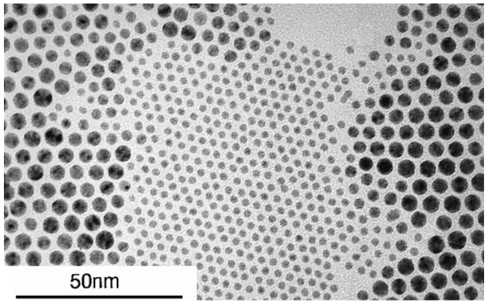
SAND2006-6186C

For presentation at the 2006 Multiscale and Functionally Graded Materials Conference, 15-18 October 2006, Honolulu, Hawaii.

Flow of concentrated, nanoparticle suspension: Multiscale modeling challenges



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Outline

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

Rheology, dispersion stability, surface self organization of 'dense' nanoparticle suspensions -- Work in progress!

Ongoing Projects

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Semiconductor-Based Nanophosphors for Scintillation Applications

Dielectric Modification of Polymers Using Nanoparticles

Integrated Sensor Is Structure (ISIS) Critical Technology Development
(subcontractor for Lockheed-Martin)

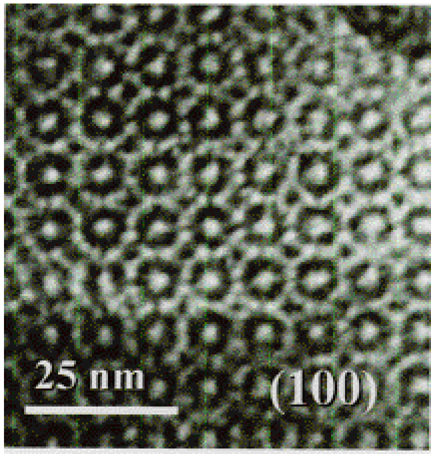
Design of Novel Nano-Catalysts for Improved Hydrogen Production
(DOE – Basic Energy Science)

Process Control ←→ Functional Material

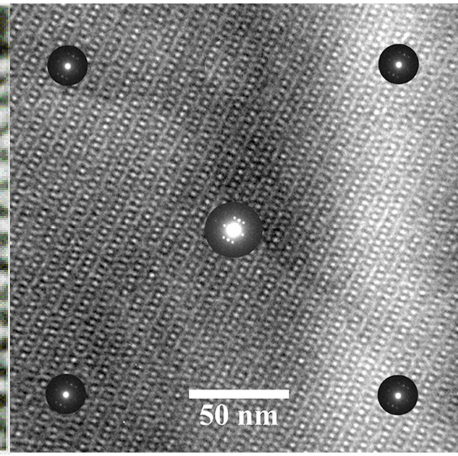
Technical Advances & Patents:
Nanosized Materials for Radiation Detection and Scintillation, SD-10005 (2005).
Dielectric Modification of Polymers Using Nanoparticles, SD-7958 (2005).
Synthesis of Aluminum and Boron Nanoclusters by Inverse Micelle and Thermal Decomposition Methods, SD-7833 (2004).
Encapsulation of Nanoparticles Using Organic Glasses, SD-7759 (2004). **Patent applied for**.
Nanocluster-Based White Light Emitting Material Employing Surface Tuning, SD-7653 (2004). **Patent applied for**.

