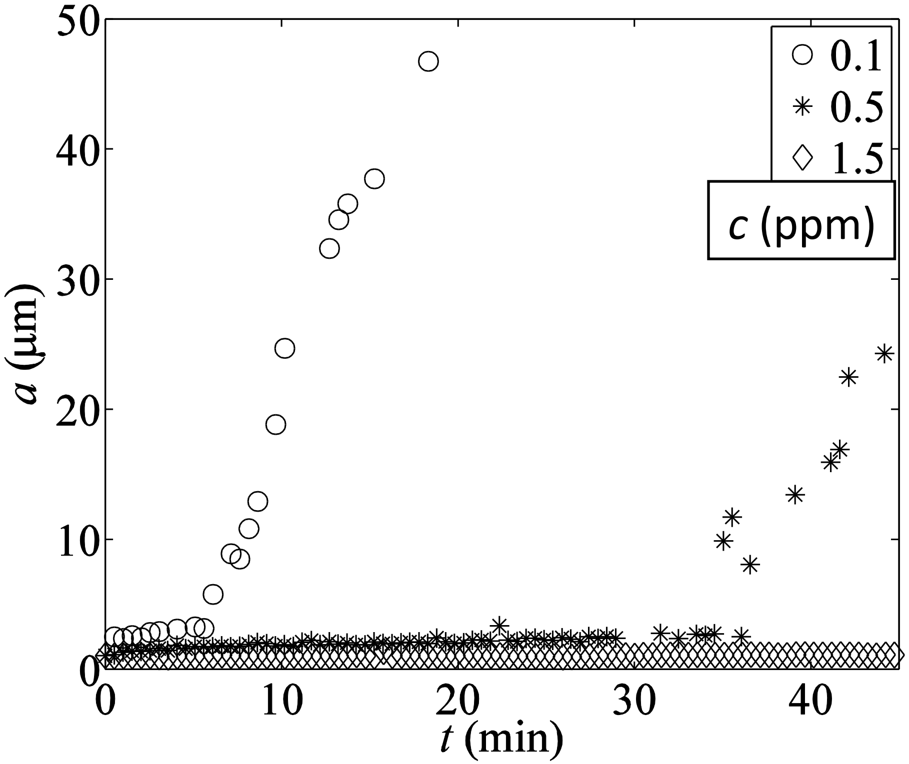
DBSA: dissolution at
c~100 ppm for SB, QAB;
c~2500 ppm for CV

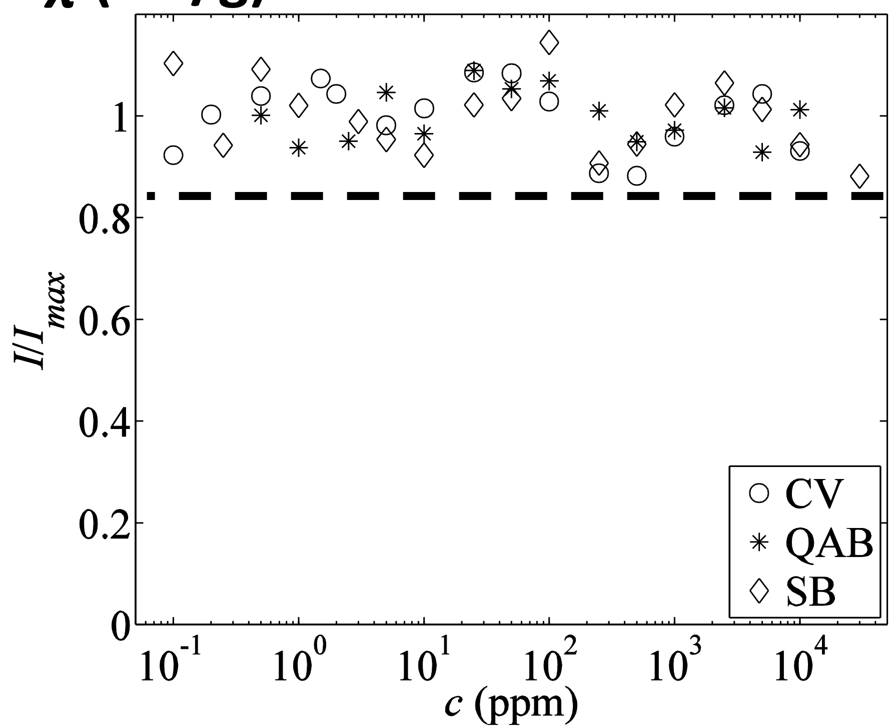
Hashmi, et. al. *Soft Matter* **8** 8778 (2012).

Stabilization without dissolution

CV χ=600 mL/g

At fixed χ (mL/g)

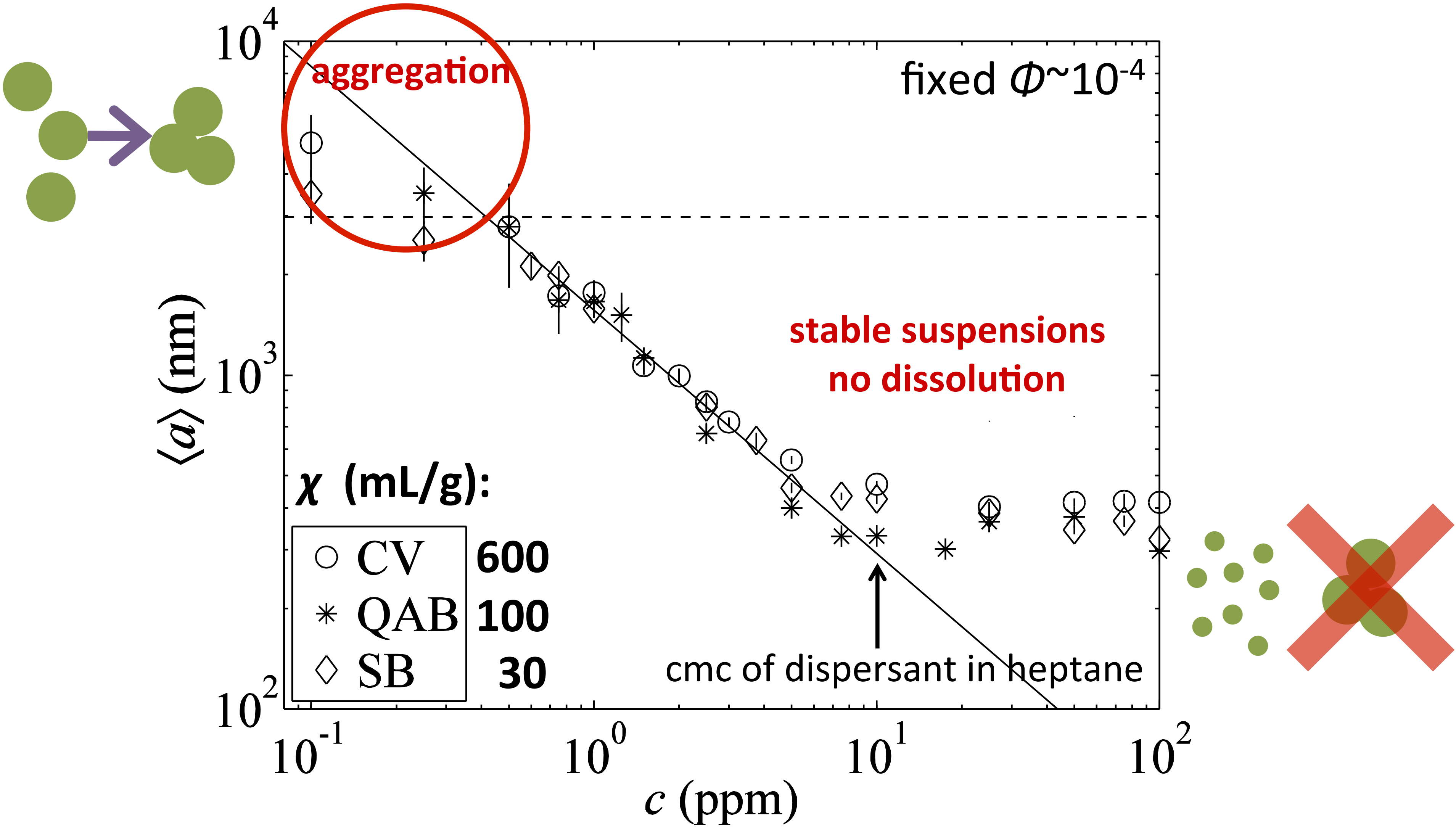




Non-ionic dispersant:
No dissolution even
above 1 wt% dispersant

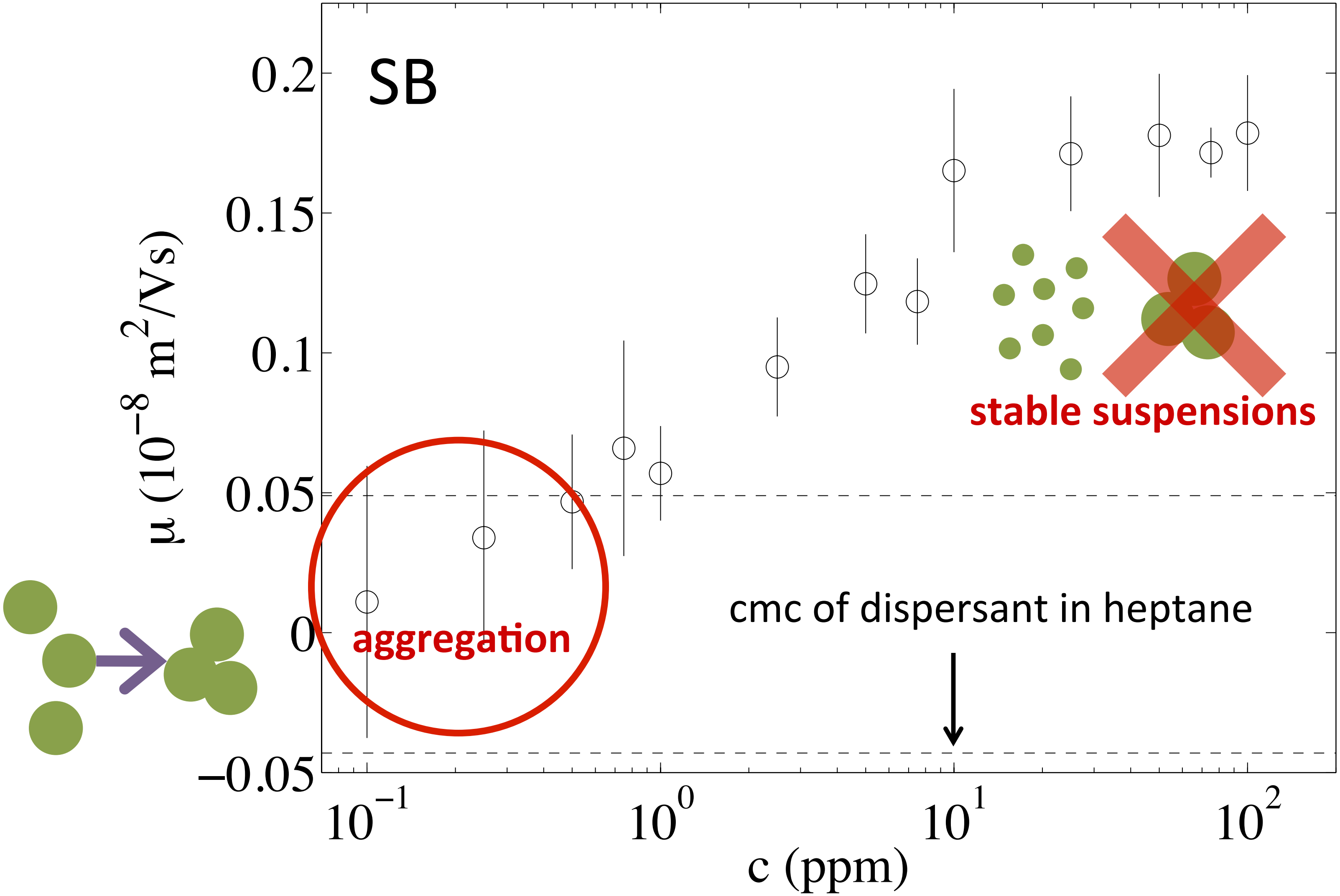
Hashmi, et. al. *Soft Matter* **8** 8778 (2012).

Particle size with non-ionic dispersant



Hashmi, Firoozabadi. *Soft Matter* **7**, 8384 (2011).

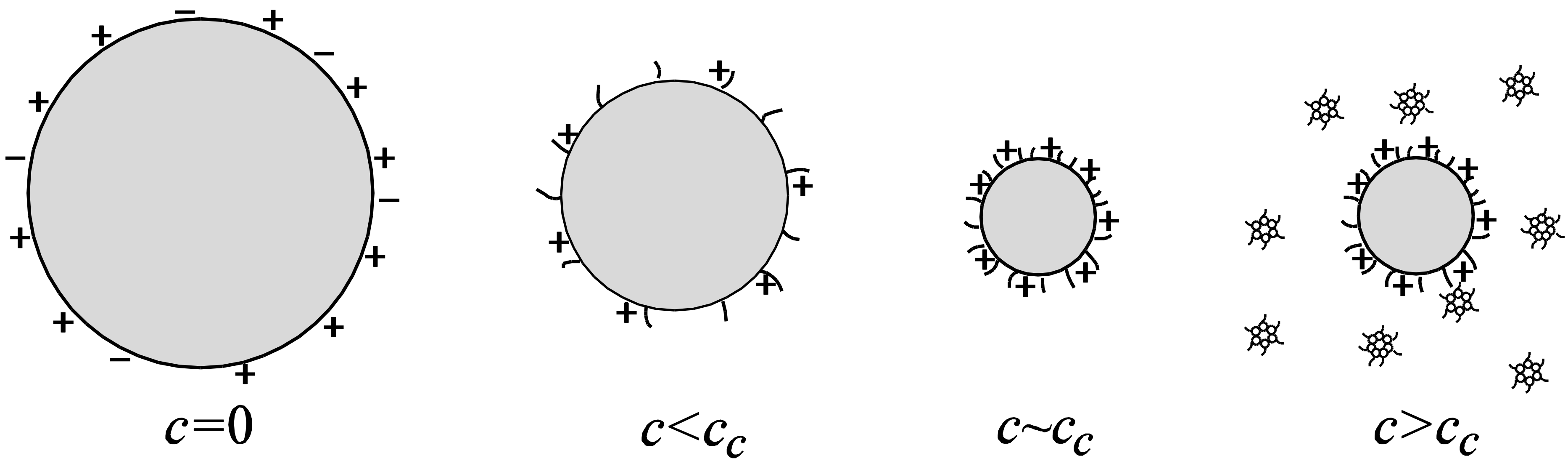
Increasing mobility with dispersant



Hashmi, Firoozabadi. *Soft Matter* **7**, 8384 (2011).

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.

Hashmi, Firoozabadi. *Soft Matter* **7**, 8384 (2011).

Water Oxidation Catalysis: Homogeneous or Heterogeneous?

Ulrich Hintermair, Staff Sheehan, Julie Thomsen

Crabtree & Brudvig Labs

Yale Chemistry

UNIVERSITY OF BATH

Water Oxidation

Goal: $2H_2O \rightarrow 2H_2 + O_2$ Water Splitting

Two Half Reactions:

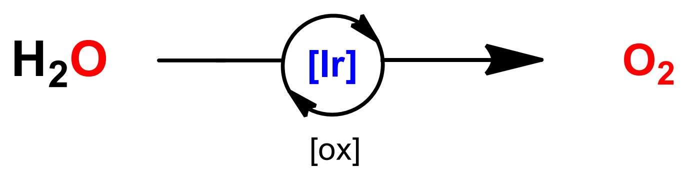
$4H^+ + 4e^- \rightarrow 2H_2$ Reduction (lower activation barrier)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Oxidation (higher activation barrier)

Oxidant: CAN ceric ammonium nitrate (high oxidative potential)

$NaIO_4$ Sodium periodate (lower oxidative potential)

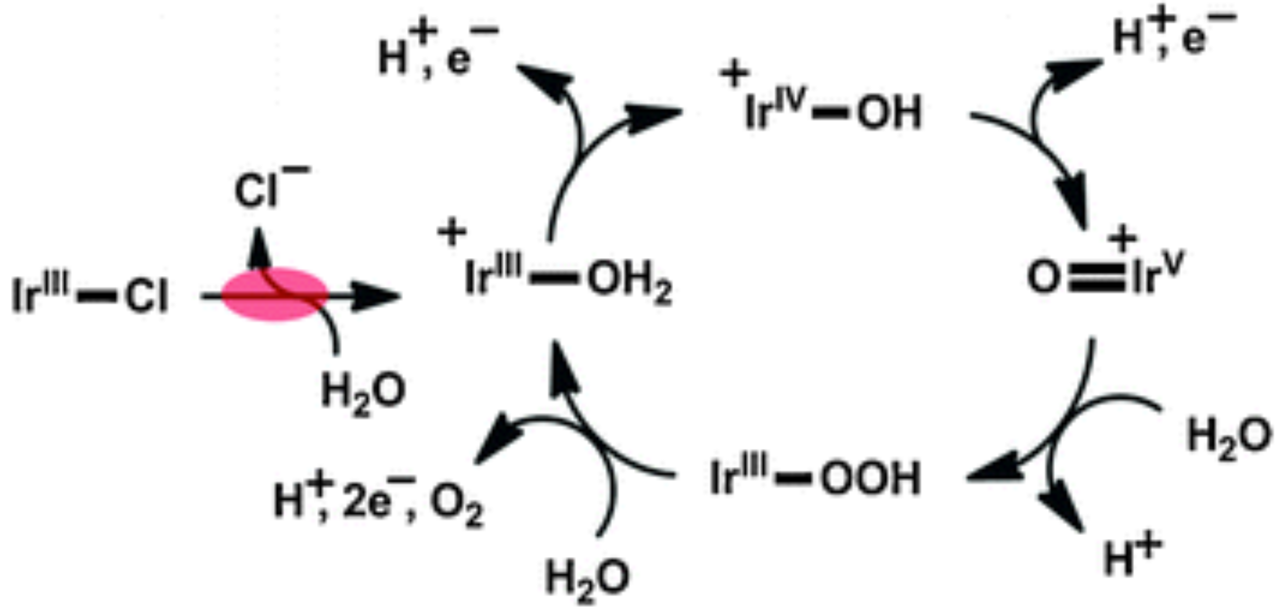
Catalyst: $Ir^{III} \rightarrow Ir^{IV}$



BDE = 115 kcal/mol *$4\ e^-$ ox.*

Oxidation Catalysis

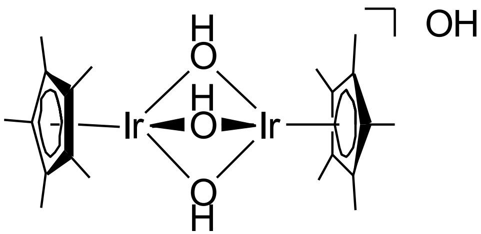
- Platinum: acid stable; not very active
- Ruthenium: active; not acid stable
- ***Iridium: active & active stable***



Garand E, et. al. *Phys Chem Chem Phys* **14** 10109 (2012).

Iridium Precursors

- Cp* = pentamethylcyclopentadienyl



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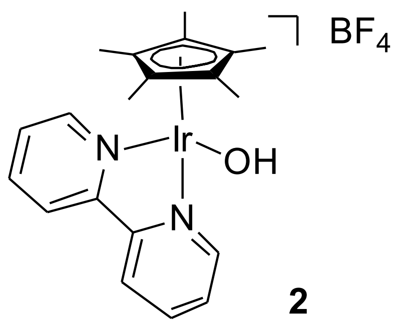

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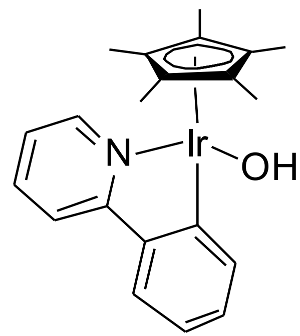

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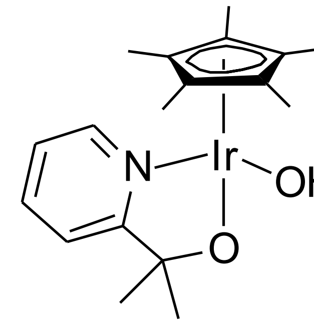
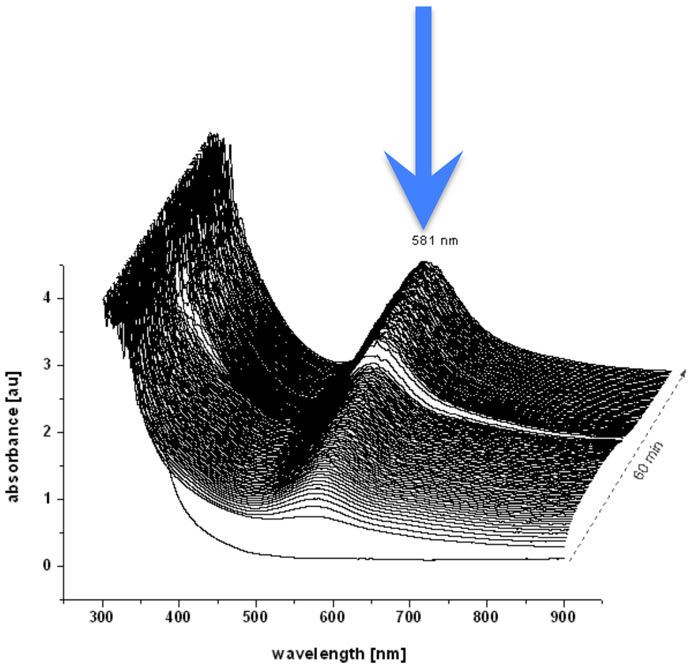


