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Application of Coarse-grained Methods to Nano-colloid Rheology

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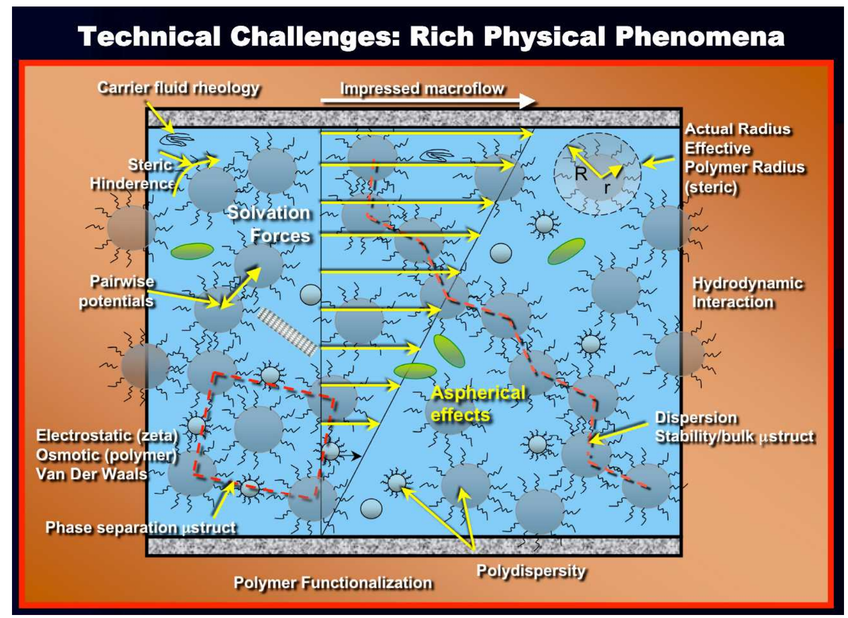
Motivation

- Nanoparticles of various sizes, shapes, and materials provide new opportunities to manufacture functionally tailored materials and devices
- Efficient processing requires understanding the rheological properties of the suspensions
- **Goals:**
  - Develop computational tools to analyze nano and colloidal suspension flows
    - Must be general, robust, accurate, and efficient
      - coarse-grained solvents
      - complex colloid interactions
      - aspherical colloids

Physical System: Total Size and Time

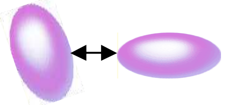
- Low Pe
  - Dispersion stability
  - Mild rheology

- High Pe: Rheology of dense, aspherical nanoparticle suspensions
  - Length and time scales
    - Some rules of thumb
      - O(10^4) particles
      - Strain O(10) box units
      - γ ~ 100 s^{-1}
      - $2a_{eff}$ ~ 10 – 1000 nm
      - Φ_{sc} ~ 0.5
    - L ~ O(0.1 – 10 μm)
    - v_s ~ O(10 – 1000 μm/s)
    - T ~ O(0.1 – 1 s)



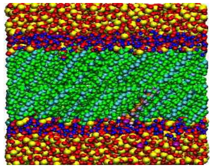
Technical Approach: Integrated, Hierarchical Capability

Molecular Dynamics

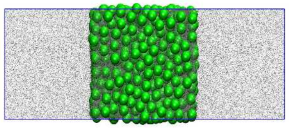


Effective potentials

Molecular scale — nanoseconds, 0.1 to 10 nm



Particle Scale — microseconds, 10 to100 nm



"Mesoscale" — milliseconds, 100 nm-10 μm

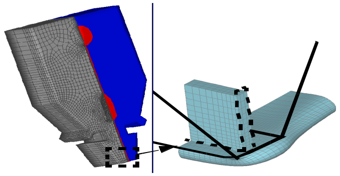
Coupled particle-fluid Interactions:
DEM-NS, SRD, DPD, SD

