Elucidating the Physicochemistry of NP Attachment to Surfaces:
Implications for Environmental Transport

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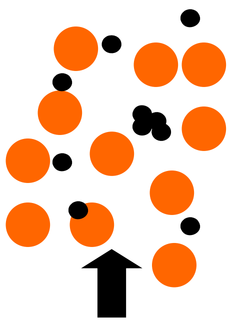
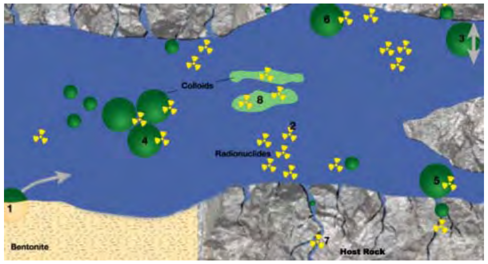
What is Transport?

Porous Media

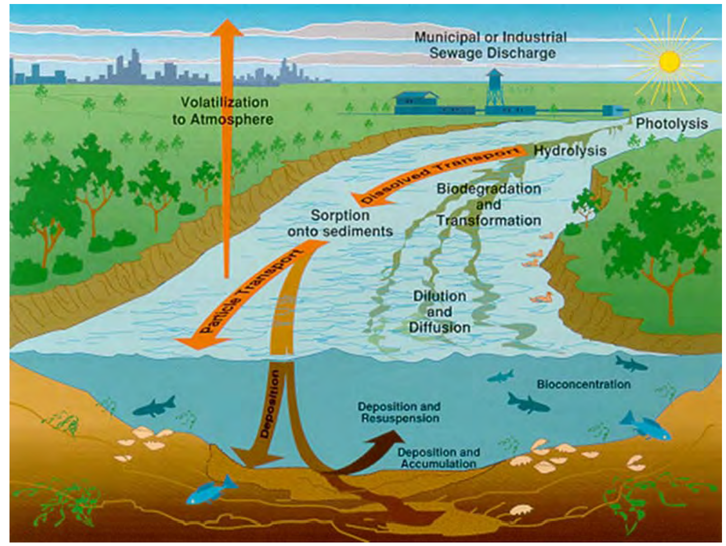


Flow

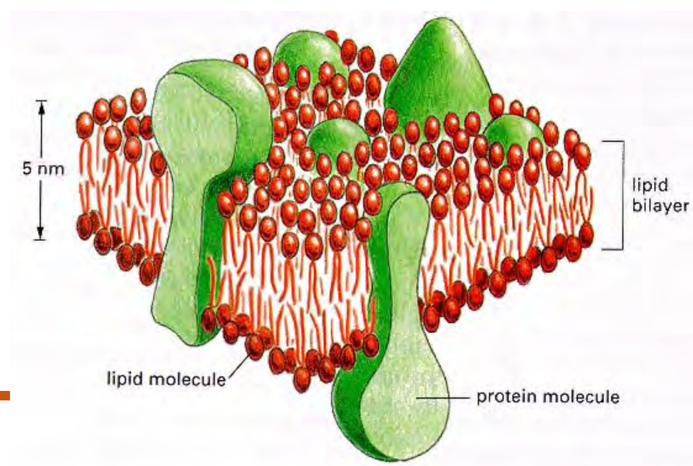


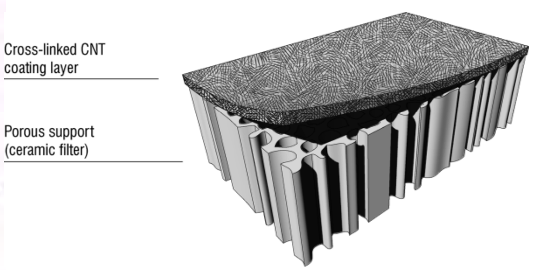
Sand Filters
Groundwater
Soil & Sediment

Cross Media



All transport is affected by <u>Aggregation state</u> & <u>Deposition</u>





Membranes

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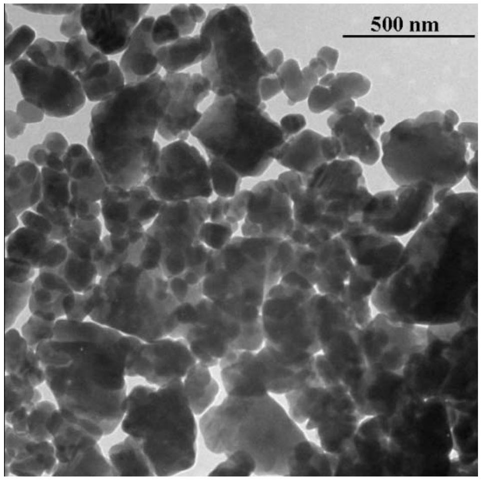
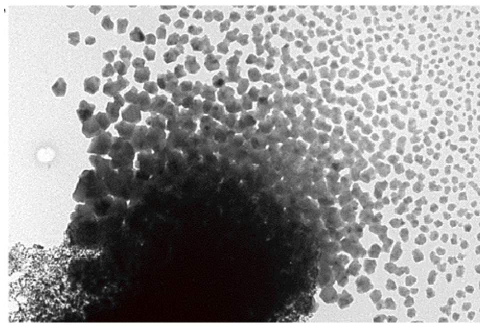
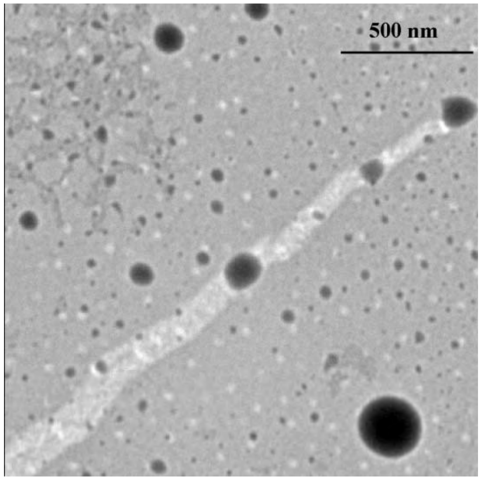
Carboxylic Acids Dissaggregate nC_{60} and Stabilize Smaller nC_{60} Clusters



aq/nC_{60}



aq/nC_{60} cluster breakup



cit/nC_{60} in 25 mM sodium citrate

Implication:

Organic acids can lead to small nC_{60} clusters whose mobility, toxicity, and physicochemical properties could differ from aq/nC_{60}

X. Chang and P.J. Vikesland, Virginia Tech

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Factors Affecting Aggregation & Deposition