4

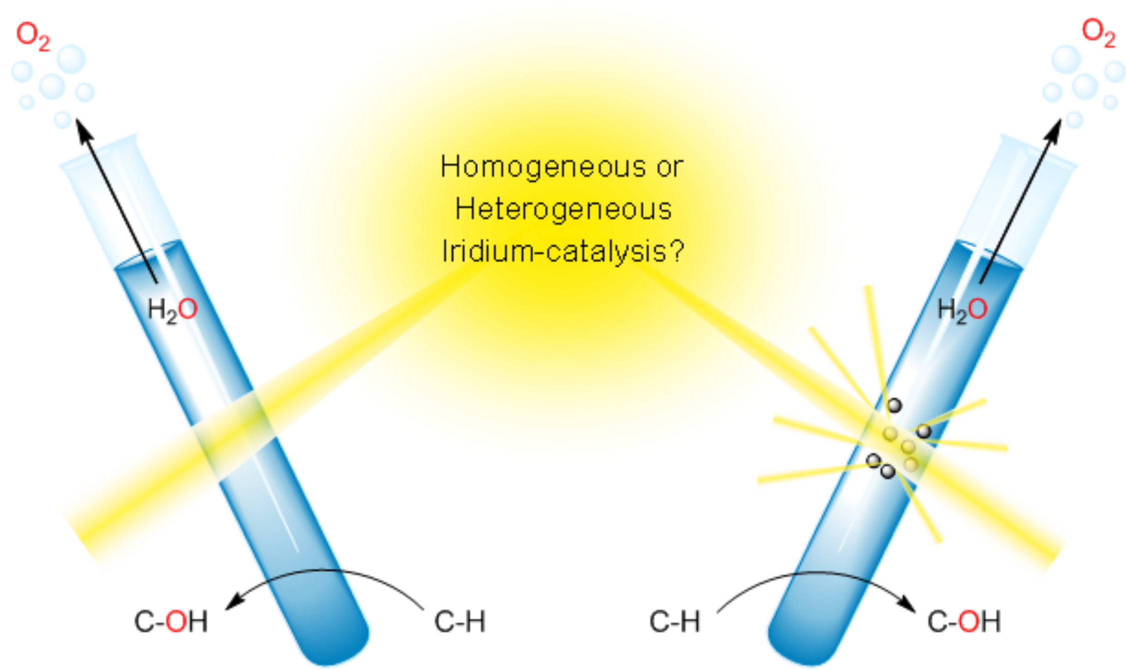
- Various ligands: tune properties of molecular materials; tune activity

Iridium Catalysis

- Blue Solution develops during oxidation reaction



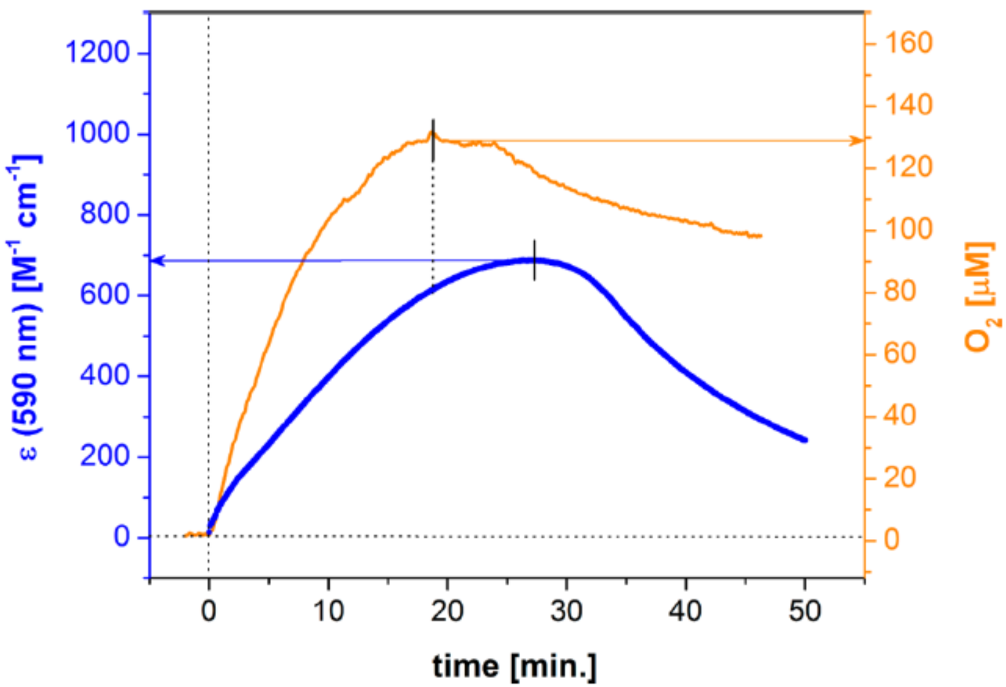
UV-vis measurements

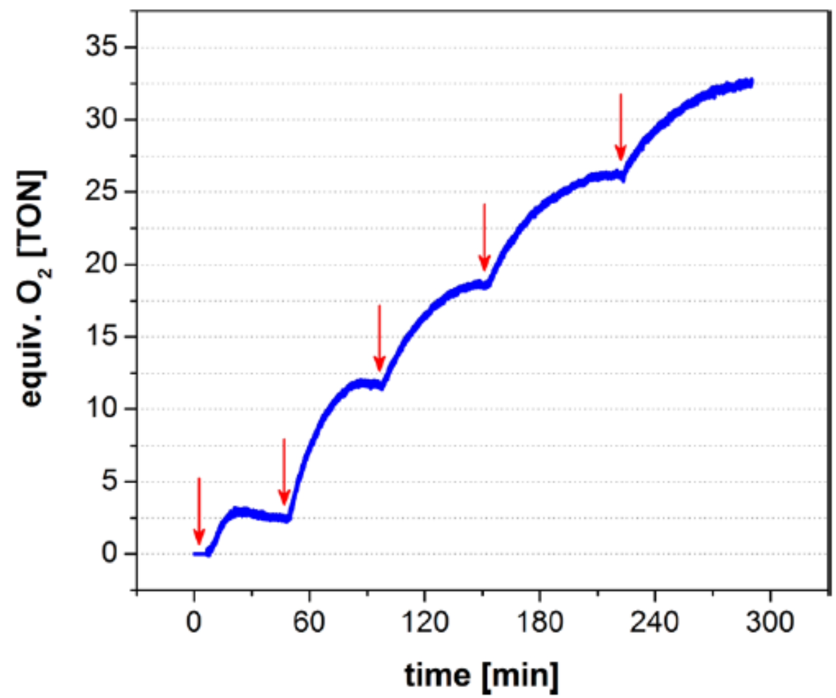


Hintermair U, et. al. *JACS* **134** 9785 (2012).

Reaction Assessed by Oxygen Generation

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



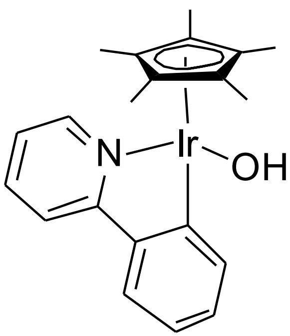


Hintermair U, et. al. *JACS* **135** 10837 (2013).

If the ligands are stable against oxidation…

- No light scattering… no particles…

→ Homogeneous catalysis



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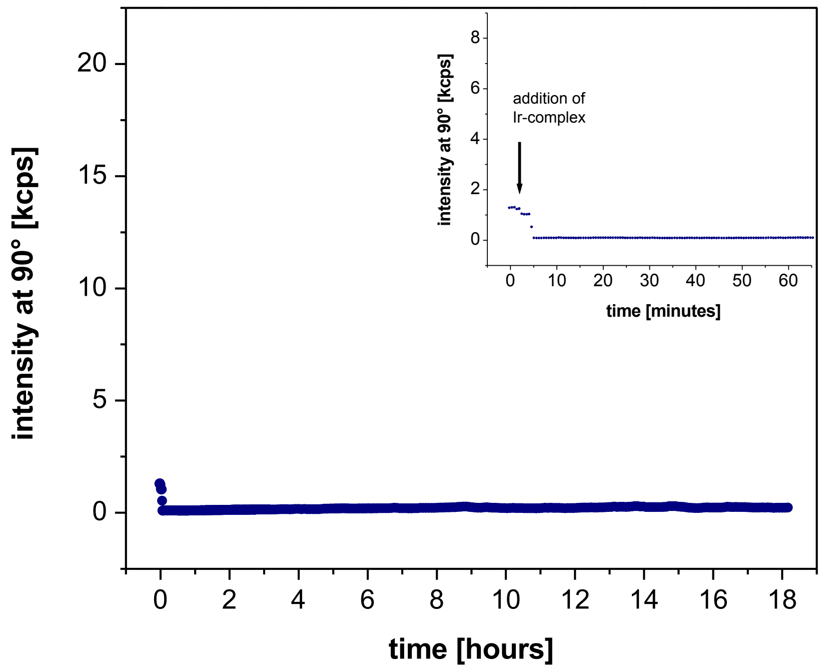

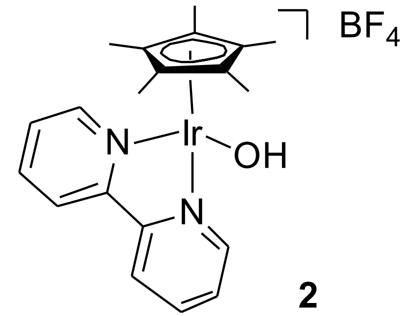

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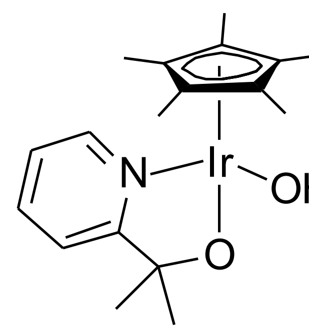

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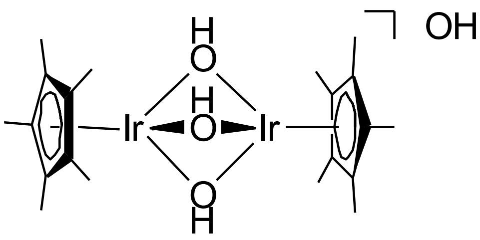
Hintermair U, et. al. *JACS* **134** 9785 (2012).

If the ligands are oxidized…

- Particles!

→ Heterogeneous catalysis



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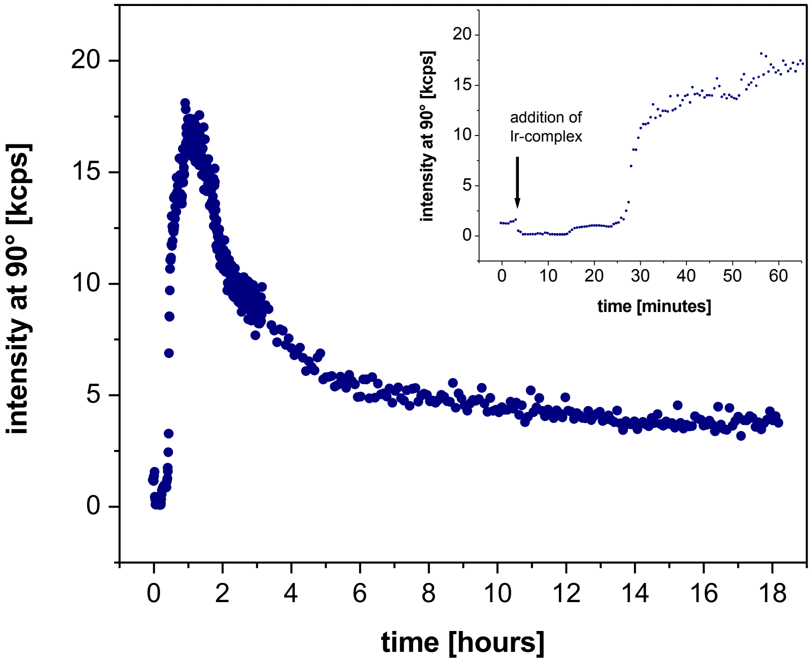
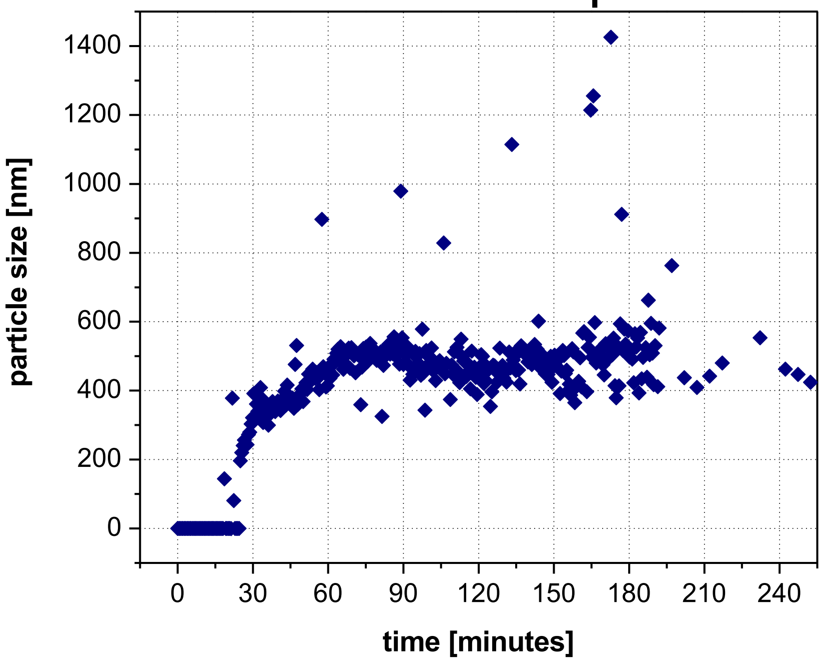
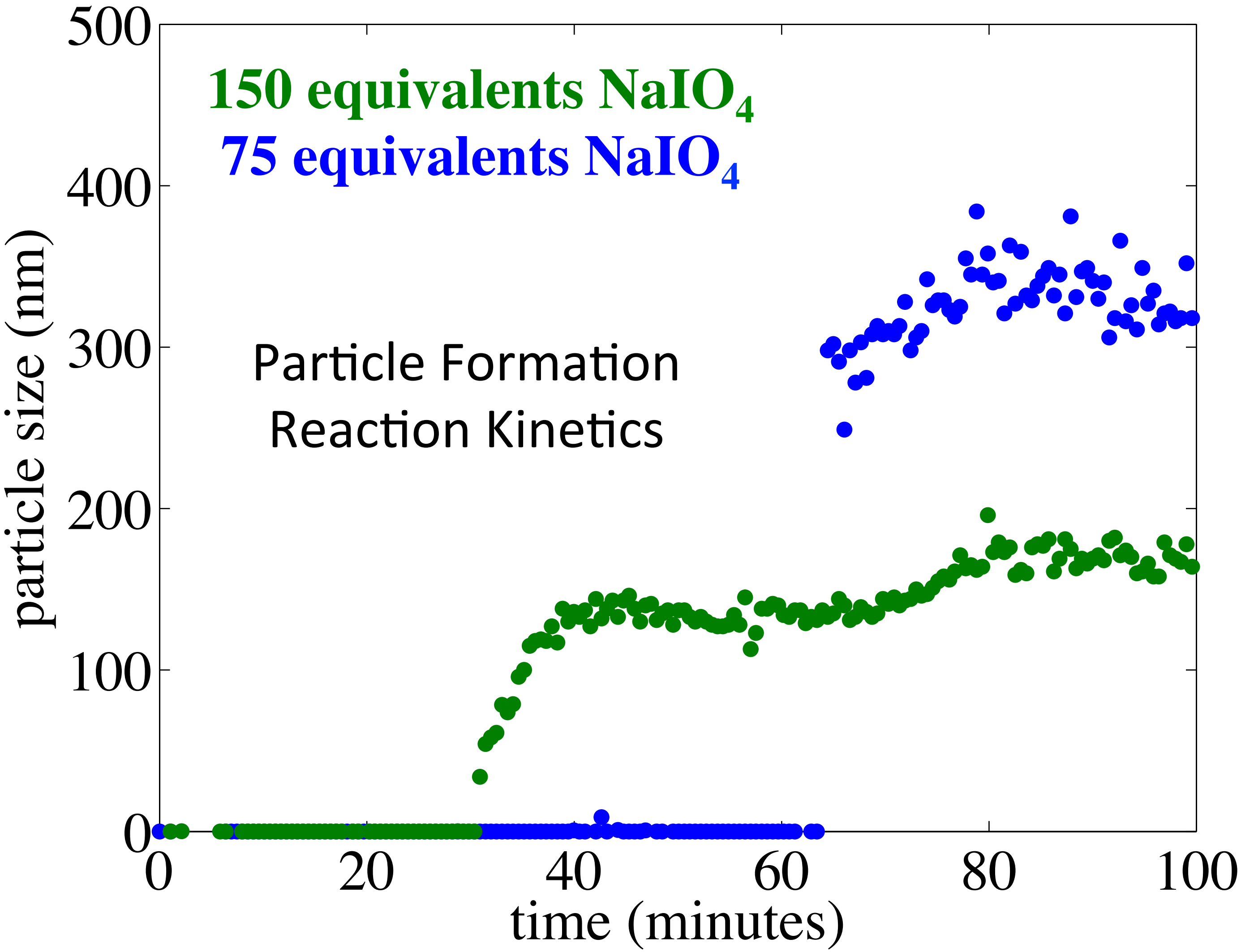




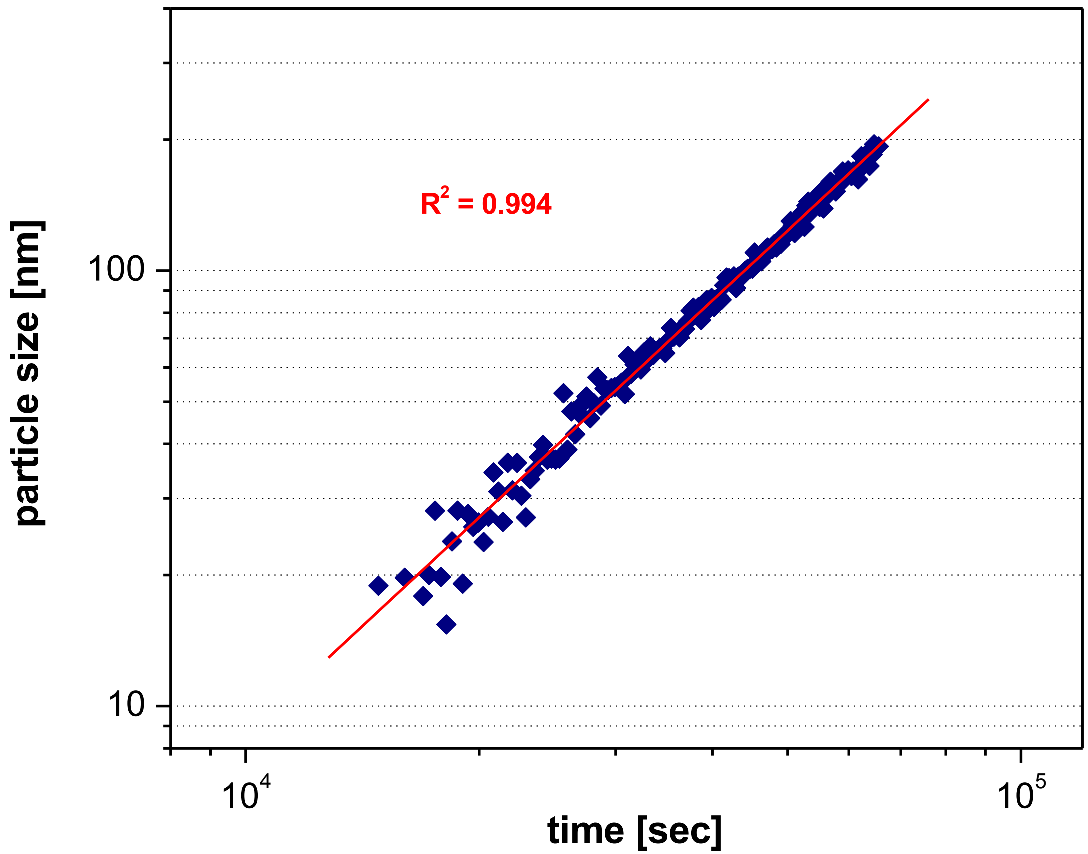
Hintermair U, et. al. *JACS* **134** 9785 (2012).