Medley of Nanostructures prepared with BES support

Membrane

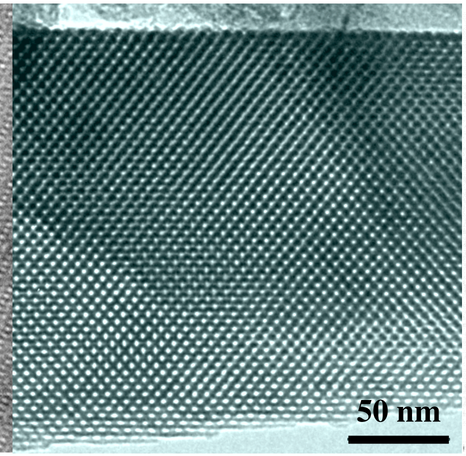


Sensor



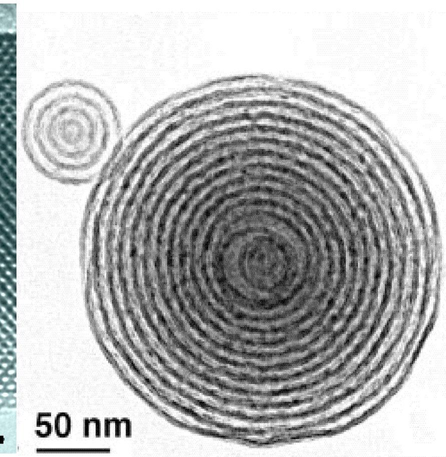
Lu et al., Nature 1997

low k



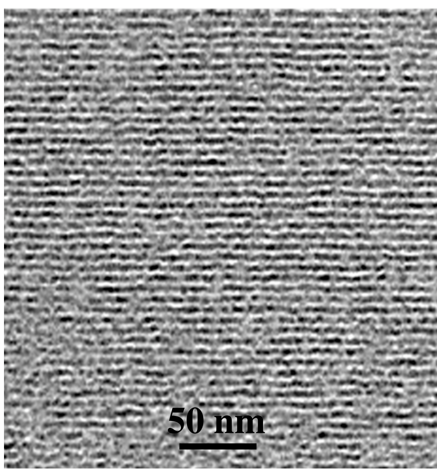
Brinker et al.,
Adv. Mater. 1999

Controlled release



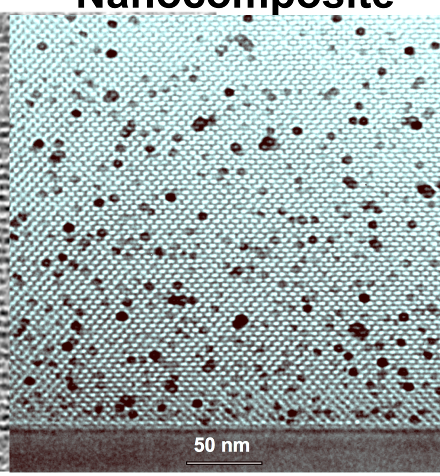
Lu, et al.,
Nature 1999

Sea-Shell



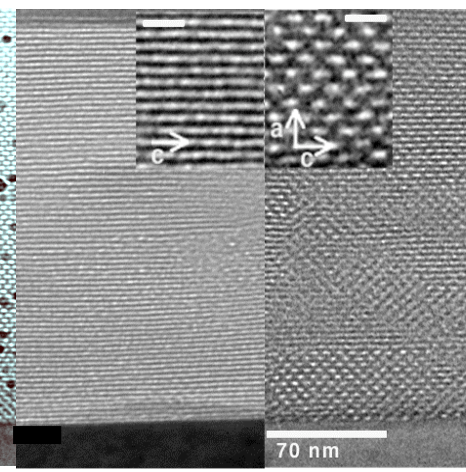
Sellinger et al.,
Nature 1998

Ag/Silica Nanocomposite



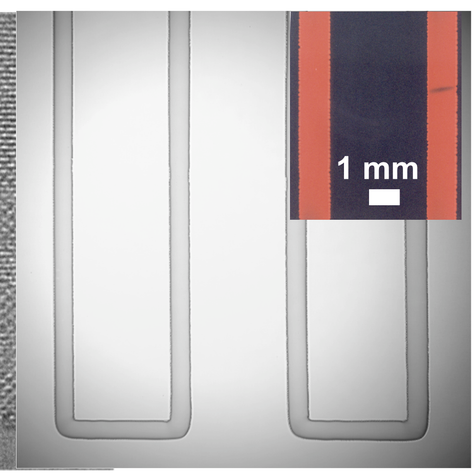
Fan et al.,
Unpublished

Phase Transition



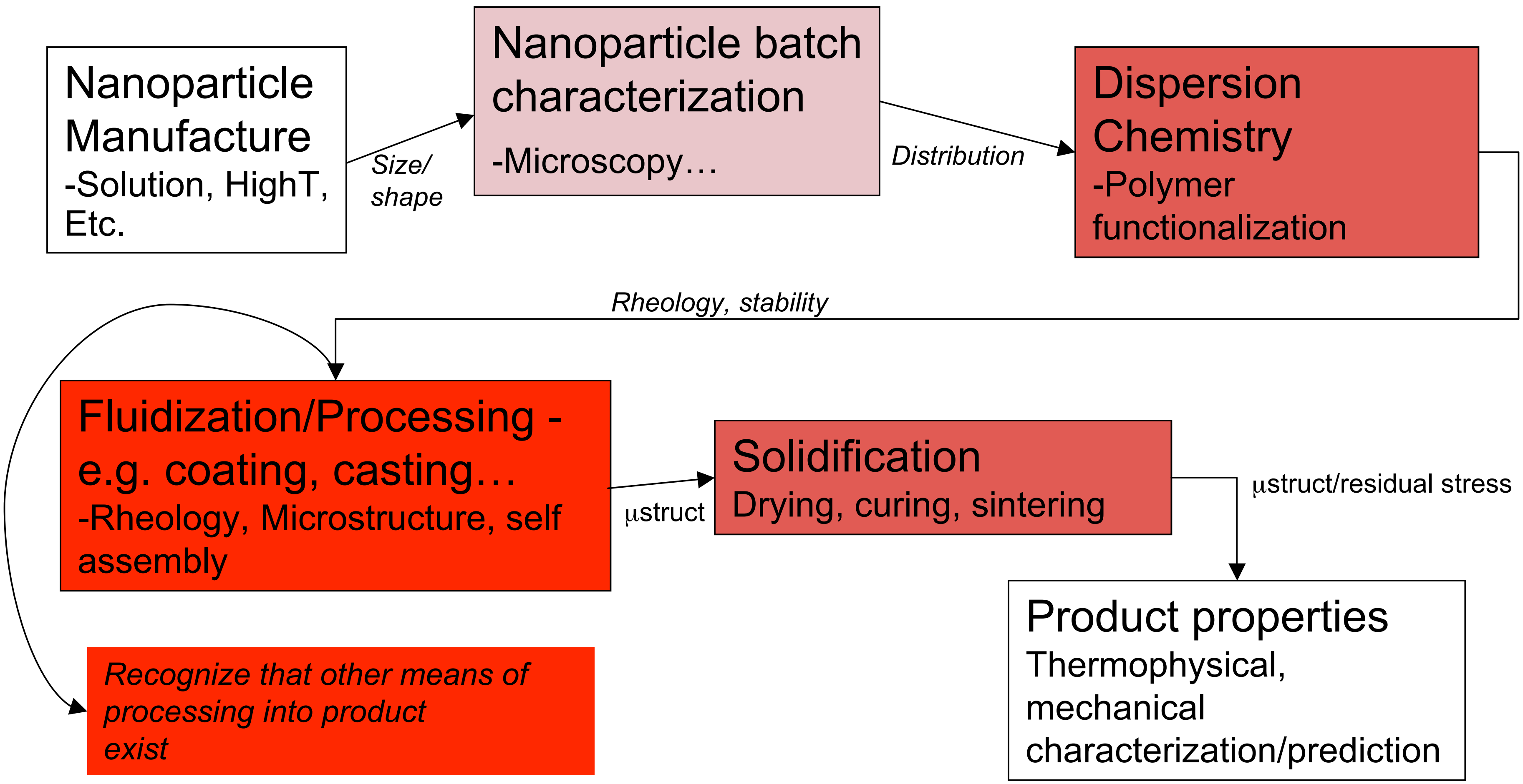
Doshi et al.,
Science 2000

Patterns



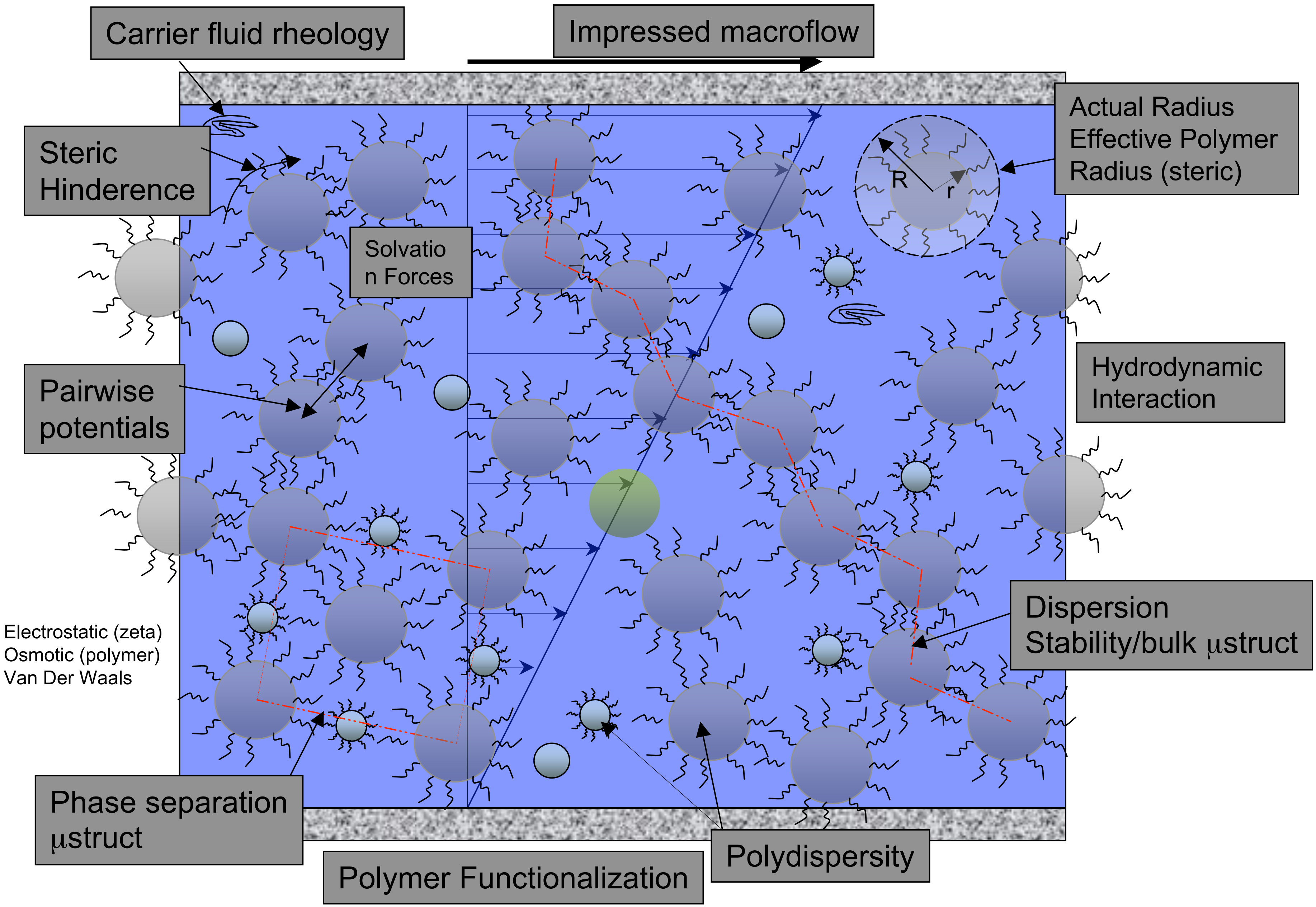
Fan et al.,
Nature 2000

Imbedding Nanoparticles in functional materials



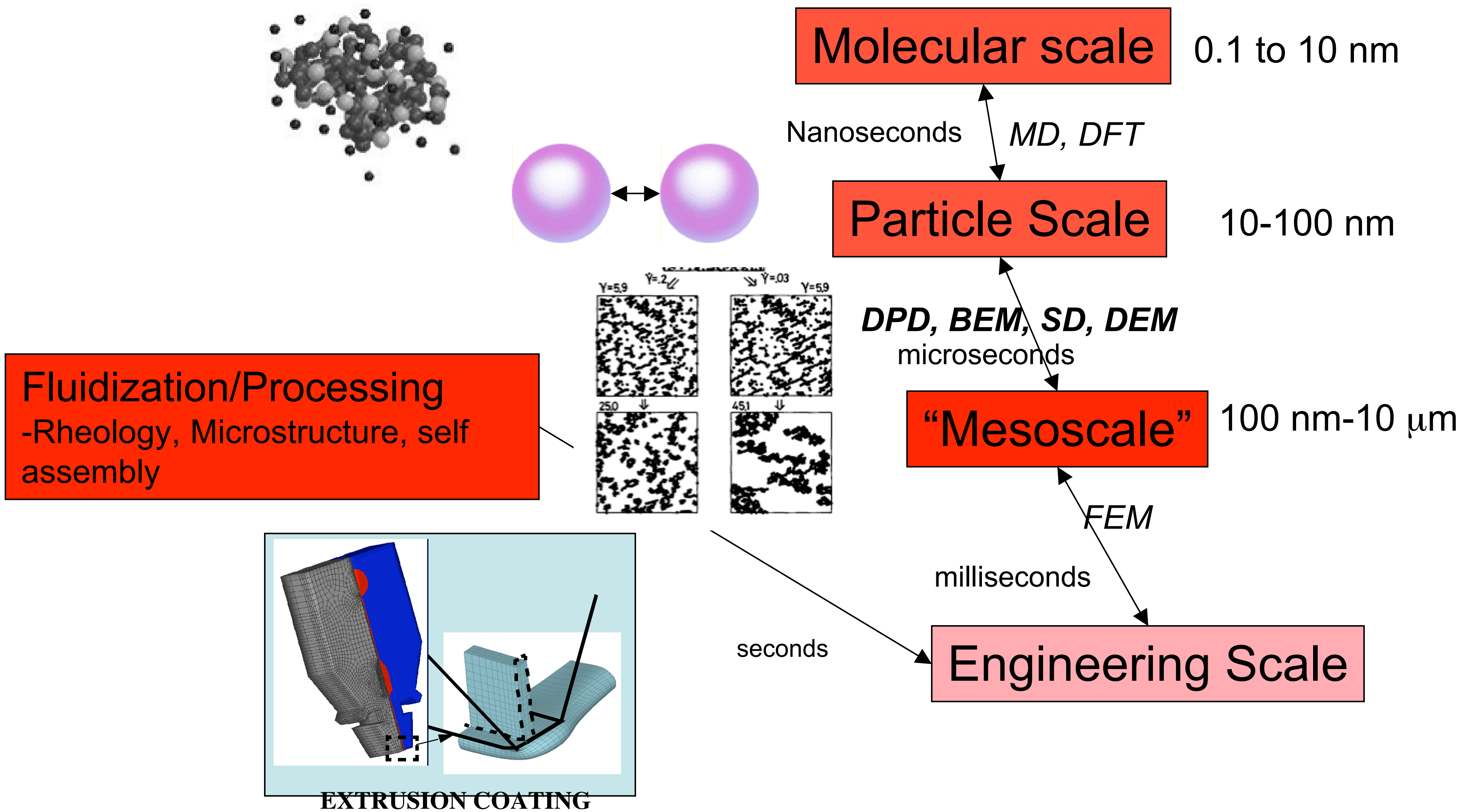
Focus is on Processing Rheology and Microstructure in Bulk and at Surfaces!

NANOPARTICLE SUSPENSIONS/DISPERSIONS GOVERNED BY FORCES, RICH IN PHENOMENA



Nanoparticle Suspensions -

Bridging Length and Time scales



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….

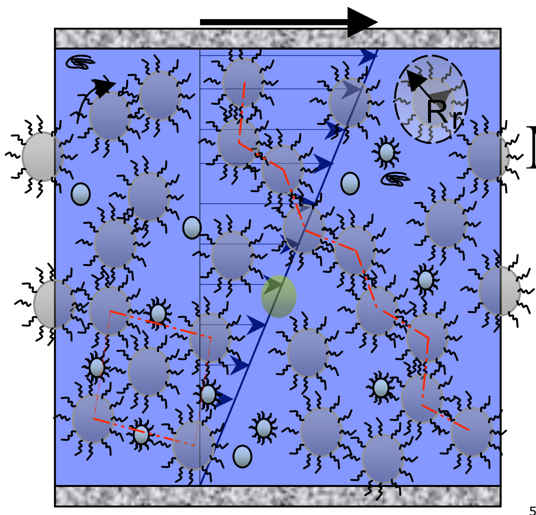
Method				
Particle	Flow	Coupling	Pros	Cons
DEM (Coarse-grained MD, CGMD)	Pair-drag model	Just another force on DEM	Simple and accurate for some Concentrated sys	No long-range hydro.
DEM (CGMD)	FEM/Pseudo-spectral	Imbedded interface (Lagrange Multipliers)	•Independent solvers readily available. •Two-way coupled. •Most general	•Expense? •Contact pathology •Subgrid-models for contact
DEM (CGMD)	Stocastic Rotation Dynamics (similar to LB)	Dual particle weighting	Good for Pe = (O) 1 Manage to keep depletion forces at bay.	Expensive for small Pe (<<1) for particle Inefficient for Pe >>1
DEM (CGMD)	BEM	Fully integrated	•Gridless for fluid •Non-spherical particles •Accurate for fluids	•Noncontinuum subgrid models •Newtonian •Expense
DEM (CGMD)	Stokesian Dynamics	Fully integrated	•Gridless for fluid •Readily available prototypes	•Spherical particles •Newtonian
DSMC	DSMC/DPD	Fully integrated	•Elegant and efficient if underlying physics models exist	•Inefficient for long time scales •Depletion forces

Discrete element modeling, Particle Potentials and Numerics

- N-Body Solver
- Parallel architectures
- Contact
- Issues:
  - Effective potentials couched in h rather than r (made necessary by aspherics and lubrication forces and surface effects)
  - Instabilities and standoff in near-contact and contact conditions

Effective Potentials

- Colloidal-level coarsening -- Use MD Code LAMMPS and build in colloidal forces, rotational DOFS, Soft contact



$$M(dr_i/dt) = \Sigma F_i \Leftarrow$$

$$F = f(\delta/d)(k_n \delta n_{ij} - m_{eff}\gamma_n v_n) + f(\delta/d)(-k_t \delta \Delta s_{ij} - m_{eff}\gamma_t v_t)$$ Hertzian/Hookean

$$U = -\frac{A_H}{6}\left[\frac{2}{(s^2-4)} + \frac{2}{s^2} + \log\left(\frac{s^2-4}{s^2}\right)\right]$$ Van der Waals