Colloid Science

- Physical Factors
  - Size of NP and media (collector)
  - Energy input (e.g. mixing or porewater velocity)
  - Heterogeneity (physical and chemical)
- Chemical Factors
  - pH
  - Ionic strength and composition
  - NOM and organic acids
    - type, concentration, conditions of exposure
  - Engineered surface coatings
    - Surfactants, polymers, and polyelectrolytes
  - Biological modifications by EPS

Less Understood

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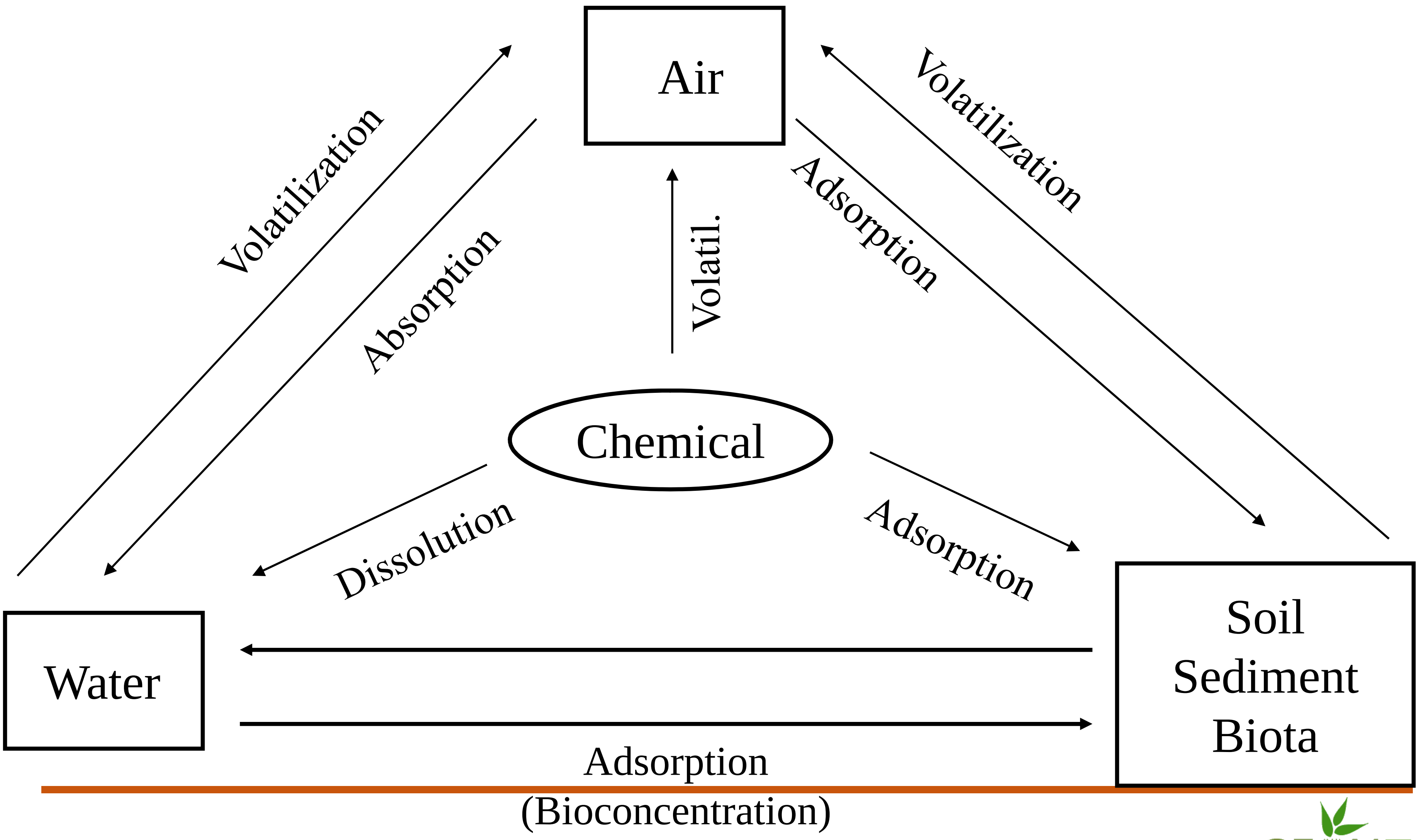
"Compartments" Approach to Determining Distribution of Environmental Contaminants



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Properties needed to Assess the Distribution of Organic Pollutants

Chemical Properties
Vapor Pressure (P^{sat})
Aqueous solubility (χ)
Octanol-Water Partitioning (K_{ow})
Environment Properties
f_{oc}, compartment volumes

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Properties needed to Assess the Distribution of Environmental Pollutants

Chemical Properties	Nanoparticles (e.g. nC_{60})
Vapor Pressure (P^{sat})	~0
Aqueous solubility (χ)	?
Octanol-Water Partitioning (K_{ow})	Very high (low for metal oxides)
Environment Properties	
f_{oc}, compartment volumes	?

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Properties needed to Assess the Distribution of Environmental Pollutants

Chemical Properties	Nanomaterials (e.g. C_{60})	Nanomaterials (proposed)
Vapor Pressure (P^{sat})	~0	N/A
Aqueous solubility (χ)	~0	Agglomeration state, Dispersion stability
Octanol-Water Partitioning (K_{ow})	Very high (low for metal oxides)	Interfacial behavior (deposition)
Environment Properties		
f_{oc}, compartment volumes	?	Ionic strength, ionic composition, pH, mixing, f_{OC}, mineral surface

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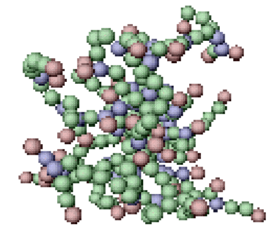
To predict transport we need to know:

- Attachment efficiency (α) and how this varies with:
  - pH, Ionic strength, ionic composition, size
  - Adsorbed NOM and other organic macromolecules
  - NP surface chemical composition, i.e. mineral phases and organic matter
  - Biological surface (collector) composition

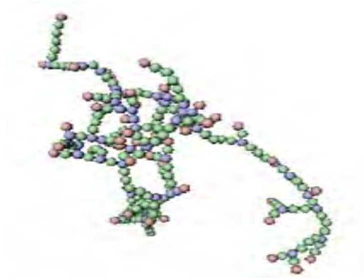
Current State-of-the-Art

- Aggregation
  - Widely studied (1000's+ papers)
  - Colloid and flocculation science



