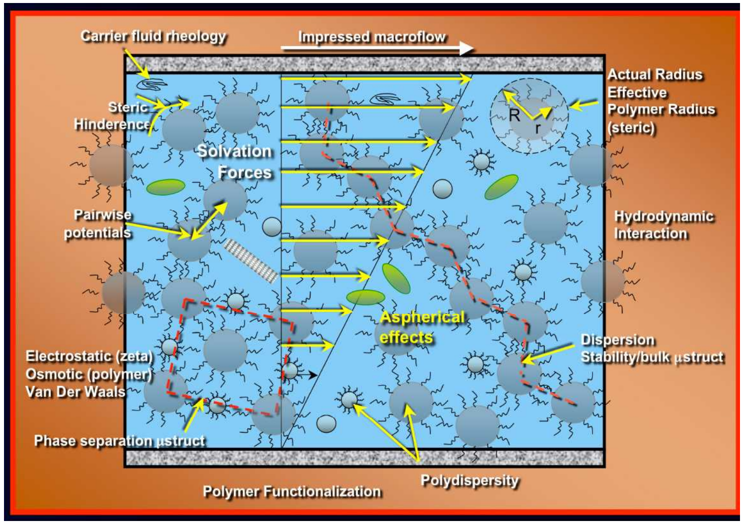
For presentation at the Nanotech 2008 Conference,1-5 June 2008, Boston, MA.

SAND2008-3731C

Flow of concentrated, nanoparticle suspensions: Multiscale modeling for Manufacturing Process Design



P. R. Schunk and J. B. Lechman

Reactive and Nanoscale Processes Department

NNSA National Nuclear Security Administration

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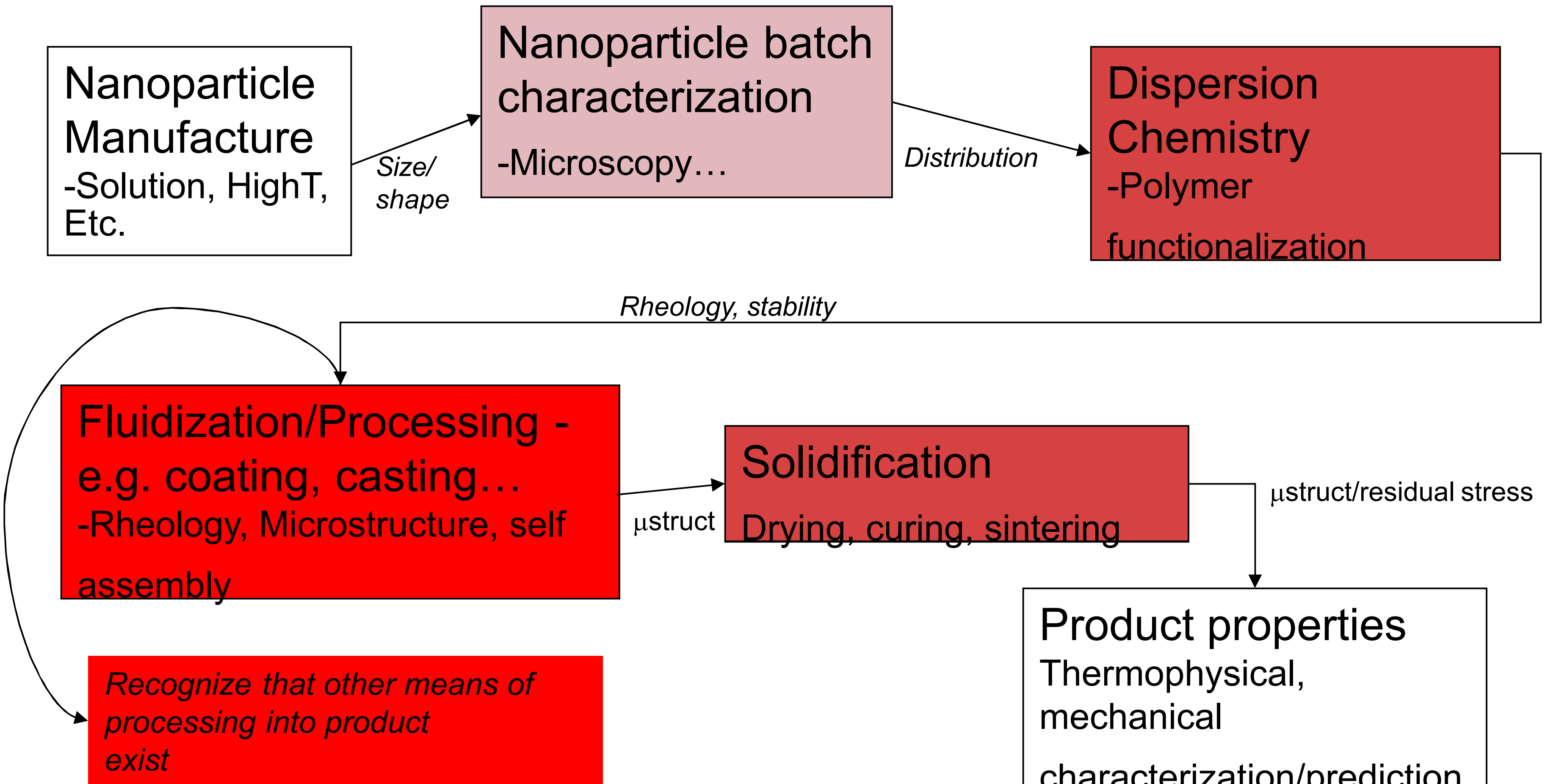
Sandia National Laboratories

Outline

- Motivation/Technology horizon
- Physics and chemistry underpinning flow of ‘concentrated’ nanoparticle dispersions
- Multiscale methods, numerical approaches
- Sample results
- Retrospective and outlook

Rheology, dispersion stability, self organization of ‘dense’ nanoparticle suspensions -- Work in progress!