Concentration limits initial growth dynamics



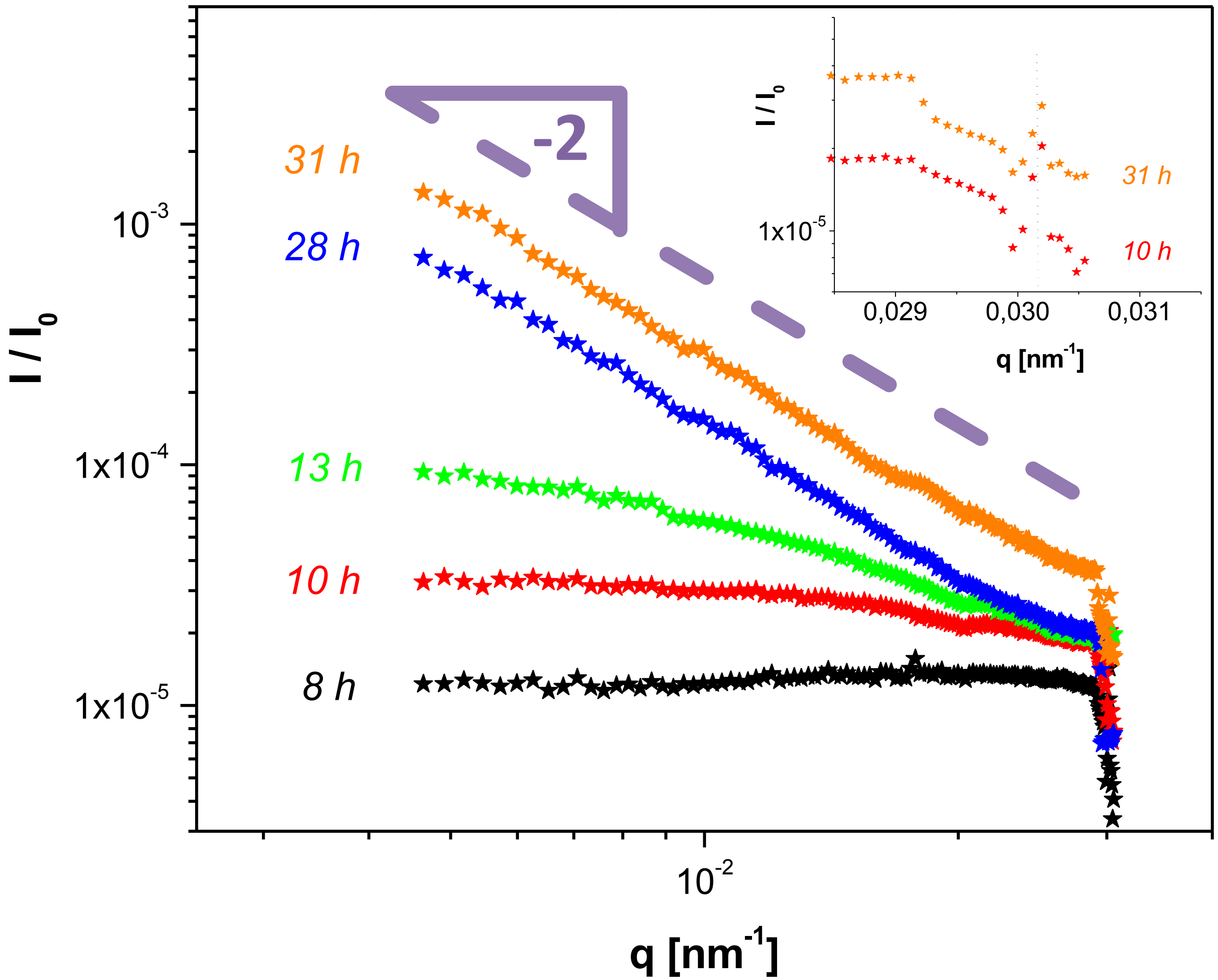
Metal Oxide Particle Synthesis

- Aggregation is diffusion controlled



Power law dynamics in aggregate growth

Aggregate Characterization



Feature at ~30 nm: primary particle size

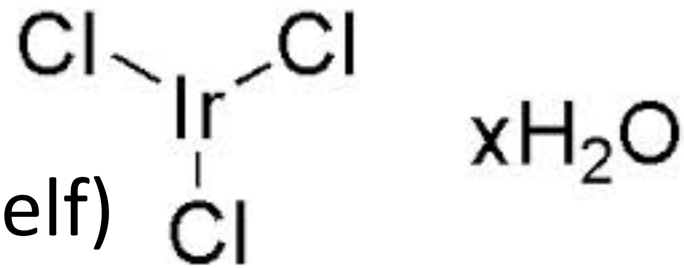
Over time D_f evolves to ~2

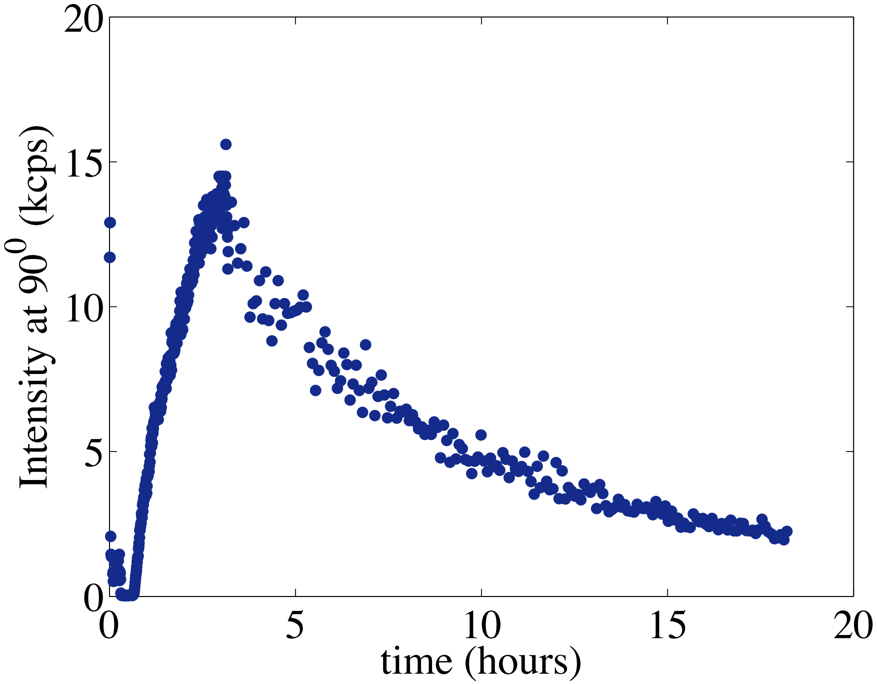
Suspension forms

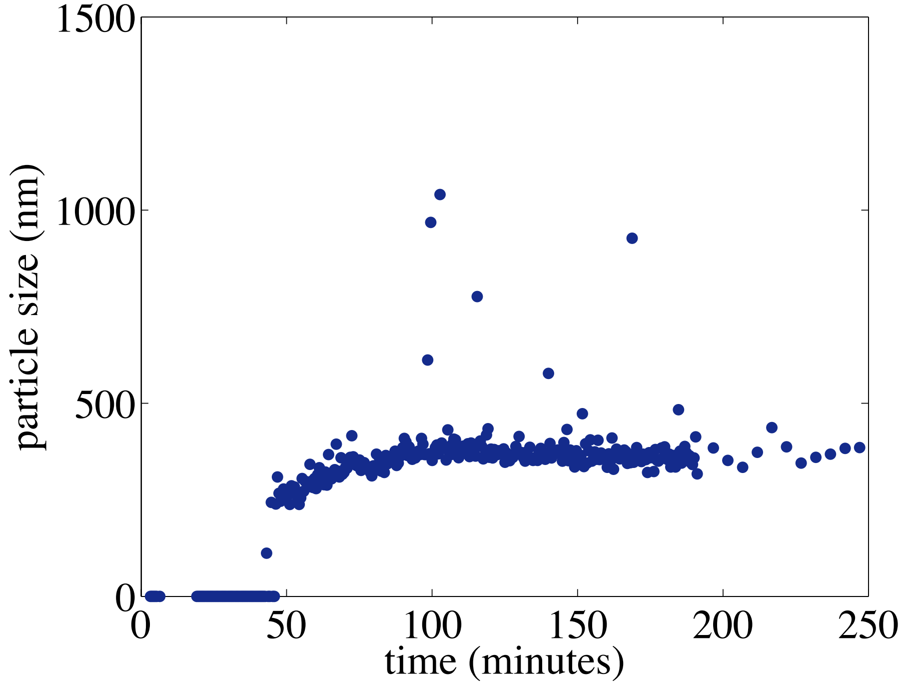
Solution only

"Green" Metal Oxide NP Synthesis

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







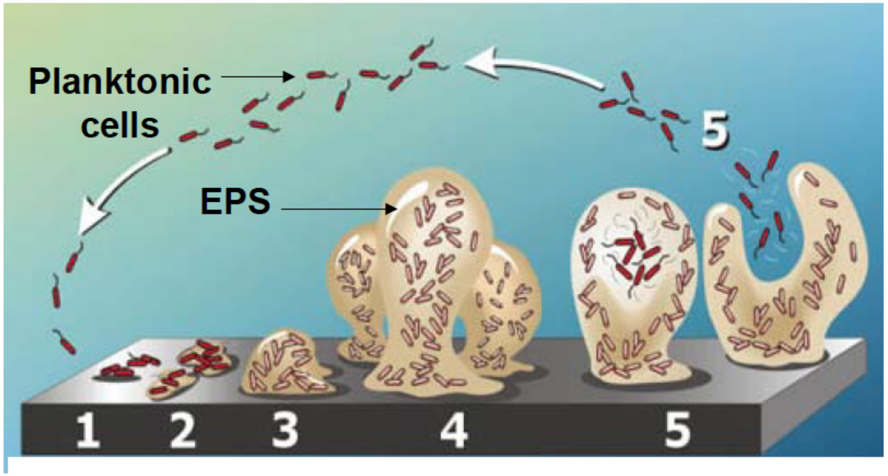
(in preparation)

Gelation in Seawater

Edo Bar-Zeev & Marissa Toussley
Elimelech Lab

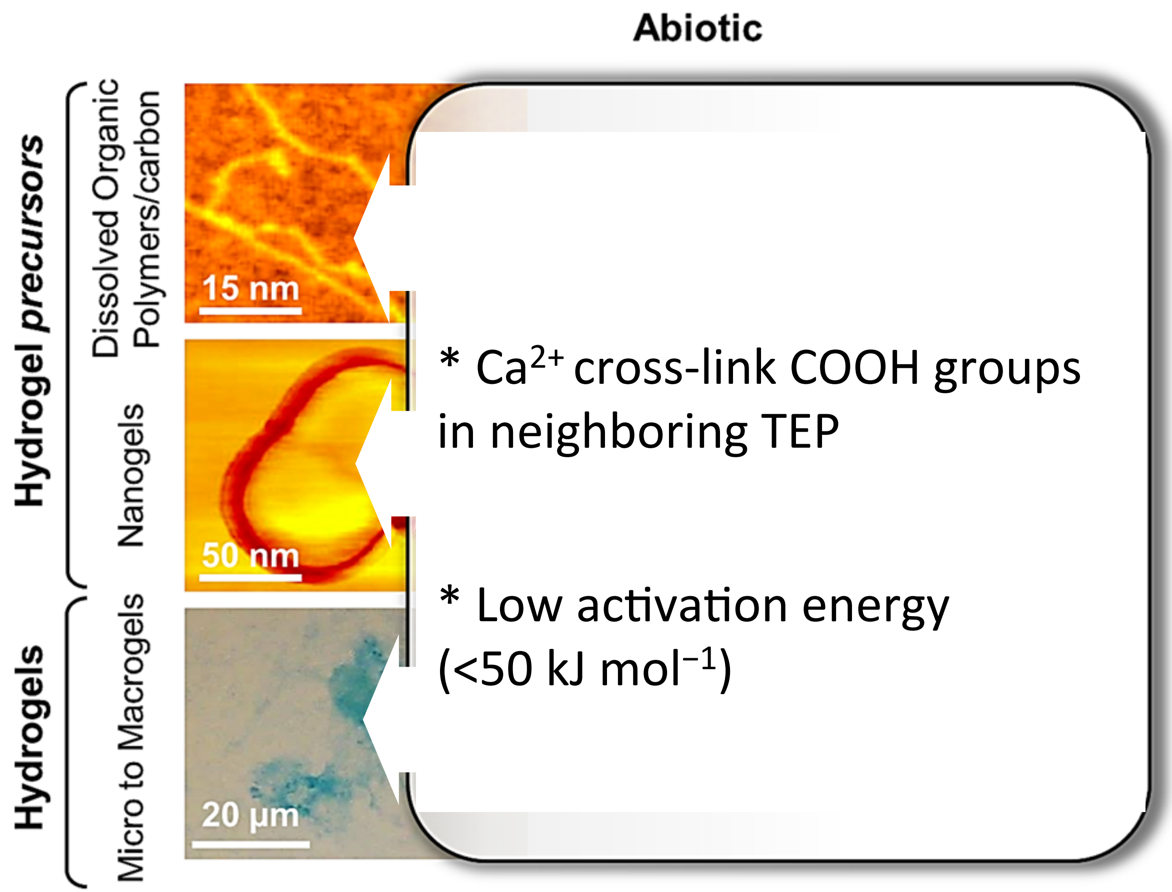
EPS = extracellular polymeric substances

- 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



Stages of biofilm development (from Stoodley et al. *Annu Rev Microbiol.* **2002**, *56*, 187

Abiotic Gel Formation



* Ca^{2+} cross-link COOH groups in neighboring TEP

* Low activation energy (<50 kJ mol^{-1})

Hydrogel kinetics will be dependent mainly by:

* Concentration,

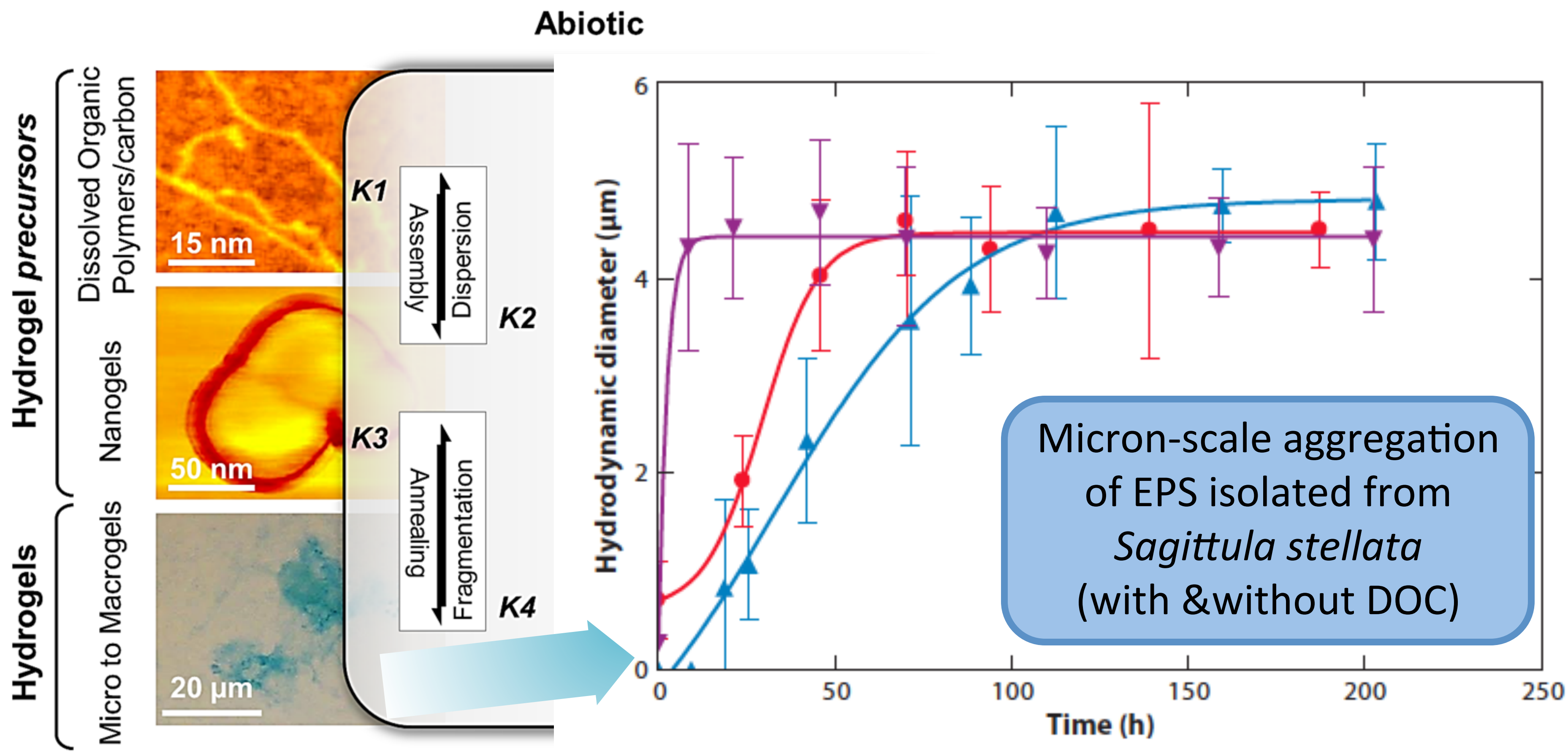
* Polymer chain size

* Charge density

* Topology (linear, branched)

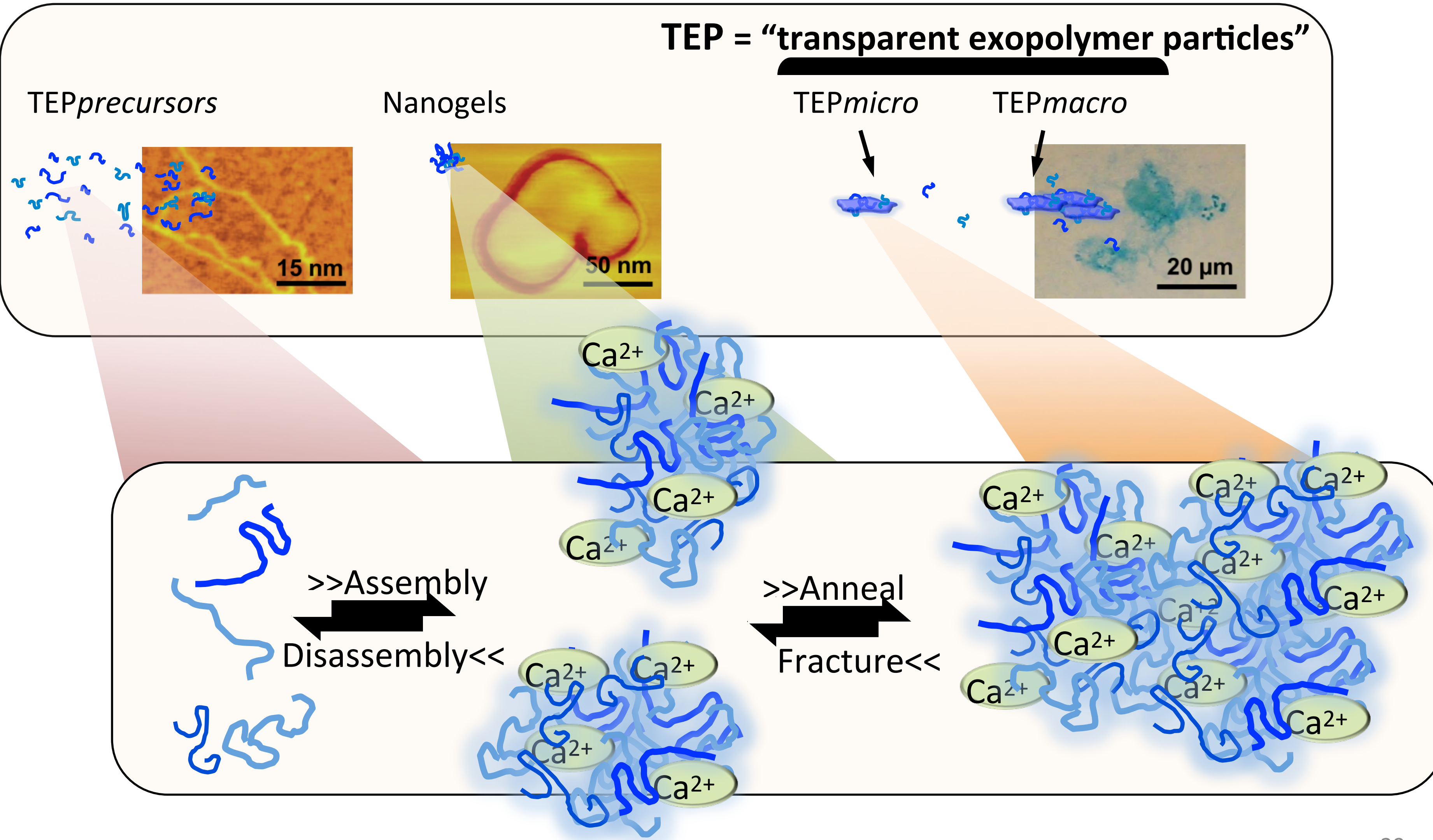
Verdugo, P. *Ann. Rev. Marine Chemistry*, **4** 375 (2012).

Abiotic Gel Formation



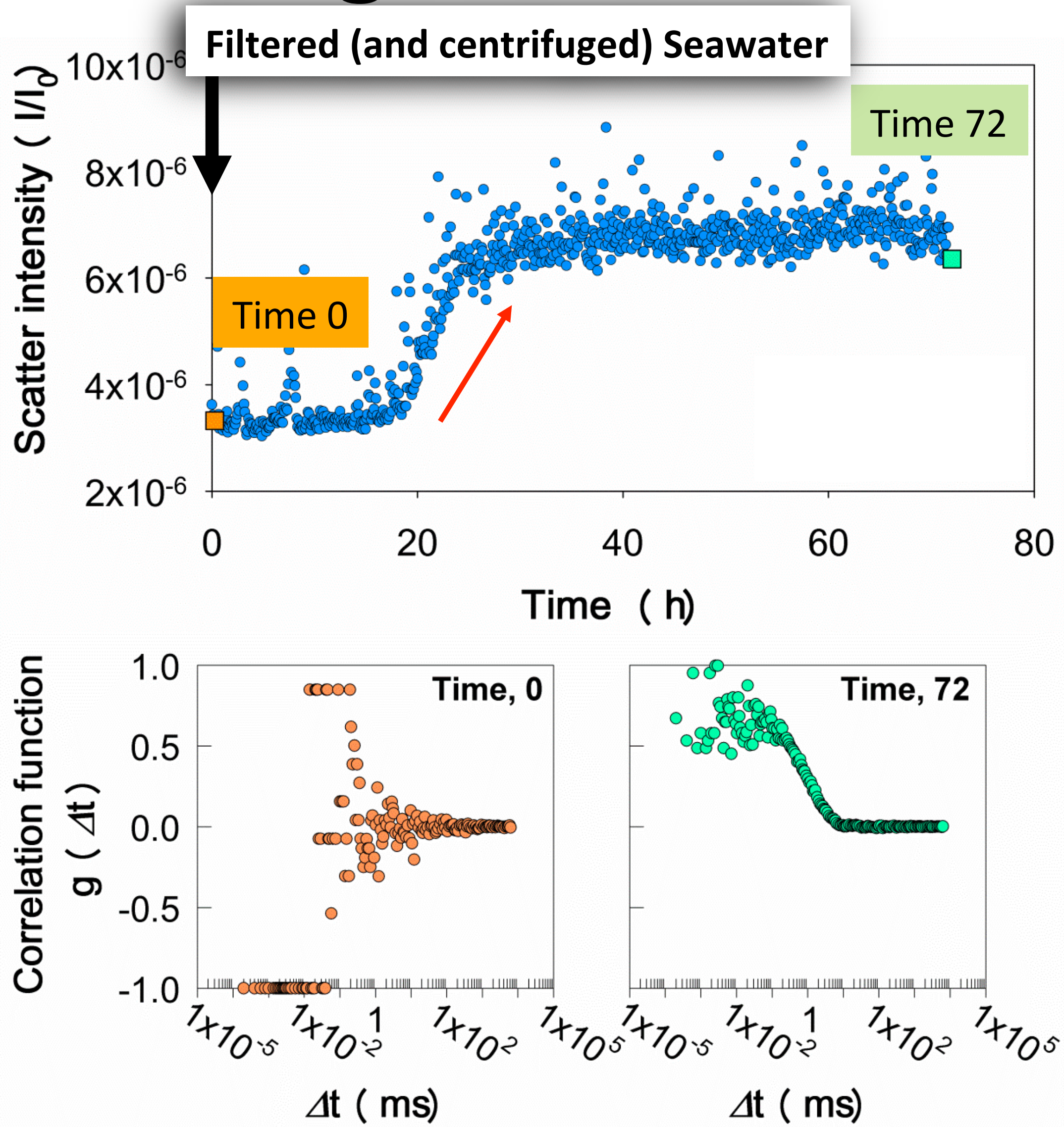
Ding, Y-X. et. al. *Marine Chemistry*, **106** 456 (2007).
Verdugo, P. *Ann. Rev. Marine Chemistry*, **4** 375 (2012).

Abiotic Hydrogel Formation



Verdugo, P. *Ann. Rev. Marine Chemistry*, **4** 375 (2012).