D_f=2.1

$$\alpha = \frac{1}{W} = \frac{k_a}{k_{a,\,fast}}$$



D_f=1.4

  - Chemistry of the problem α is handled empirically or stochastically
  - Predicting the effects of NOM and adsorbed macromolecules on α and D_f is not possible

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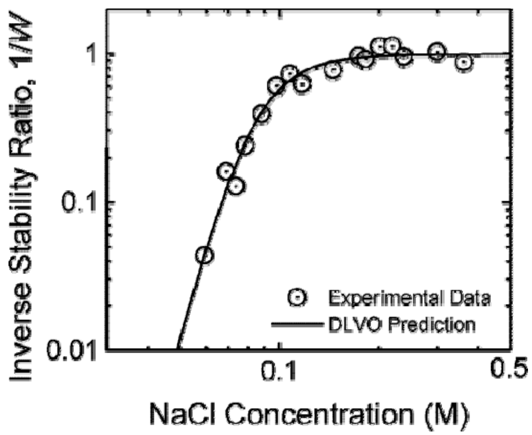
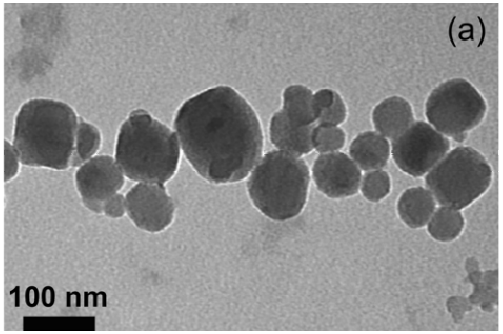
Aggregation state-of-the-art

- Measure
  - Particle size and aggregation kinetics by light scattering
  - Electrophoretic mobility
  - All as a function of [salt]
- Model attachment efficiency with DLVO
  - Hydrodynamic model *assumed*