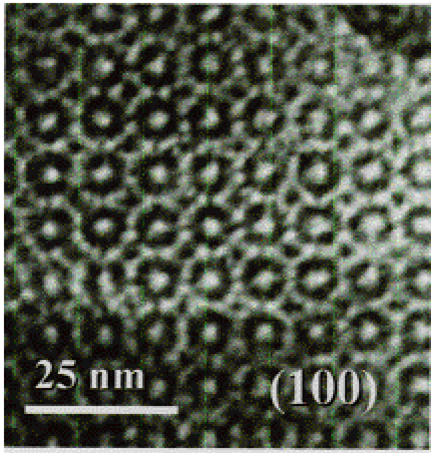
Imbedding Nanoparticles in functional materials



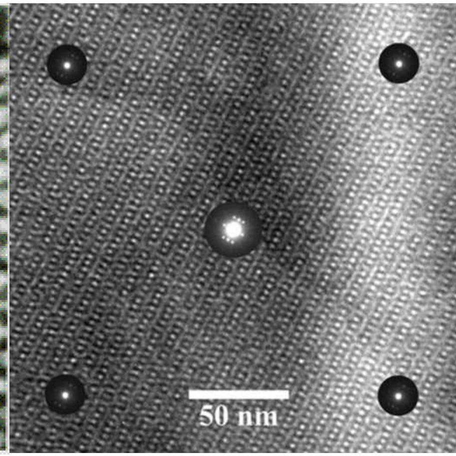
Focus is on Processing Rheology and Microstructure in Bulk and at Surfaces!