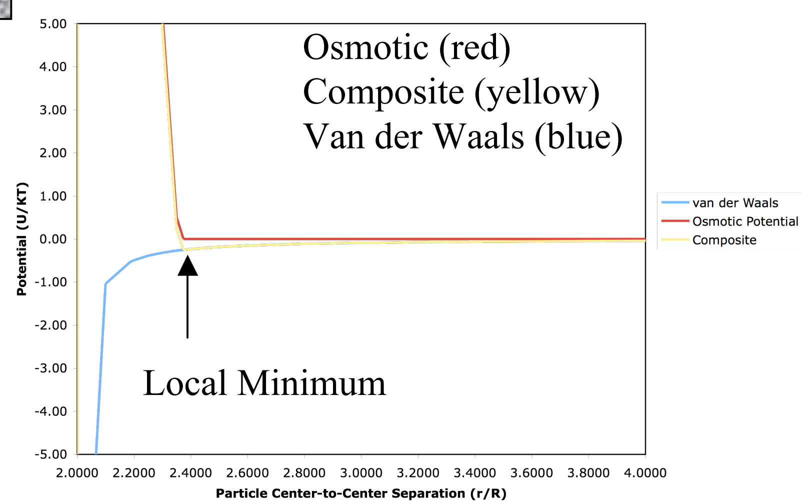
$+$

$$U = \frac{4\pi a_s kT}{\upsilon_1}(\bar{\phi}_2^a)^2\left(\frac{1}{2}-\chi\right)\left(\delta - \frac{h}{2}\right)^2$$ Osmotic

$$\langle F_B \rangle$$ Brownian

$$F = (\vec{v}_{rel}, \vec{r})\vec{r}\left[\frac{6\pi r_{avg}^2}{r - r_1 - r_2}\right]$$ Short-range Hydrodynamic

Interparticle Potentials

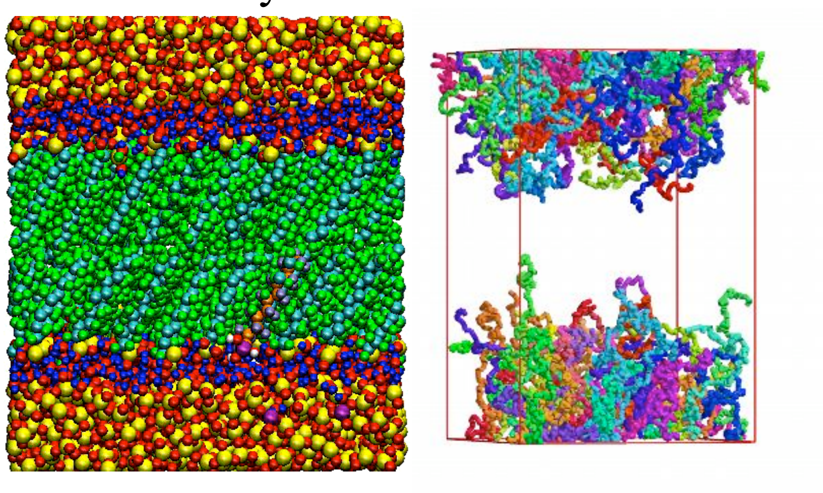


- *Also plans for Metropolis MC code with same inputs for equilibrium stability prediction*

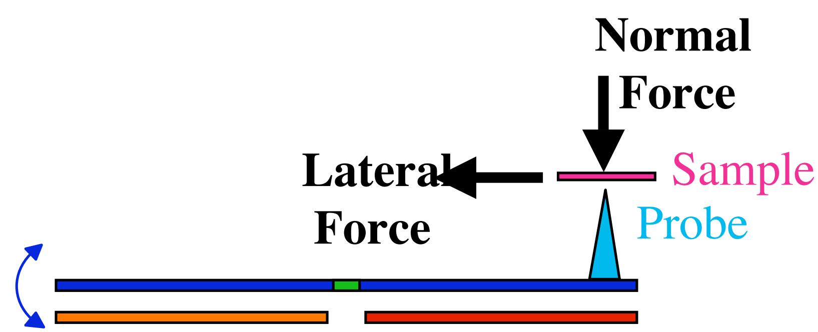
Effective Potential Development

- Molecular dynamics (polymer, solvent, particle) in shear. How small can we go with continuum mechanics principles?

Alkylsilane SAMs



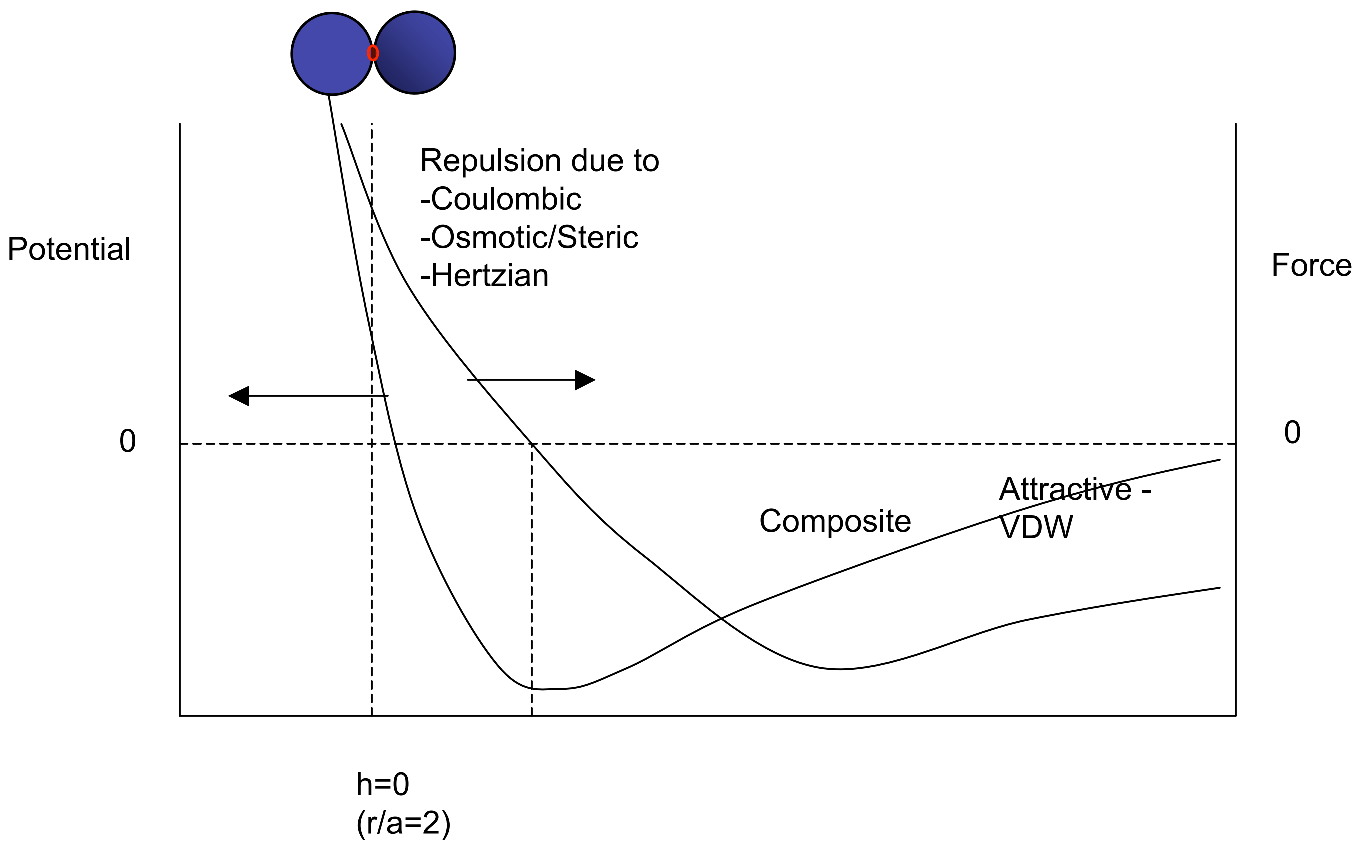
Atomistics/MD



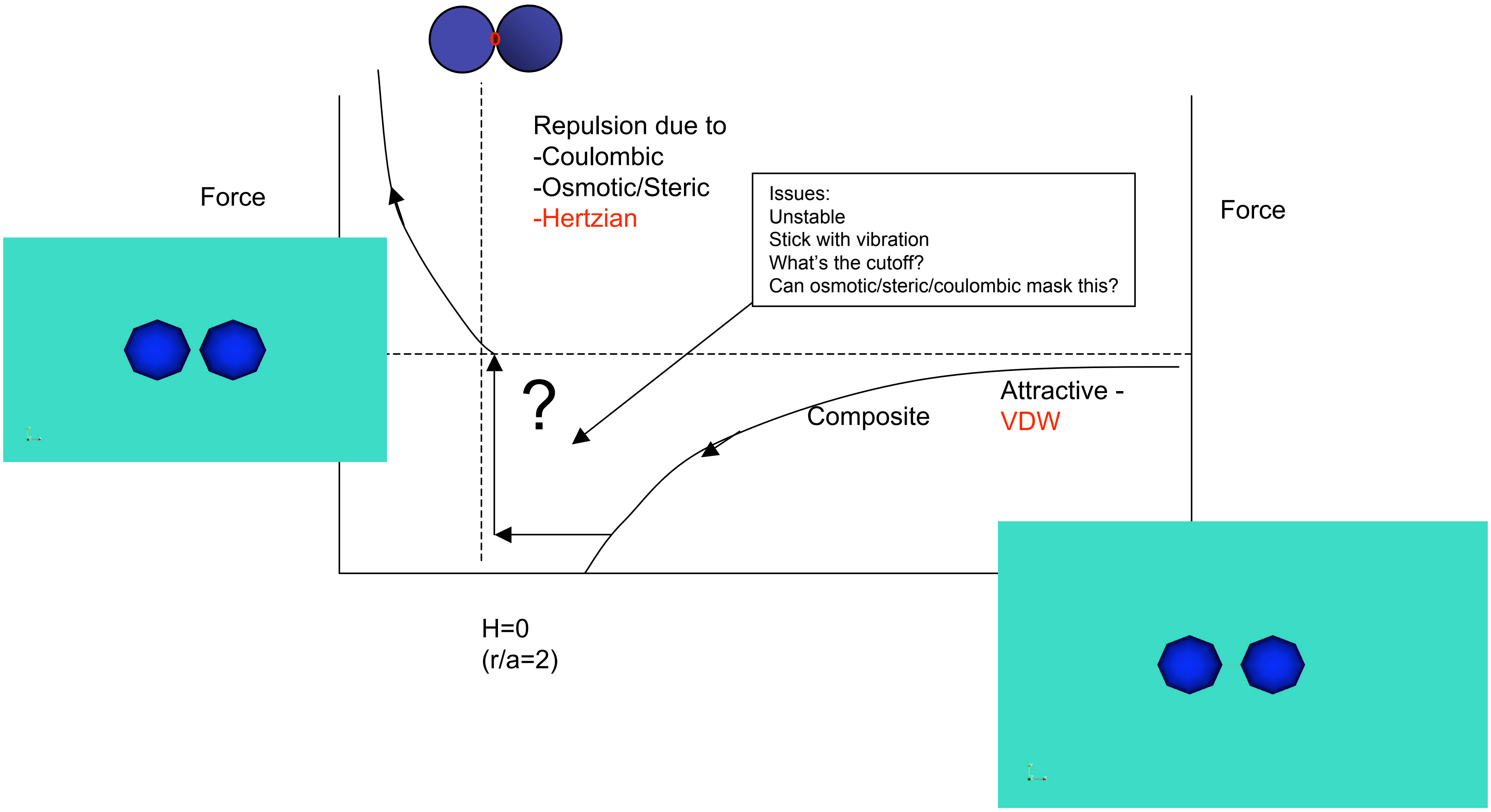
IFM Measurements

Accurate effective pair potentials required for simulations of nanoparticles in suspension