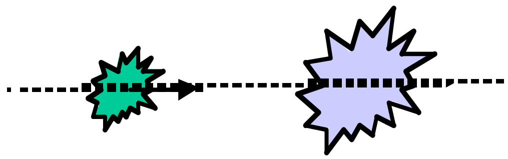


Chen and Elimelech, *Langmuir* 22 10994, 1996

Models for particle aggregation

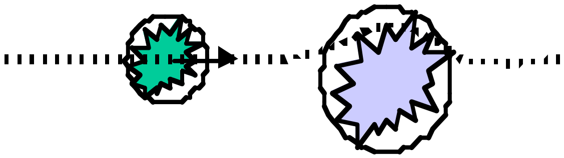
Collision rate constants

Rectilinear Model



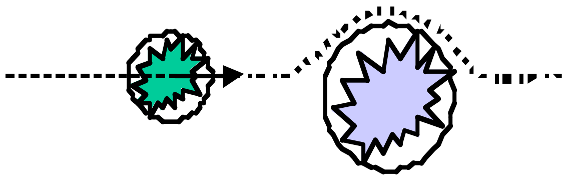
Smoluchowski, 1917

Intermediate model



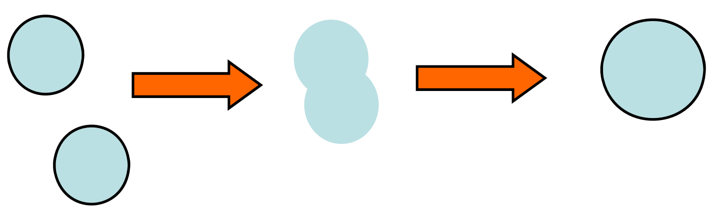
Veerapaneni and Wiesner, 1997

Curvilinear Model

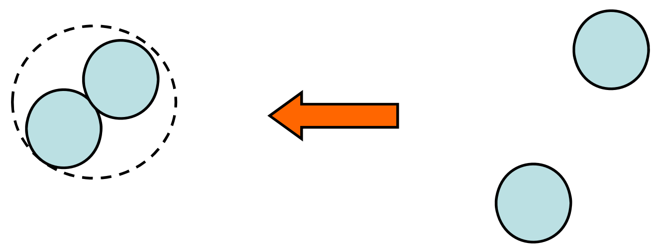


Han and Lawler, 1992

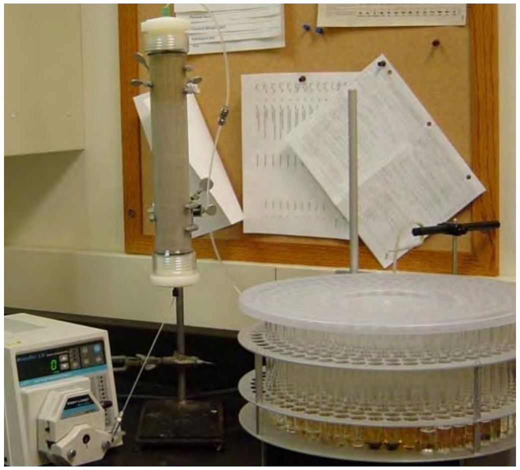
Coalescing spheres



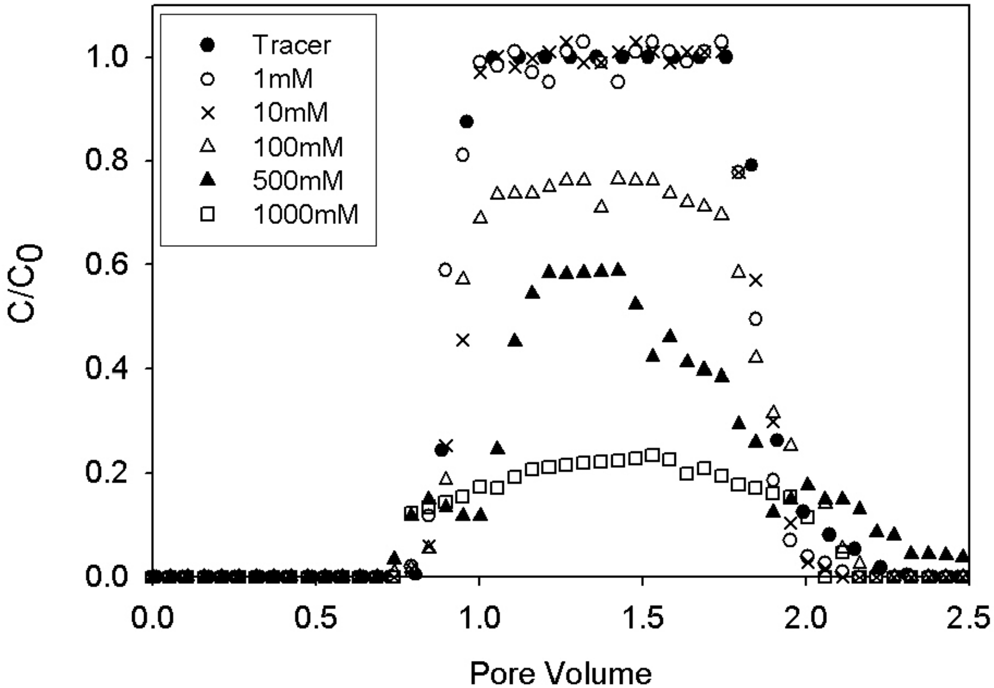
Porous aggregates



Deposition State-of-the-art



Glass beads
Sand
Model Soil
Soil

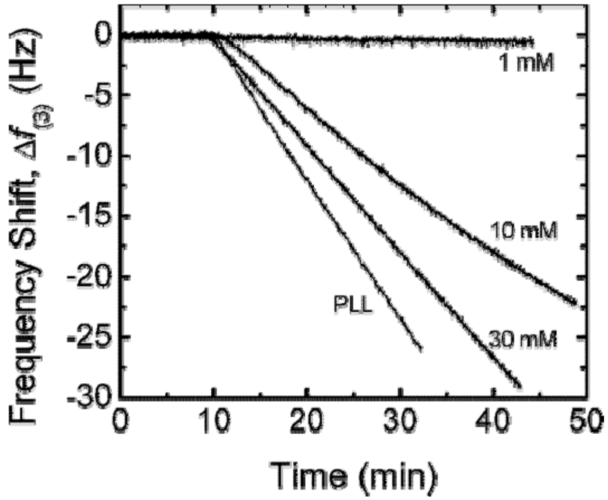


Saleh et al., 2008 Environ. Sci. Technol. 42 3349.

$$\alpha = \frac{\eta}{\eta_o} - \ln\left(\frac{C_e}{C_o}\right)\left(\frac{4a_c}{3(1-n)\eta_o}\right)$$

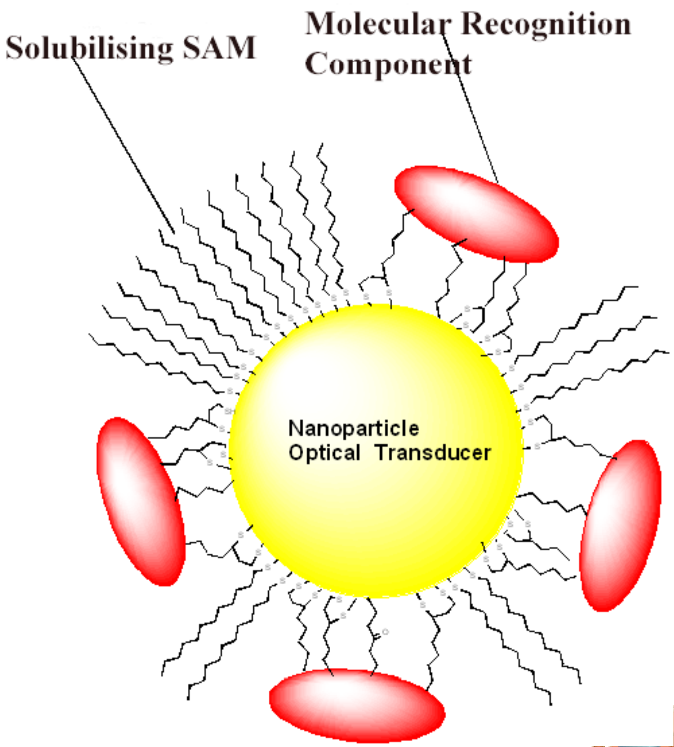
Deposition State-of-the-art

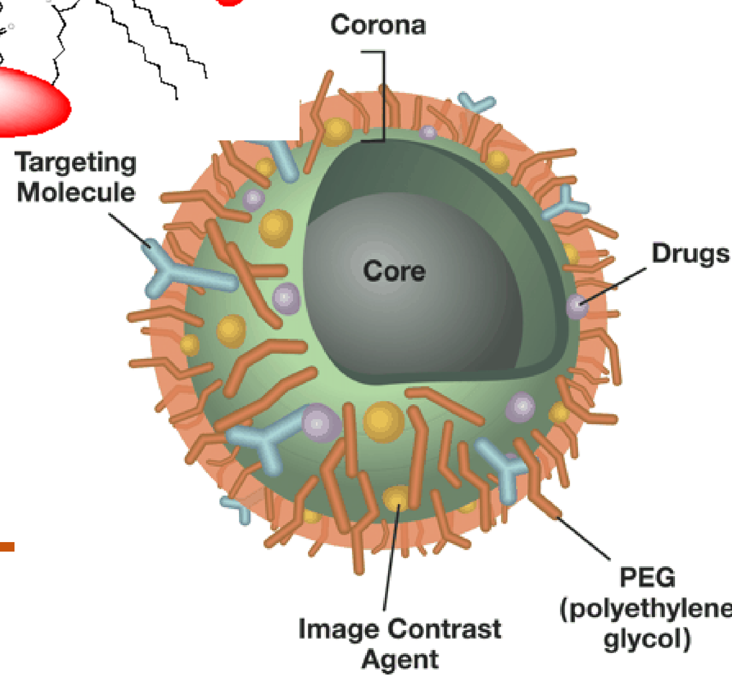
- QCM-D
  - Quartz Crystal Micro-balance with Dissipation
  - Change in frequency of crystal oscillation indicates adsorbed mass
  - Energy dissipation indicates structural properties of adsorbed layer
    - Determined from time for energy dissipation after power is shut off
  - Many metal-oxide coated quartz crystals now available
    - Highly idealized systems



Chen and Elimelech,
Langmuir 22 10994, 1996

Most Nanomaterials are Coated



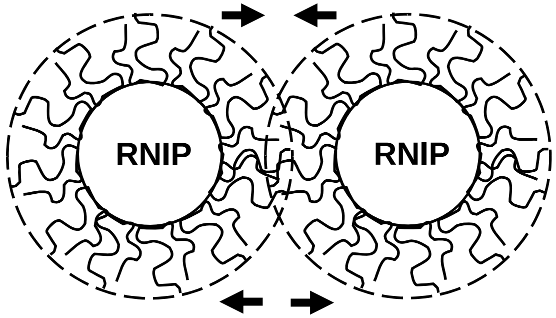


Coatings provide…

- Dispersion stability
- Functionality
- Targeting capabilities
- Biocompatibility