Medley of Nanostructures prepared with BES support

Membrane

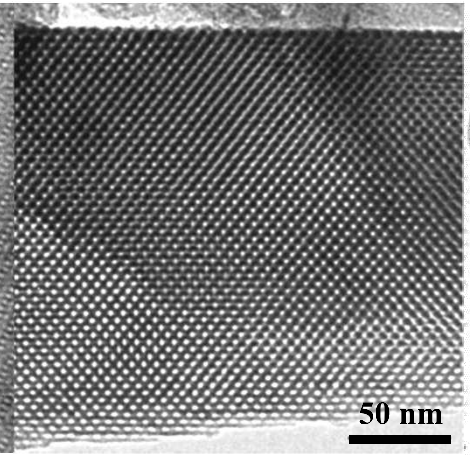


Sensor



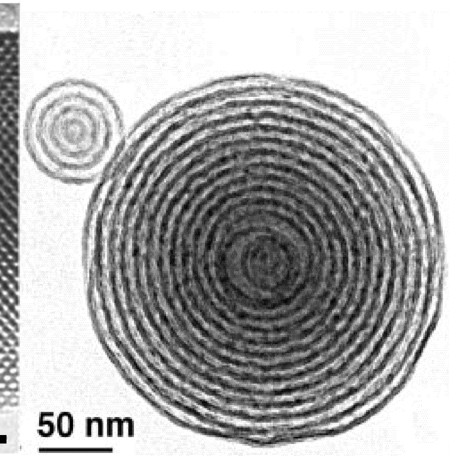
Lu et al., Nature 1997

low k



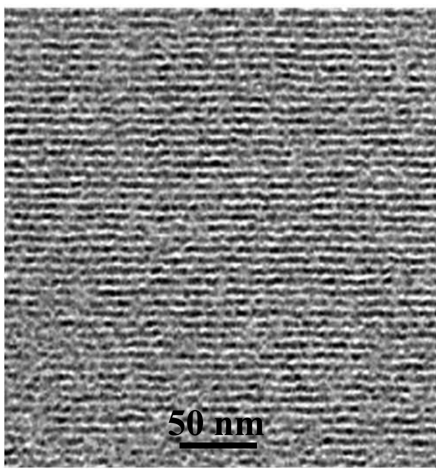
Brinker et al.,
Adv. Mater. 1999

Controlled release



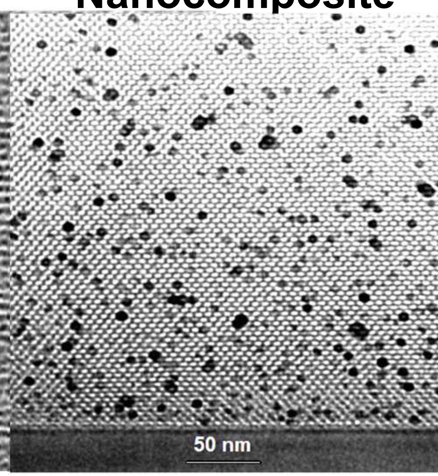
Lu, et al.,
Nature 1999

Sea-Shell



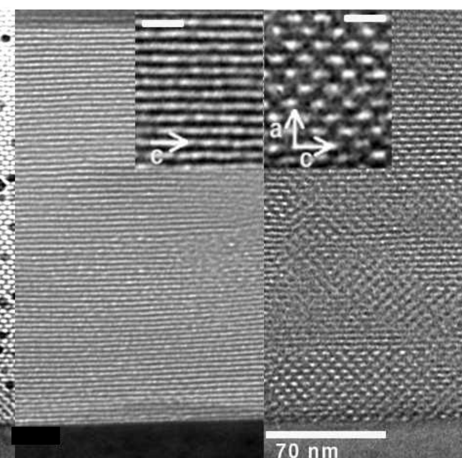
Sellinger et al.,
Nature 1998

Ag/Silica Nanocomposite



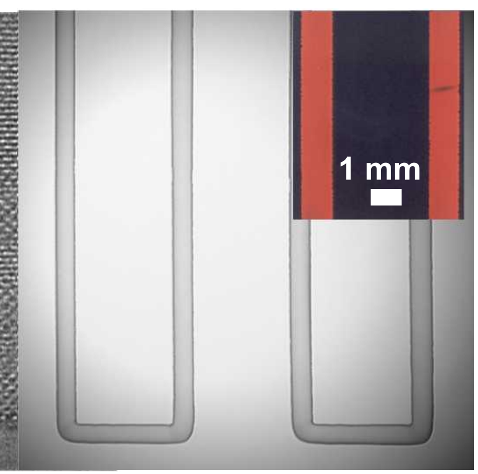
Fan et al.,
Unpublished

Phase Transition



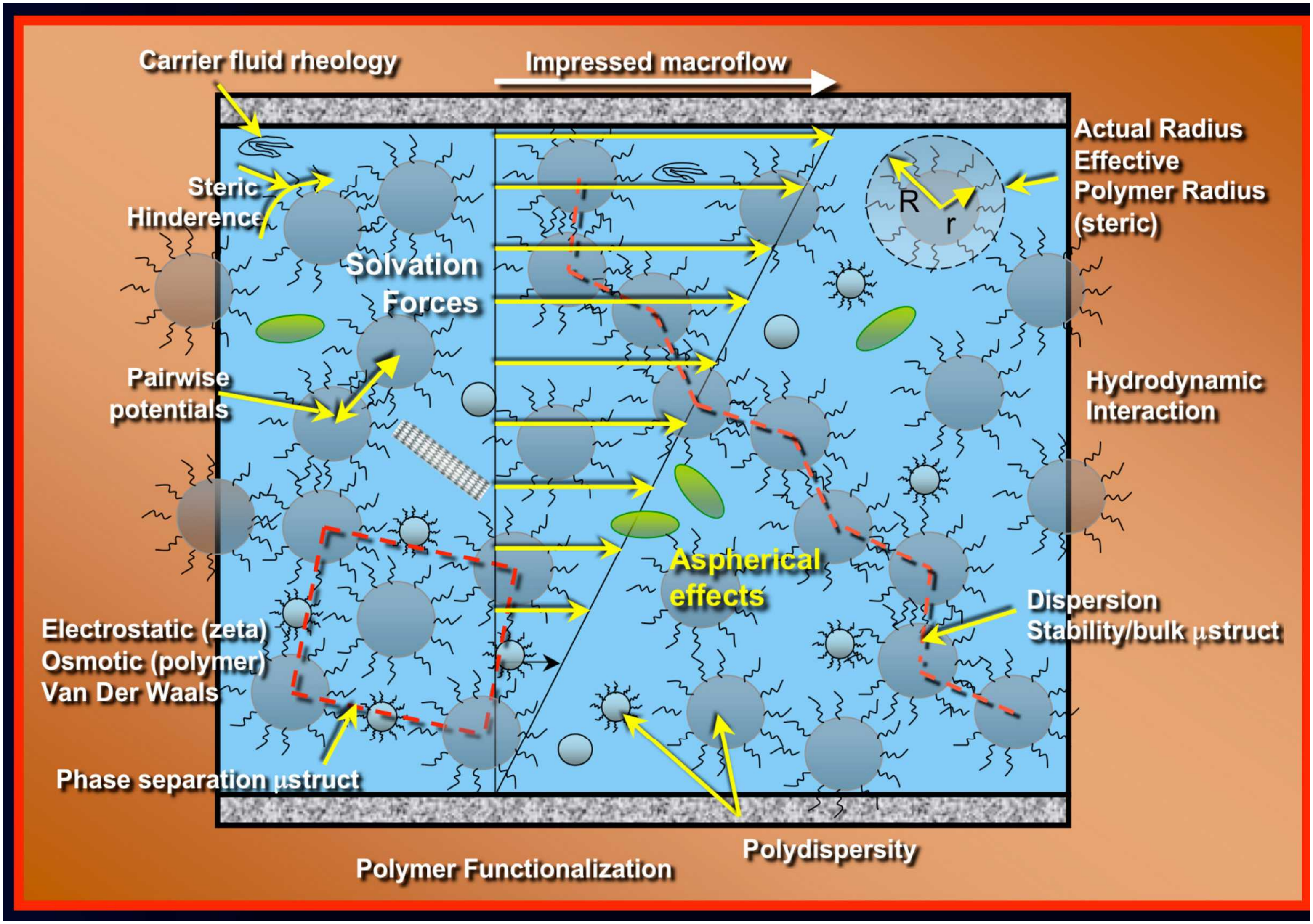
Doshi et al.,
Science 2000

Patterns



Fan et al.,
Nature 2000

Technical Challenges: rich physical phenomena



What effects Computational Requirements?

- Predictive capability aimed at
  - Particles (10 nm-1μm) in water at moderate to high concentrations. Polydisperse but *mainly spherical or near spherical shape*
  - Solvent/suspending fluid is Newtonian (continuum)
  - Physics includes interparticle forces (Static: Van Der Waals, Steric/physical, osmotic, electrostatic, solvation. Dynamic: hydro,Brownian)
  - Phenomenology: Micro/meso mechanics discovery, macro-rheology and viscometric fluid mechanics, stability, surface self assembly/organization
  - Other phenomenology of potential interest: nanoparticle effects on wetting/spreading, product performance.

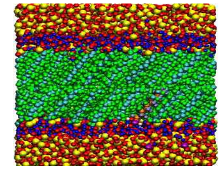
All at intermediate to "high" concentrations, which sets this effort apart….

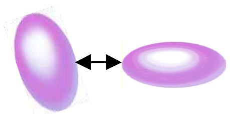
Technical Approach: Integrated Capability

Molecular Dynamics

Molecular scale

nanoseconds
0.1 to 10 nm

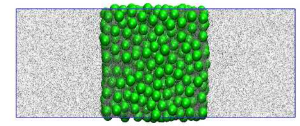




Effective potentials

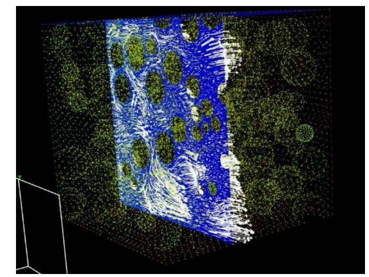
Particle Scale

microseconds
10 to100 nm



“Mesoscale”

milliseconds
100 nm-10 µm

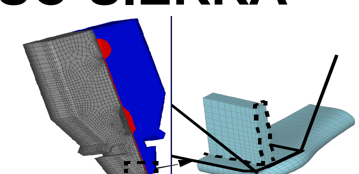


Coupled particle-fluid Interactions:
DEM-NS, SRD, DPD, SD

Constitutive Relations **Micro-structure**

Integrated Modeling and Simulation Tool
Integrating Tools Across Scales
Experimental Validation
Research (Materials/Numerical methods)

FEM, ASC SIERRA APPS:
ARIA,
GOMA

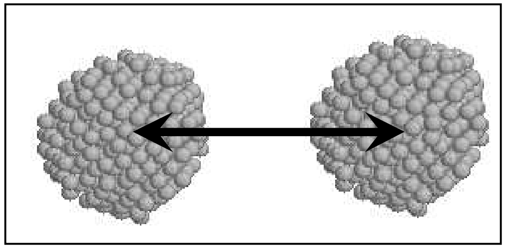


Engineering Scale

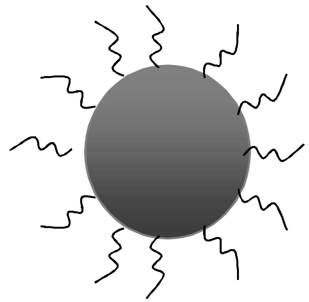
Seconds
mm

About Coarse Graining - What is needed?

