For Presentation at the 81st Annual Meeting of the Society of Rheology, Madison, Wisconsin, 16 2009.

SAND2009-6809C

Performance of Mesoscale Modeling Methods for Predicting Rheological Properties of charged Polystyrene/Water Suspensions

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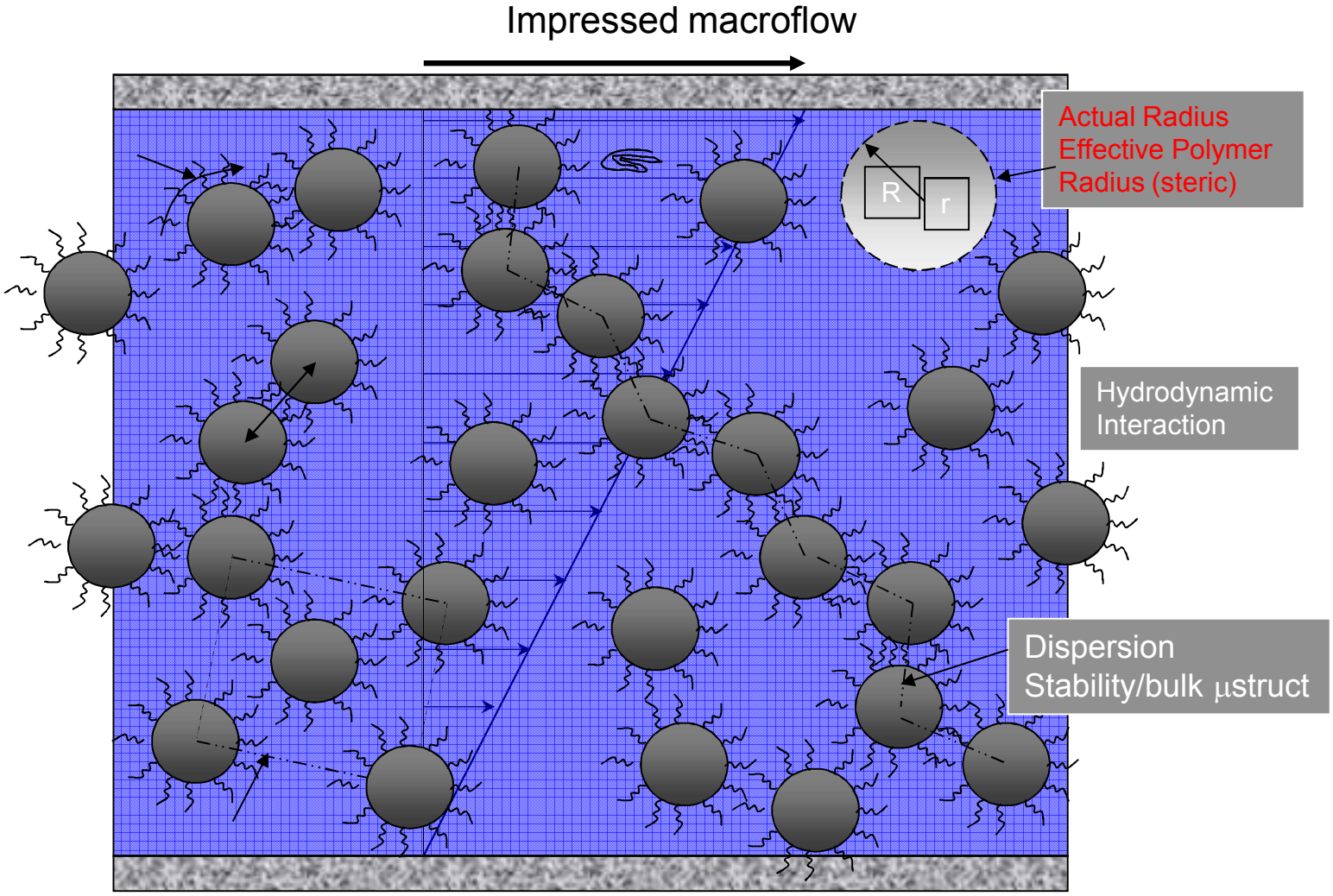
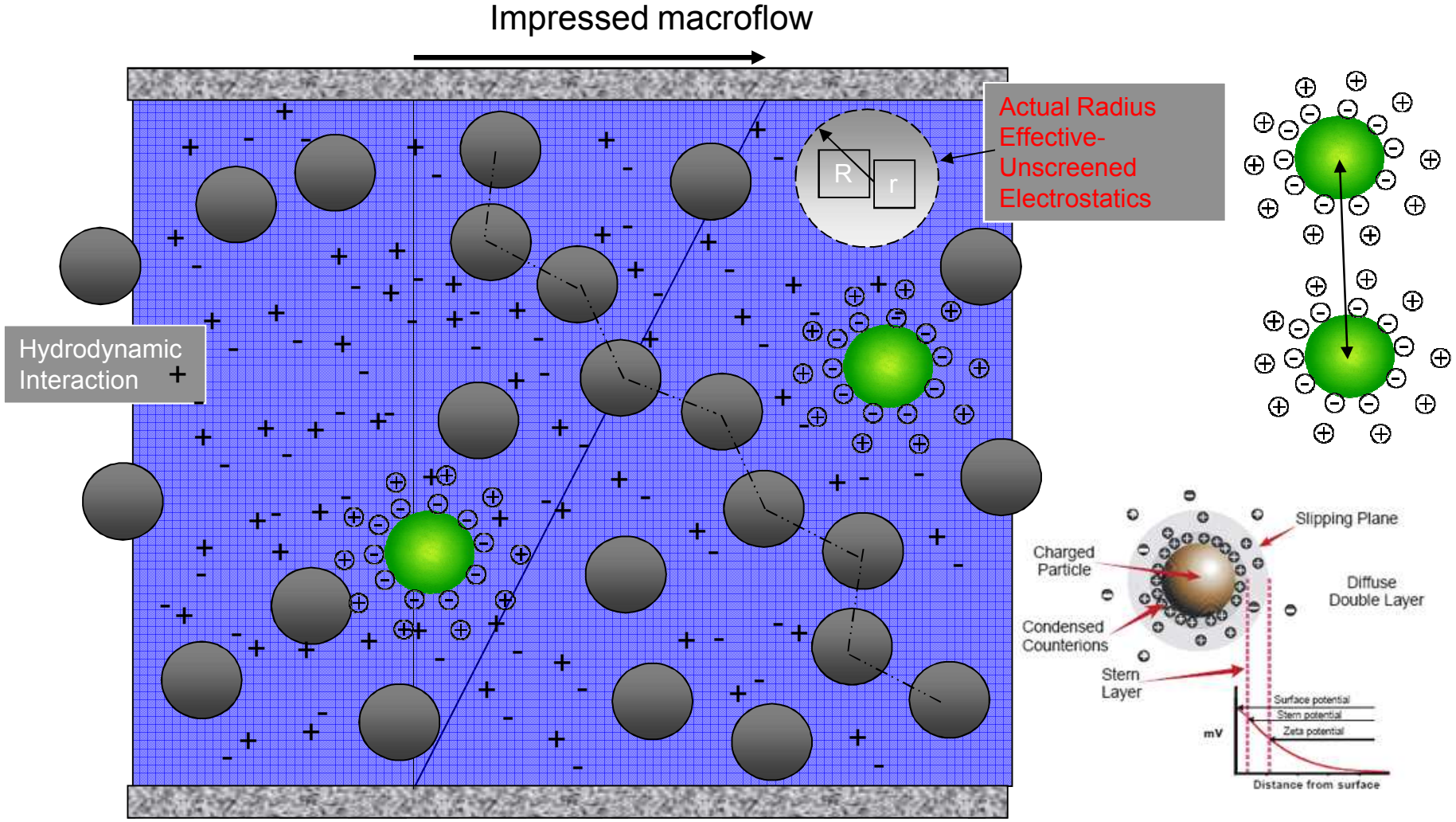
Outline