Coatings Dominate the Interaction Energies between Particles

Attraction due to $V_{vdw}+V_M$



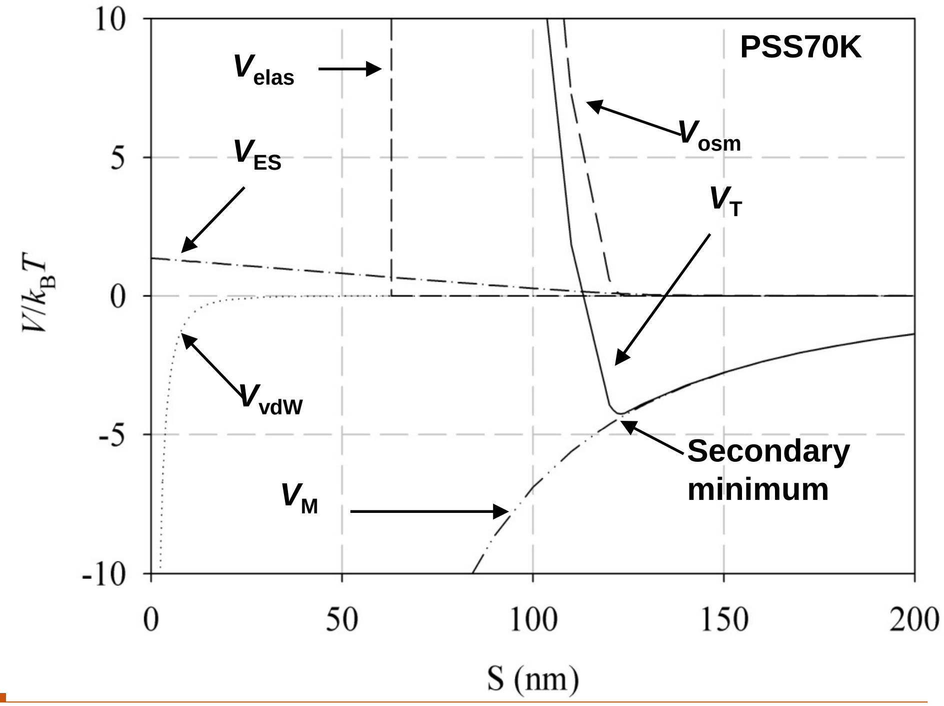
Repulsion due to $V_{ES}+V_{osm} + V_{elas}$

Need to consider:

V_{elas}, V_{osm}

due to polyelectrolyte

V_{osm} is strong repulsive force and results in <u>agglomeration</u>



Phenrat, et al. *J Nanopart. Res.* Vol. 10 p 795-814

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Deposition Predictions need to include chemistry of surface coatings

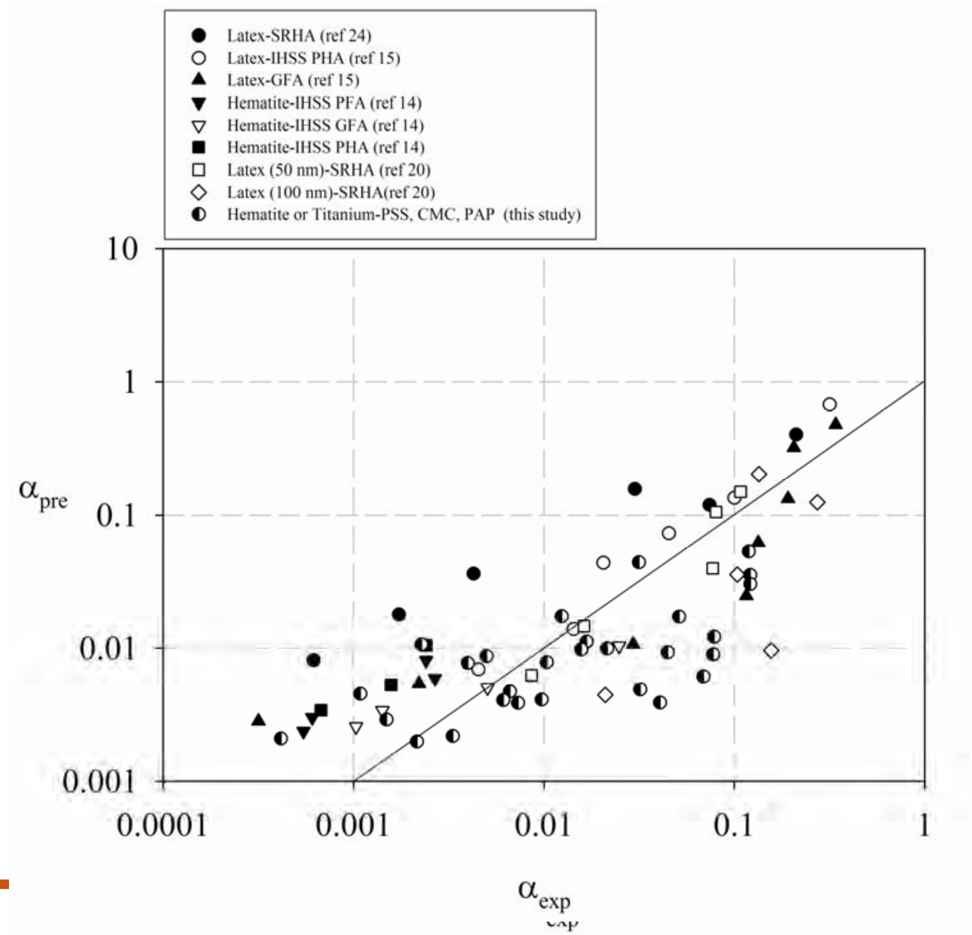
$$\alpha_{pre} = 2.53x10^{-3} N_{Lo}^{0.70} N_{E1}^{-0.31} N_{E2}^{3.51} N_{DL}^{1.35}$$

(J. Colloid Interface Sci. 1999, 218, 488-499)

$$N_{LEK1} = \frac{d_p d_M^2 u_s \Gamma N_a \rho_p}{\mu M_W}$$

Dimensionless number accounting for NP coating properties

$$\alpha_{pre} = 10^{-1.35} N_{LO}^{0.39} N_{E1}^{-1.17} N_{LEK1}^{-0.10}$$



What is needed for success?