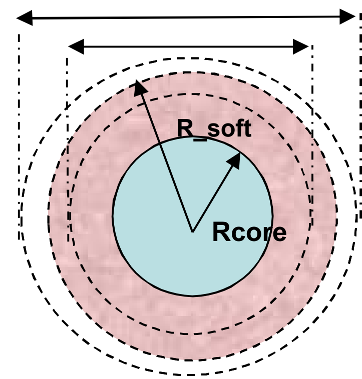
Particle



Integration to Hammaker's Equation and equivalent



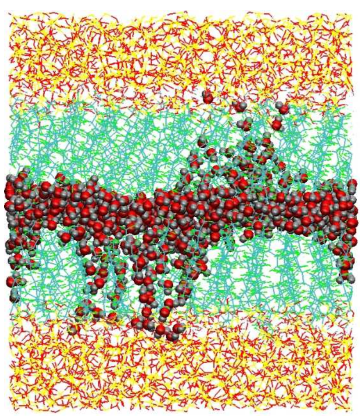
Osmotic and steric/structural representation



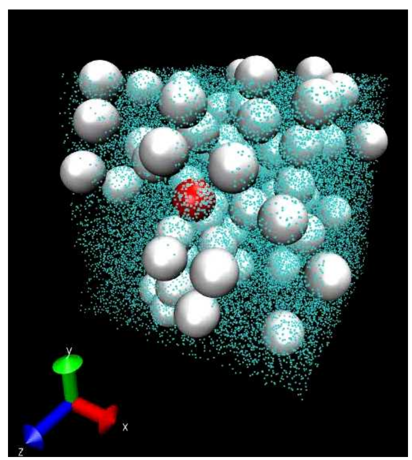
- Computational standoffs
- Porous constants
- Polymer layer parameters
- Structural constants (polymer
- And hard sphere)