- Meso-scale Modeling Methods for Nanoparticle Suspension Flows
  - *–SRD, DPD, FLD, FEM for solvent*
  - *–DEM with LAMMPS code for particles (www.lammps.sandia.gov)*
- Sample preparation and Rheological Testing
  - *–Charged polystyrene in water. 950 nm*
  - *–Shear rheology (steady and oscillatory)*
- Equilibrium structure properties, diffusivities, shear viscosity
  - *–Methods cross compare (performance and agreement)*
- Validation results
- Conclusions and Outlook

Mesoscale Models of Suspension Dynamics



Mesoscale Models of Suspension Structure/Dynamics- Charged Systems



Overview of Nanoparticle Flow Project

Colloidal (Nano) Particle Mechanics

Methodology (Algorithms, Platforms, Requirements)
- •N-body Newton-equation solver (translation/rotation)
- •N-body Equilibrium Solver (long time)
- •Distributed/parallel or of suitable performance
- •Interface to add any effective pair-wise potentials
- •LAMMPS or similar, expandable platform
- •LAMMPS infrastructure changes (Particle Layers)
- •Capable of handling massive contact/aspherics
- •10000 Particles, 3D.

Long, Intermediate Range Interaction Models
- •Effective potential development
- •Solvent effects (solvation, brownian)
- •Particle temperature (thermostat)
- •Polymer brush effects (potentials)- attributes
- •Coarse graining with aggregates
- •…

Colloidal Contact Models
- •Minorly aspherical
- •Composite Particle structures
- •Generally aspherical
- •Elastic/Hertzian
- •Viscoelastic

Active effort

Eliminated per requirements

Flow Solver

Algorithms, Platforms, Requirements
- •High performance (parallel, or whatever)
  - •ARIA, Goma, other
- •Multiphase flow approach (effective Darcy Law, …)
- •Numerically stable at contact/near contact (stress singularities)
- •FEM/FDM
  - •ARIA, Goma (Explicit, SemiImplicit, body-fitted grid/imbedded)
- •Stoksian Dyn. (Specialized)
- •BEM (Specialized)
- •SRD (Pe of colloid part O(1). Too expensive otherwise.
- •DPD (limited Peformance Depletion forces)
- •LB (depletion forces)
- •FLD - Frame-invariant pair-drag model

Subgrid Models (contact/near contact)
- •Dominate viscous modes
- •Effect of polymer graft
- •Effect of surface roughnes
- •Aspherical

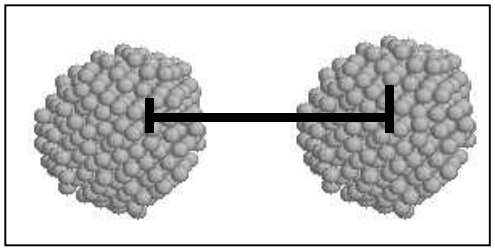
Coupled Multiphase Solver

Methodology
- •CDFEM/DLM/Distributed volumetric source (Glowinski)
- •Body fitted grids: remeshing and remapping as needed)
- •Hybrid scheme: Imbedded interfaces + one-level adaptivity to capture surface
- •Intrinsic: BEM, Stoksian Dynamic
- •Implicit Solvent
- •Explicit coarse-grained solvent/colloid collision

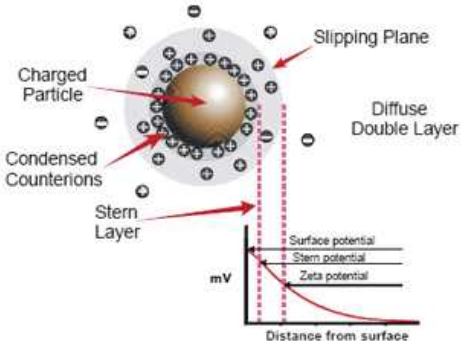
Platform
- •LAMMPS
- •ARIA
- •Home grown

About Coarse Graining - What is needed?

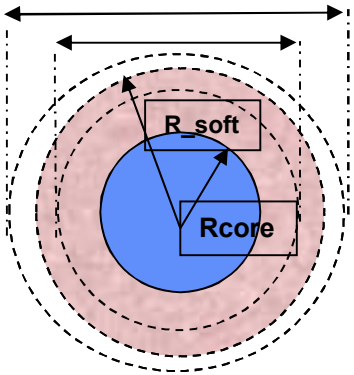
Particle



e.g. Integration to Hamaker's equation and DLVO

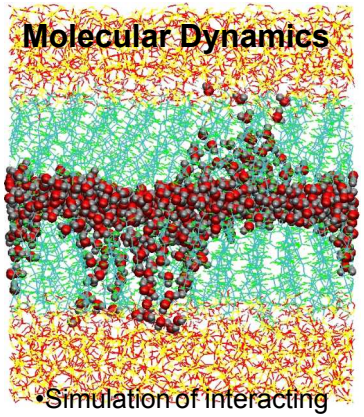


electrostatic
Structural representation



- Computational standoffs
- Polymer layer parameters
- Screening layer thickness
- Structural constants (polymer and hard sphere)

Solvent



- Simulation of interacting
- polmer/solvent/particle

Blobs->SRD/DPD
Dual particle approach

QuickTime™ and a YUV420 codec decompressor are needed to see this picture.

Continuum

QuickTime™ and a Motion JPEG OpenDML decompressor are needed to see this picture.

Framework + Methods Implemented and Tested

www.lammps.sandia.gov

LAMMPS - DEM Solver

"COLLOID" Package for Pairwise Potentials (e.g. DLVO)

EXTERNAL HYDRODYNAMICS SOLVERS

MEZZO (ARIA) - Incompressible Finite element flow solver

•Coupled with LAMMPS through overset grid CDFEM.

•Advantages: completely general.