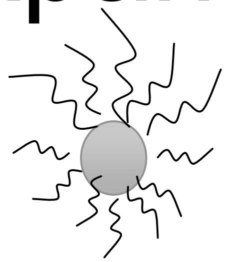
Effective potentials/forces at near contact and contact



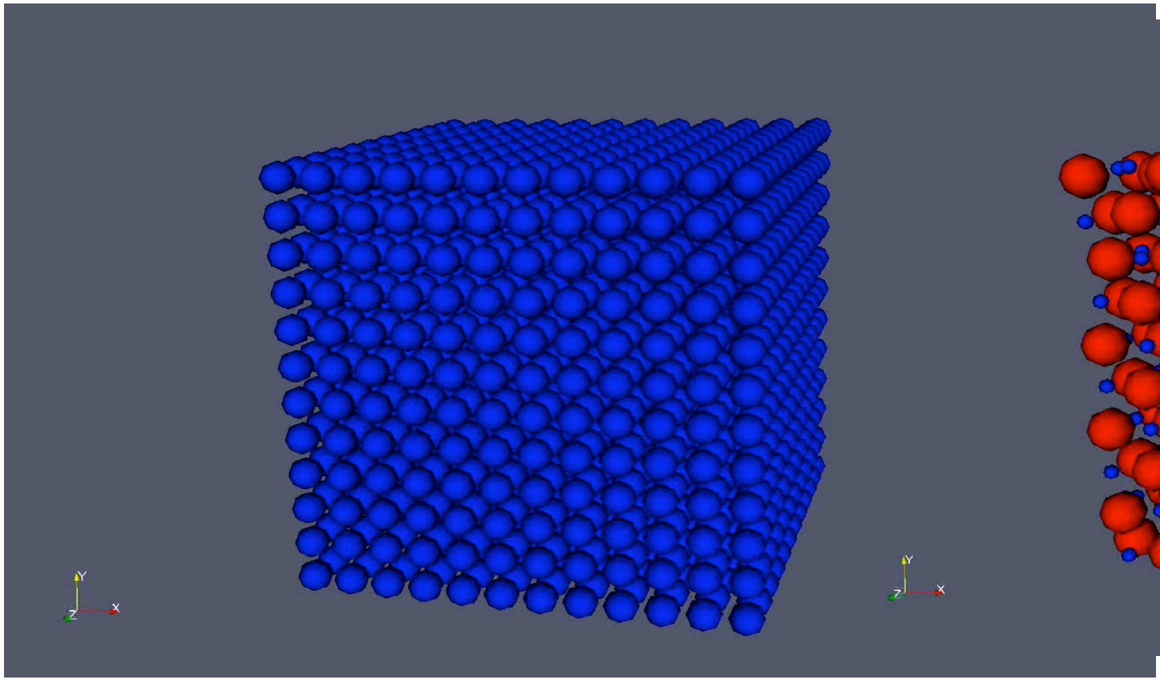
Effective potentials/forces at near contact and contact

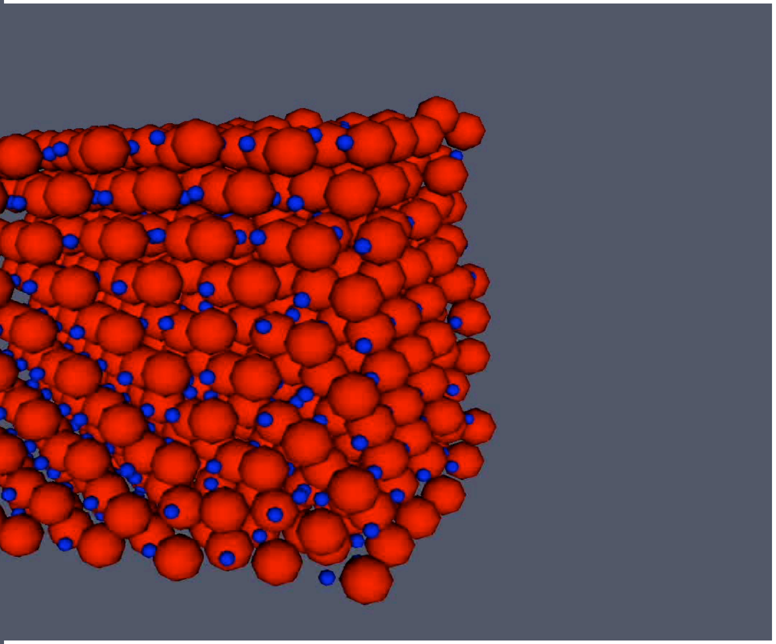


Osmotic/VDW- Elastic Expansion (Gold/Thiol)

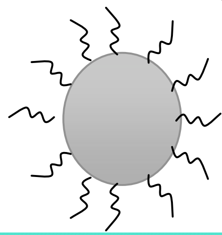


Show potential curves here

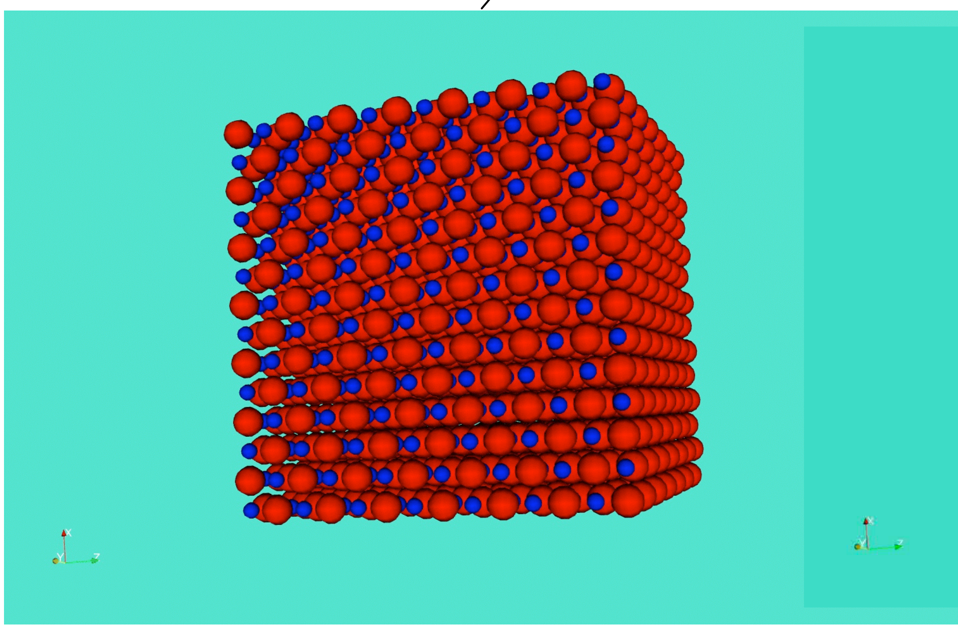


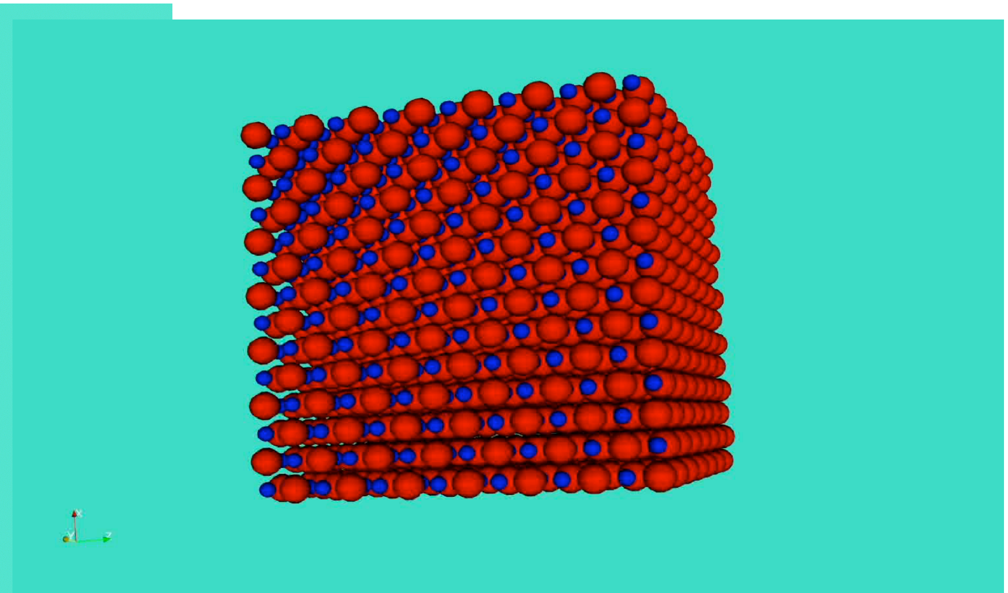


Brownian/VDW/Hertzian (LS Silicate)