Solvent

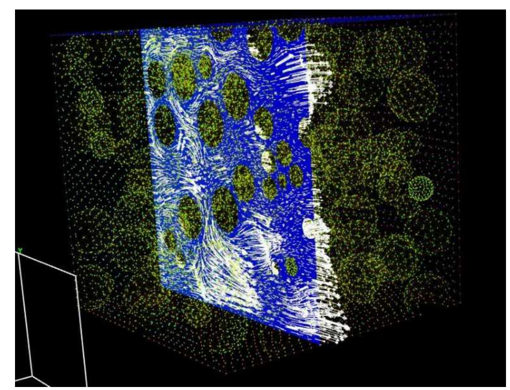
Molecular Dynamics



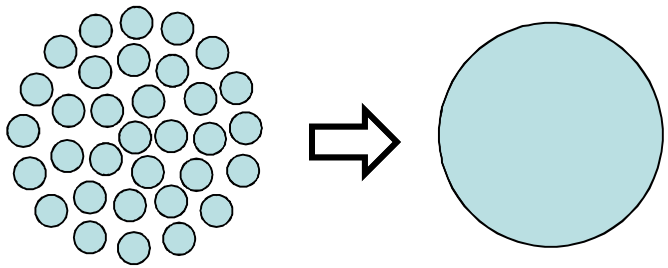
Blobs->SRD/DPD: dual particle approach

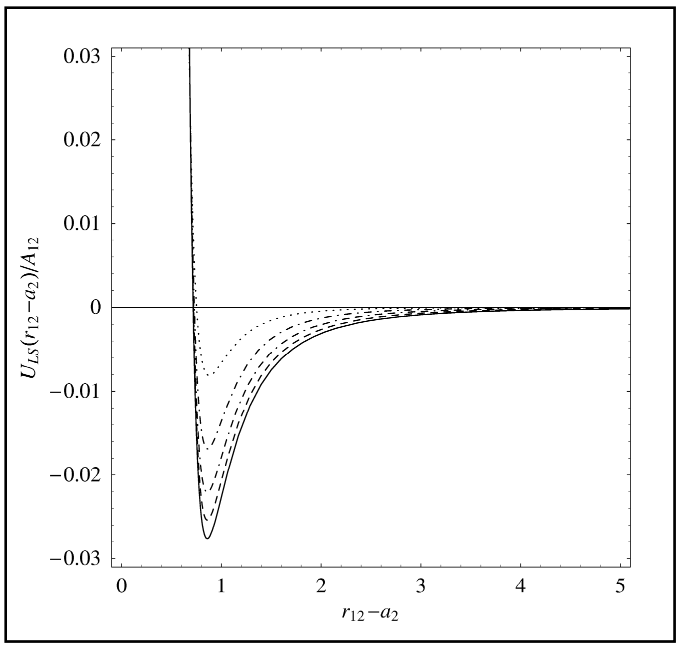


Continuum: FEM, SD



Colloidal Model: First Approach



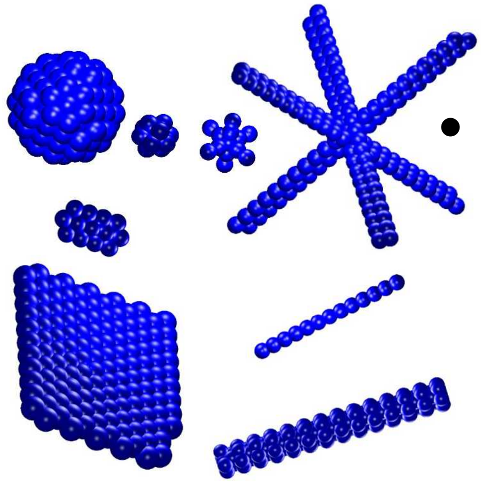


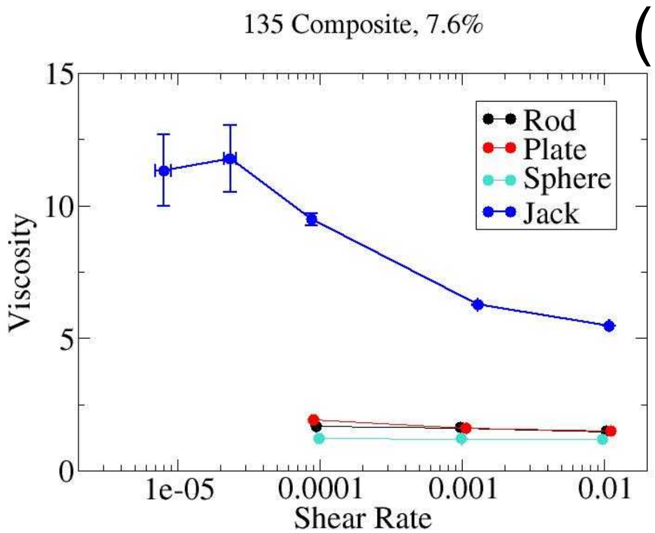
- **Integrated Lennard-Jones potential represents colloidal particle[1]**
  - **Hard spheres are poor model since they phase separate for disparate sizes**
- **Compared to Lennard-Jones - harder at short range but softer at long range**
- **Guarantees long-range interaction between colloidal particles through long-range attractive contribution**
- **Addition of colloid-solvent and solvent-solvent interactions**
- **Hamaker constant A_{ij} represents pairwise interaction strength**

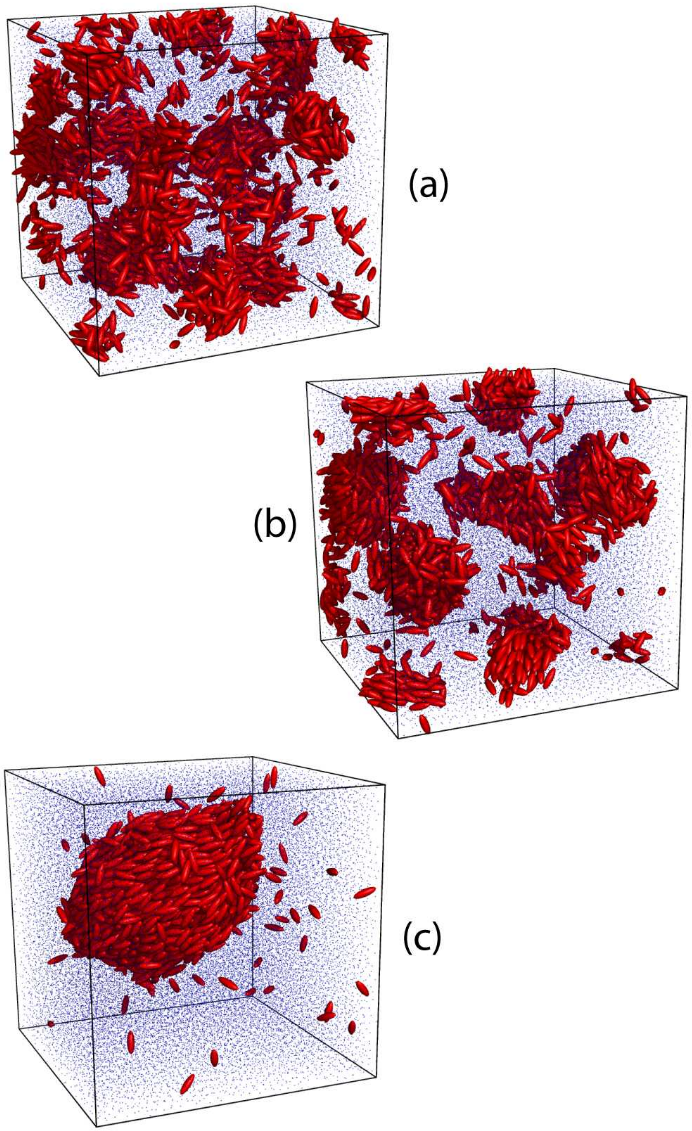
[1]R. Everaers and M.R. Ejtehadi, Phys. Rev. E ***67***, 41710 (2003)

Aspherical Effects

- Composites
- Analytical shapes
  - R. Everaers and M.R. Ejtehadi, PRE ***67***, 41710 (2003)

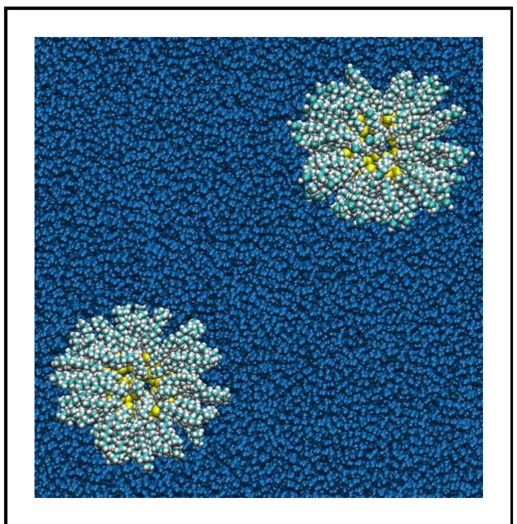




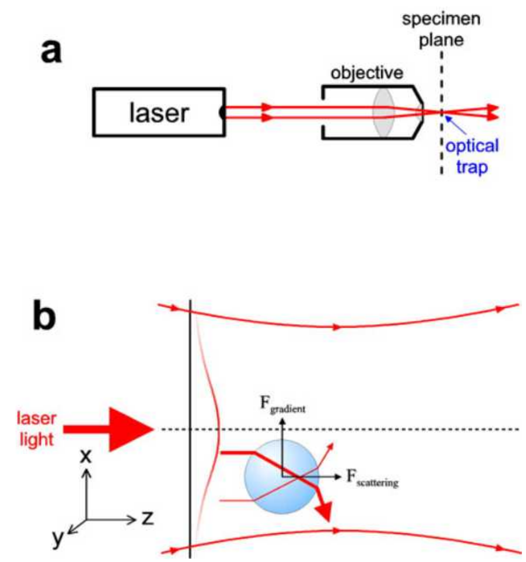


Effective Potential Development

- Molecular dynamics. How small can we go with continuum mechanics principles? Determining interparticle potentials for mesoscale?
- Direct force measurement (IFM, Optical Trapping)