•Disadvantages: performance?

LAMMPS PACKAGES FOR COARSE-GRAINED EXPLICIT HYDRODYNAMICS

DPD - Dissipative Particle Dynamics

•Explicit Solvent "particles". Molecular dynamics framework. Solvent potentials.

•Advantages: no grid. Full HI,

•Disadvantages: relatively more expensive. Difficult to map to real system (coarse grained)

SRD - Stochastic Rotation Dynamics

•Explicit Solvent "particles". Molecular dynamics framework

•Advantages: Full HI. Highly scalable. Intrinsic Brownian.

•Disadvantages: Difficult to map to real system

LAMMPS PACKAGES FOR IMPLICIT HYDRODYNAMICS

SD - Stokesian Dynamics with FLD simplification

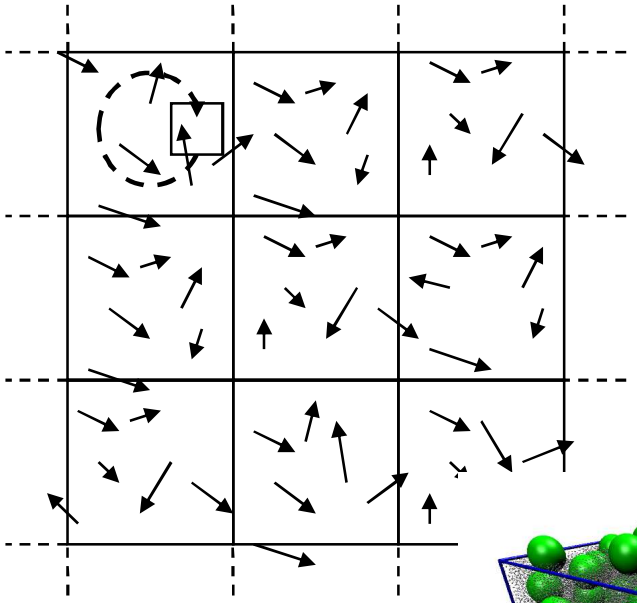
•Ball-Melrose pair-drag models and FLD. Implicit, explicit integrator. Hydro through pairwise interactions and Long-range isotropic tensor

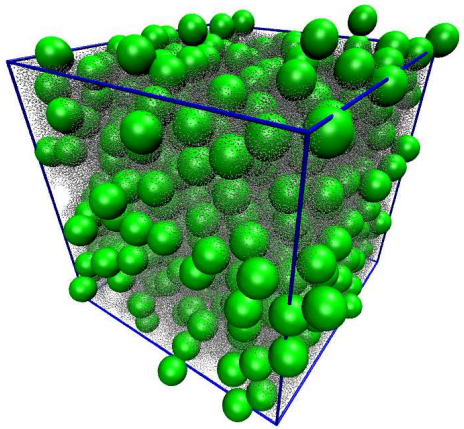
•Advantages: Scalable.

•Disadvantages: spherical, needs tuning

SRD - Stochastic Rotation Dynamics
MPCD - Multi-Particle Collision Dynamics

- SRD is a point particle based fluid (mass, velocity), wherein the fluid interacts through collision operations
- Conserves linear momentum
- Produces fluctuating hydrodynamic behavior
- Computational efficient
  - -No pair wise potential
  - -SRD rotation does not limit time step
  - -10^3 improvement over explicit Lennard-Jones solvent





390 nm charged polystyrene In water being sheared (500 colloids+ 400000 srd particles)

A. Malevanets, R. Kapral, J. Chem. Phys. **110**, 8605 (1999)

A. Malevanets, R. Kapral, J. Chem. Phys. **112**, 7260 (2000)

DPD - Dissipative Particle Dynamics

- Approach similar to Non-equilibrium Molecular Dynamics
  - Apply driving force
  - Measure response
- For suspension viscosity use Couette flow
  - Apply known shear rate
  - Measure system stresses
- Use Lees-Edwards BC and DPD thermostat
- Two types of particles
  - Solid (larger)
  - Fluid (smaller)
- Interaction forces
  - Solid-solid
    - DLVO theory for colloids
  - Solid-fluid
    - Standard DPD forces from literature
    - Currently working on highly viscous fluid
  - Fluid-fluid interactions
    - Standard from literature (Groot-Warren)

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

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are needed to see this picture.

J. M. V. A. Koelman and P. J. Hoogerbrugge, ŅDynamics Simulations of hard-sphere suspensions under steady shearÓ, *Europhys. Lett.*, **21**, 363-368 (1993).

R. D. Groot and P. B. Warren, ŅDissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulationÓ,J. Chem. Phys. 107, 4423-4435 (1997).

FLD - Fast Lubrication Dynamics

Higdon, Kumar et al. UIUC

Hydrodynamic Interaction

PME Stokesian Dynamics ***O(N log N)***

$$R = (I - \mathcal{R})^{-1} R_{1B} + R_{lub}$$

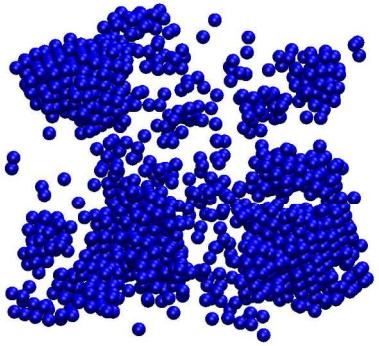
Fast Lubrication Dynamics ***O(N)***

$$R = R_0 + R_\delta$$

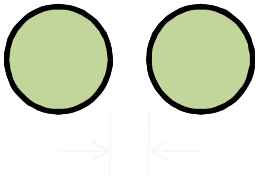
Isotropic Constant

δ FLD ~ 1/ δ

δ-logδ FLD ~ 1/ δ + ln(1/ δ)



390 nm charged polystyrene In water being sheared into phase separation



Wednesday, 21 October, 10:10 AM. Paper Number - SC32
Session Suspensions and Colloids. A. Kumar and J. Higdon
Charge effects on microstructure, rheology and order-disorder transitions for sheared colloidal crystals and suspensions

CDFEM and Fluctuating Hydro and Colloidal Dynamics with Sierra/Mezzo

- Coupled Aria and LAMMPS in Mezzo

  Monodisperse spheres

  $\rho_f = 0.6$

  $k_B T = 1.0$

  $\nu = 1.67$

- Can do 3D, no problem
- Parallel, no problem
- Currently
  - Quasi-static fluid (creeping Stokes) - novel velocity/pressure decoupling solver
  - Explicit time integration of colloid dynamics

QuickTime™ and a
Motion JPEG OpenDML decompressor
are needed to see this picture.

$$\mathbf{v}^{n+1} = \mathbf{v}^n + \frac{\Delta t}{m}(\mathbf{R}\mathbf{v}^n + \sum \mathbf{f}^n)$$

$$\left(\frac{\Delta x}{\Delta t}\right)^{n+1} = \mathbf{R}^{-1}\sum \mathbf{f}^n$$

QuickTime™ and a
Motion JPEG OpenDML decompressor
are needed to see this picture.