Initial Vol Frac = 0.4. Show potential curves here

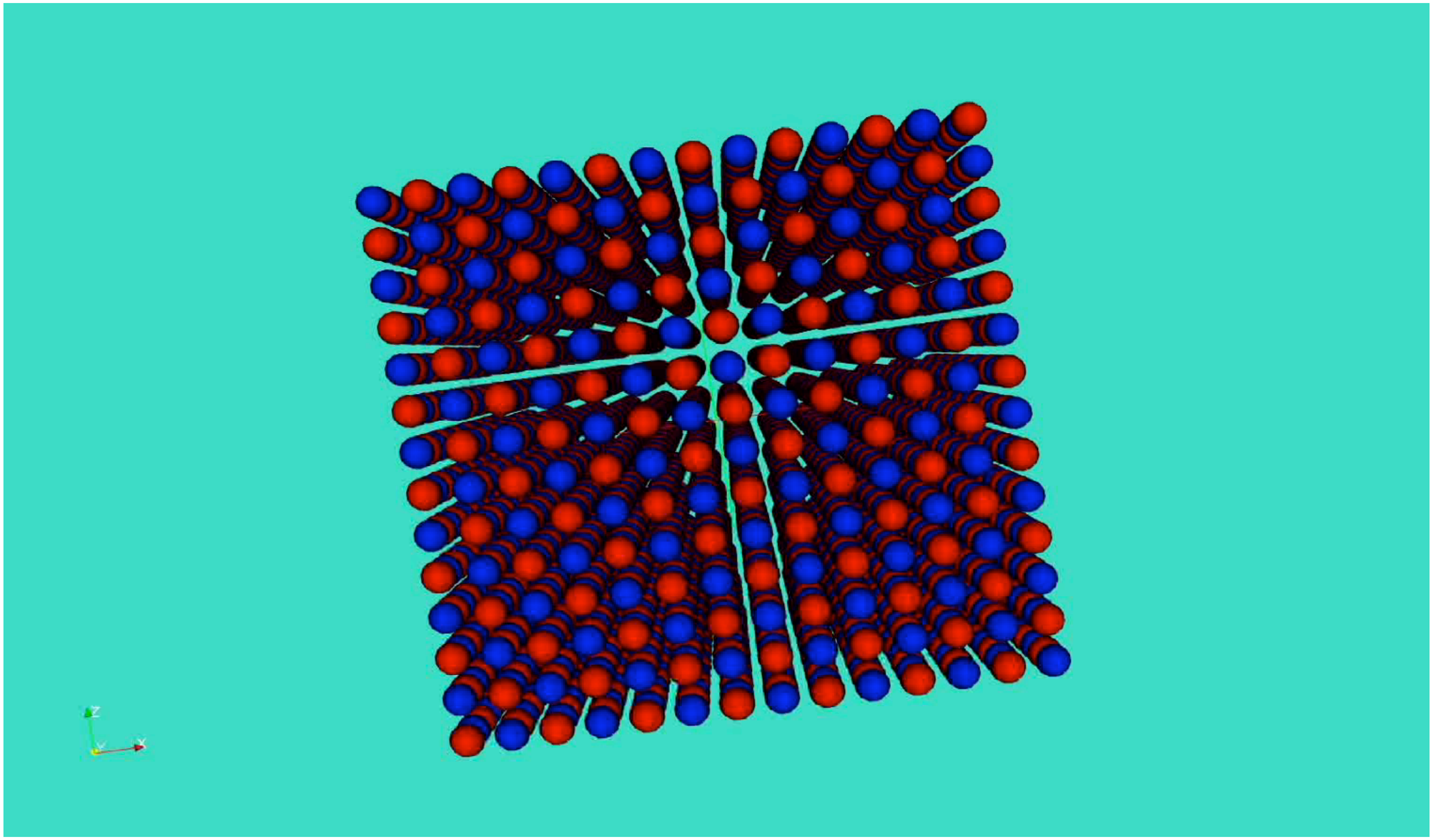




Small particles - Van Der Waals

All particles - Brownian, Hertzian

Brownian/VDW/Hertzian (LS Silicate) - All particles



Issue 1: Hydrodynamics and Coupling

- Platforms for development

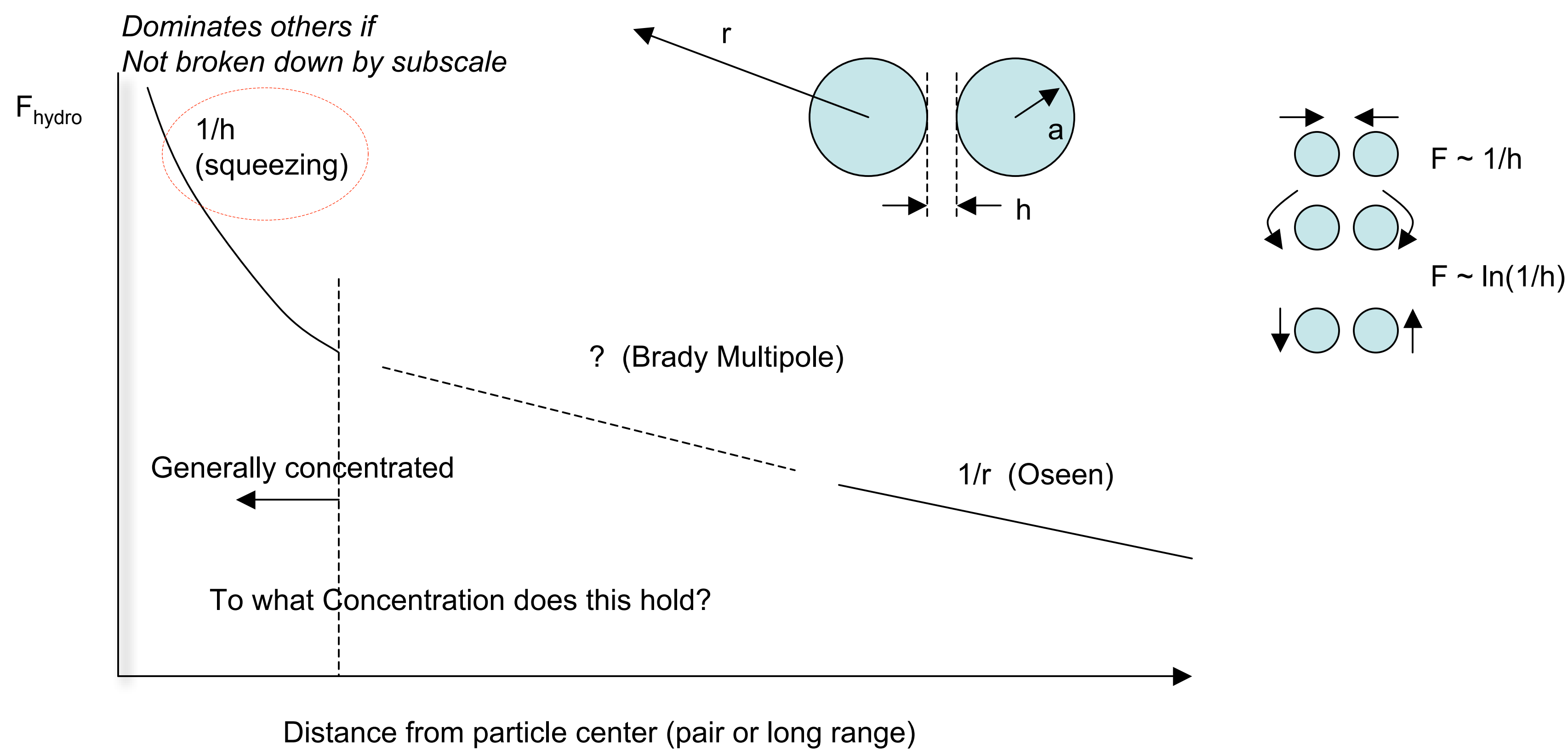
  LAMMPS, SIERRA, Home-grown
- Suitable flow solvers

  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

Hydrodynamic Forces: Pair-drag models (region of applicability)



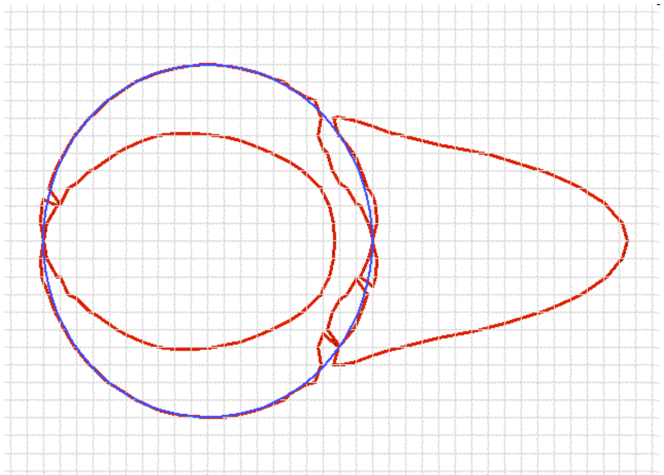
Nanoparticle Flow, Ordering and Self-Assembly

- Current Work/Progress - FY06
  - Coupled Flow/DEM Solver

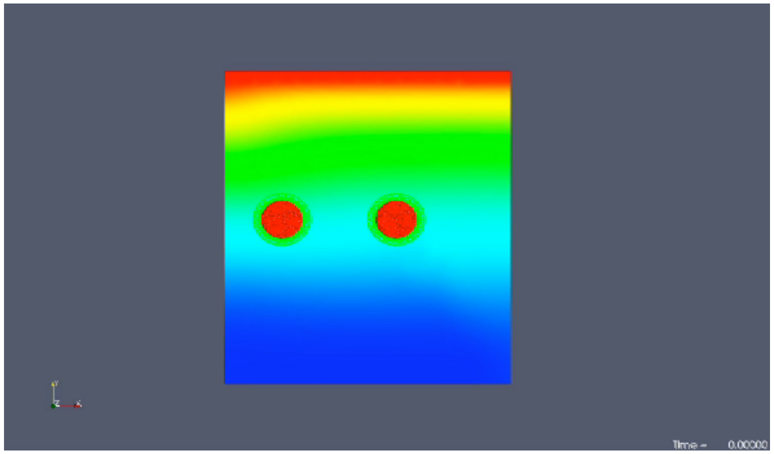
    LAMMPS for particle mechanics

    +

    BEM/FEM/PSFEM flow solver



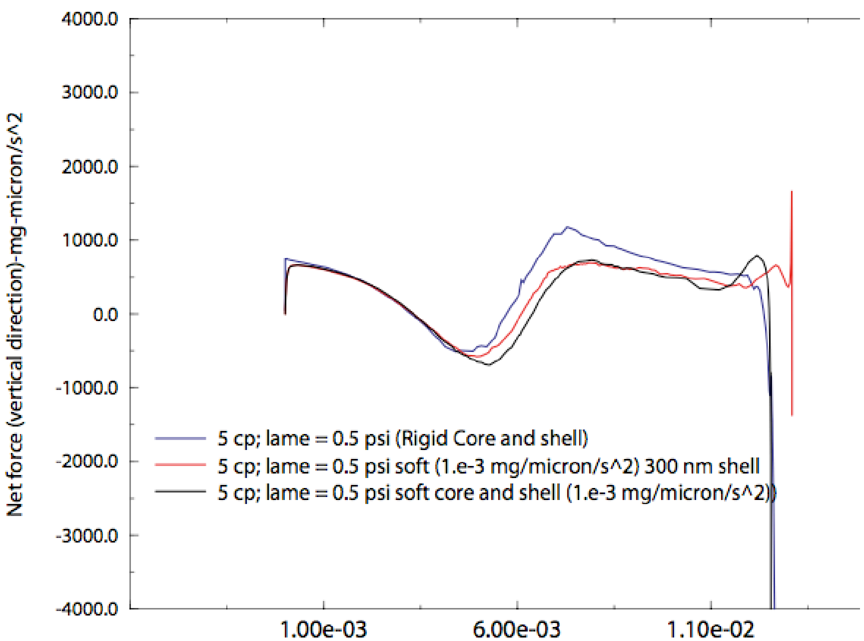
Imbedded Interface Methods - e.g. DLM
(Prototyping now with a PS-FEM code)