MD of actual Silica/PEO/Water System (Dynamic and Equilibrium)



Optical Tweezers Measurements

Accurate effective pair potentials required for simulations of nanoparticles in suspension

Hydrodynamics and Coupling

- Platforms for development

  LAMMPS, SIERRA, Home-grown
- Suitable flow solvers

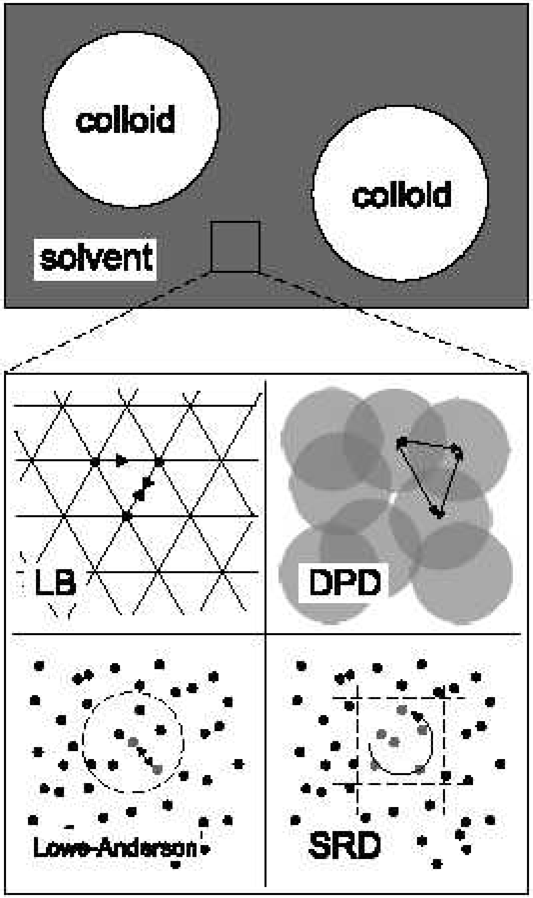
  FEM, BEM, DPD, SRD
- Suitable n-body Newton solvers

  Effective potentials, contact, aspherical

Note that all this has been accomplished for dilute systems, small collections of particles, and with a wider number of candidate specialty techniques

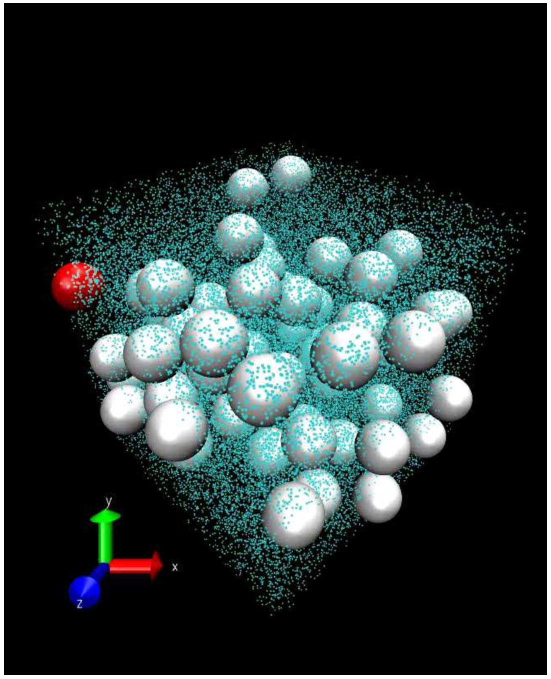
Simulating the Solvent

- Computational cost
  - **Explicit atomistic solvent requires calculation of all pair-wise solvent-solvent/colloid interactions**
    - **typically *many* orders of magnitude more solvent atoms than solute particles**
    - **light, relatively fast dynamics => short timesteps**
  - **Coarse-grain: Average over fast degrees of freedom**
    - **all => Generalized Langevin dynamics of colloids**
    - **some => coarse-grained solvent with reduced # of solvent particles, larger mass, longer timesteps (e.g., softer potentials)**



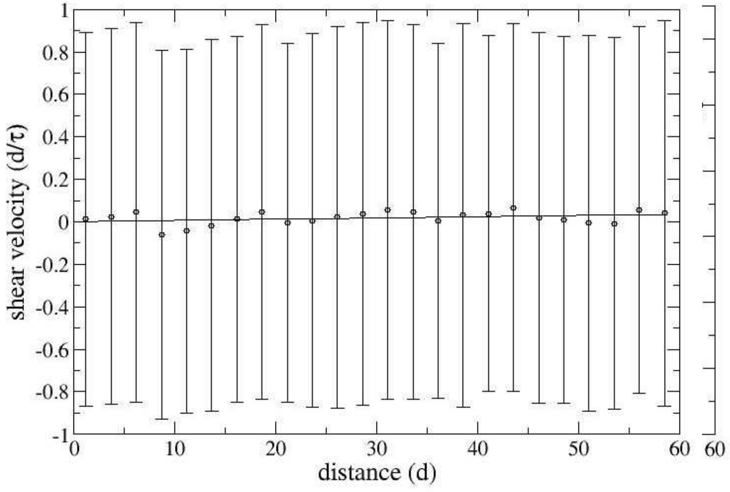
- Multiple "coarse-grained" methods to capture hydrodynamics
  - **MD-like, coarse-grained, "explicit" solvent**
    - **DPD solvent**
    - **SRD solvent treated as massive, ideal fluid, point particles**
  - **NS-based ("continuum") "implicit" solvent**
    - **BD (approximate hydrodynamics – $F_H \sim 6\pi\mu a$)**
    - **SD/BEM (creeping Stokes equations)**
    - **LB**
    - **Solve full continuum Navier-Stokes equations numerically (e.g., FEM)**