Validation Tests, Experimental Program

- **System Characteristics**

  Bangs Labs. Nominally 950 nm monodisperse. Required 0.003M SDS surfactant for stability. Zeta potentials measured with Malvern Zetasizer ZS (Light-scattering velocimetry)

Salt Concentration	κ	Ψz	Ψ_0
1e-4 M	3.25e7 m^{-1}	112.4 mV	114 mV
1e-3 M	1.03e8 m^{-1}	116.6 mV	118mV
1e-2 M	3.25e8 m^{-1}	124.2 mV	125 mV

$$\sigma = \sqrt{\varepsilon\varepsilon_0 kT}\,\sinh\left(\frac{e\psi_0}{2KT}\right)c_{i0}^{1/2} \qquad \sigma = \frac{2\varepsilon\varepsilon_0\kappa KT}{e}\left[\sinh\left(\frac{e\Psi_d}{2KT}\right)+\frac{2}{\kappa a}\tanh\left(\frac{e\Psi_d}{2KT}\right)\right] \qquad \frac{1}{\kappa} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{1000e^2 N_{Av} c_{i0}}}$$

- **Particle Diffusivities**

  BASF: Measurements forthcoming.

- **Dynamic Tests**

  –Shear/Oscillatory. RFS Rheometer (TA Instruments).

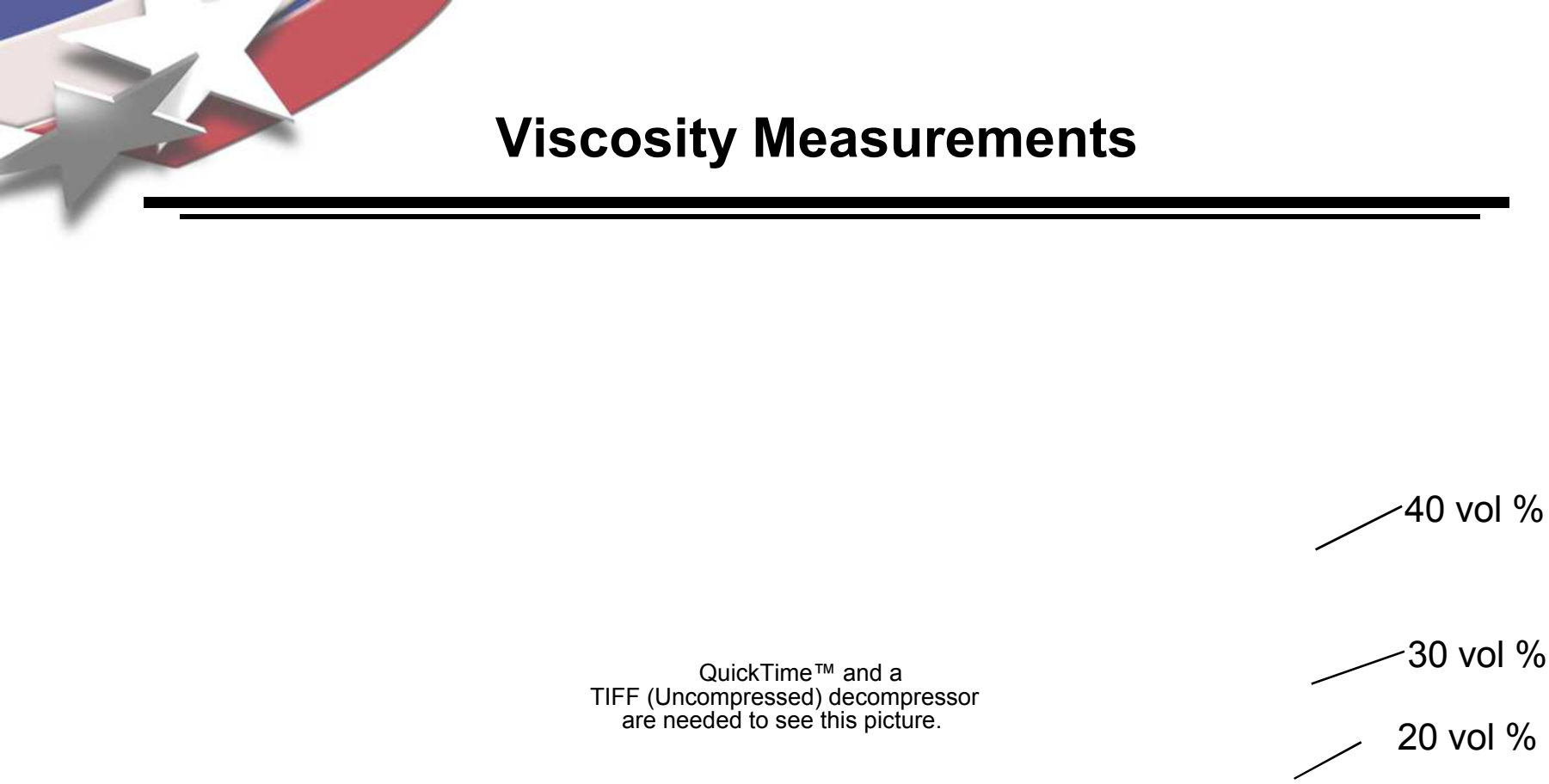
  –Viscosity is reproducible, though data is very scattered at low shear rates (No indication of settling or aggregation)

  –Preshear at steady shear rate 10 s^{-1} for 300 seconds.

  –Run a shear rate step test for 60s each at 1 s^{-1}, 10 s^{-1}, 100 s^{-1}, and 10 s^{-1}

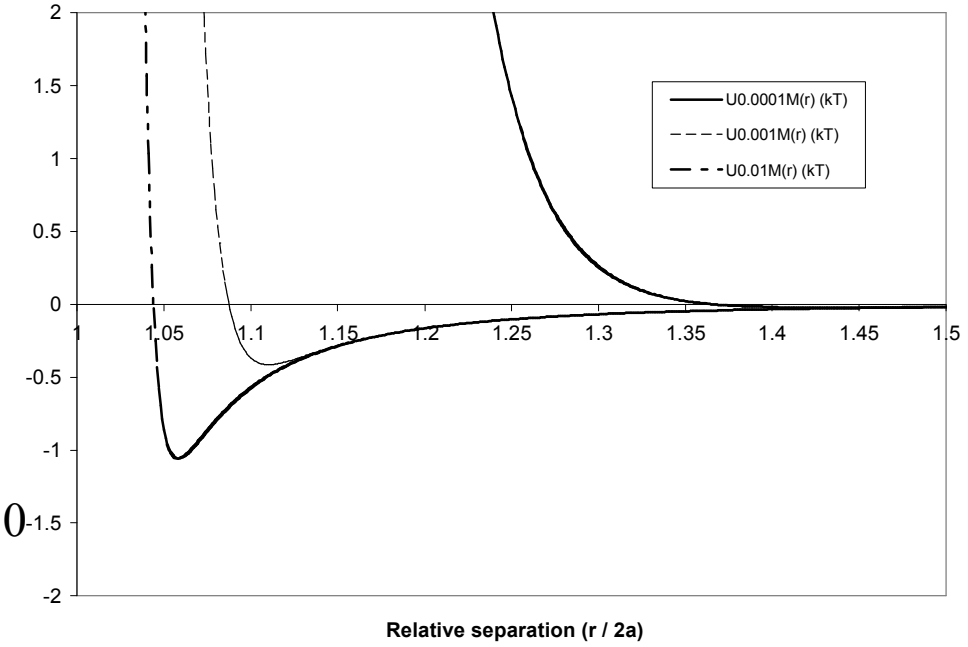
  –Run a shear rate step test for 60s each at 100 s^{-1}, 200 s^{-1}, 300 s^{-1}, and 500 s^{-1}.