Nanogel Formation: Kinetics & Size



Scattered Intensity

Increasing scatter indicates

Gel formation with time

Dynamic Light Scattering

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

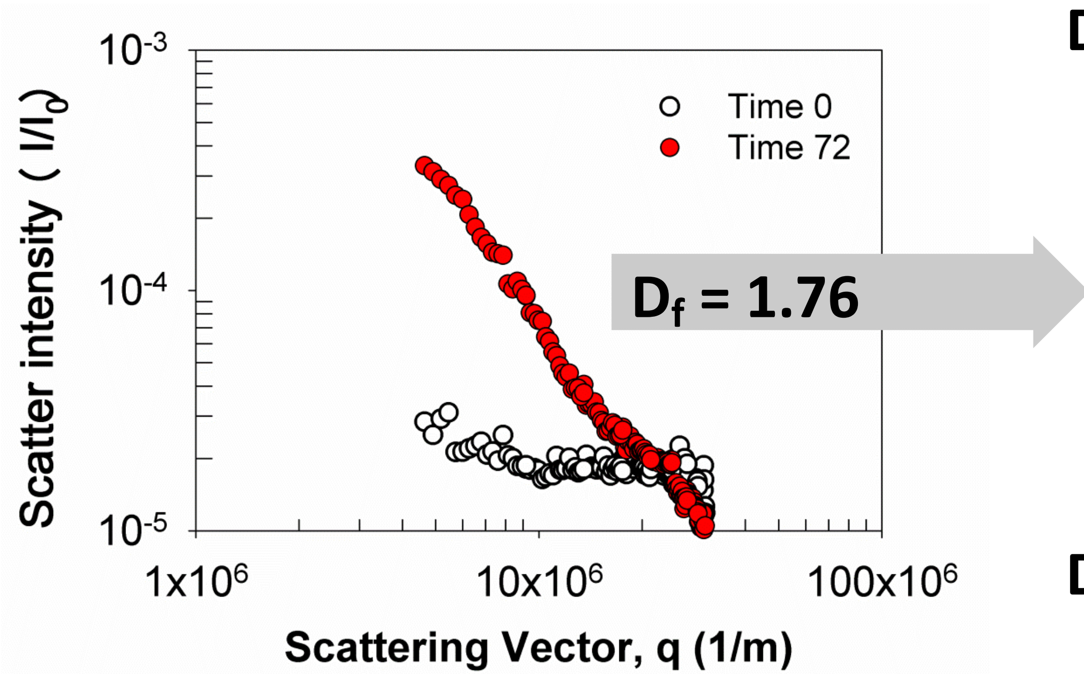
0 - - - ***Time*** - - - 72 h

Bar-Zeev et al. in progress

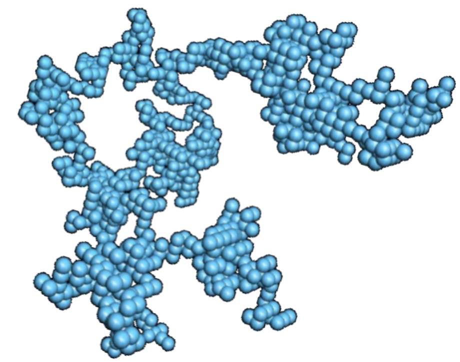
Nanogel Structure

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

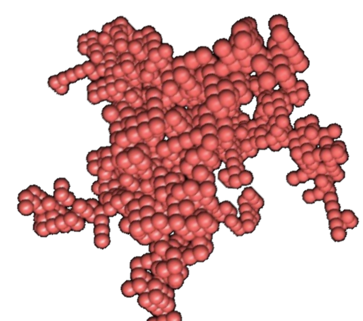
Static Light Scattering (SLS)



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



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



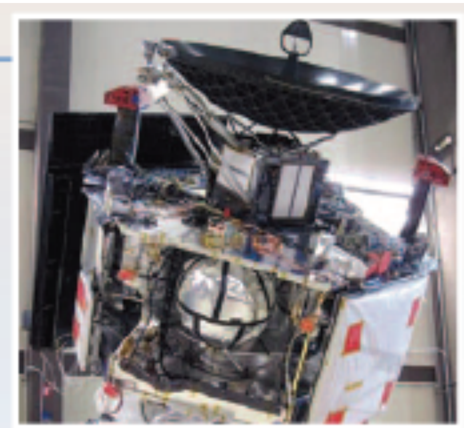
Bar-Zeev et al. in progress

Carbon Nanotubes Dispersion ←→ Function

Leanne Pasquini, Seyla Azoz
Zimmerman & Pfefferle Labs

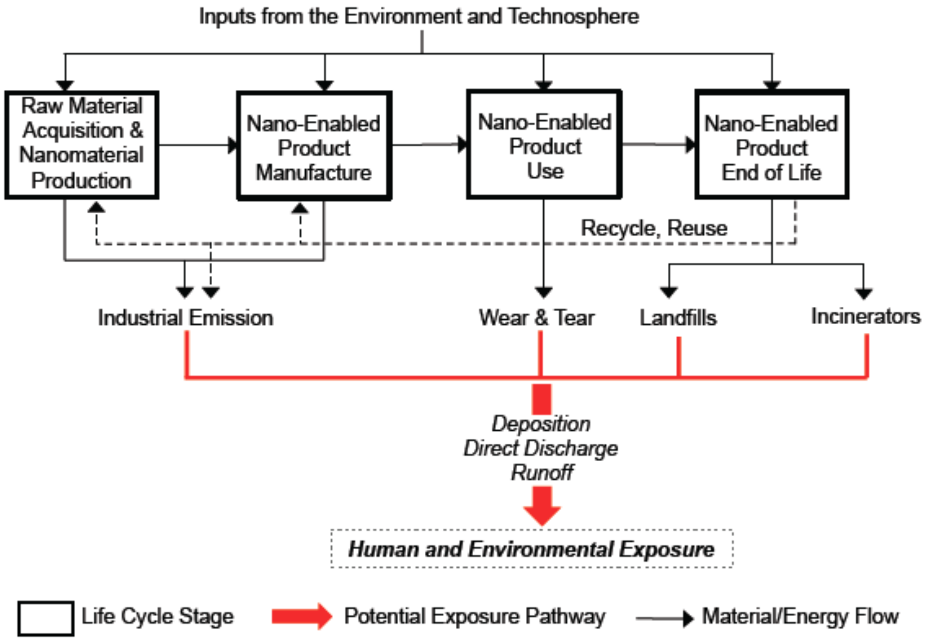
Environmental Impacts of CNTs

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



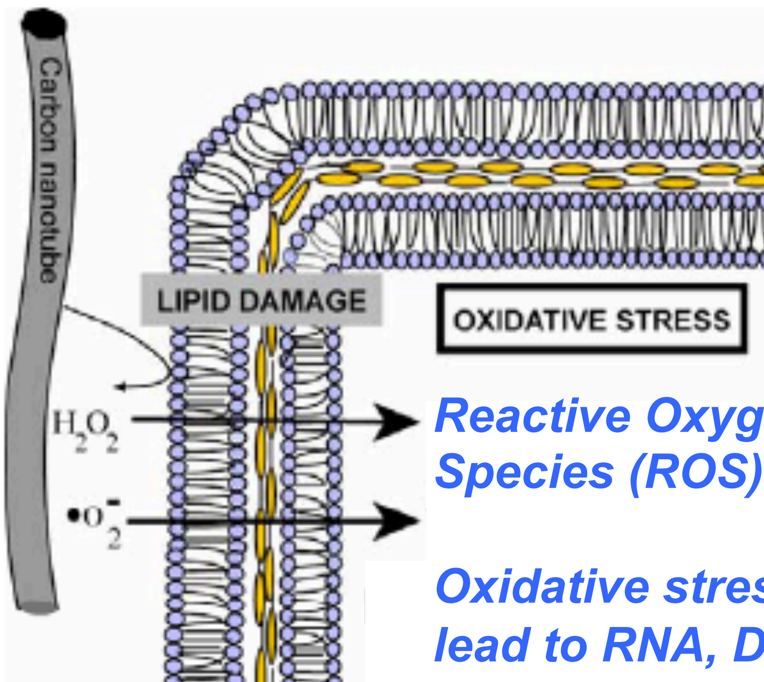
Juno spacecraft uses CNT ESD shield

Winning Tour de France bicycle uses CNT composite



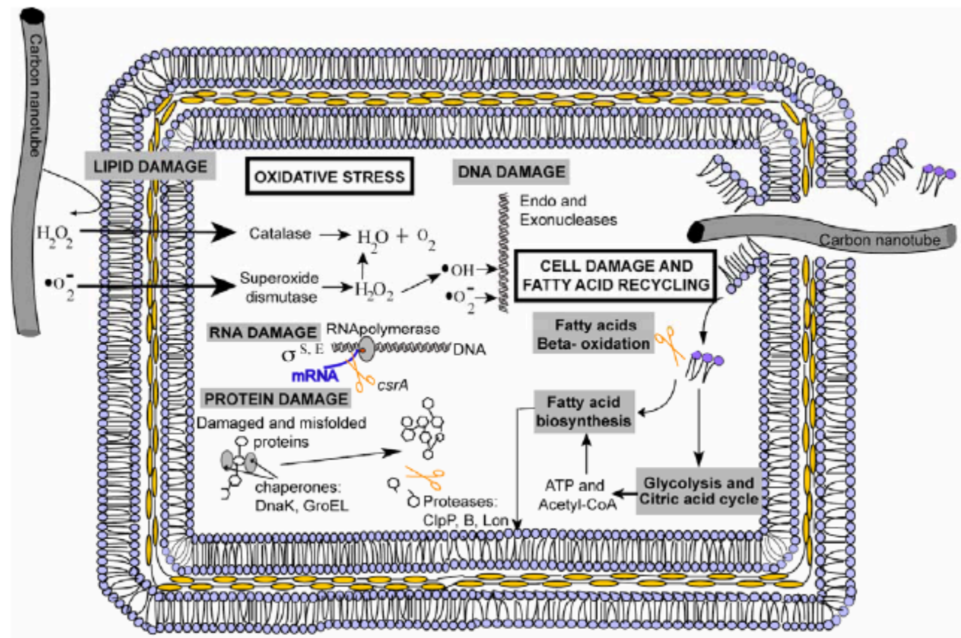
Proposed Cytotoxicity Mechanism

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



Reactive Oxygen Species (ROS)

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

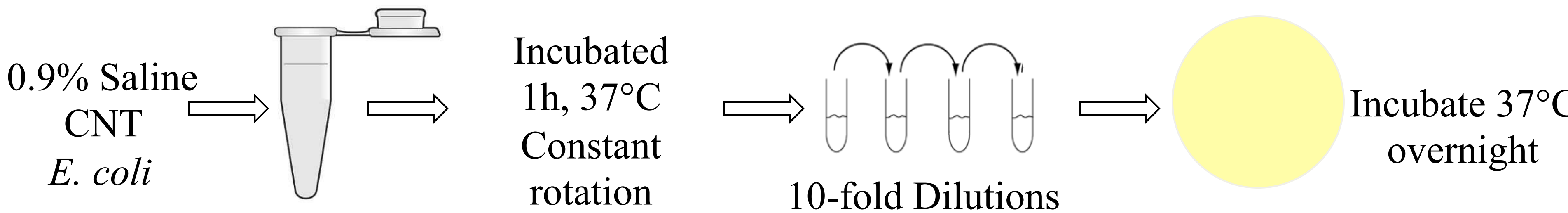


Kang, S., et al. Langmuir, 2008, **24**, 6409-6413.

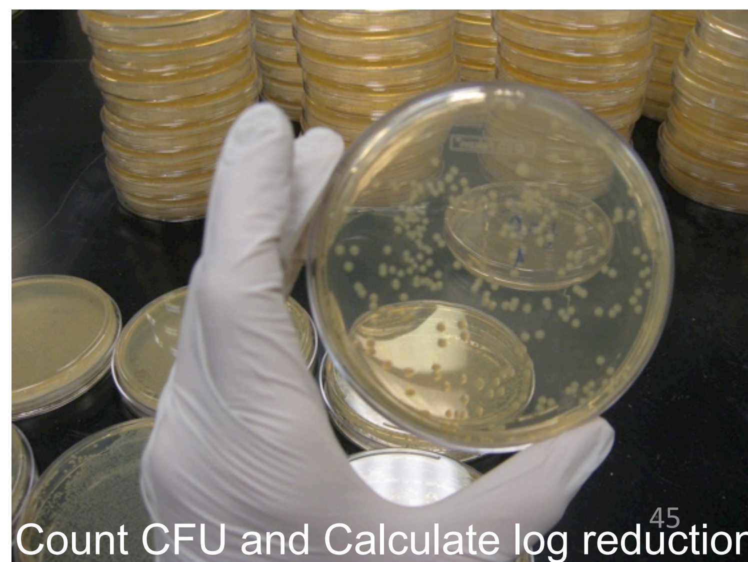
In Vivo Cytotoxicity

Escherichia Coli K12 are exposed to CNTs in aqueous suspension

(alternate assay: on a membrane)

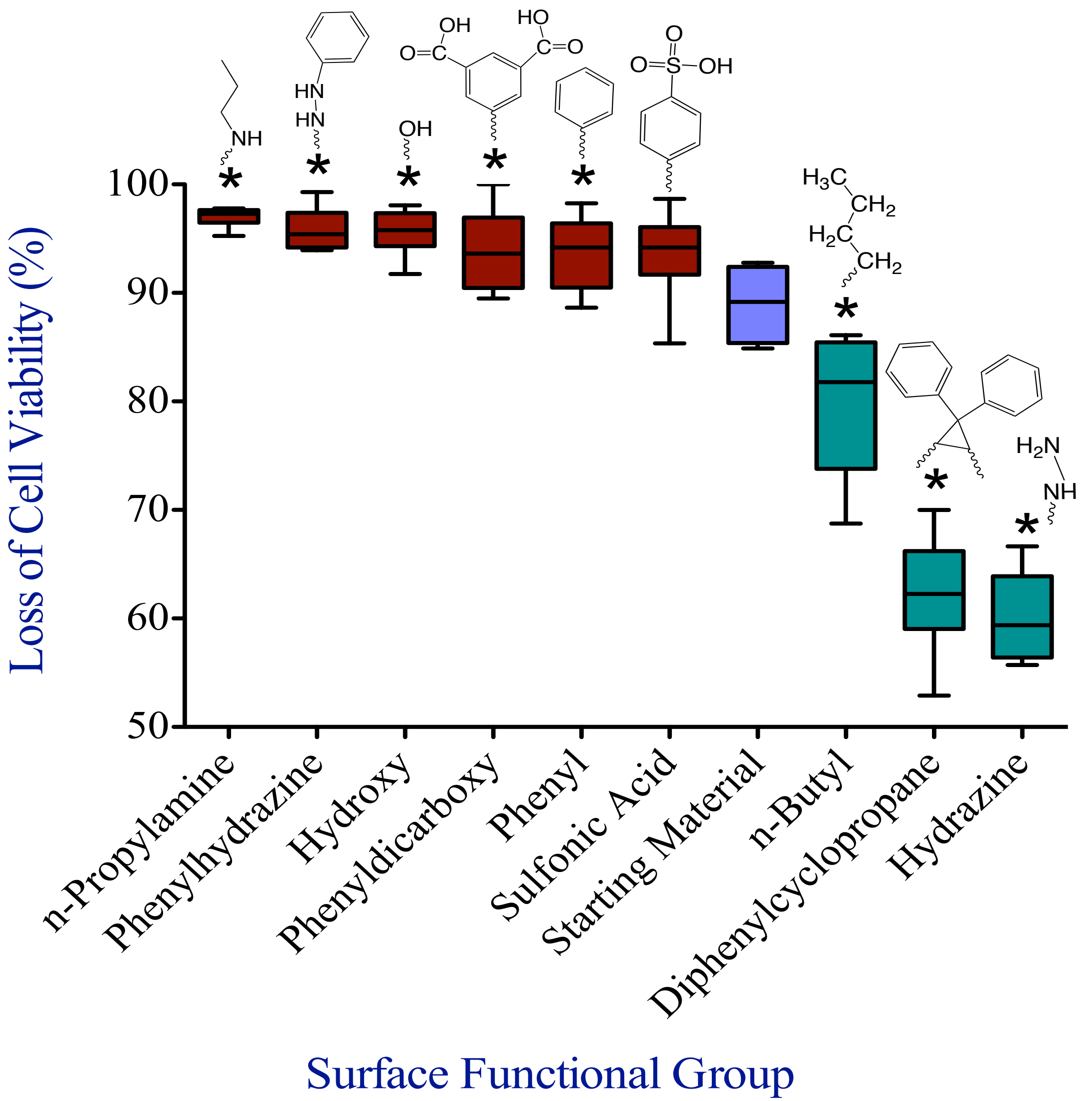


Plating: Assess reduction of Colony-Forming-Units / mL



Pasquini, L. M. et al. ES&T, 2013, **47**, 8775-8783.

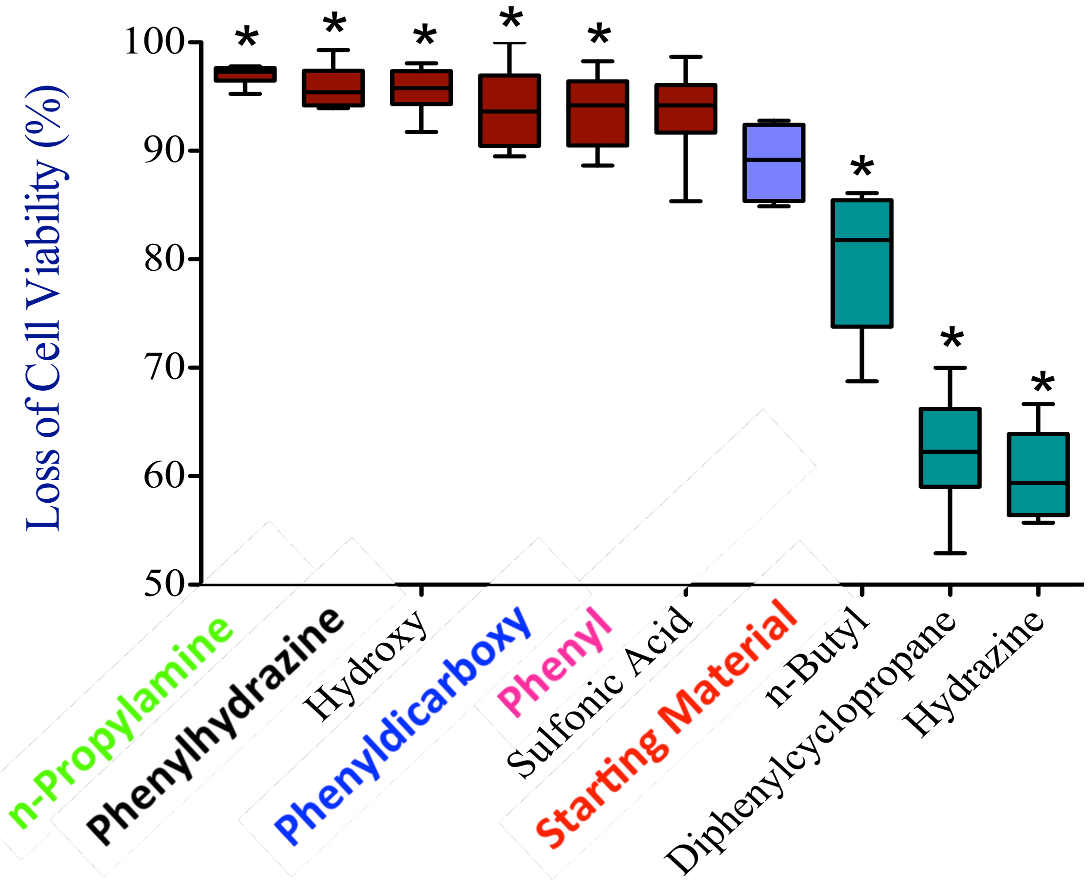
Functionalized SWNT Cytotoxicity



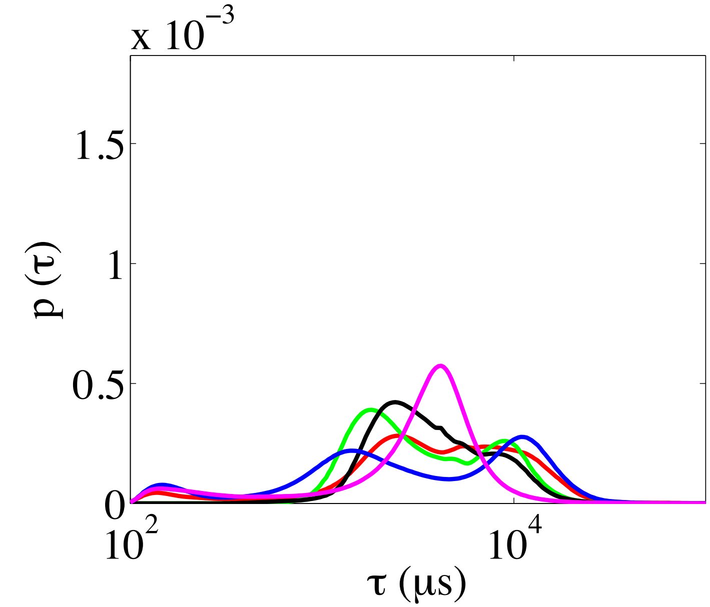
- Identify specific physicochemical properties that correlate with the cytotoxicity.
- Ultimately leading to future safer design of SWNTs
- Maintain functionality; minimize negative impact

Pasquini, L. M. et al. ES&T, 2012, **46**, 6297-6305.

How does functionalization affect stability?