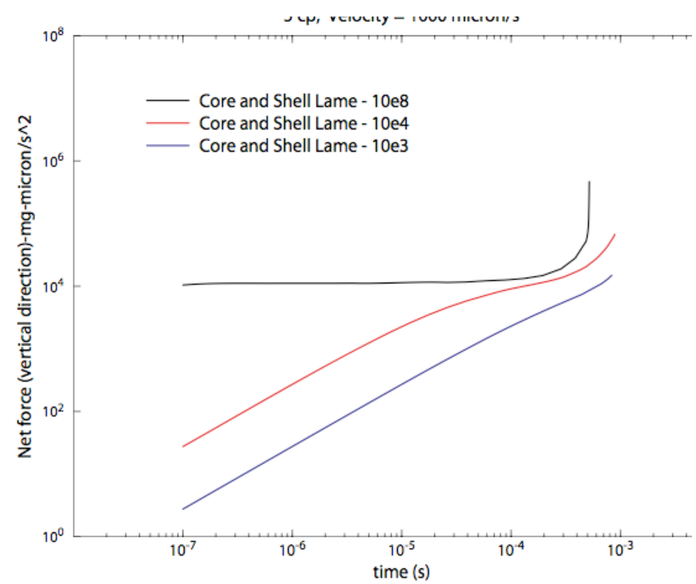


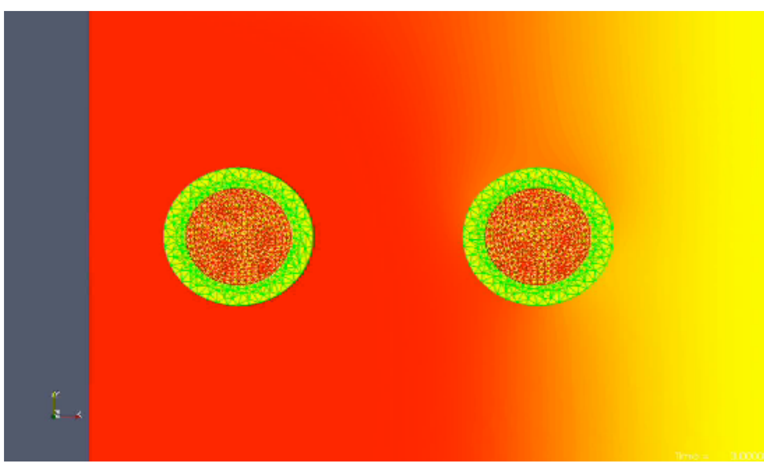
Overset Grid Methods - e.g. DLM
(Prototyping now with a FEM code)

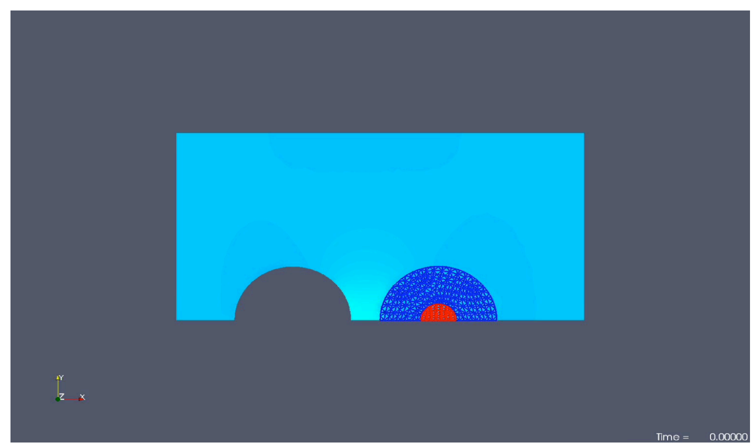
Nanoparticle Flow, Ordering and Self-Assembly

- Current Work/Progress - FY06



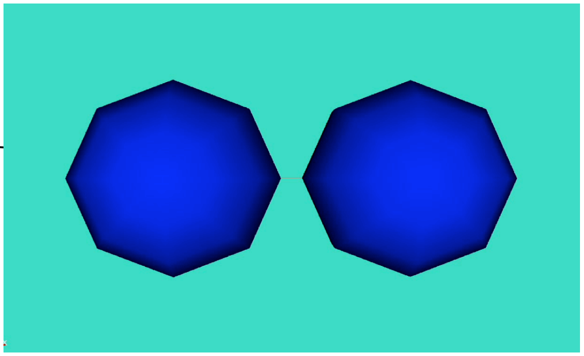


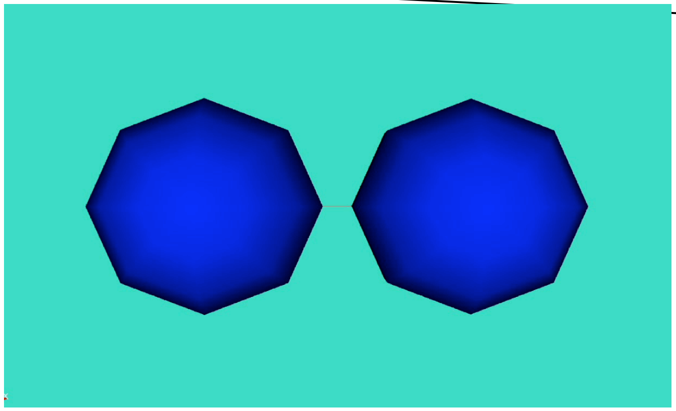




Two-Particle Interactions (with and without Hydro)