Viscosity Measurements



Target Physical Parameters and Simulation Parameters

- Particle diameter – 950 nm
- Particle density – 1050 kg/m^3
- Surface potential – 0.112-0.124 V
- Solvent viscosity – 0.001 Pa-sec
- Solvent density – 1000 kg/m^3
- Temperature – 298 K
- Hamaker constant – 1.37E-20 J
- Nominal Particle volume fraction – 0.30



$$U_{vdw,att}(r) = -\frac{A_{cc}}{6}\left[\frac{2a^2}{r^2-4a^2}+\frac{2a^2}{r^2}+\ln\left(\frac{r^2-4a^2}{r^2}\right)\right]$$

$$U_{vdw,rep}(r) = \frac{A_{cc}}{37800}\frac{\sigma^6}{r}\left[\frac{r^2-14ar+54a^2}{(r-2a)^7}+\frac{r^2+4ar+54a^2}{(r+2a)^7}-2\frac{r^2-30a^2}{r^7}\right]$$

$$U_{el}(r) = \frac{64\pi kT\rho_{NaCl}(\infty)a\psi_0^2}{\kappa^2}e^{-\kappa(r-2a)}$$

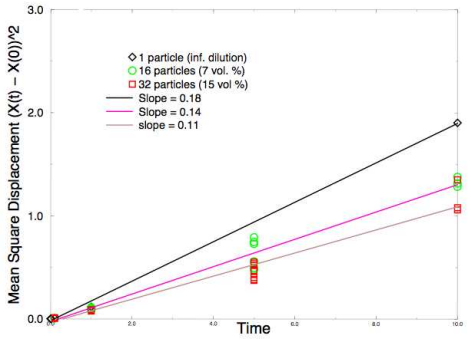
Target Colloidal Dispersion Properties for V&V

- Equilibrium Structure Properties

  Pair distribution function, Coordination number, Cluster size distribution, Nearest neighbor distance, System energy per colloid, Cell density distribution, Order parameter

- Particle Mobility - Short-time and long-time diffusivity

  Measure mean-square displacement



- Shear viscosity (steady)

  TriClinic Deforming Box,

  Muller-Plathe for bulk shear

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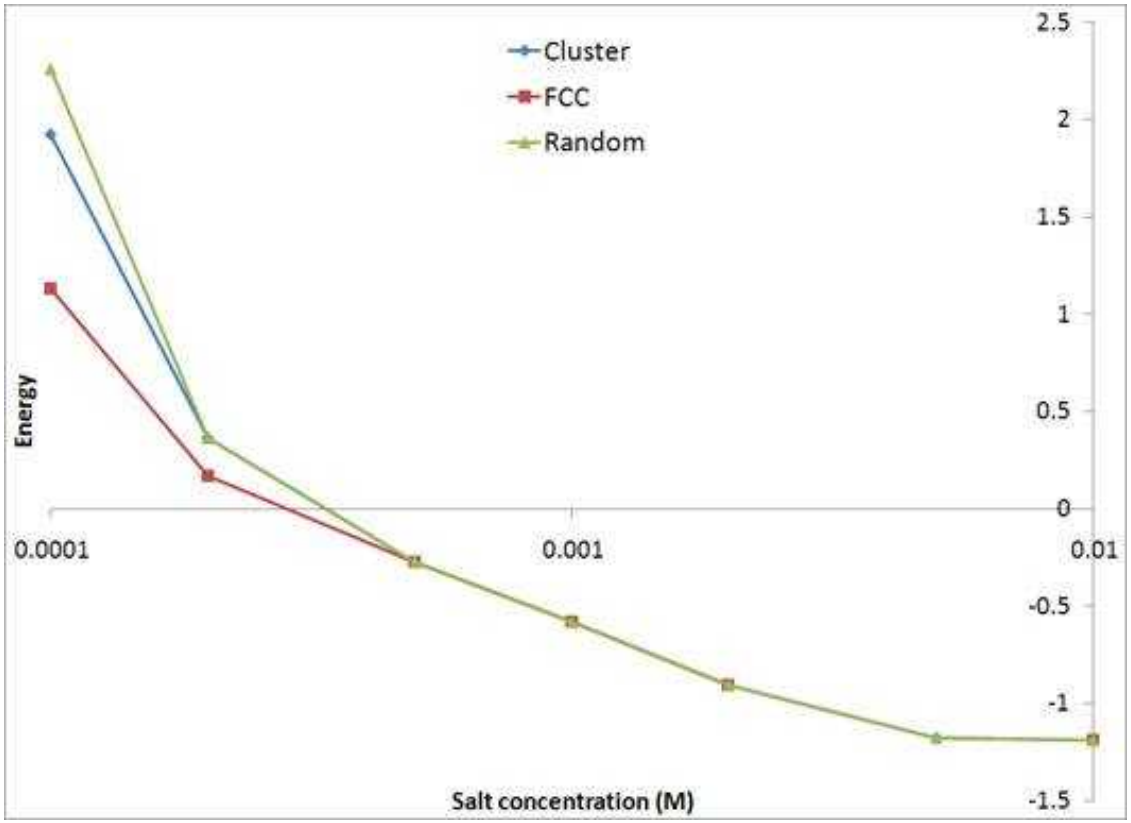
- G', G"

  Triclinic deforming box - FLD only

Equilibration

- Monte Carlo Simulations - System Energy per Colloid. Volume Fraction 0.3



Under 5 x10^{-4} M salt concentrat ion, the systems can arrest at a lo cal equ ilibrium.