- Understand fate, then transport
  - Partitioning behavior first
    - Show that α is predictive of partitioning
  - Rates of transfer between phases second
- Get some chemistry into α for NPs coated with organic macromolecules
  - Understand interface (2 to 3 nm)
  - Effect of pH, ionic strength, ionic composition, surface properties (e.g. charge), NP size
  - Need models that include *polydispersity* and *disaggregation*

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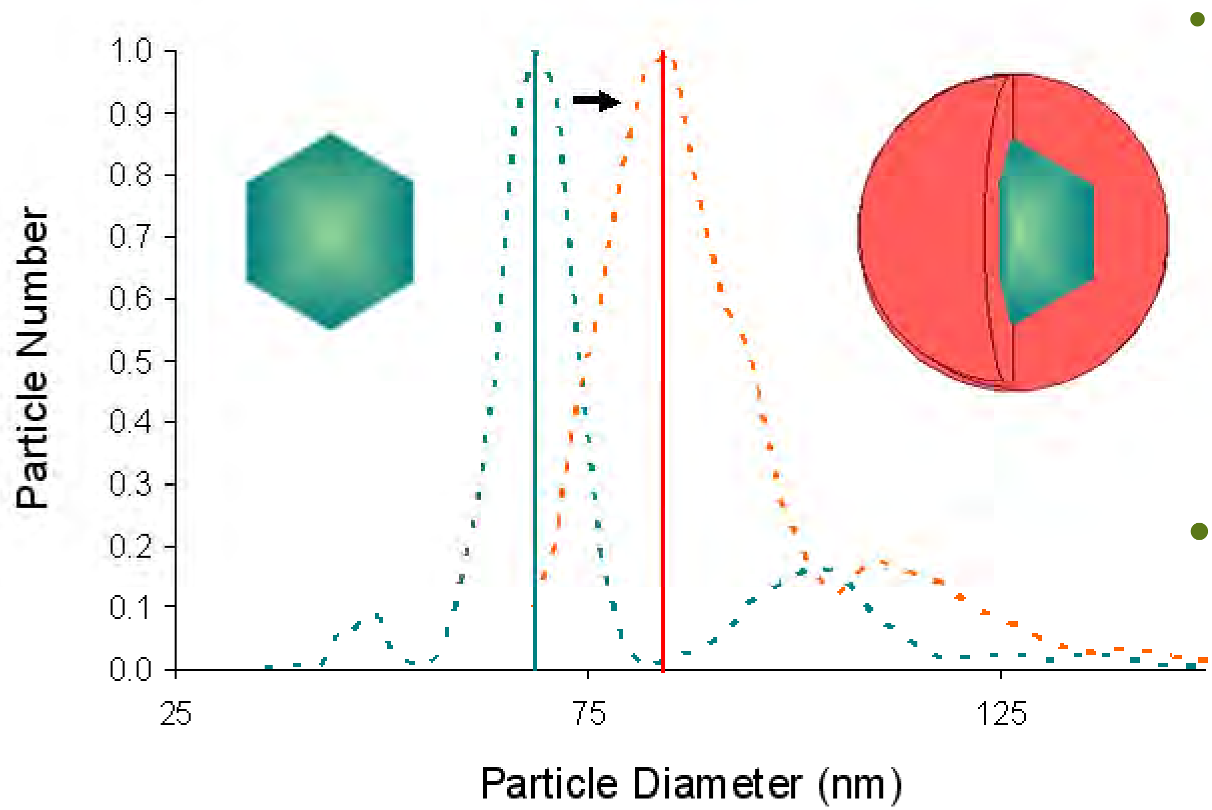
What is needed for success?

- Understand attachment to biological surfaces
  - Bacteria, plant roots, etc.
  - May strongly affect bioavailability
- Understand transformations that affect NP aggregation and deposition
  - Redox reactions, biological reactions, condensation of organic matter
  - Numerical models for NP-macromolecule interactions
    - Kinetic rather than thermodynamic

Questions?

Organic coating formation on aerosolized NPs

Objective: Determine the effect secondary organic acid coatings on nanoparticles emitted into the lower atmosphere



- Results:
  - Measured PSL particle growth in presence of a-pinene and ozone
  - Model predicts 5 to 10-nm growth of SOA per hour
- Implication:
  - NP properties in soil and water determined by coating properties

Neil Donahue and Erica Trump-CMU

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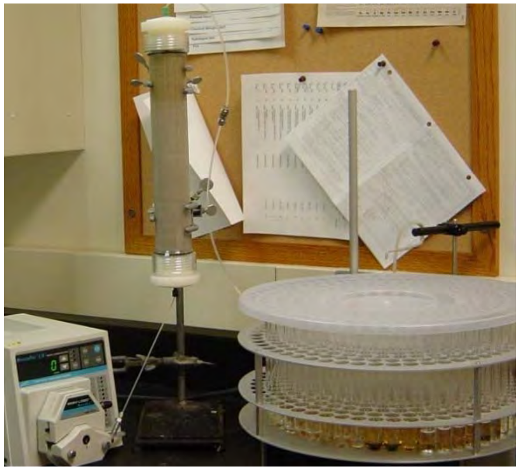
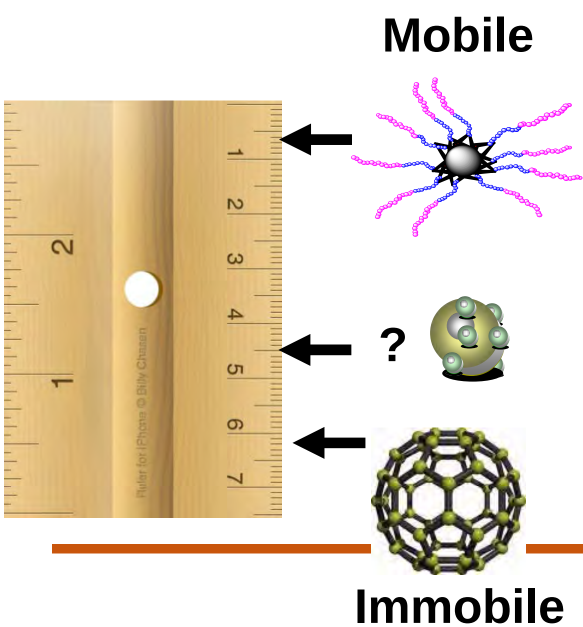
NP Attachment and Deposition



$$\alpha = -\ln\left(\frac{C_e}{C_o}\right)\left(\frac{4a_c}{3(1-n)\eta_o}\right) = \frac{\eta}{\eta_o}$$

- Objectives:
  - Develop models for NP attachment linear combination of surfaces
  - include chemistry of adsorbed macromolecules
  - Determine benchmarks for mobility based on measureable NP properties