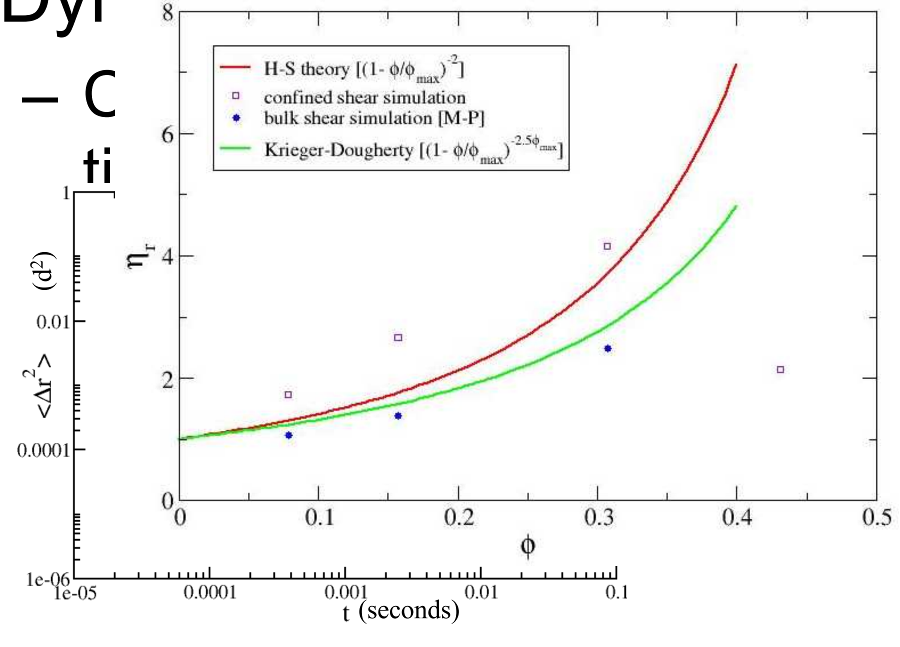
SRD-Colloid Coupling Verification



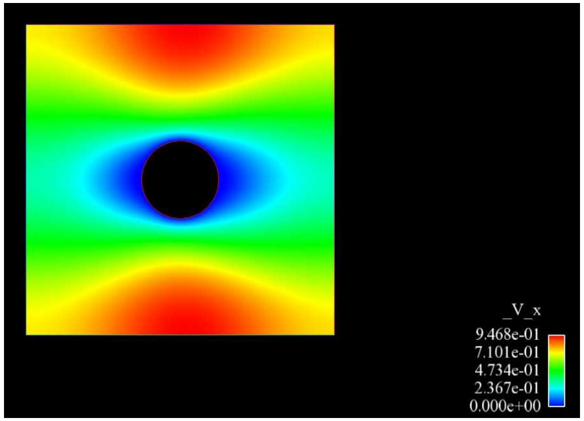
- Computationally inexpensive but
  - Newtonian
  - Pseudo-compressible, Ma_{srd} > Ma_{actual}
  - Re_{srd} > Re_{actual}, etc.
- Dynamic Similarity
  - C