Simulation Parameters

•**Method**	μ	ρ	**U[r]**	**T**	No. Colloids	☐ Pe/Cld*
•FLD	0.001 Pa-s	1000 kg/m^3	As Shown	298K	256-1370	196/3
•FEM	0.001 Pa-s	1000 kg/m^3	As Shown	298K	256-??	196/3
•SRD	1e-8 Pa-s	1000 kg/m^3	A=1.4e-25 J	2.8e-3K	256	196/2.9
•DPD	<0.001 Pa-s	1000 kg/m^3	As Shown	298K	216	196**/2.9

$$m_i \frac{d^2 \underline{r}_i}{dt^2} = \underline{F}_i^{\,H} + \underline{F}_i^{\,B} + \sum_j \underline{F}_{ij}^{\,P}$$

$$Pe = \frac{ColloidAdvectiontime}{Colloiddiffusiontime} = \frac{8\mu\dot{\gamma}a^3}{kT} \qquad Cld = \frac{ColloidalForces}{Hydrodynamicforces} = \frac{A_{cc}}{kT}$$

**Based on 100 s^{-1}, 298K*

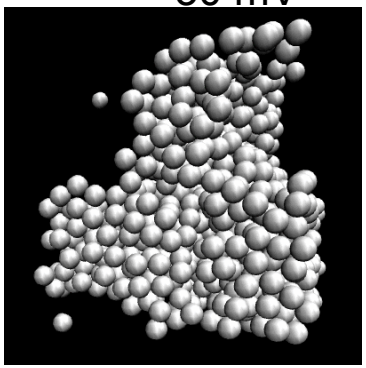
***Achieved by adjusting the effective shear rate*

Sample Results (SRD)

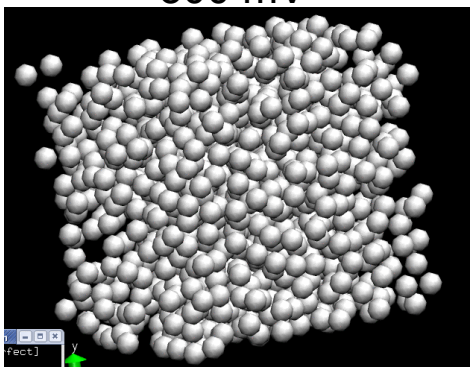
Shear-Rate 85 s^{-1}

- Volume fraction 0.30; Surface potential 33 mV and 300 mV;