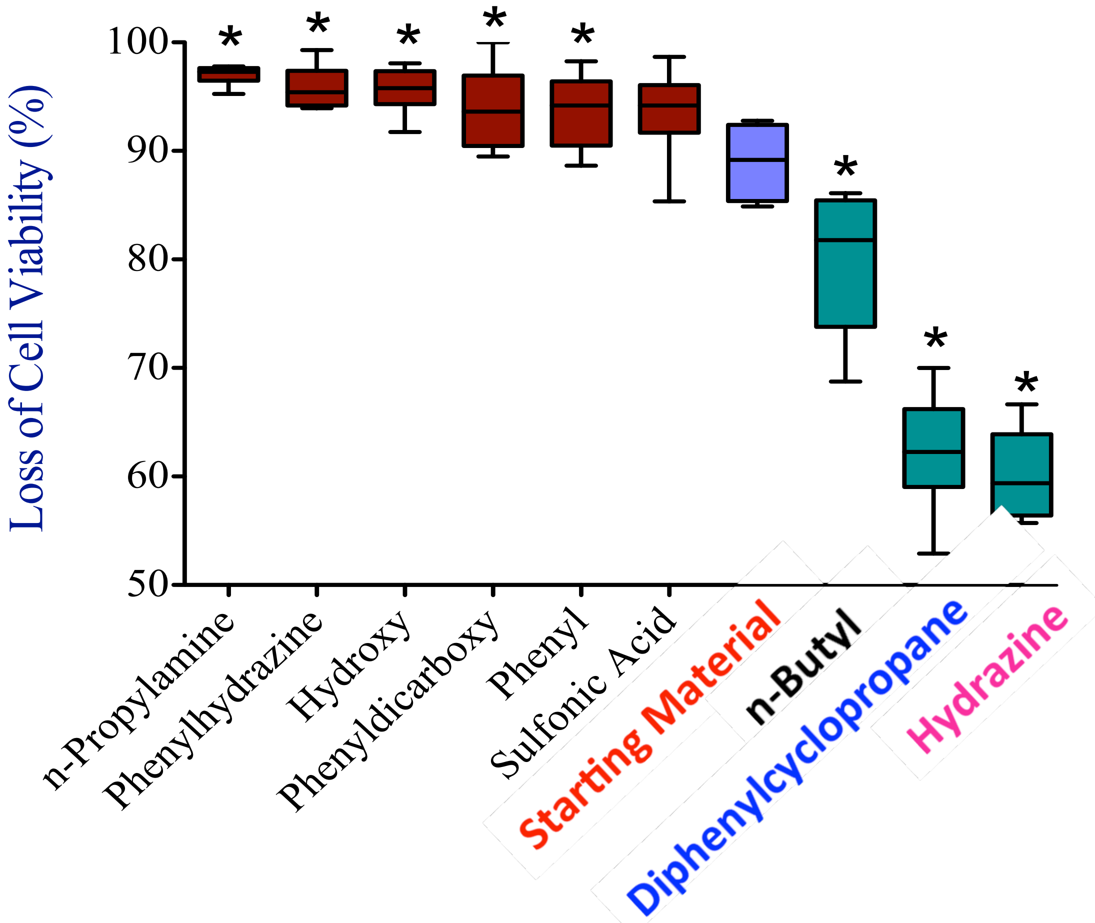
Very broad distributions



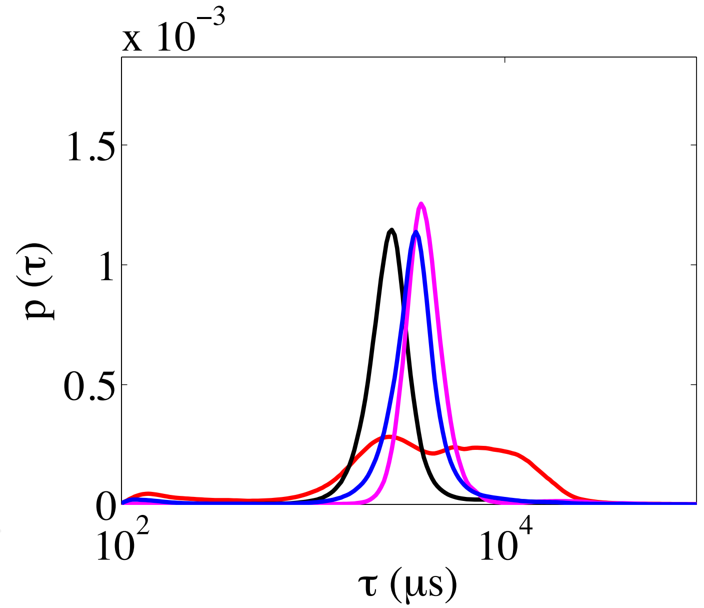
Compare diffusive time scales (non-spherical)

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

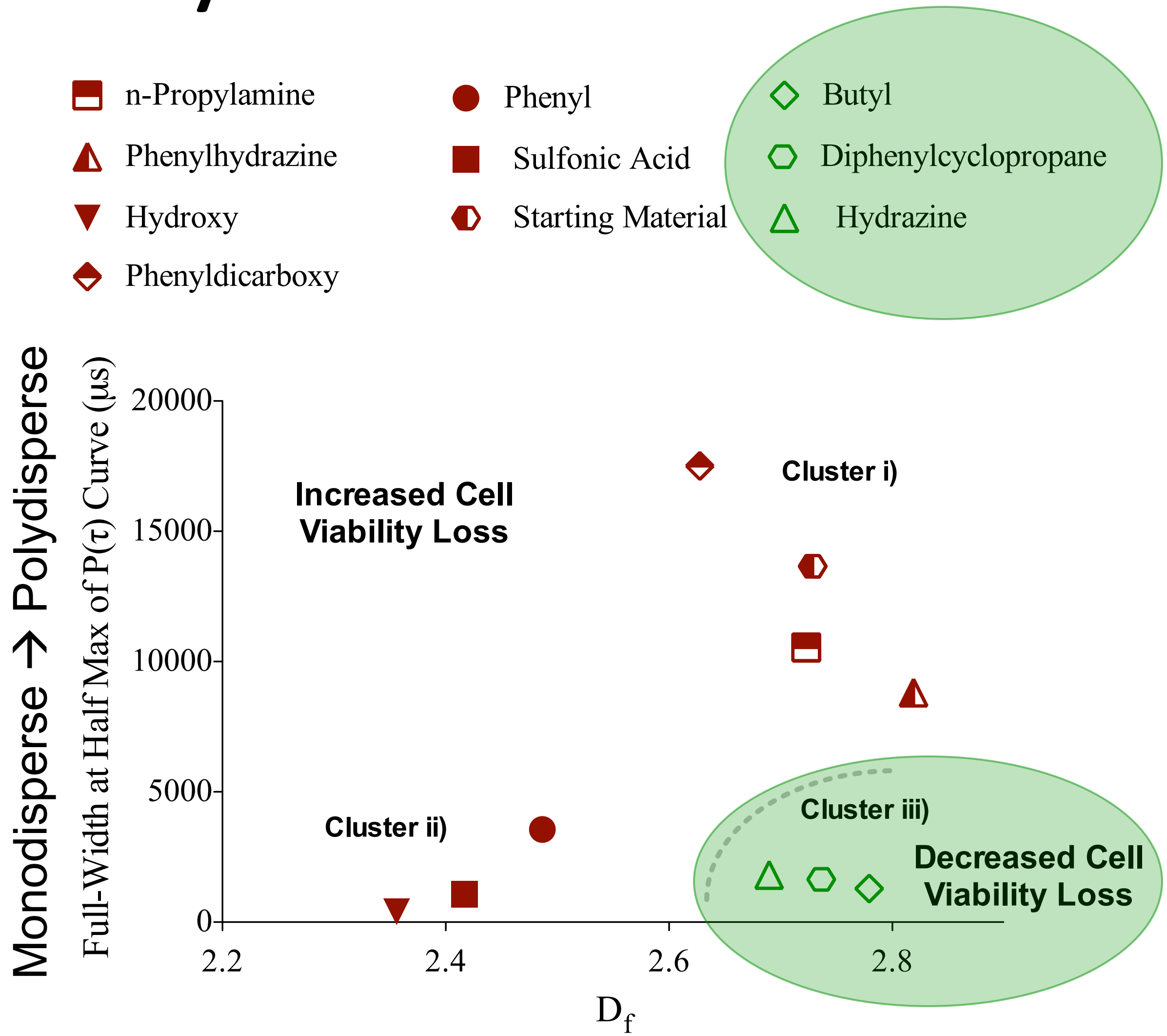
Surface functional groups

↕

Dispersed aggregate state

↕

SWNT toxicity

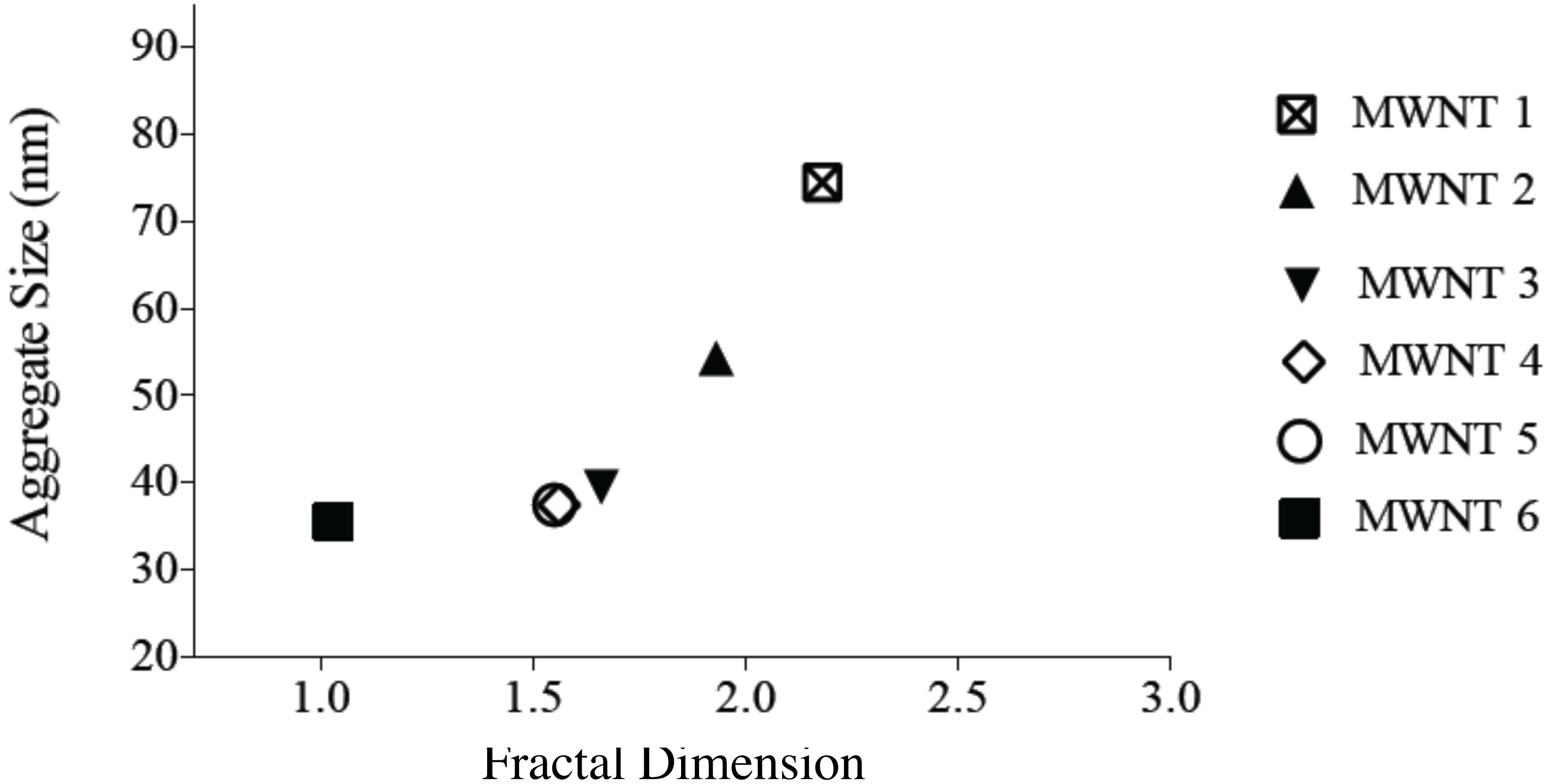


Less Compact → More Compact

Pasquini, L. M. et al. ES&T, 2012, **46**, 6297-6305.

Controlling MWNT Dispersions

Nitric Acid Treatment Time (hrs)



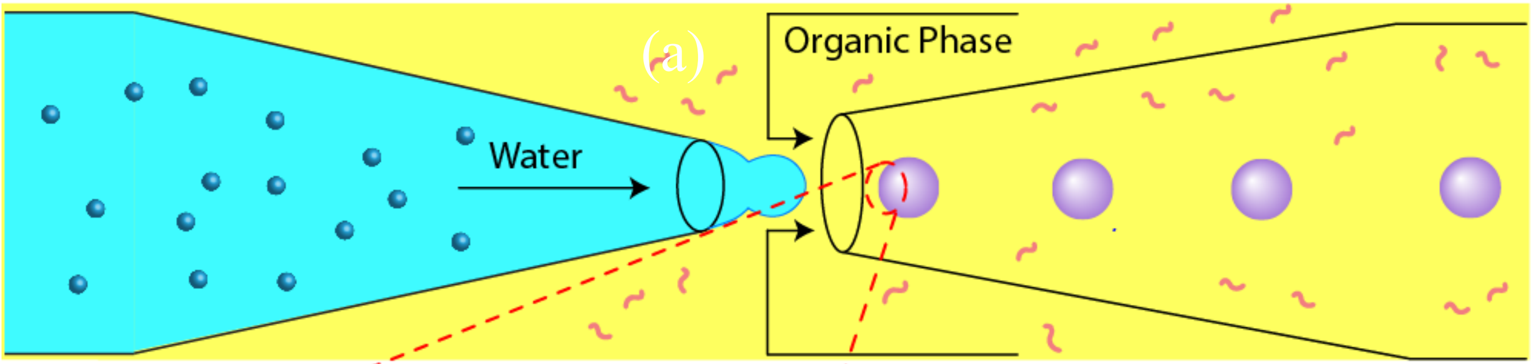
HNO_3 treatment increases surface oxygen (COOH)

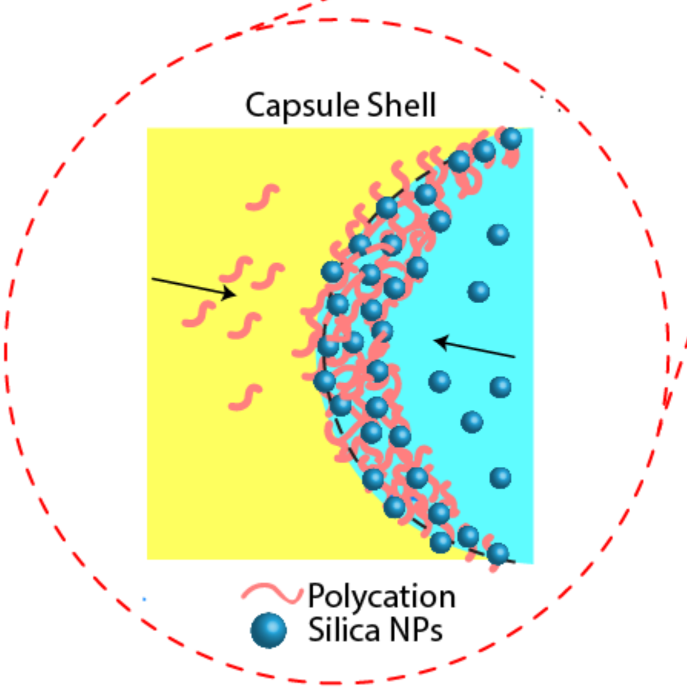
Facilitates more well-dispersed rod-like structures

Pasquini, L. M. et al. ES&T, 2013, **47**, 8775-8783. **SWNT in water: Azoz et.al. (*in preparation*).**

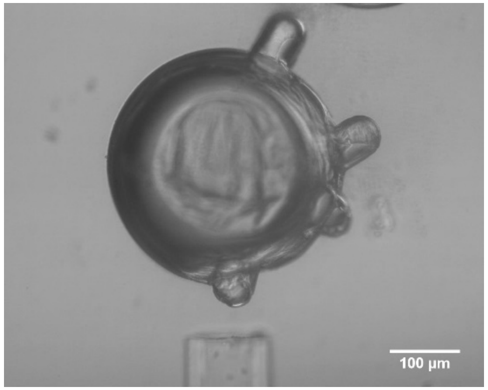
Additional Projects

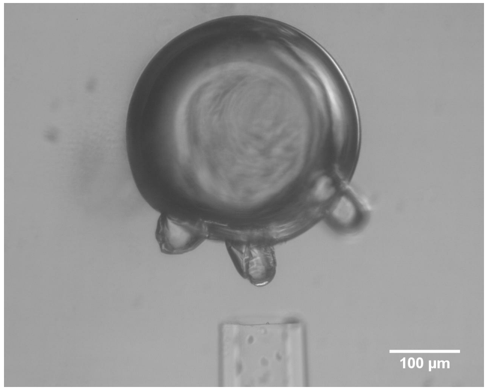
Silica NPs/s-SEBS microcapsules





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

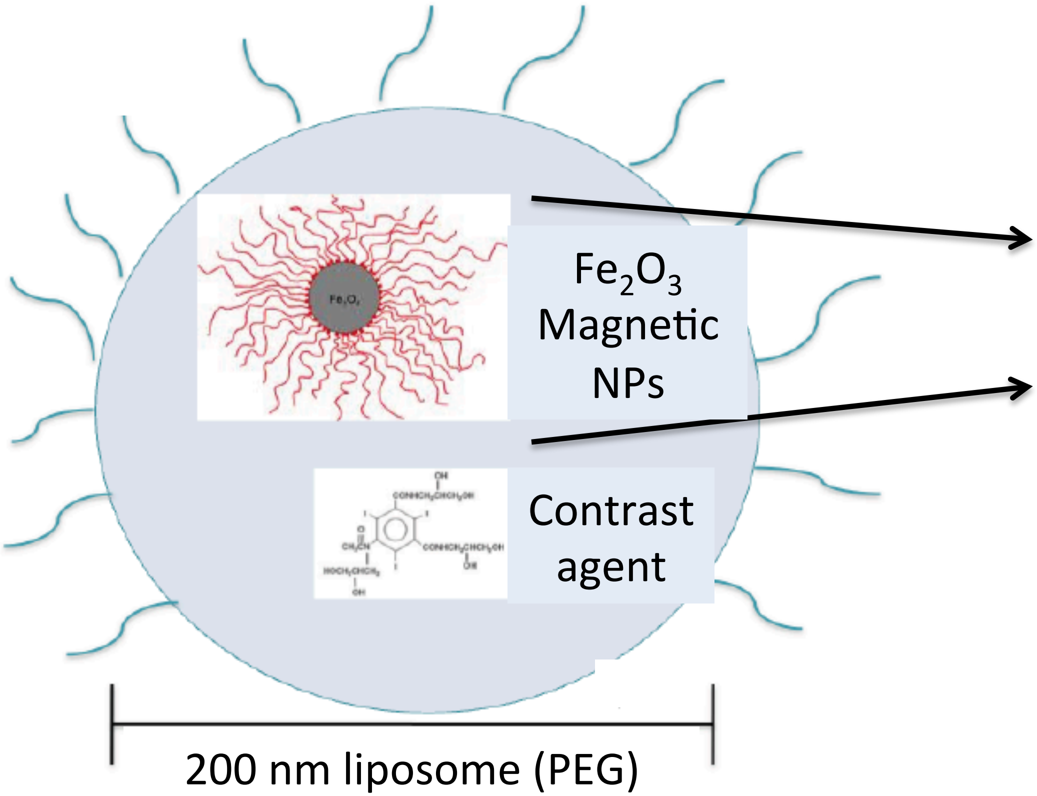




Gilad Kaufman, Raphael Sarfati, Osuji Lab

Liposomes with Magnets & Contrast Agent

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



EXTERNAL MAGNET to retrieve contrast agents after imaging

Encapsulation of contrast agent to avoid biological interaction

Trey Turner & Candice Gurbatri, van Tassel Lab

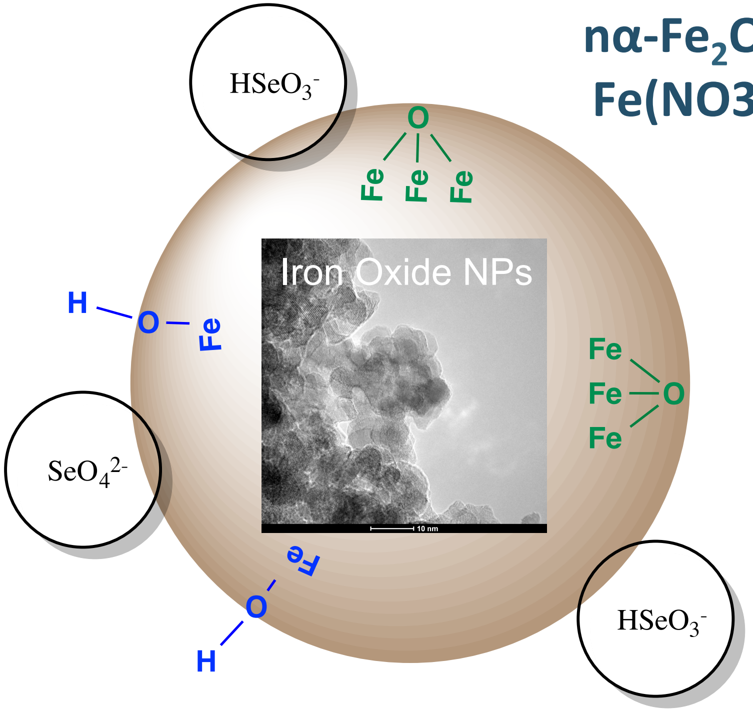
Selenium Remediation via nano-Hematite

Selenium in the Environment

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

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

nα-Fe_2O_3 from Fe(NO3)3 salt



Hematite (α-Fe_2O_3)

- *Iron oxides = nature's adsorbent*
- *Thermodynamically stable*
- *Cheap & abundant*

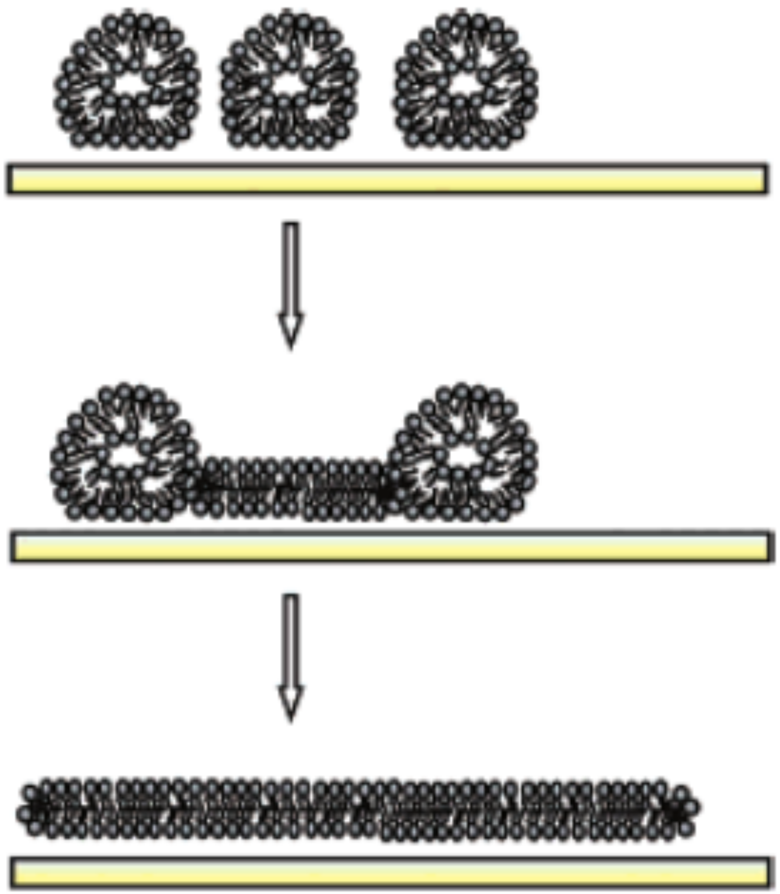
Nano Hematite (nα-Fe_2O_3)

- *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)

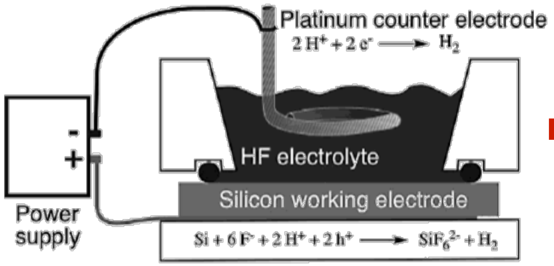


Richter, R., Bérat, R. & Brisson, A. *Langmuir* 3497–3505 (2006).