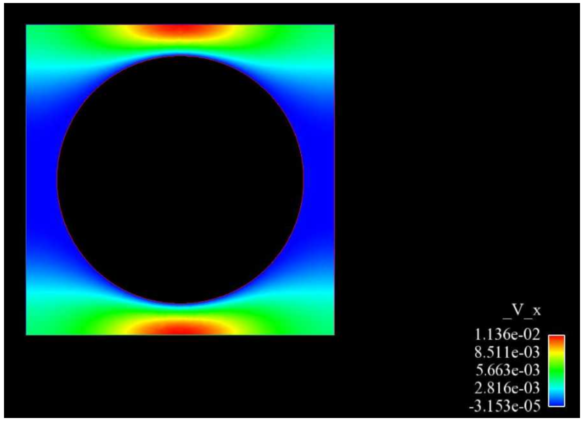
ti

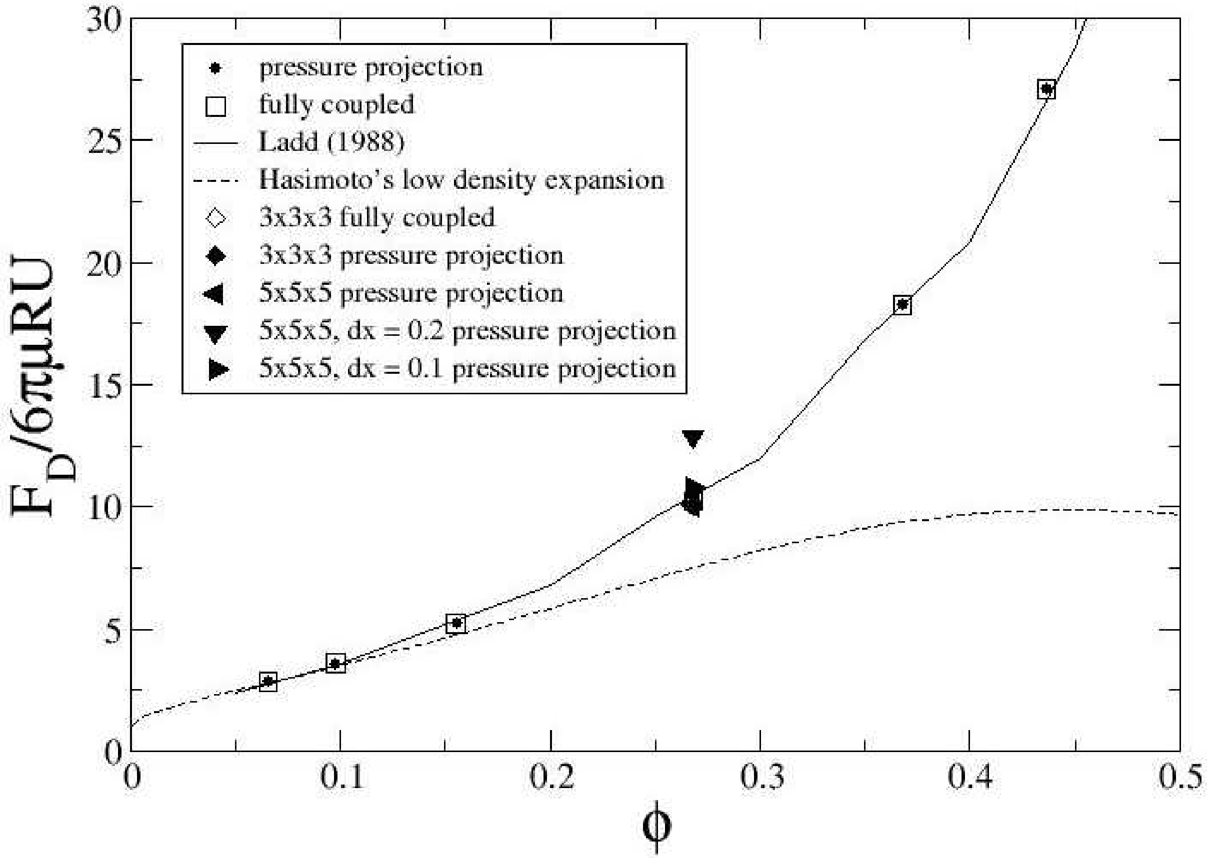




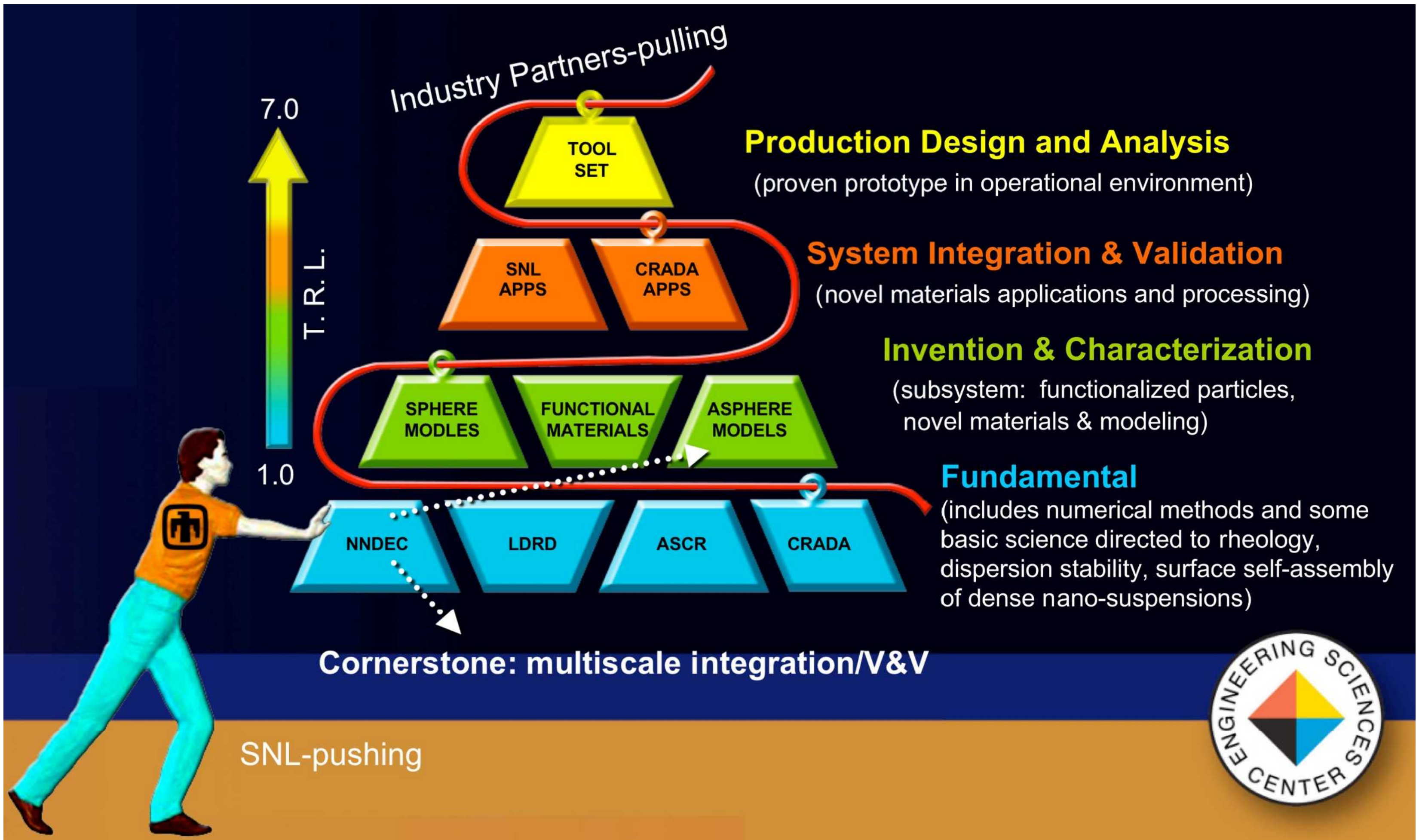
Continuum FEM Accuracy: Translational Friction Coefficient in Stokes Flow







Nanoparticle Suspension Rheology: Predictive Manufacturing Capability



Retrospective and Outlook

- **Nanostructured Materials achieved through suspension based processing of nanoparticles requires understanding of**
  - ***-bulk rheology***
  - ***-dispersion stability***
  - ***-induced assembly and structure from volume reduction***

- **We are advancing a mod/sim platform to meet these needs which targets a scale that bridges between the molecular regime and the engineering regime**

- **Our vision is a computational platform to shorten the experimental/test cycle time for designing nanocomposite materials.**

Acknowledgements

- Gary Grest
- Matt Lane
- Matt Petersen
- Ahmed Ismail
- Steve Plimpton
- Mike Brown