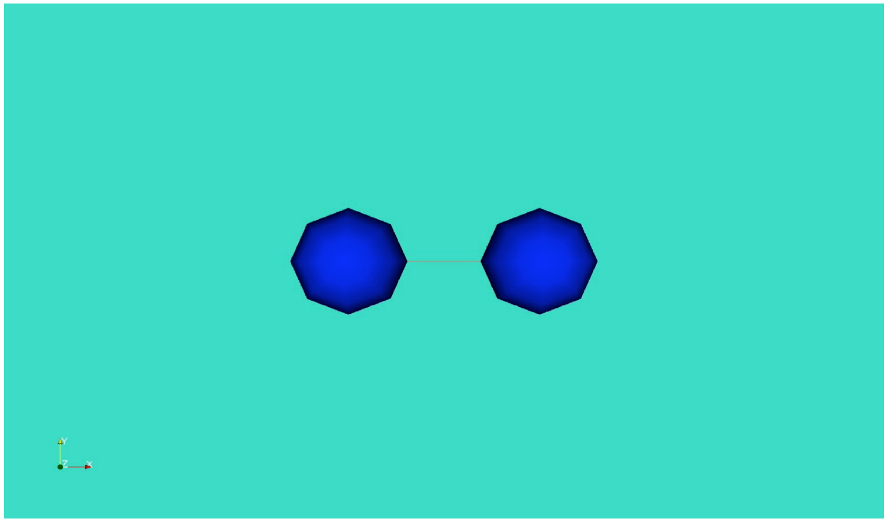
- 10KT
- 100 KT



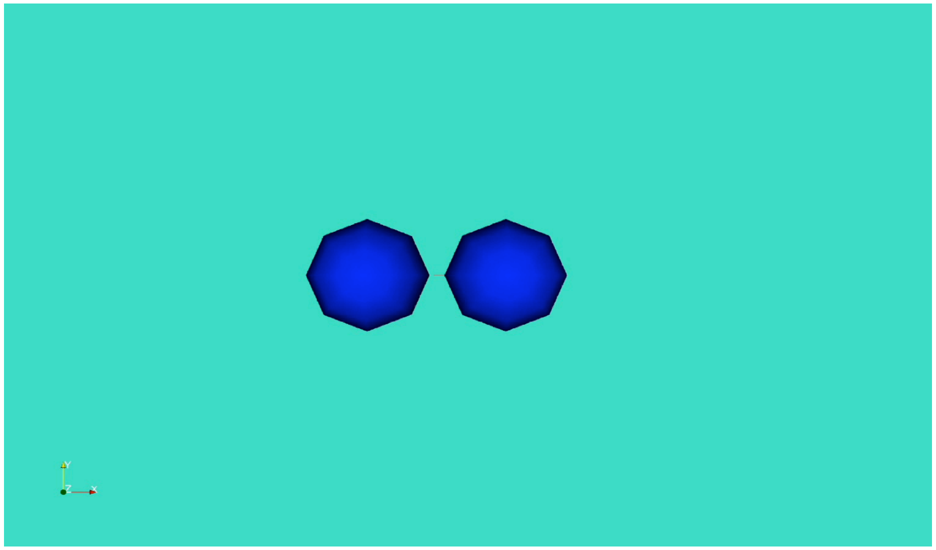


…Now add Short-Range Hydrodynamic Model 1/h

Force at 100 KT, reverse at 100 KT

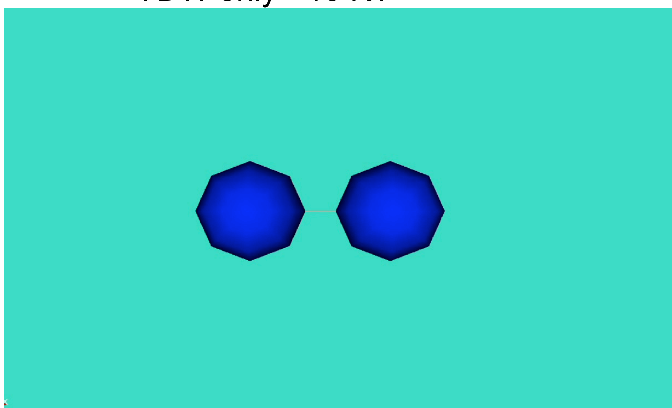


Force at 100 KT, reverse at 10 KT

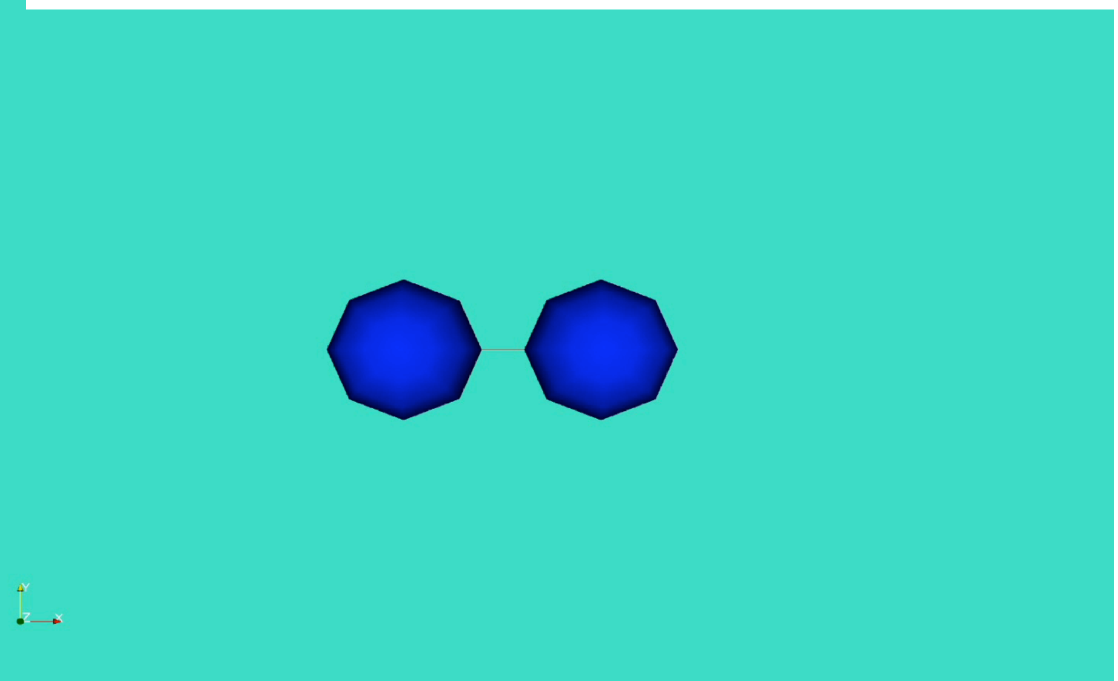


Two-Particle Interactions (with and without Hydro) - 45 deg

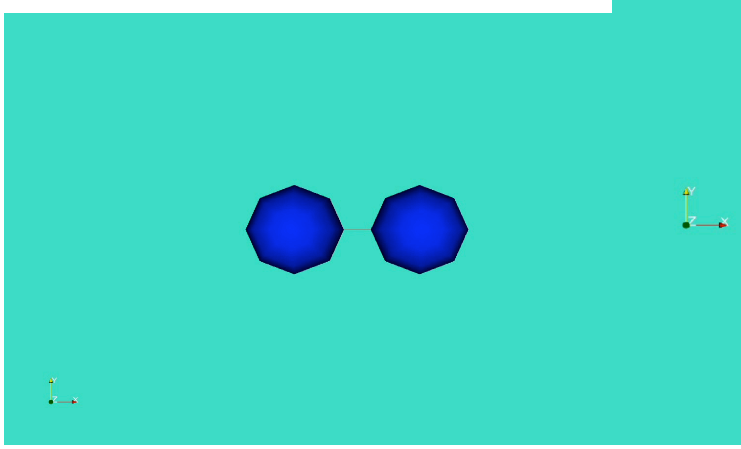
VDW only - 10 KT



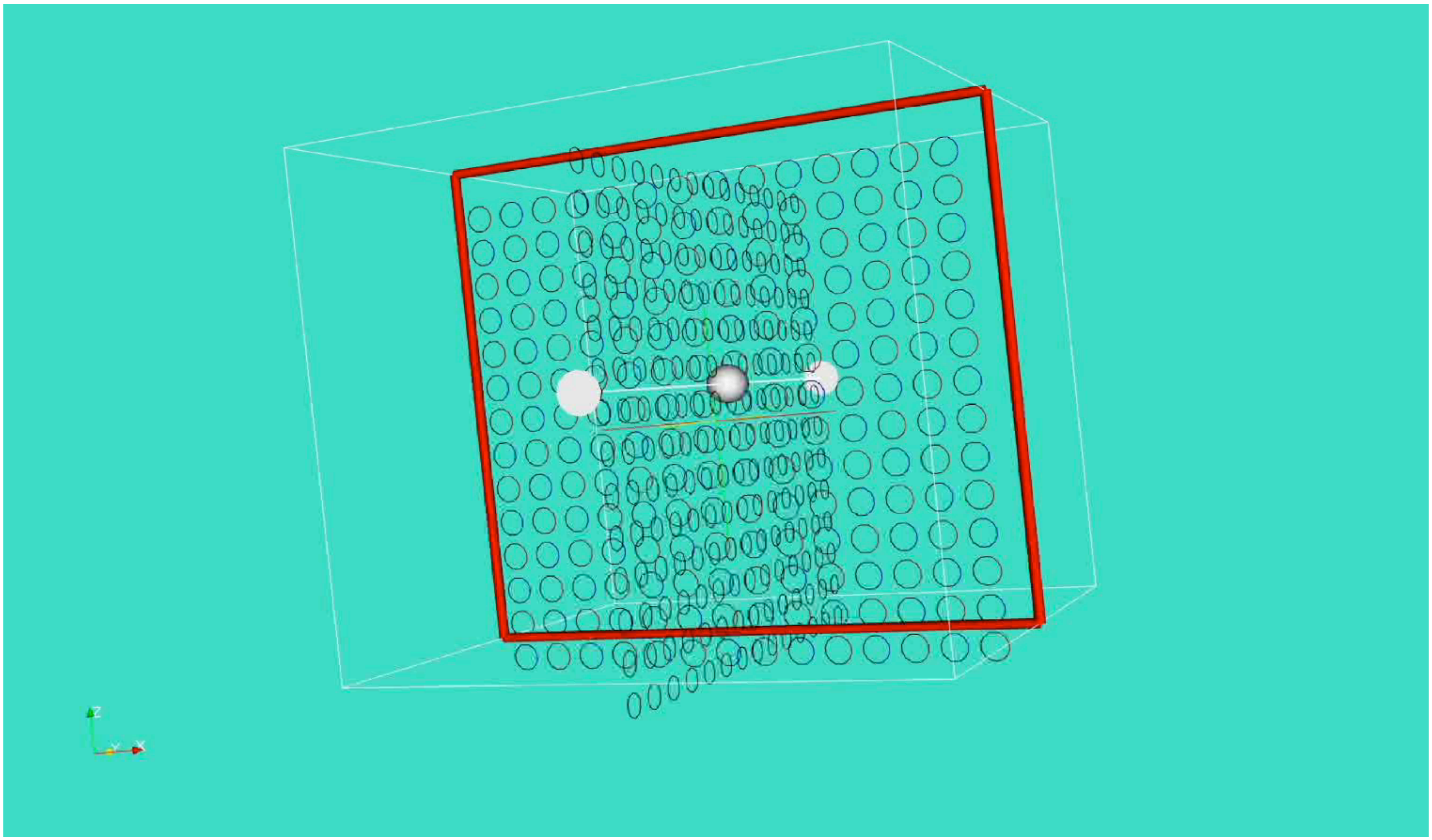
VDW/Hydro/hertzian - 10 KT



VDW only - 100 KT



Hydro/Brownian/VDW/Hertzian (LS Silicate) - Shear flow (Periodic)

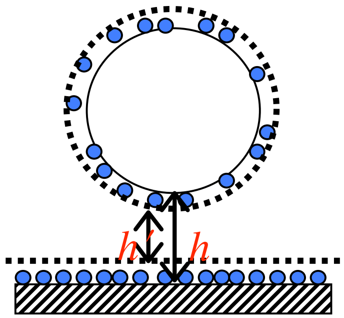


Experimental Highlights (SNL)

- Interfacial force microscopy
- Confocal Microscopy
- Acoustic spectroscopy
- Suspension Rheology
- Other: Raman Spectroscopy, etc.

Replace analytical patch with one that combines colloidal and hydrodynamic forces

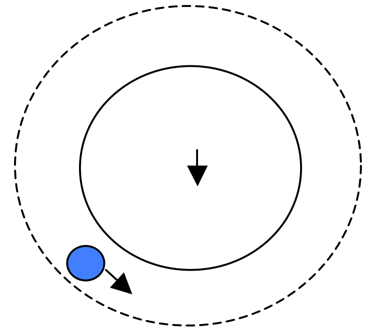
Example: Friction Force, Dissipative Particle Dynamics



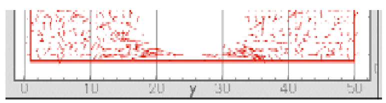
Friction: $\boldsymbol{F} = \gamma\omega^2 \boldsymbol{u}_{surf}$

Range ≈ Diminished Separation ($h \rightarrow h'$)??

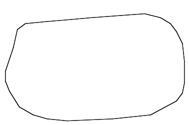
Normal to the object: $\boldsymbol{rn} = \boldsymbol{ri} - \boldsymbol{robj}$

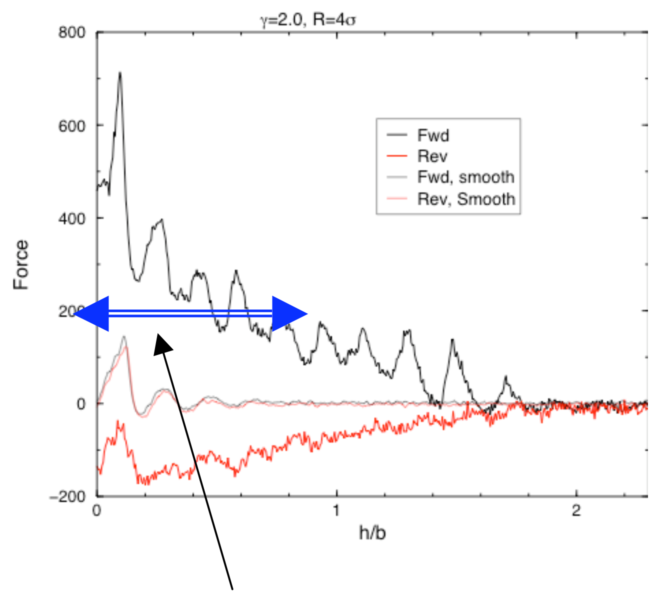


- Relative Velocity : $\boldsymbol{u}_{rel} = \boldsymbol{u}_i - \boldsymbol{u}_{obj}$
- Velocity $\perp_r$ to Surface : $(\boldsymbol{u}_{norm} = \boldsymbol{u}_{rel} \bullet \boldsymbol{r}_n)\, \boldsymbol{r}_n / |\boldsymbol{r}_n|$
- Velocity along Surface : $\boldsymbol{u}_{surf} = \boldsymbol{u}_{rel} - \boldsymbol{u}_{norm}$



Atomistic simulation





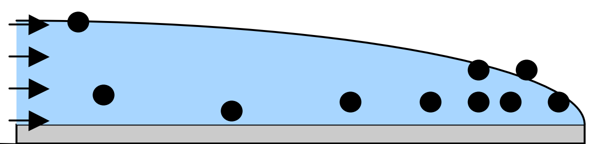
Combined Surface/Sphere Cutoff

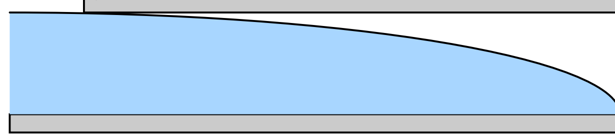
- Effect of friction goes far beyond its range
- Layer-by-layer transition during drainage is prominent, though severely dampened during flooding

Nanoparticle Flow, Ordering and Self-Assembly

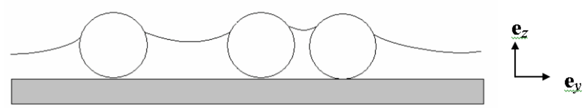
- Current Work/Progress - FY06
  - Surface self assembly

- Drying suspension of particles situated at the surface

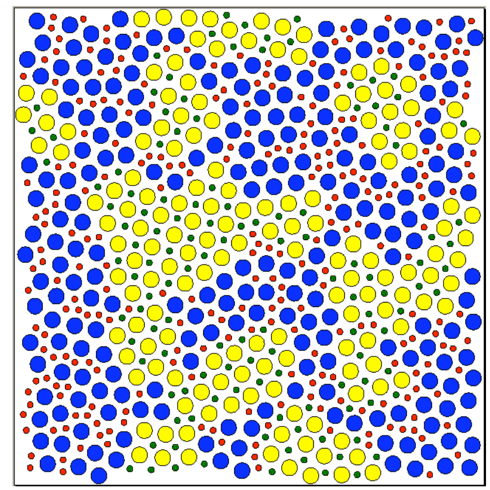


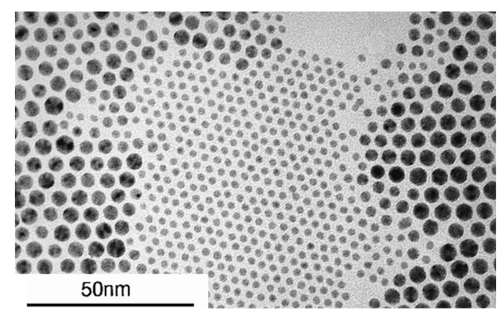


- Forces
  - Drag
  - Van der Waals
  - Electrostatic
  - Capillary
  - Brownian
  - Hydrodynamics