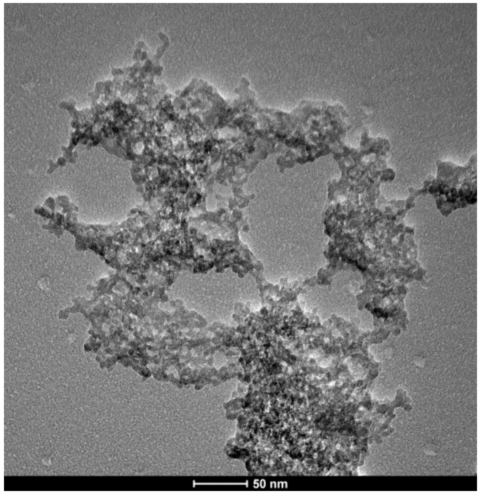
Jay Werber, Elimelech Lab

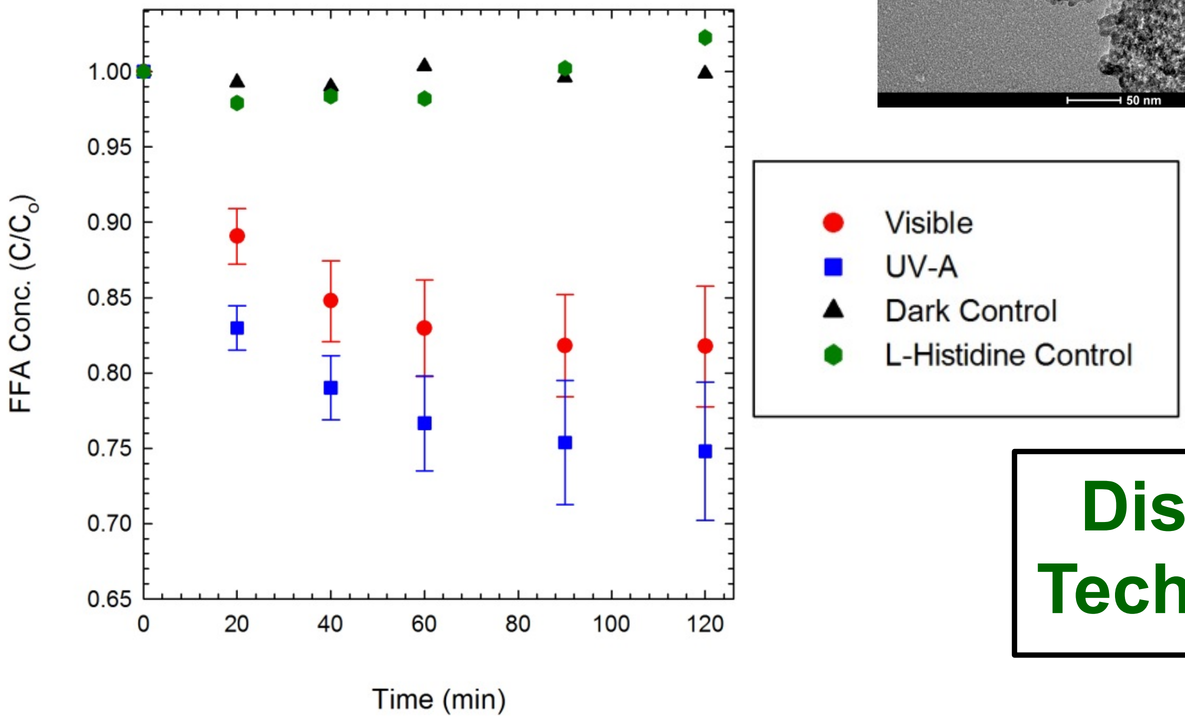
Porous Silicon (pSi)

Etch Cell: HF eats silicon wafer



sailorgroup.usc.edu





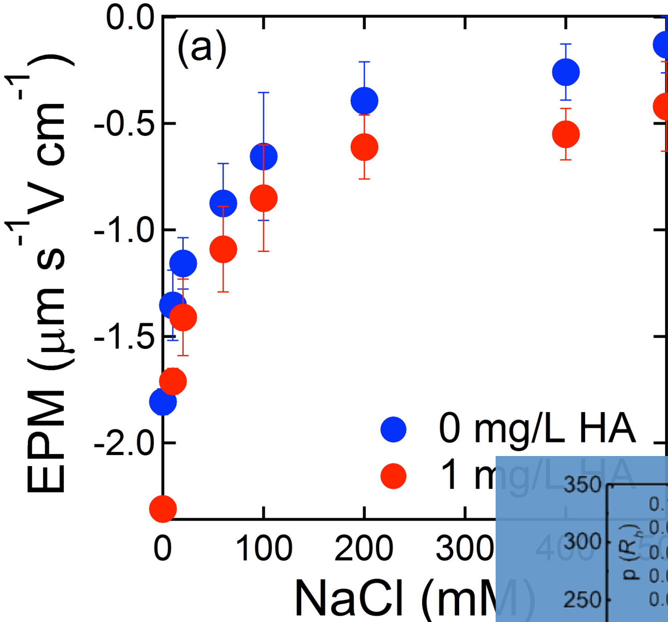
- Photoluminescence indicates average band gap $E_g \sim 1.89$ eV
- Interaction with light can produce singlet oxygen (ROS)

Disinfection Technologies?

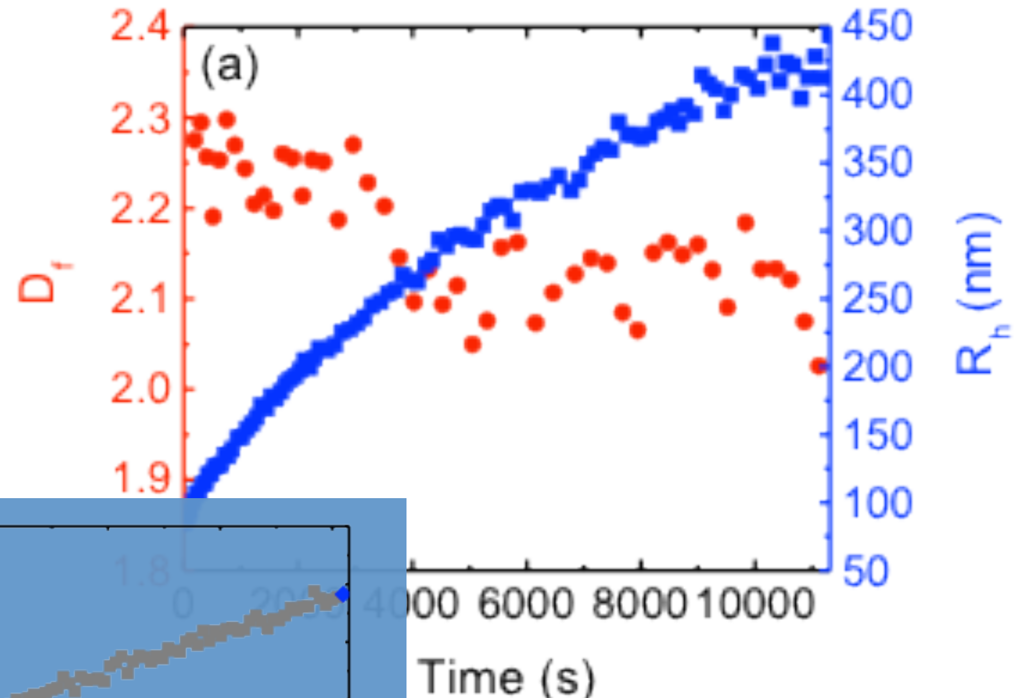
Kyle Moor, Ezra Cates, Kim Lab

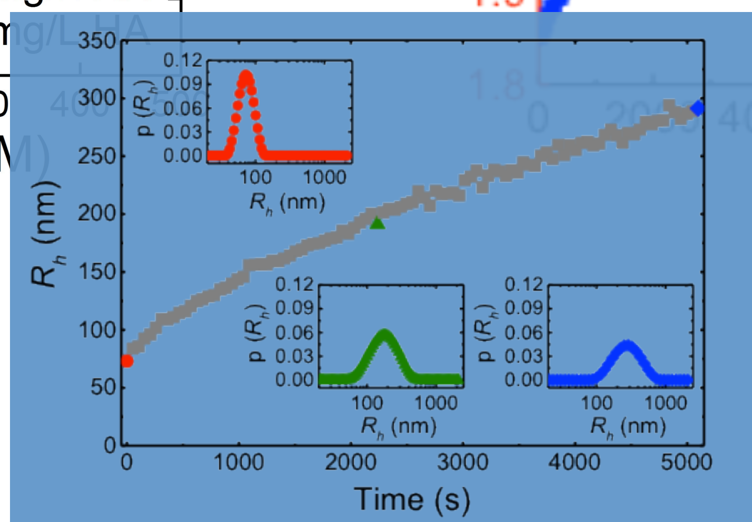
Fullerene aggregation

Salt reduces magnitude of surface charge; destabilizes suspension



500 mM NaCl + FNPs

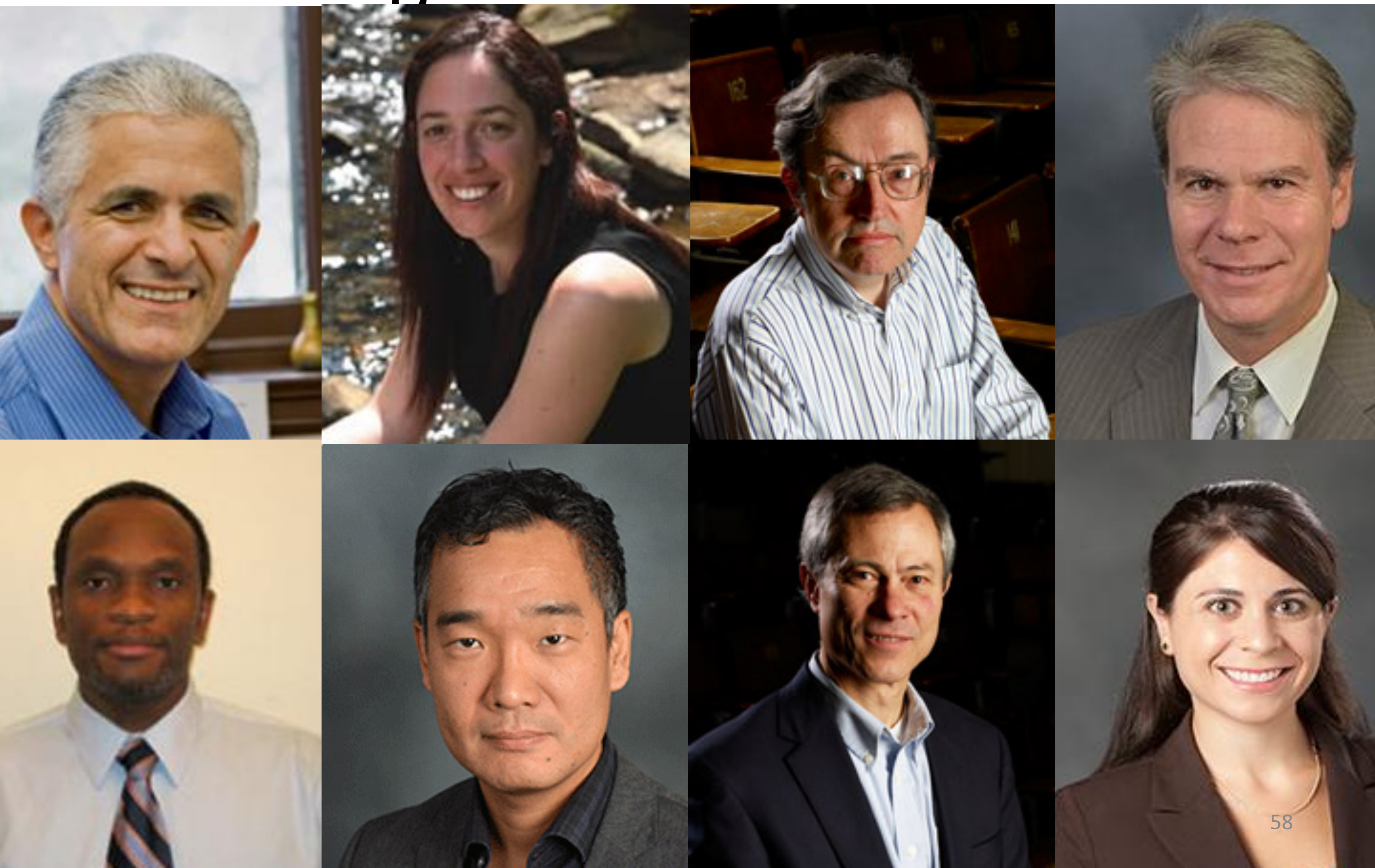




Meng, Z. et al. Langmuir

Zhiyong Meng, Elimelech Lab

Acknowledgements



Acknowledgements

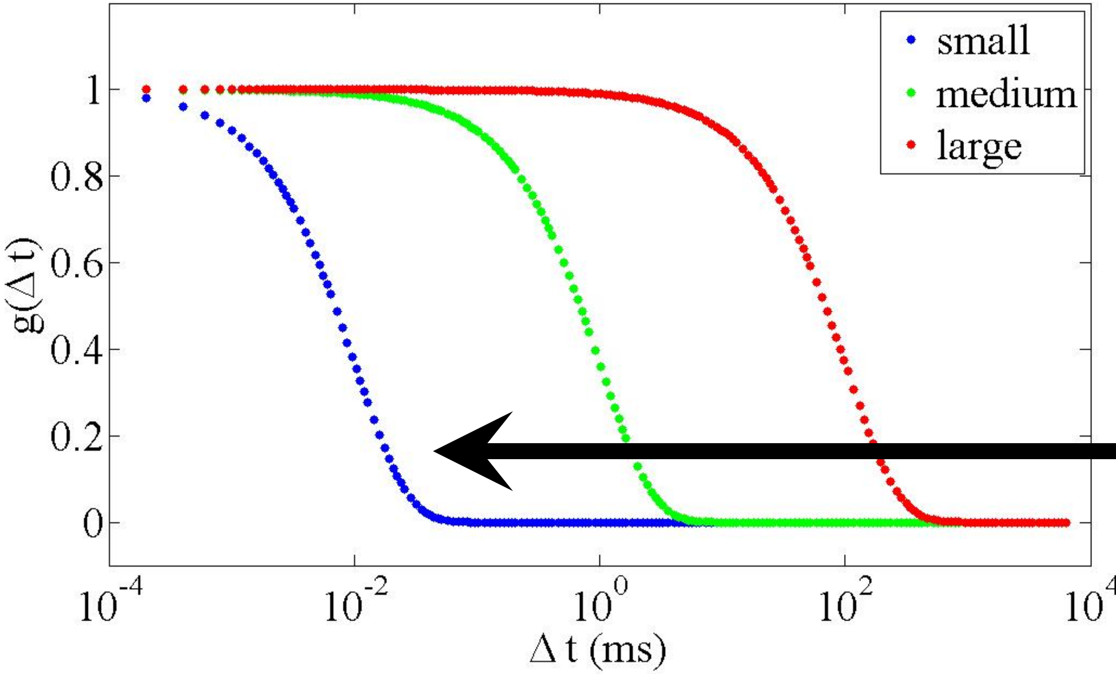
- Meny Elimelech: Edo Bar-Zeev, Marissa Toussley, Jay Werber
- Julie Zimmerman: Leanne Gilbertson, Amanda Lounsbury
- Chinedum Osuji: Gilad Kaufman
- Paul van Tassel: Trey Turner, Candice Gurbatri
- Jaehong Kim: Kyle Moor
- Bob Crabtree/Gary Brudvig: Ulrich Hintermair, Julie Thomsen, Staff Sheehan

Thank You!

Questions?

Extra Slides

How Small?



In water; 532 nm; 90^0

10^{-2} ms → ~2 nm

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

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

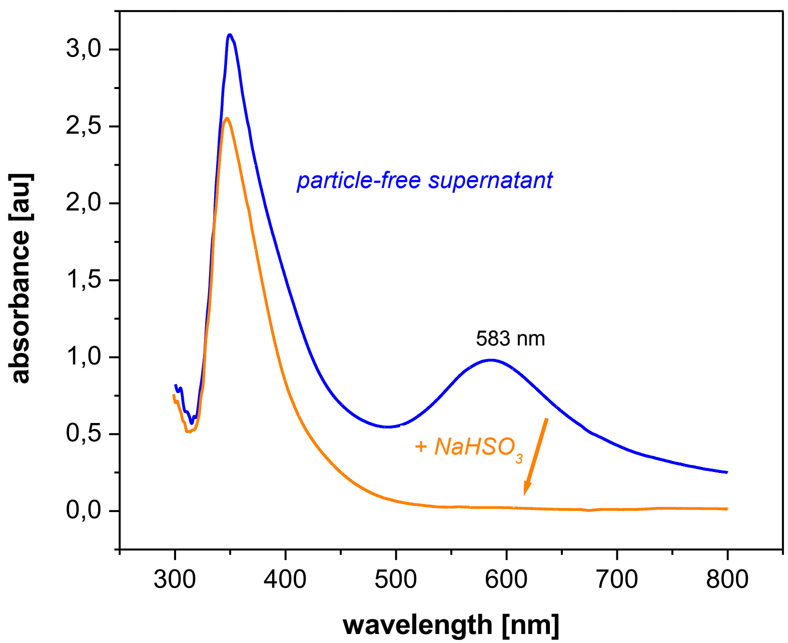
$$\tau = 1/2q^2 D$$

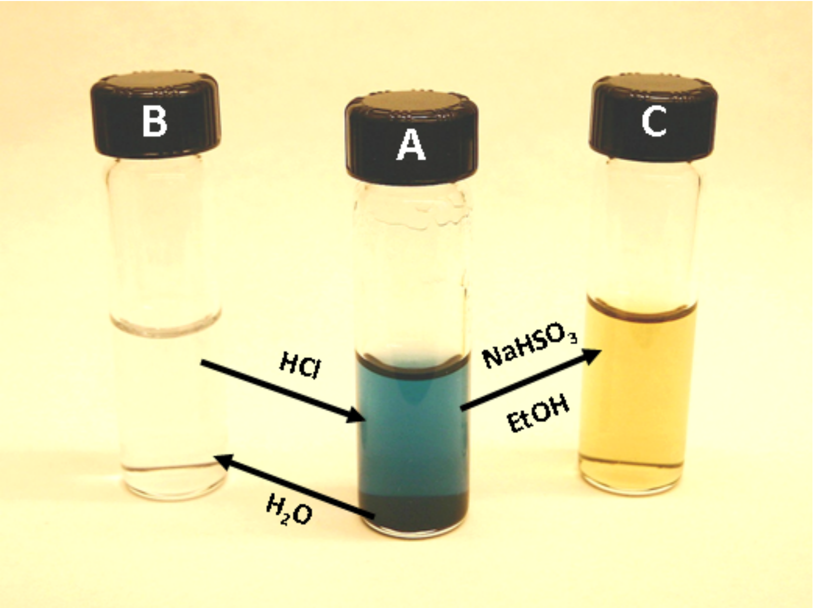
$$D = \frac{k_B T}{6\pi\mu a}$$

Particle size measurement : ***spherical approximation***

Interconversion

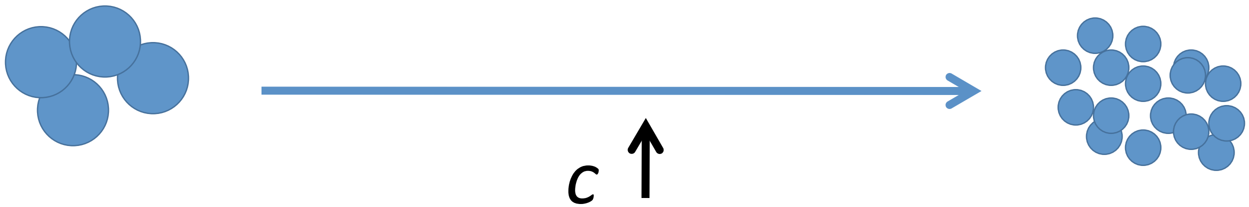
- Molecular species → particles (blue) → reduction to molecular species (yellow)

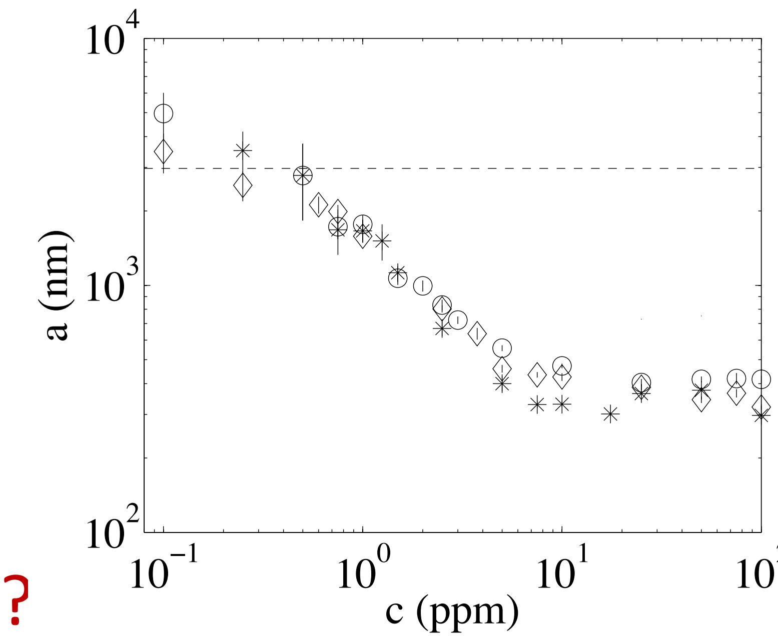




Hintermair U, et. al. *JACS* **134** 9785 (2012).

Understanding particle size decrease





Dispersant increases surface area; no dissolution: $SA/V \propto c$

Spheres: $SA/V \propto a^{-1} \rightarrow a \propto c^{-1}$

What if the particles aren't spherical?

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

Hiemenz & Rajagopalan. *Principles of Colloid & Surface Chemistry*, (1997).