•30 mV

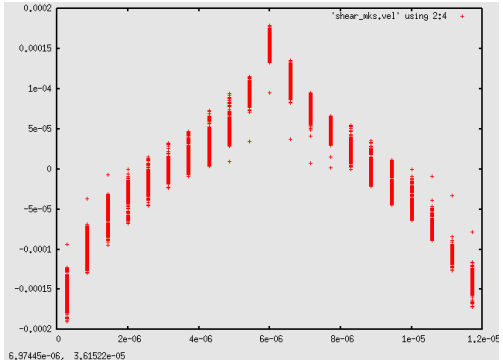


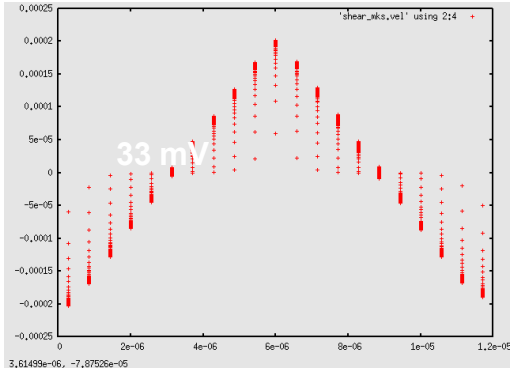
•300 mV



•300 mV, Electrolyte concentration 0.0001 M

•Electrolyte concentration 0.1 M





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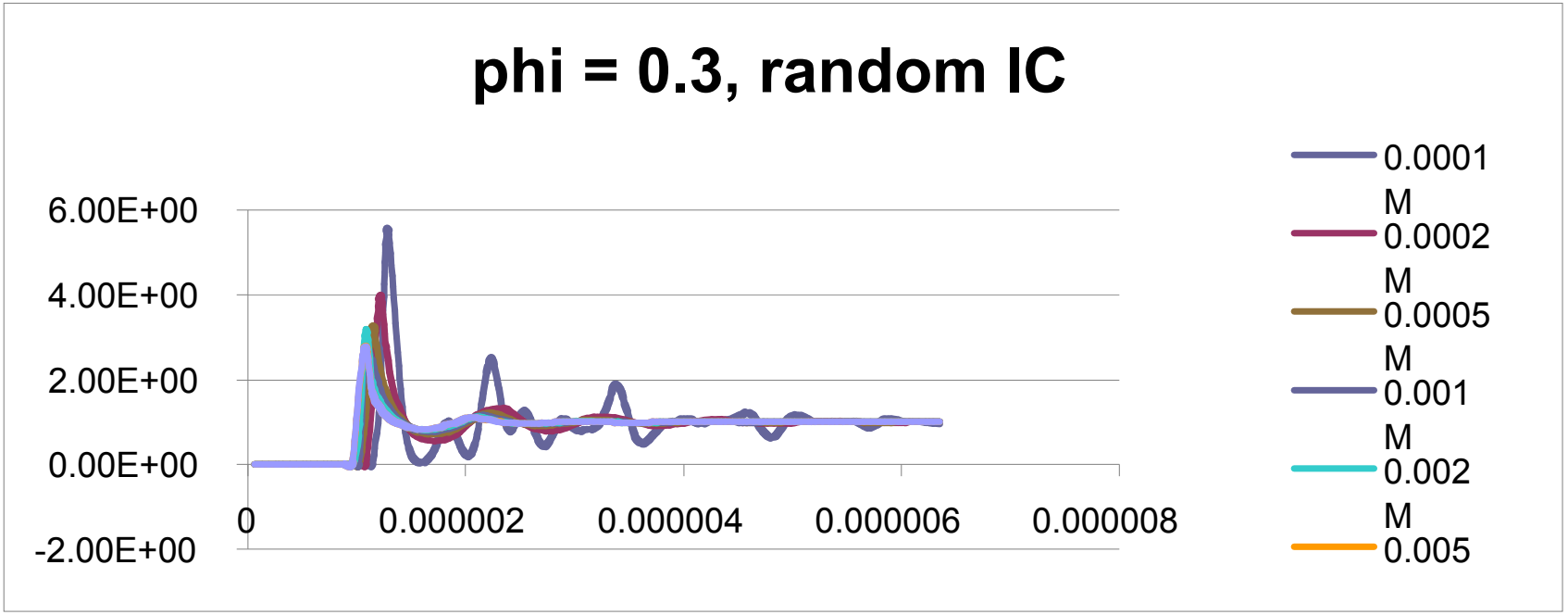
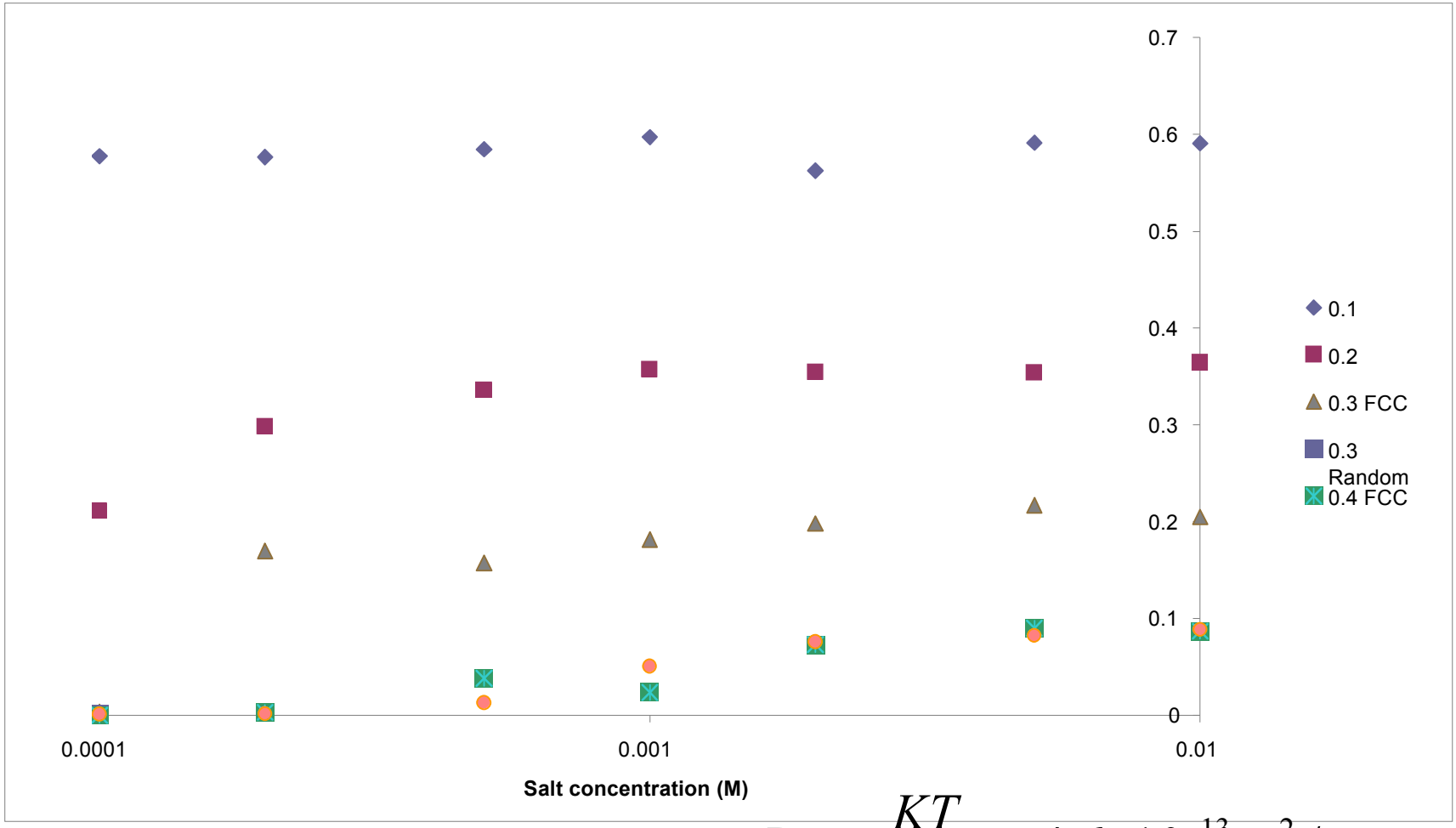
YUV420 codec decompressor
are needed to see this picture.