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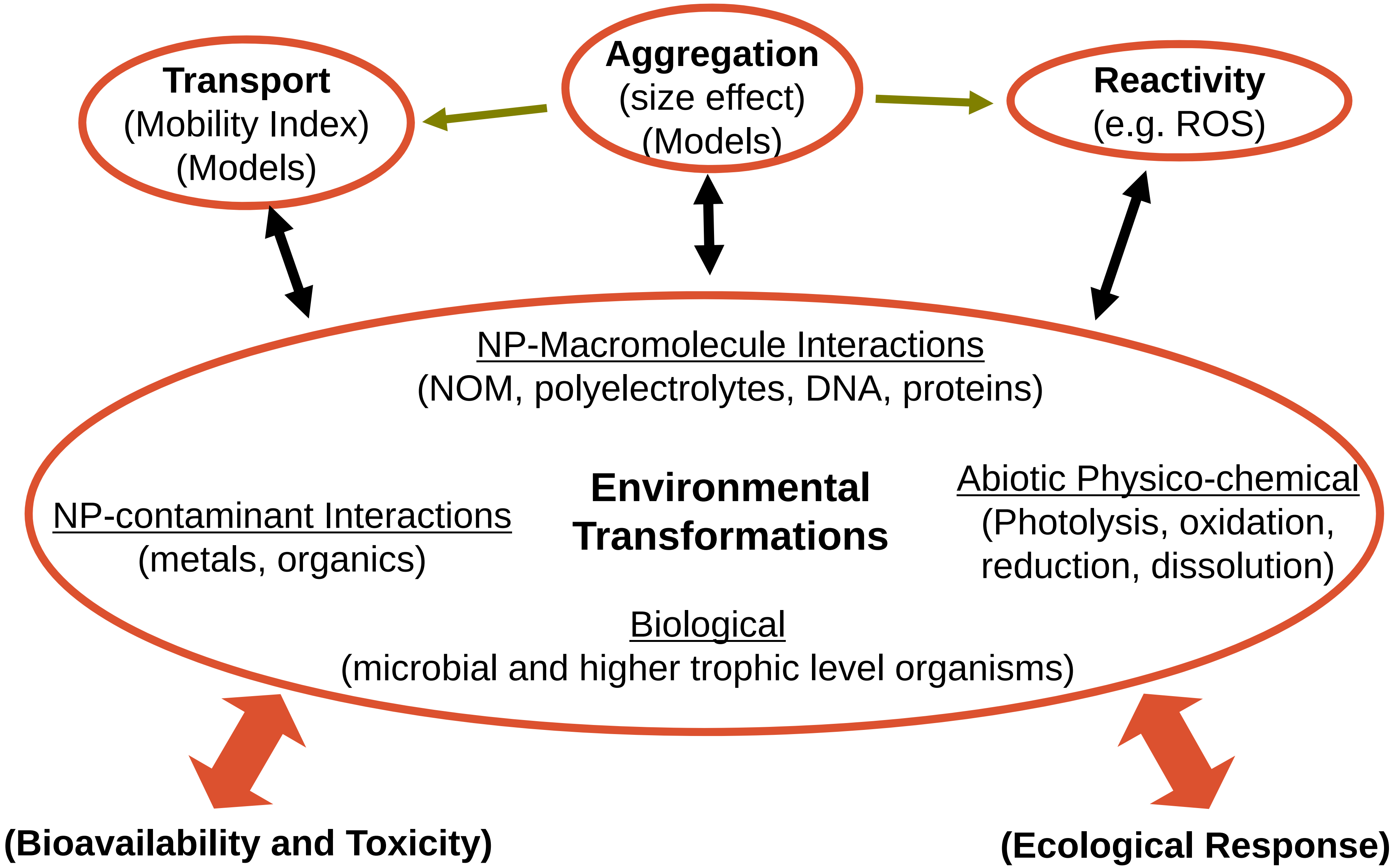
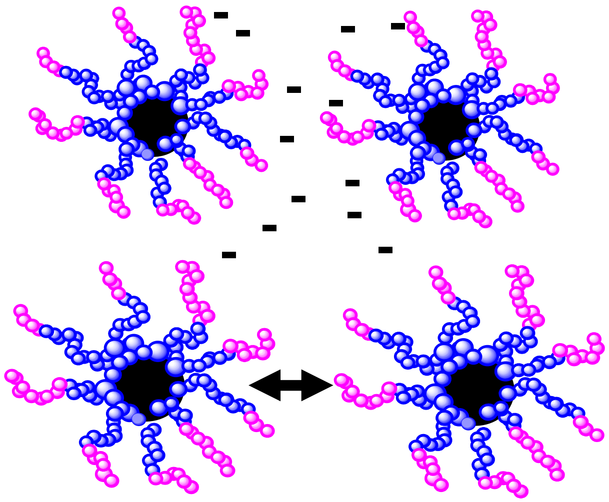
Research Activities