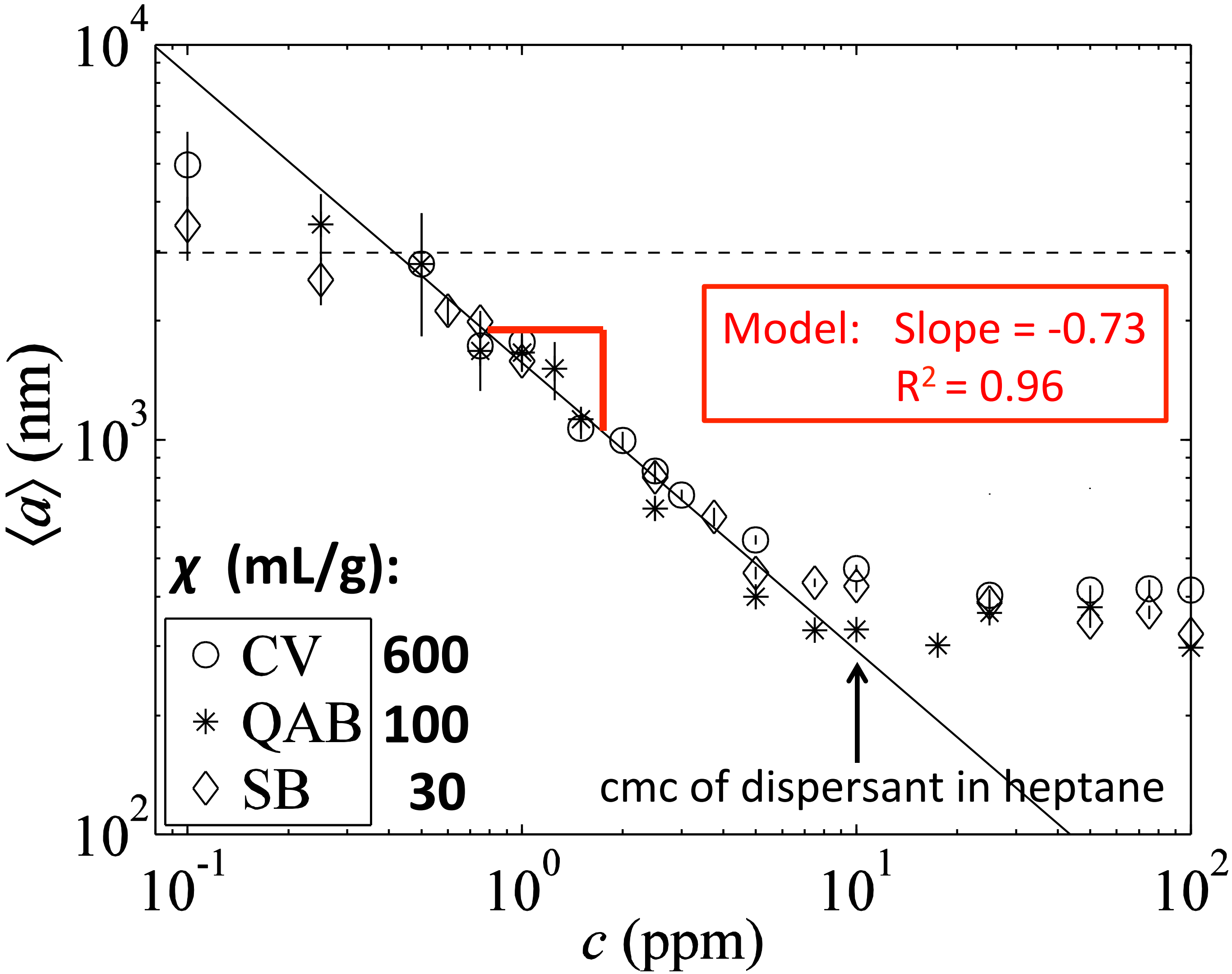
Evidence for surface adsorption

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

Model requires measure of D_f

By SLS:

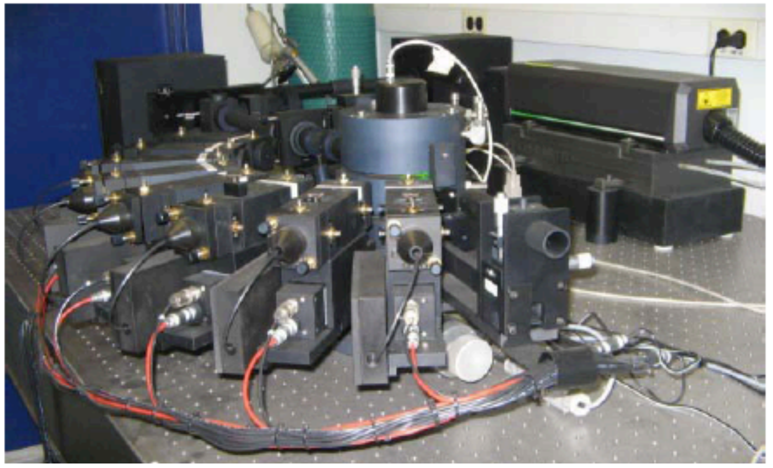
$$D_f = 1.63$$



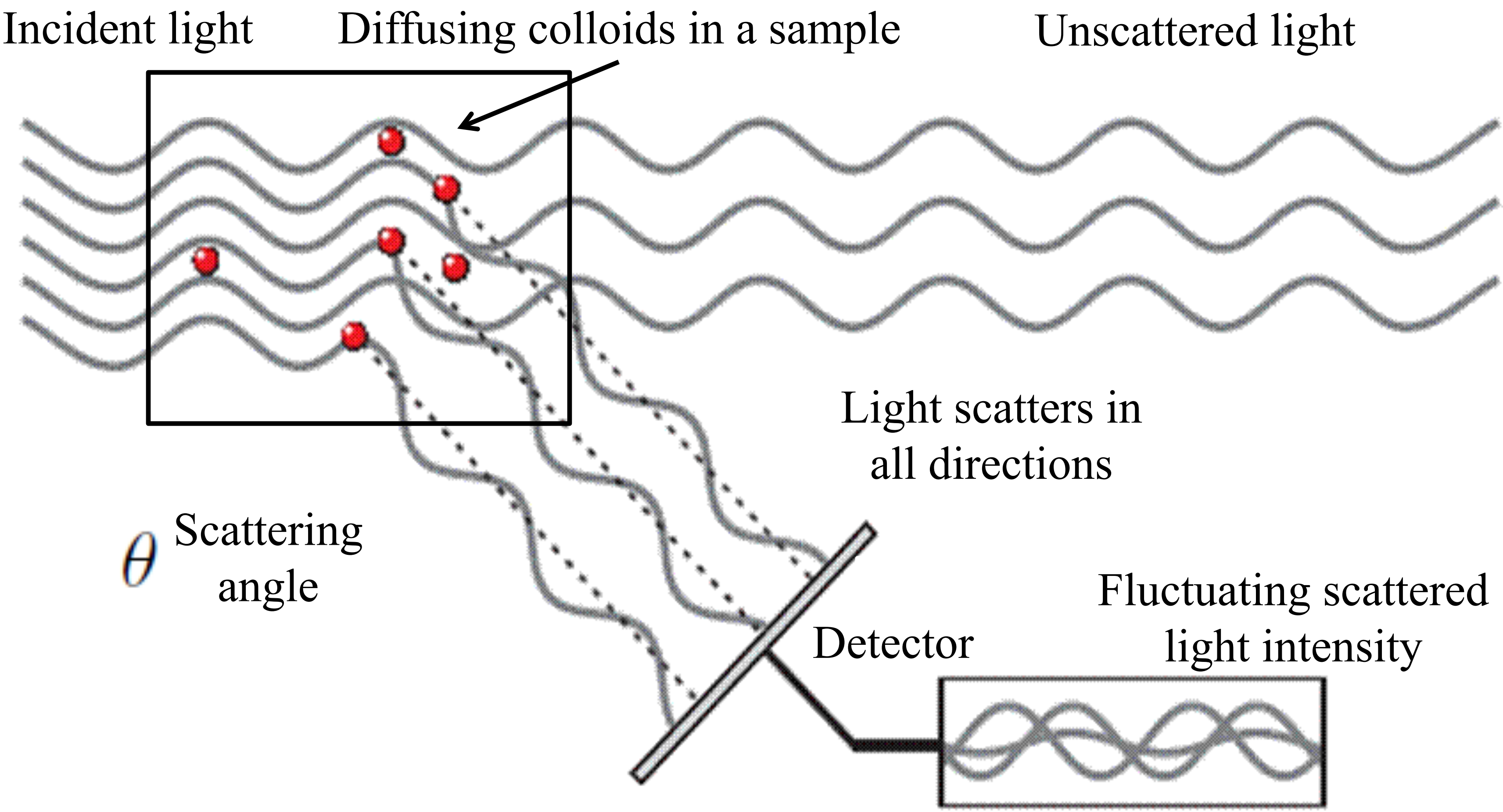
Hashmi, Firoozabadi. *Soft Matter* **7**, 8384 (2011).

Instrument Setup

- ALV 5000 goniometer + Verdi laser (Coherent)
- Instrument parameters: wavelength λ, scattering angle θ, temperature T
- Suspension parameters: index of refraction n, viscosity μ



Dynamic Light Scattering: Setup



Fluctuations in scattered light arise from diffusion

Size Distributions: non-monodisperse

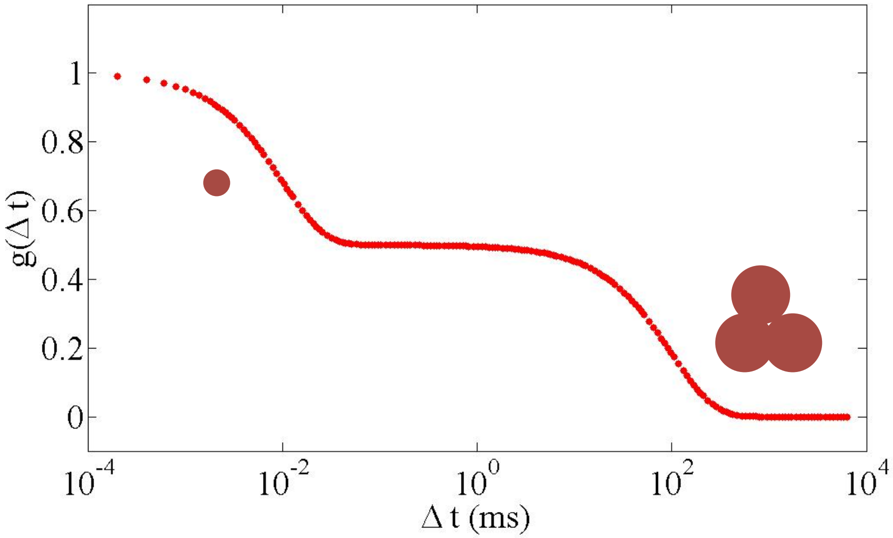
CONTIN: Provencher (1982)

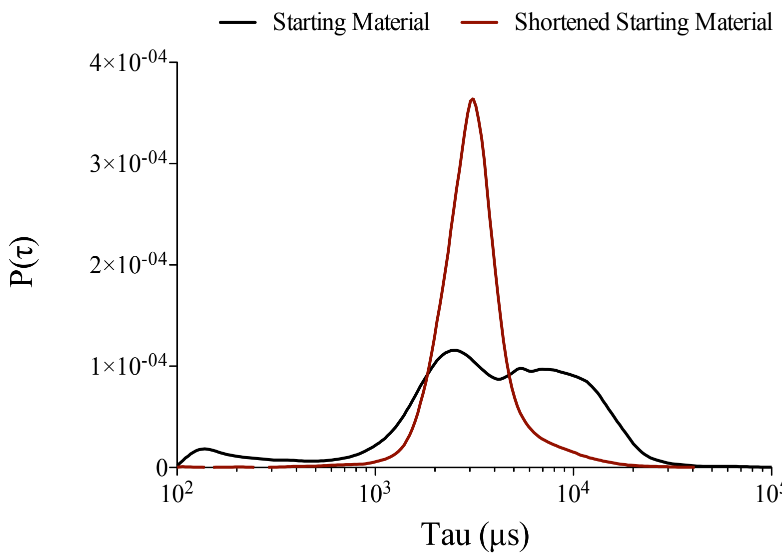
No assumptions about shape of distribution

Distinct decays indicate distinct particle populations

$$g(\Delta t) = \int p(\tau) exp(-\Delta t/\tau) \mathrm{d}\tau$$

$$p(\tau) \rightarrow p(a)$$

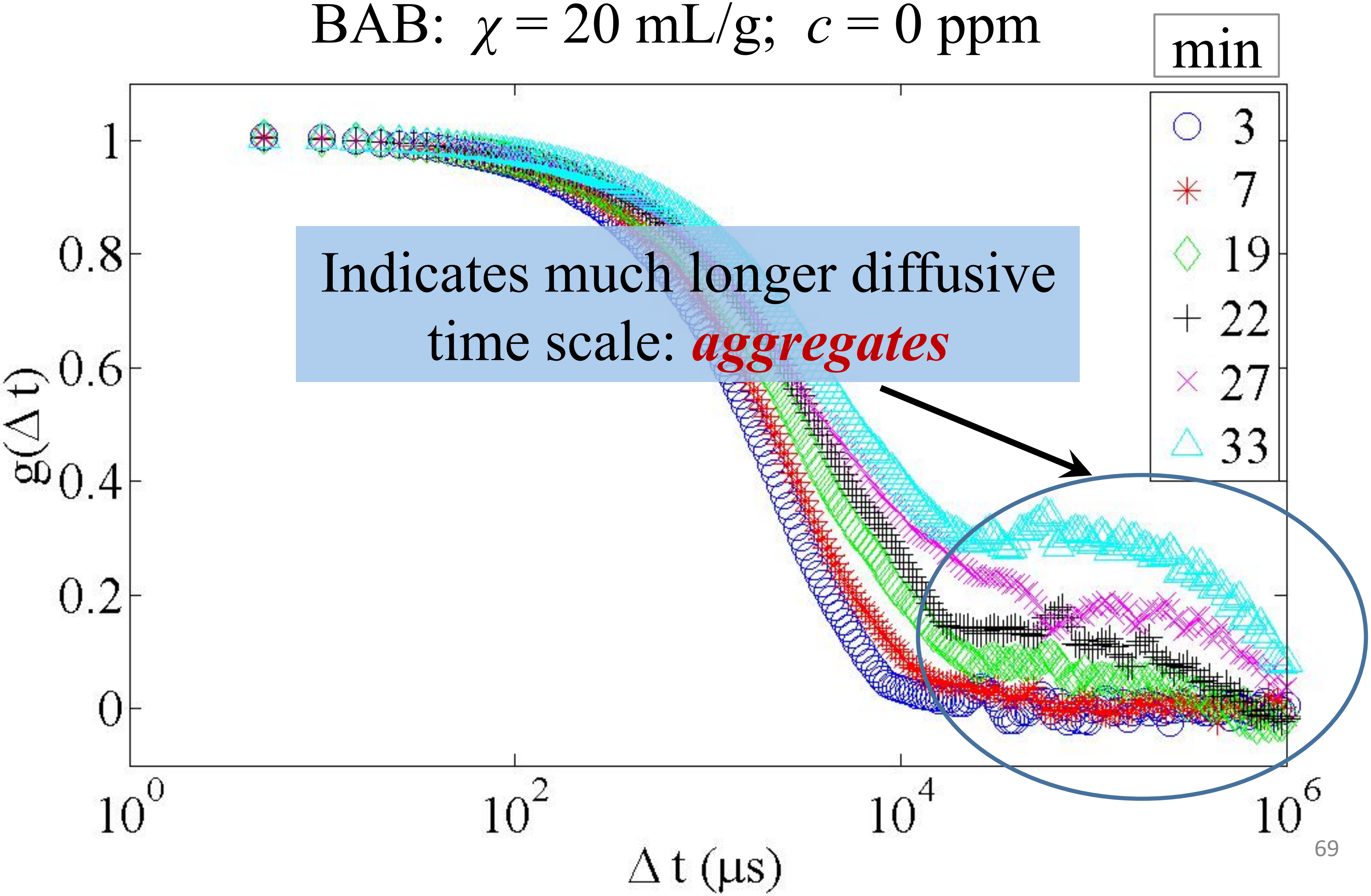




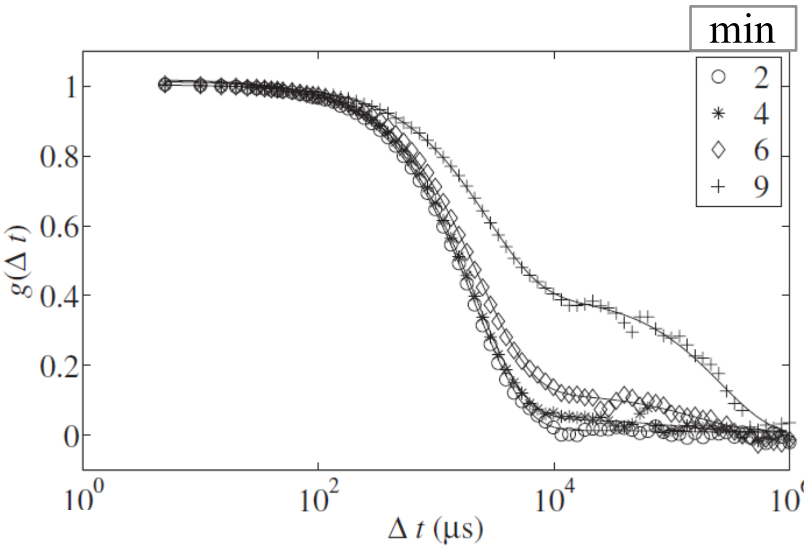
Freely available; implemented in Fortran, C; data handling can be done in Matlab

DLS Measurements Over Time

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



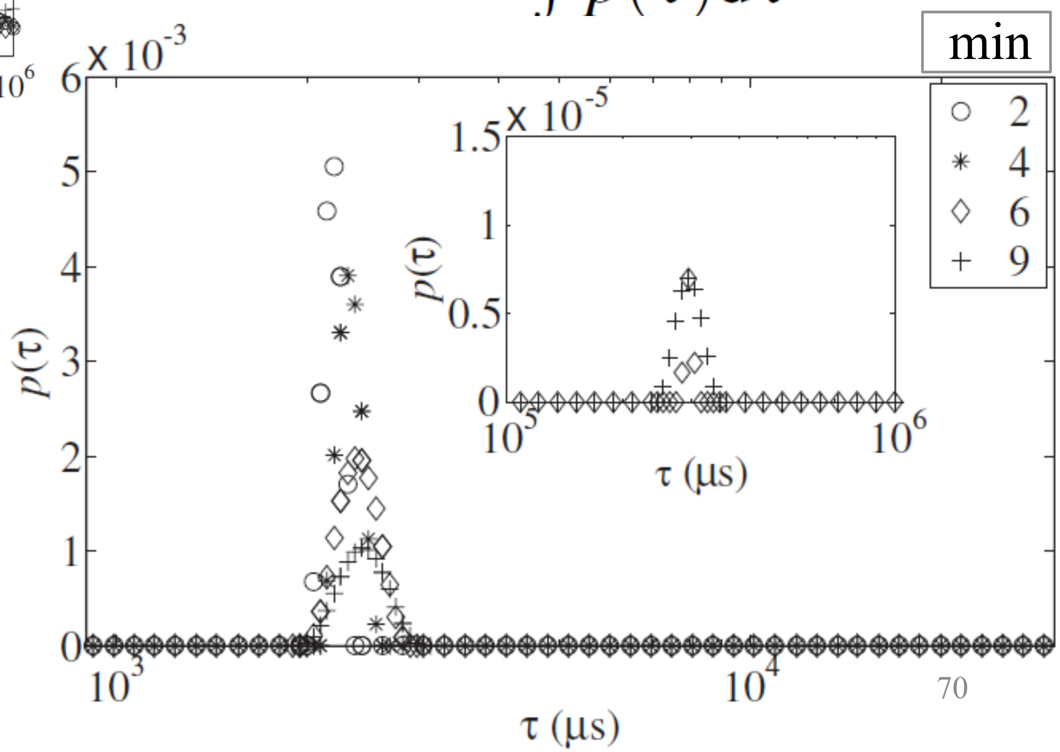
CONTIN Analysis



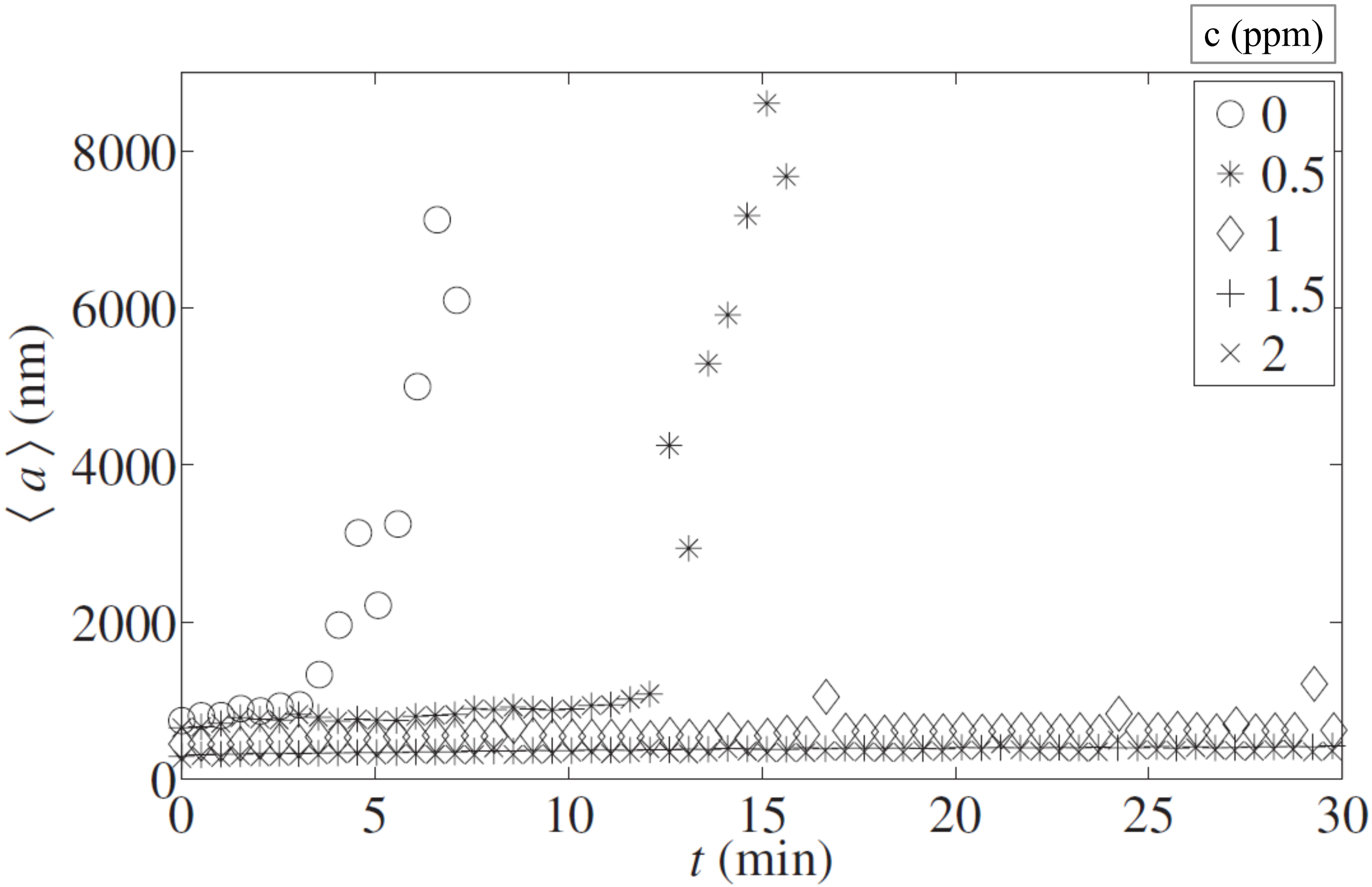
$$g(\Delta t) = \int p(\tau) exp(-\Delta t/\tau)\mathrm{d}\tau$$

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

SB: $\chi = 30$ mL/g;
$c = 0$ ppm



Composition Dependent Growth



Adding dispersant → delays, suppresses aggregation

Hashmi & Firoozabadi. *Journal of Physical Chemistry B* (2010) **114** 15780.