Constitutive Relations

Micro-structure

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

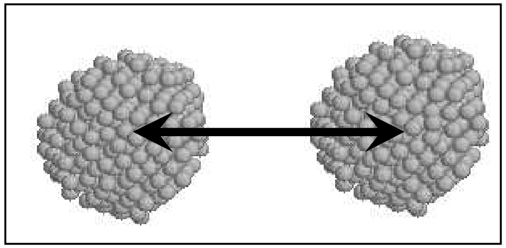
FEM, ASC SIERRA APPS:
ARIA



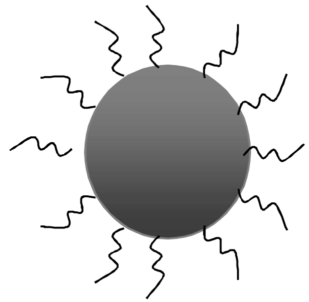
Engineering Scale — Seconds, mm

What is needed? - Coarse Graining

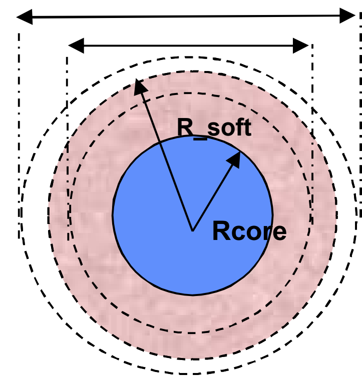
Particle



Integration to Hammaker's Equation and equivalent



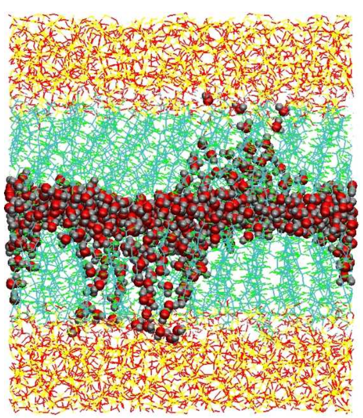
Osmotic and steric/structural representation



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

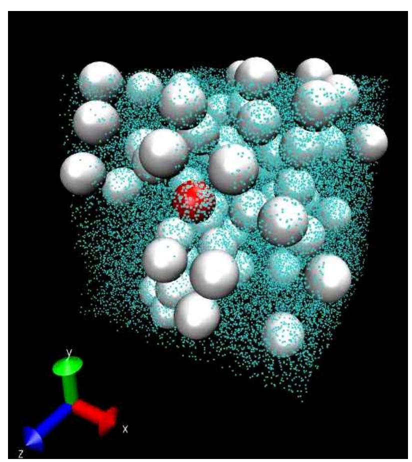
Solvent

Molecular Dynamics

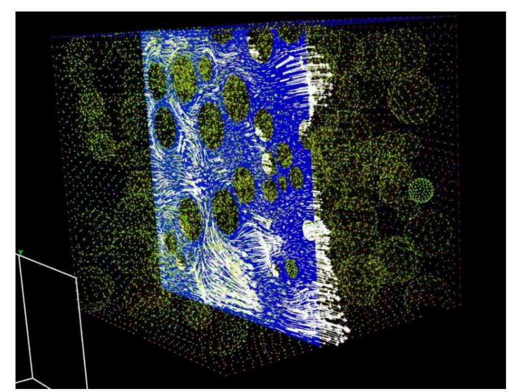


Grest et al.