- Dynamic Simulation
  - Langevin equation
  - Integrate particle positions forward in time





Retrospective and Outlook

- Seek to build a nanoparticle suspension flow/dispersion simulator accurate and efficient enough for predictive rheology, stability, self assembly
- Multiscale methods to bridge scales: atomistics->effective potentials. Two-particle -> effective potentials. Imbedded interfaces in fluid -> long range hydrodynamic forces

NANOPARTICLE SUSPENSION FLOW COMPONENTS/REQUIREMENTS: THE BIG PICTURE

Colloidal (Nano) Particle Mechanics

Methodology (Algorithms, Platforms, Requirements)

- N-body Newton-equation solver (translation/rotation)
- N-body Equilibrium Solver
- Distributed/parallel or of suitable performance
- Interface to add any effective pair-wise potentials
- LAMMPS or similar, expandable platform
- Capable of handling massive contact/aspherics
- …

Colloidal Chemistry Models

- Effective potential development
- Solvent effects (solvation, brownian)
- Particle temperature
- Polymer brush effects (potentials)
- Coarse graining with aggregates
- …

Colloidal Contact Models

- Computational geometry
- Minorly aspherical
- Composite Particle structures
- Generally aspherical
- Elastic/Hertzian
- Viscoelastic
- …

Active effort
Researching/surveying

Flow Solver

Methodology (Algorithms, Platforms, Requirements)

- High performance (parallel, or whatever)
  - ARIA, Goma, other
- Numerically stable at contact/near contact (stress singularities)
- FEM/FDM
  - ARIA, Goma
- Stoksian Dyn. (Specialized)
  - No capability exists, coupling implicit
- BEM (Specialized)
  - Capability available, easy coupling
- SRD (Pe of colloid part O(1). Too expensive otherwise.
- DPD (limited)
  - Depletion forces
- LB (depletion forces)
  - Capability available.
- Frame-invariant pair-drag model (long-range/short-range) - (Approx.)
  - Some drivers exist. For long range, no relative motion.

Subgrid Models (contact/near contact)

- Dominate viscous modes
- Effect of polymer graft
- Effect of surface roughnes
- Aspherical

Coupled Multiphase Solver

Coupling Methodology

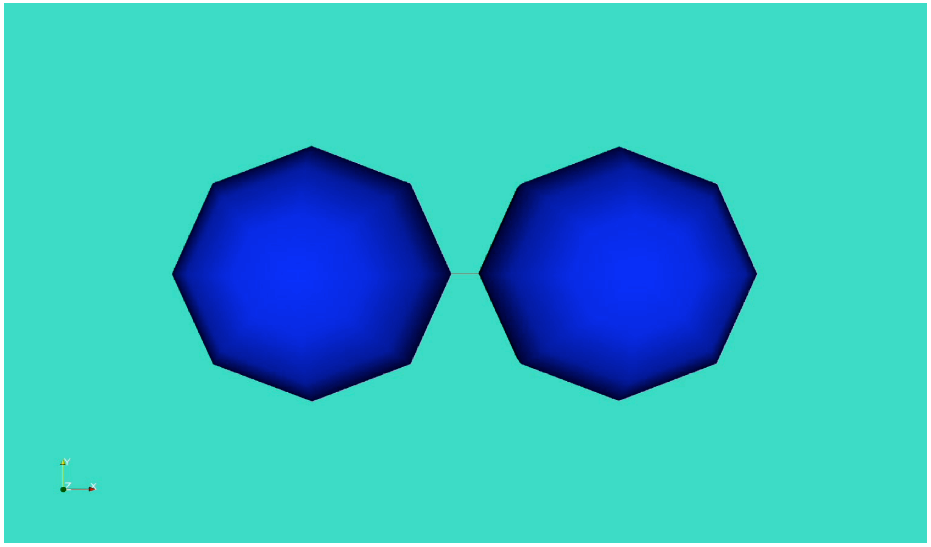
- DLM/Distributed volumetric source (Glowinski)
- Intrinsic: BEM, LB, DPD, Stoksian Dynamic
- Effective potential for flow (approx. fluids)

Platform

- LAMMPS
- ARIA
- Home grown

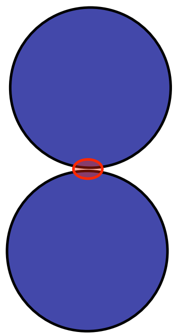
Two particle Tests: Force comparison

- VDW only: Attract to contact (hertzian), and then vibrate--Need better sticking model - video below
- VDW/Short-range hydro: Takes forever for dispersion forces to pull particles together: 1/r vs 1/r/r - ah-dah!   - no video
- Hydro 1/h forces dominate.   Is there a breakdown point? Need to adjust the hydro-cutoff to see if you can get contact.



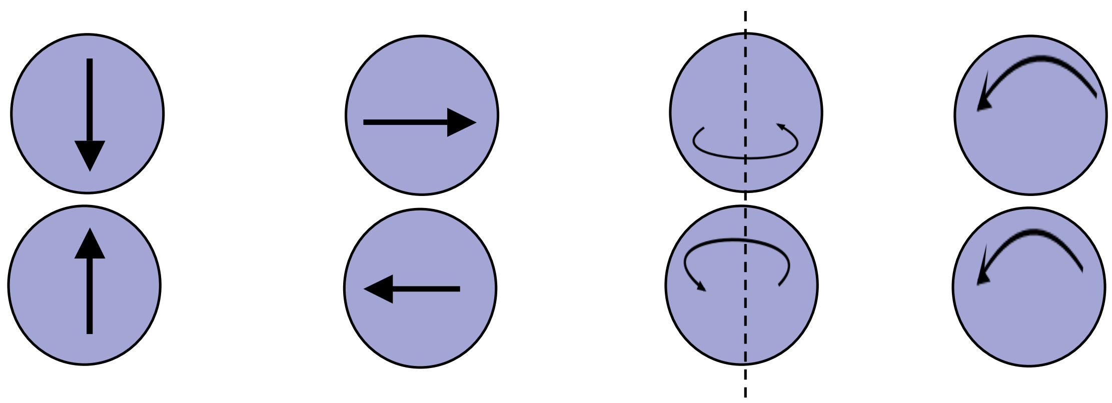
New 3D Boundary Element Method
LANL/UNM/SNL (from Mondy, Ingber et al.)

The hybrid BEM (HBEM) can combine the hydrodynamic forces with other methods such as MD simulations results. This enables us to couple the macroscale modeling and the microscale modeling directly which is not possible in other techniques.



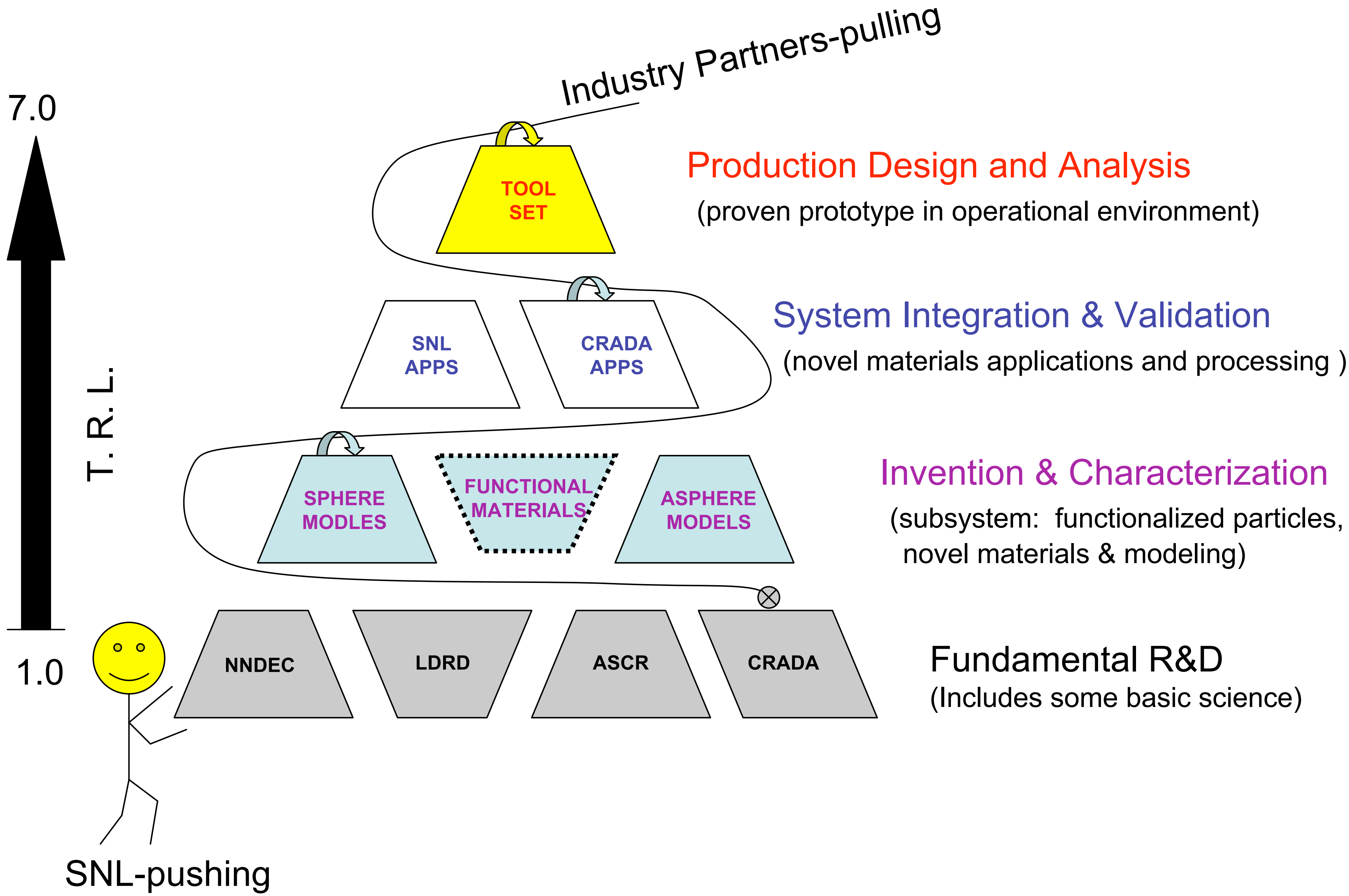
The forces on the the majority (blue part) of the sphere are obtained by solving the hydrodynamic equations with the BEM.

In the close contact region (red part), the force solutions come from either analytic analysis*, MD simulations, or both.



*The relative particle motions can be decomposed into four basic relative motions.

Cox and Brenner, Chemical Eng. Sci. 1967, Vol. 22, pp1753
O'Neil and Majumdar, ZAMP, 1970, Vol. 21, p180
Jeffrey and Onishi, ZAMP, 1984, Vol. 35, p639



Industry Partners-pulling
7.0
T. R. L.
1.0
TOOL
SET
Production Design and Analysis
(proven prototype in operational environment)
SNL
APPS
CRADA
APPS
System Integration & Validation
(novel materials applications and processing)
SPHERE
MODLES
FUNCTIONAL
MATERIALS
ASPHERE
MODELS
Invention & Characterization
(subsystem: functionalized particles,
novel materials & modeling)
NNDEC
LDRD
ASCR
CRADA
Fundamental R&D
(Includes some basic science)
SNL-pushing