•Velocity Profile - MP Method

Cross-Comparison: Equilbrium Structure Properties

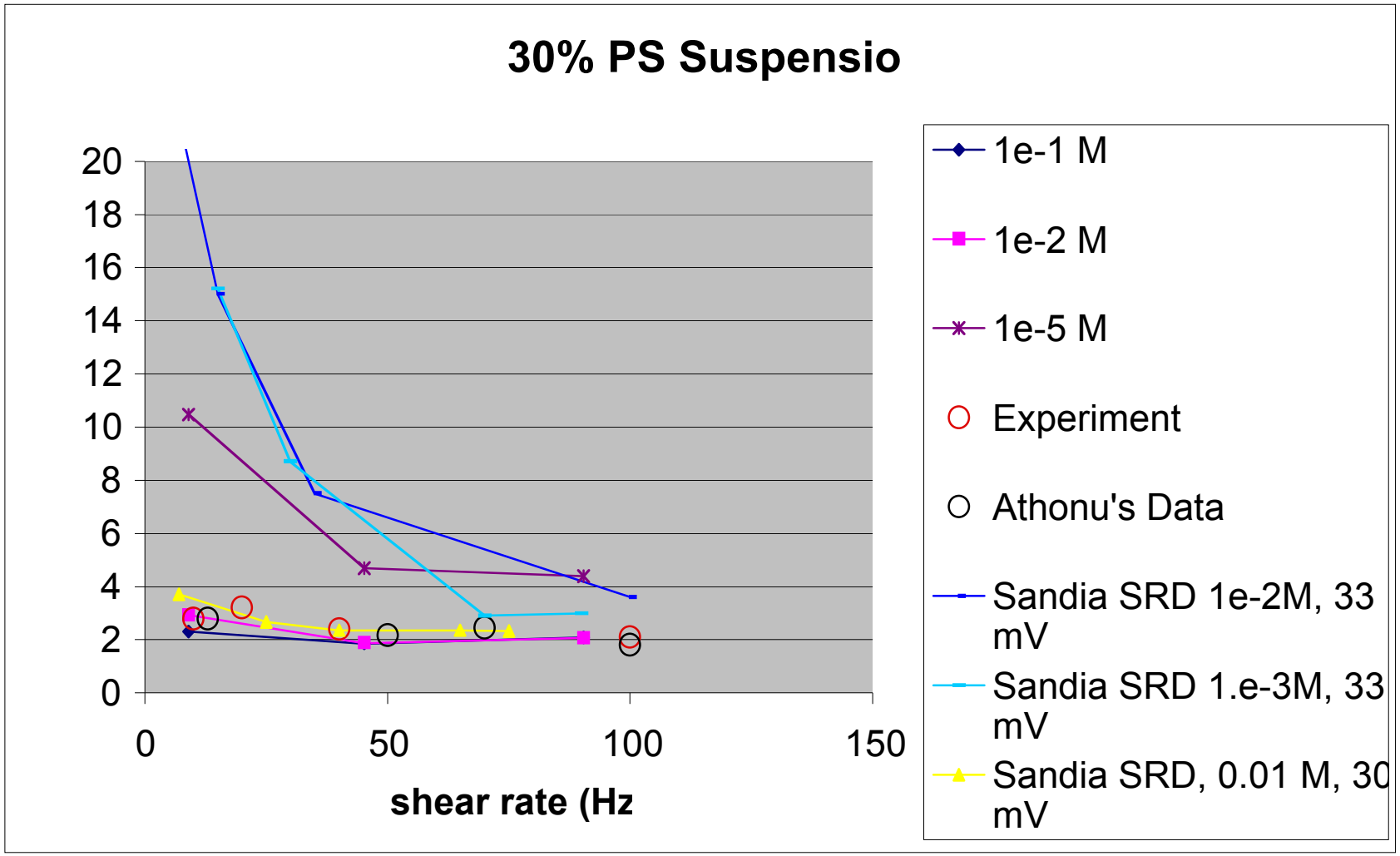


Cross-Comparison: Diffusivities



$$D_0 = \frac{KT}{6\pi\mu a} = 4.6x10^{-13}\, m^2/s$$

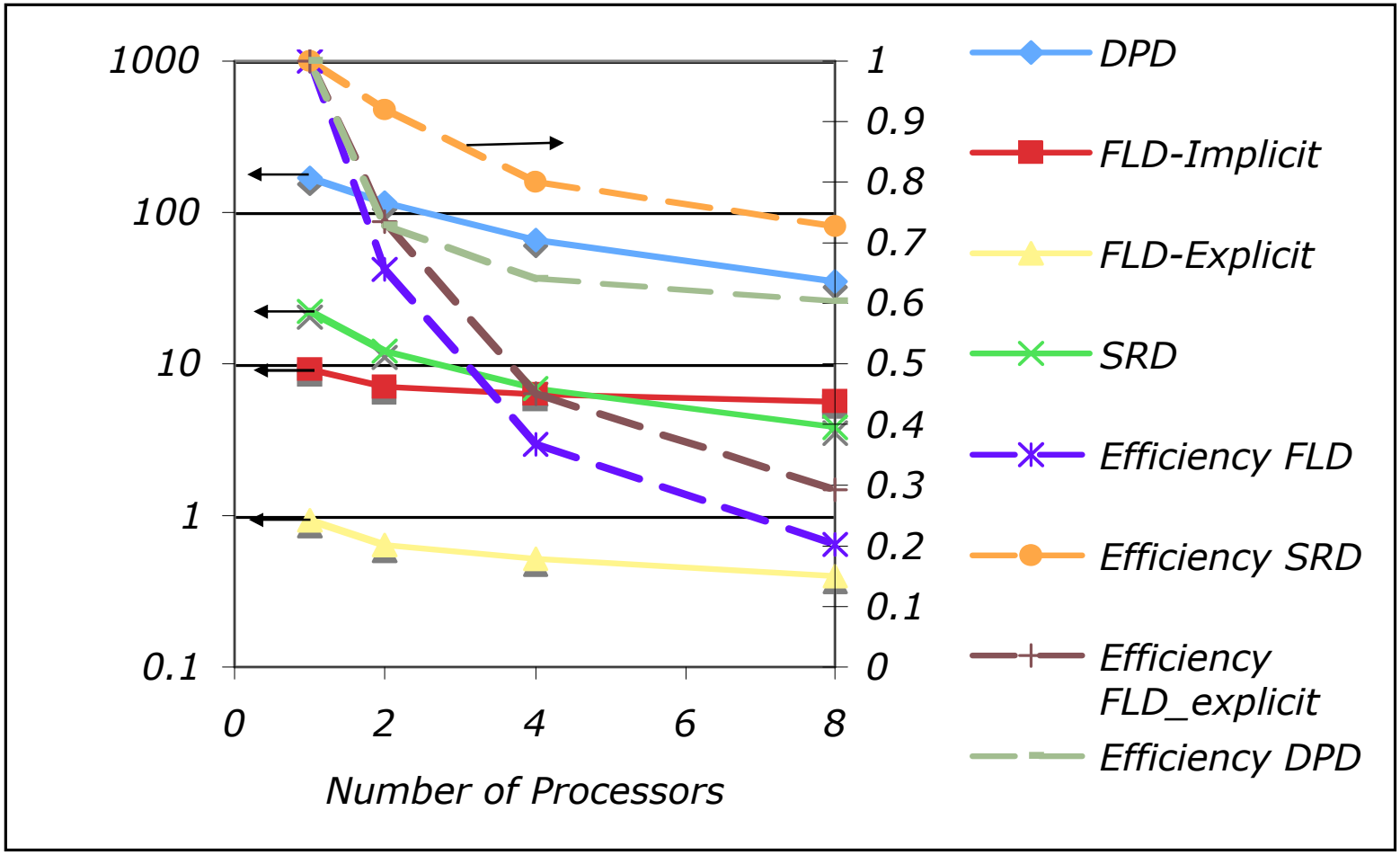
Cross Comparison for Rheology. Experimental comparison



Performance Comparison

0.3 Vol. % PS in Water, 0.001M NaCL, ~220-256 Colloids

- Time reported for 1000 time steps for equilibration/diffusion measurement run. Timings on 8000-node T-Bird Machine: Dual 3.6 GHz Intel EM64T Processors.



Performance Comparison - The Real Story

0.3 Vol. % PS in Water, 0.001M NaCL, ~220-256 Colloids

- Parallel Performance of FLD-Implicit:

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

- Wall-Clock Time to Integrate to 1 s real time (4 Proc):

FLD	FLD_expl	SRD	DPD
124 s	49,961s (13.8 hrs)	69,000 s (~19 hrs) ~2 hrs on 32 proc	~300 hrs

•So why no simply go with implicit FLD? Accuracy and Stokes…

Retrospective and Outlook

Implemented/Developed and demonstrated four solver-methods for dynamics of meso-scale simulations of colloidal suspensions -- *Our work is aimed at the nanoparticle scale.*

Presented verification and validation results (cross-compare and comparisons with experimental test data)

-Radial distribution functions compare well across all methods, verifying potentials

-Diffusivities predicted by FLD and SRD agree at 0.2 and 0.3 volume fraction. DPD-predicted diffusivities suspect at all volume fractions.

-Viscosity at moderate shear rates (1-100 s-1) predicted well vs. volume fraction.

SRD shows the best parallel scalability. FLD-Impl the most cost-effective despite its limitations.

Considering the overall criteria of “Better, faster”:

-Winner: Give to FLD_impl for overall efficiency.

-Loser: Give to DPD for lack of efficiency and accuracy.

SDS confounding our validation effort and in some sense spoiling it. Suspected that a coating is influencing the effecting Hamaker constant and influencing the effective potential.

DPD is just too compute-intensive for this class of problem to be practical, notwithstanding its issues with accuracy. Reasons are primarily time-step limitations, and inefficient solvent respresentation.

Acknowledgements

- Chris Brotherton, Sandia
- Roger Bonnecaze, UT Austin
- Nanoparticle Flow Consortium (NPFC)