Surface Coatings Affect Attachment

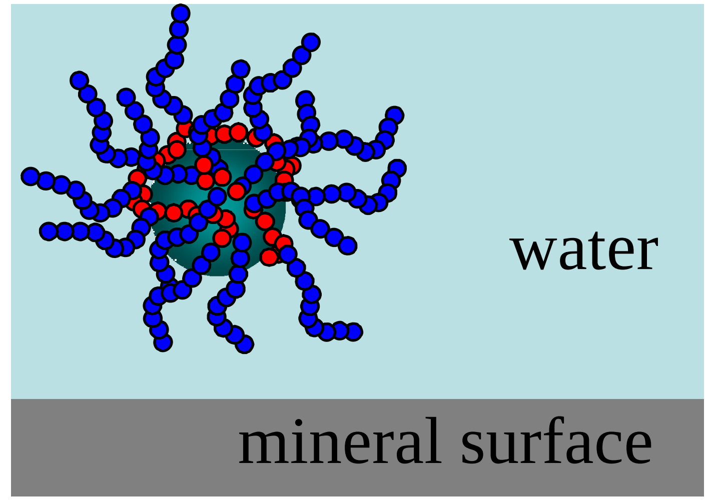
Inhibits Aggregation

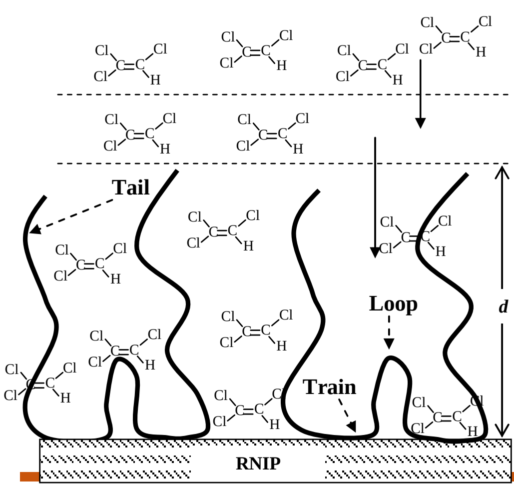


Charge Stabilization

Steric Stabilization

Inhibits Deposition

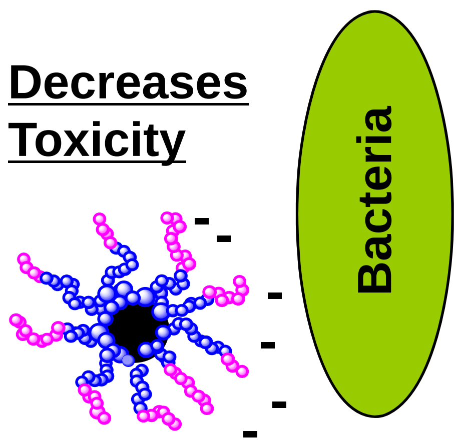


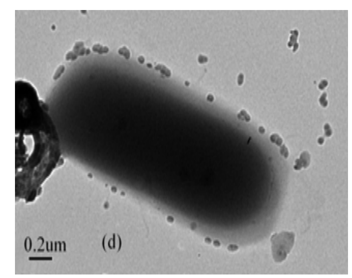


Lowers Reactivity

Phenrat et al., 2008
ES&T 43 1507

Decreases Toxicity





Empirical correlations developed to <u>estimate</u> α from particle and collector properties

Elimelech's correlation **(Water Res. 1992, 26, (1), 1-8)**

$$\alpha = 2.57x10^{-2} N_{col}^{1.19}$$

N_{col} represents a force balance between van der Waals attraction and *electrostatic* repulsion

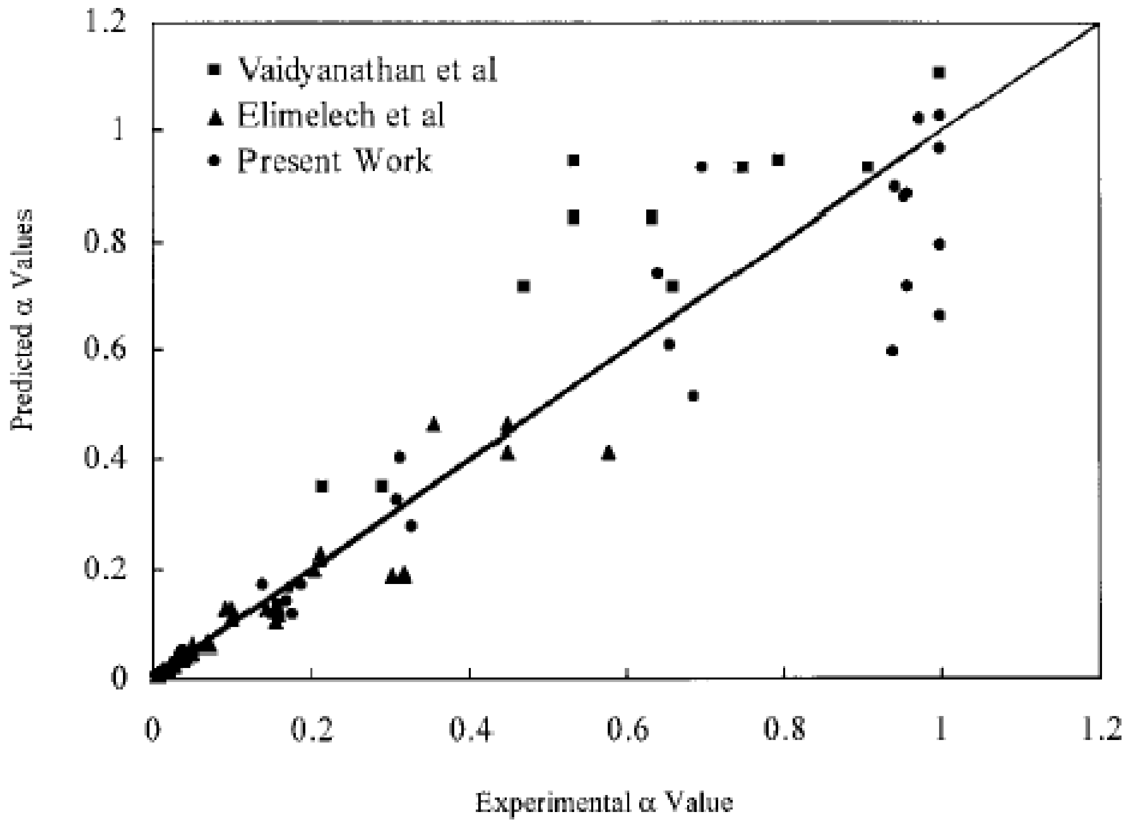
Bai and Tien 's correlation **(J. Colloid Interface Sci. 1999, 218, 488-499)**

$$\alpha = 2.53x10^{-3} N_{Lo}^{0.70} N_{E1}^{-0.31} N_{E2}^{3.51} N_{DL}^{1.35}$$

Also van der Waals attraction and *electrostatic* repulsion but includes velocity term

Predicted deposition of electrostatically stabilized colloids

Bai, R.; Tien, C. (*J. Colloid Interface Sci.* **1999**, *218*, 488-499).



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Additional Dimensionless Parameter

Determined from Buckingham-Pi Theory

$$N_{LEK1} = \frac{d_p d_M^2 u_s \Gamma N_a \rho_p}{\mu M_W}$$

Correction for [salt] on layer confirmation

$$d_M = d_{M0}\left[\frac{I}{I_{ave}}\right]^{-2/3}$$

Predicted α for Coated NPs

$$\alpha_{pre} = 10^{-1.35} N_{LO}^{0.39} N_{E1}^{-1.17} N_{LEK1}^{-0.10}$$

Refs. for the relationship between *d* and *I

R. Hariharan; C. Biver; J. Mays; W. B. Russel, *Macromolecules* **1998,** 31, (21), 7506-7513.
J. F. Argiller; M. Tirrell, *Theor. Chim. Acta* **1992,** 82, (5), 343-350
N. I. Abu-Lail; T. A. Camesano, *Biomacromolecules* **2003,** 4, (4), 1000-1012.

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