Application to Carbon Nanotubes

- DLS measures Diffusion constant D →
  - Can be used to obtain Diameter:Length ratio

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

rods

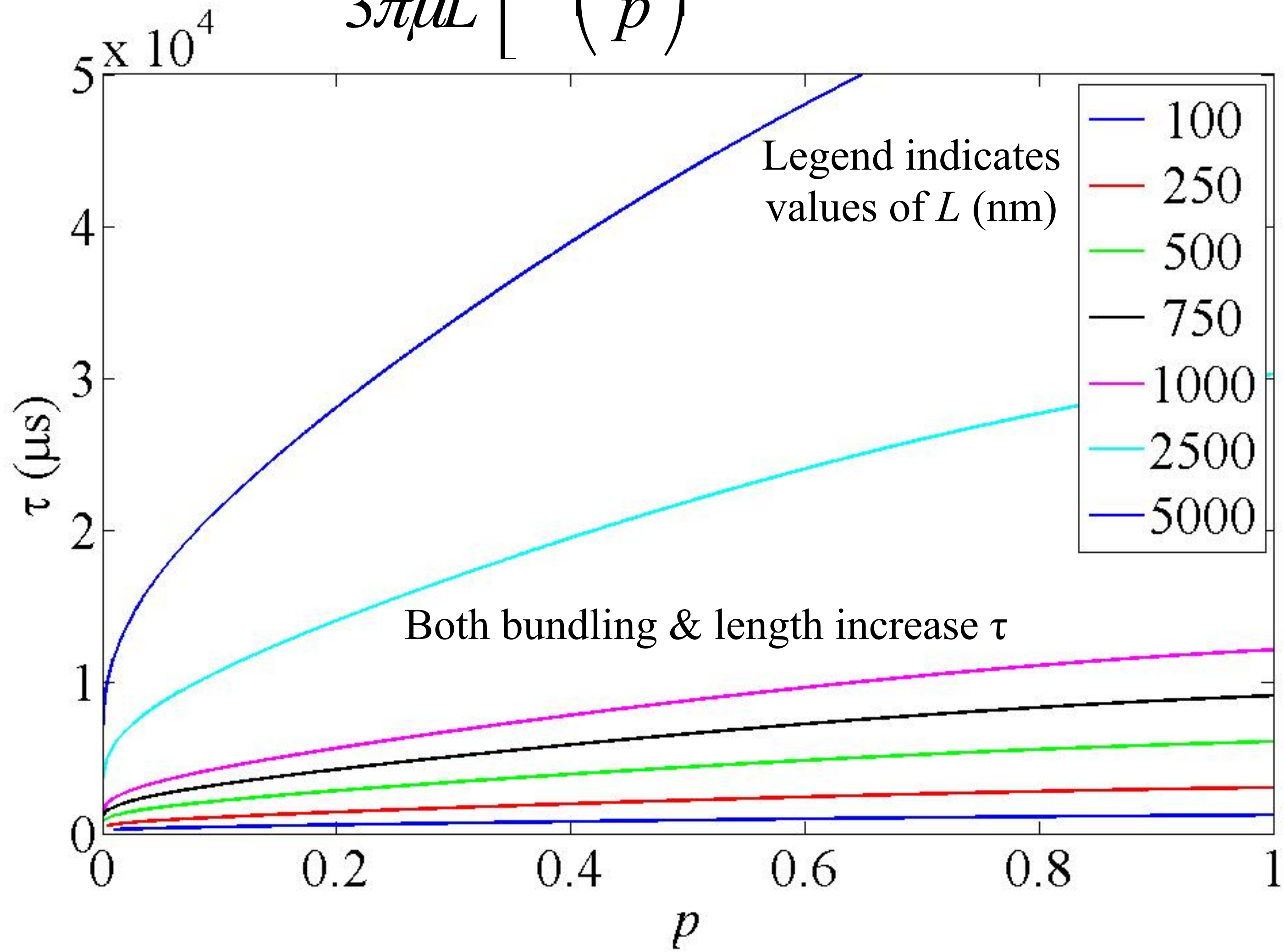
$$D = \frac{k_B T}{3\pi\mu L}\left[\ln\left(\frac{L}{D}\right) + 0.316 + 0.5825\left(\frac{D}{L}\right) + 0.050\left(\frac{D}{L}\right)^2\right]$$

van Bruggen, Lekkerkerker, Dhont, *Physical Review E* (1997) **56** 4394.

Brancaa, Magazu, Mangione. *Diamond & Related Materials* (2005) **14** 846.

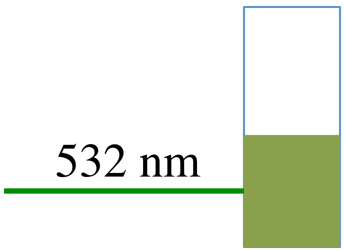
Dependence on Aspect Ratio

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

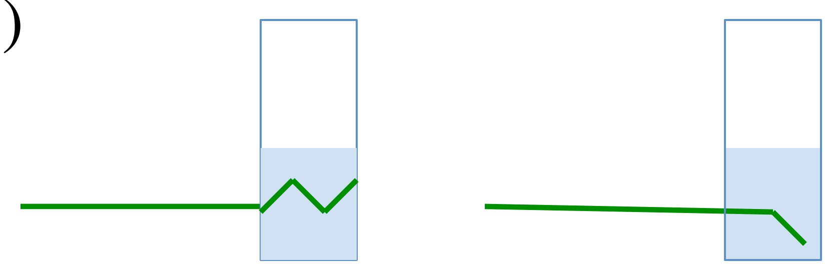


Practical Considerations

- Sample Preparation
  - Absorption at λ
    - Confirm/check with UV-vis spectroscopy

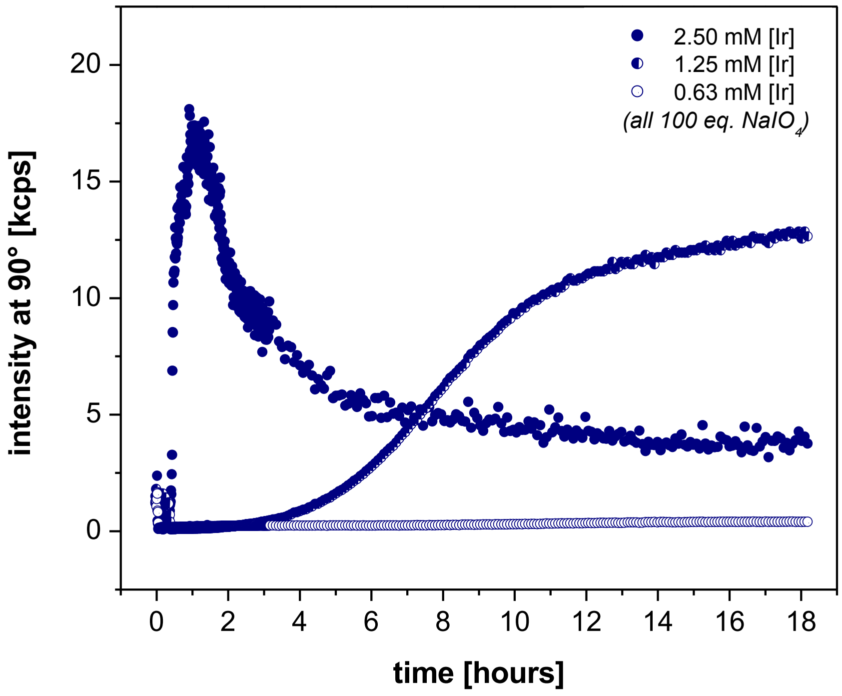


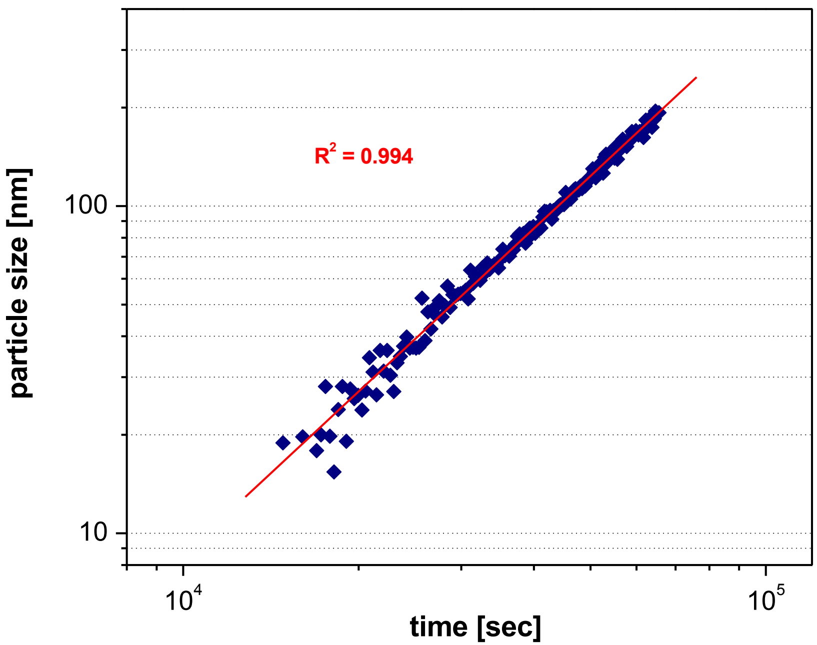
  - Concentration
    - Need 'enough' particles; avoid multiple scattering
    - Other methods can accommodate multiple scattering (back-scattering, DWS)



  - Particle size
    - Estimate given system/sample parameters

Understanding dynamics: Ir NP's





Power law growth – diffusion limited aggregation
Exponential growth – reaction limited aggregation

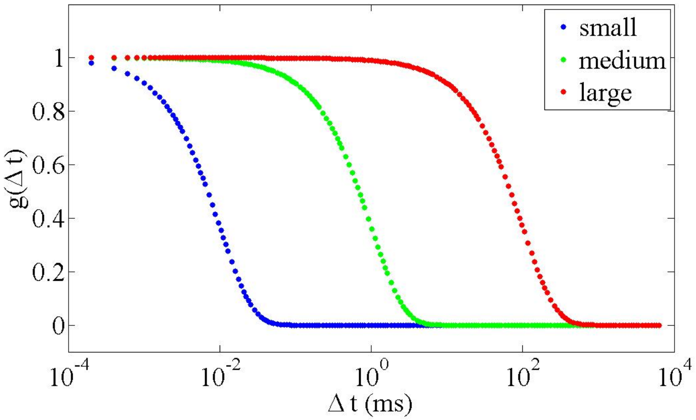
What Can SLS Measure?

- 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



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

$$D = 1/2q^2\tau$$

$$a = \frac{2q^2\tau k_B T}{6\pi\mu}$$

Parameters (water)

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

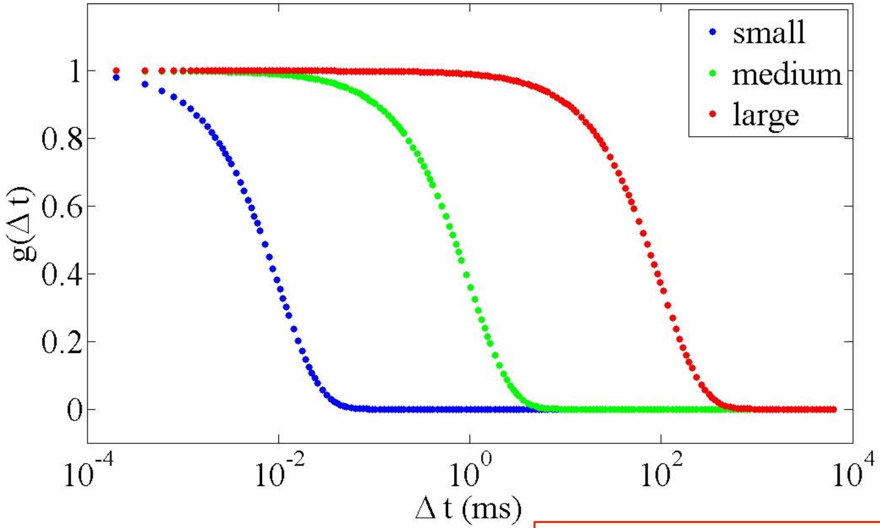
$\lambda = 532$	nm
$\theta = \pi/2$	Radians
$n = 1.333$	
$\mu = 0.001$	Pa.s
$T = 298$	K

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

$$\tau \approx 10^{-4} \ \text{s}$$

$$a \approx 40 \ \text{nm}$$

Size Distributions: Monodisperse



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

Instrument assumes Gaussian distribution

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

Average $\Gamma = 1/\langle\tau\rangle$ Variance σ^2

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

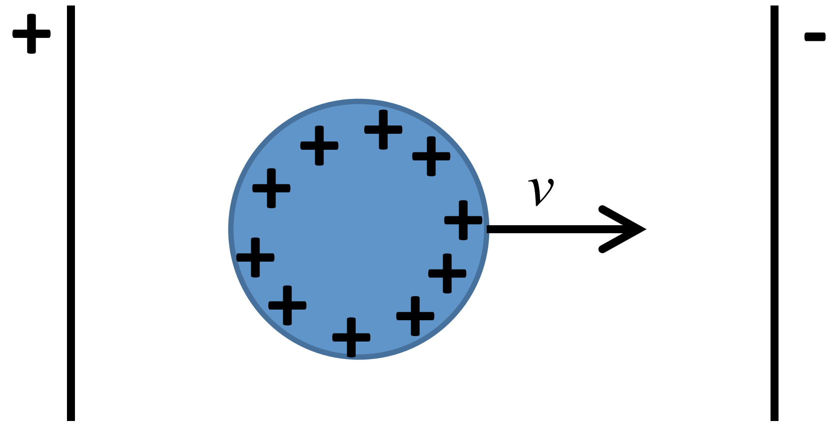
Second Order Cumulant $g(\Delta t) = \exp(-\Delta t \Gamma + \sigma^2 (\Delta t)^2 / 2)$

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

When 2nd order Γ ~ 3rd order Γ; Gaussian is good approximation

Electrophoretic mobility

$$\mu \equiv \frac{v}{E}$$



Balance electrostatic and hydrodynamic forces: $\mu \approx \dfrac{Qe}{6\pi\eta a}$

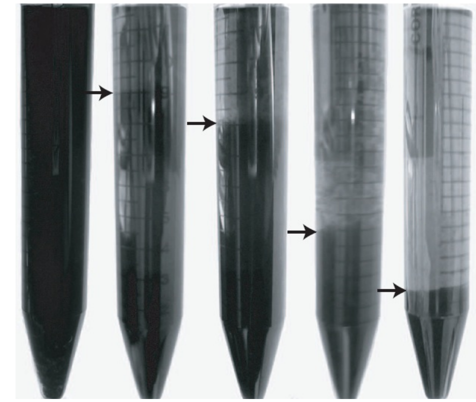
Hückel Theory: $\zeta = \dfrac{3\mu\eta}{2D\varepsilon_0}$ Valid for low ionic strengths: $\kappa^{-1} > a$

Mobility measurements respond to *particle velocity*

Instrument resolution ~ 3 x 10^{-10} m^2/Vs

Controlling Precipitation

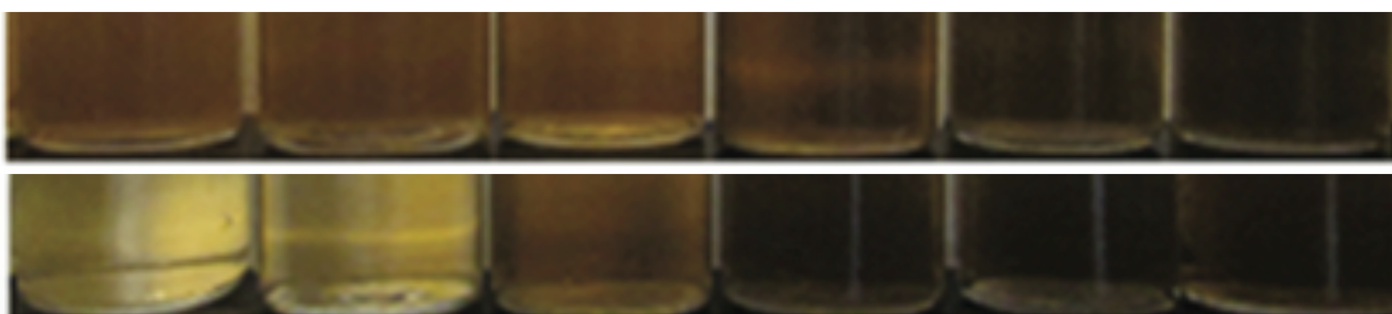
- Mix oil with precipitant (heptane)
- Filter to Isolate asphaltenes
- Dissolve in toluene → 'model oil'
- Reprecipitate in heptane; add dispersants



Dodecyl benzene sulfonic acid

Mix:

Centrifuge & decant:

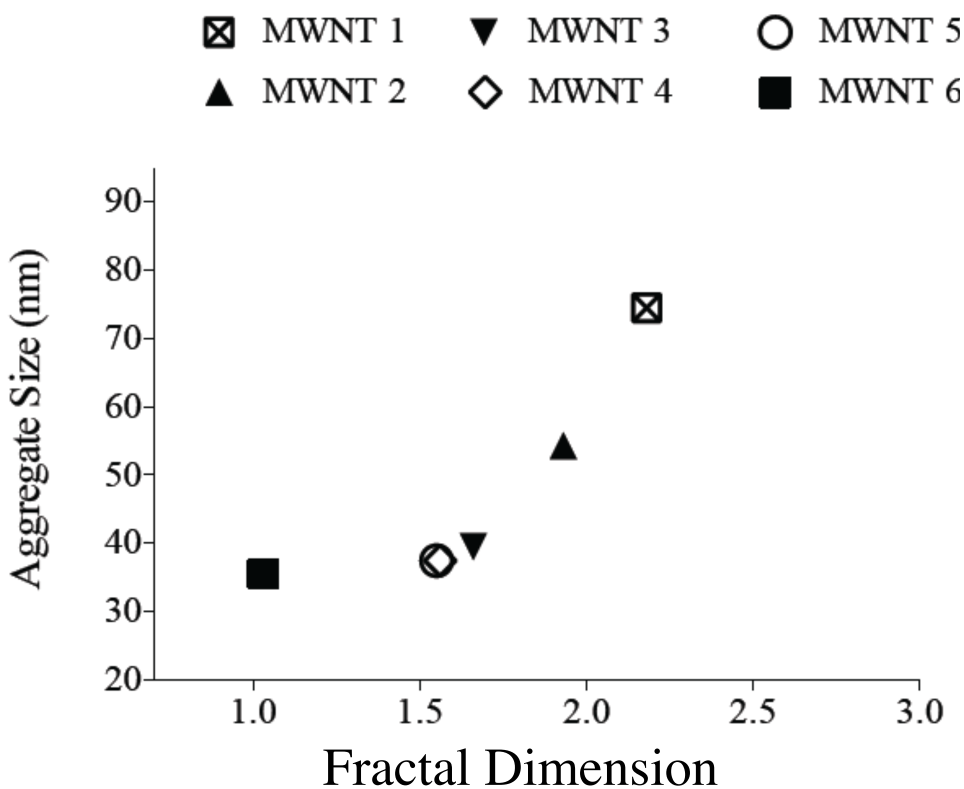


DBSA: 50 250 750 2,500 7,500 10,000 ppm

Hashmi, et. al. *Soft Matter* **8** 8778 (2012).

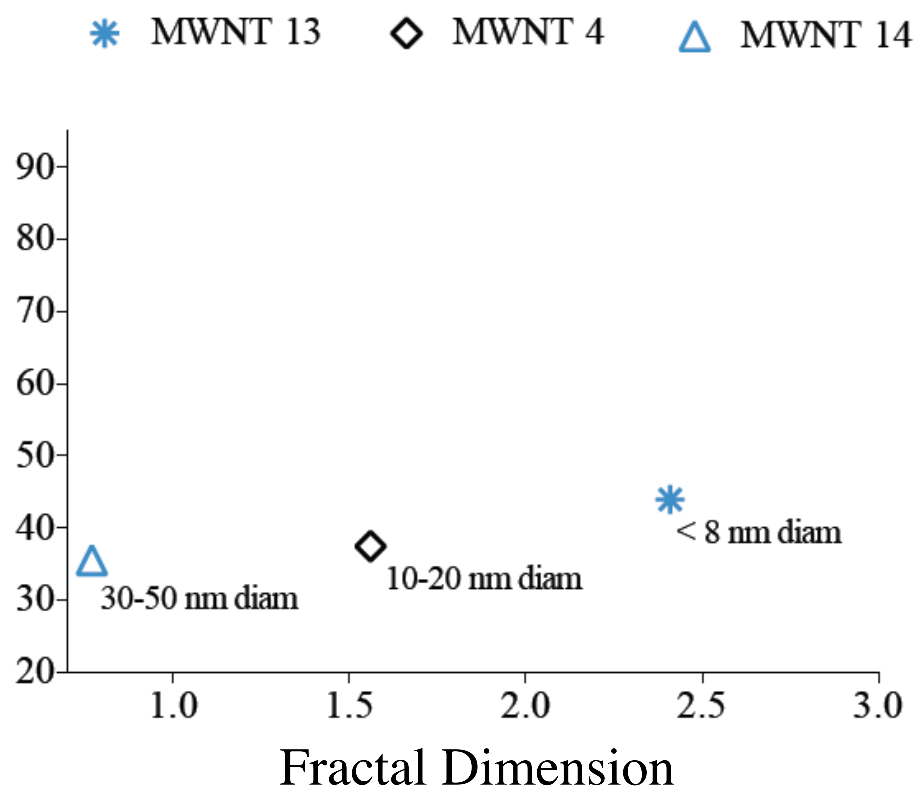
Controlling MWNT Dispersions

Nitric Acid Treatment Time



HNO_3 treatment increases surface oxygen (COOH)

Tube Diameter



Pasquini, L. M. et al. ES&T, 2013, **47**, 8775-8783.