Blobs->SRD/DPD: dual particle approach

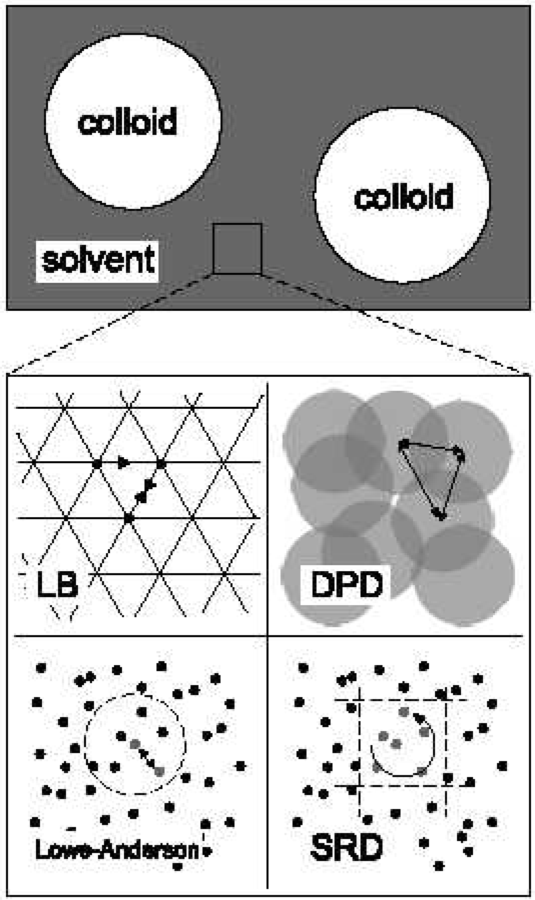


Continuum: FEM, SD



Solvent Methods

- **Multiple methods to treat hydrodynamics**
  - Particle-based ("explicit") treatment of solvent
    - Atomistic solvent (e.g. LJ solvent)
    - "Approximate" coarse-grained solvent
      - DPD solvent
      - SRD solvent treated as ideal fluid particles with a mass
  - Continuum approaches
    - BD – Stokes drag, Oseen tensor, FLD, etc.
    - SD/BEM
    - Solve continuum Navier-Stokes equations numerically

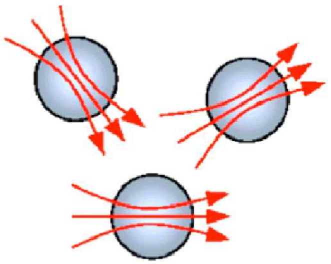


- **Computational cost**
  - MD requires the calculation of all solvent-solvent interactions which are typically *many* orders of magnitude larger in number than the solute particles
  - SRD computational cost scales as N

Governing Equations

- **Langevin Equation**

$$m\frac{dU}{dt} = F^H + F^B + F^P$$

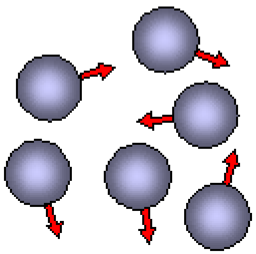


- **Hydrodynamic Force**

$$F^H = -R\,U$$

- **Brownian Force**

$$\begin{aligned} < F^B > &= 0 \\ < F^B F^B > &= 2kTR/\Delta t \end{aligned}$$

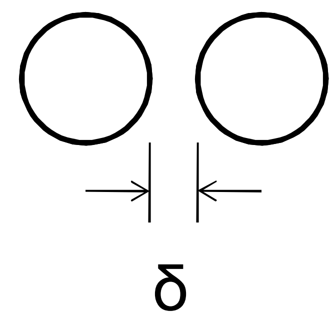


Hydrodynamic Interaction

- **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

Tuned to Match

Average Mobility

Asymptotic lubrication Interaction only

δ FLD ~ 1/ δ

δ-logδ FLD ~ 1/ δ + ln(1/ δ)

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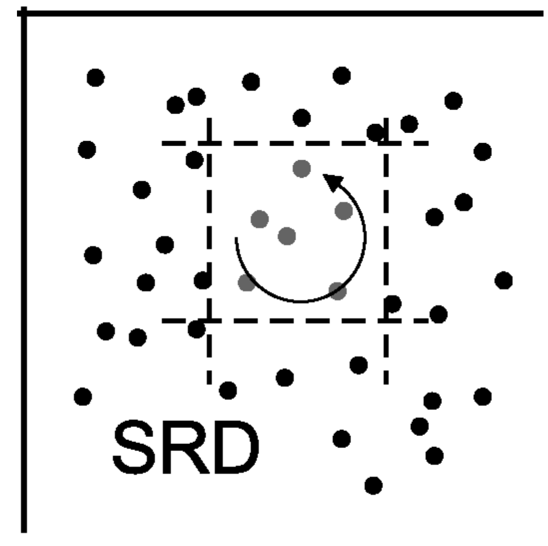
Stochastic Rotation Dynamics (SRD)

- Simulation domain divided up into cubic cells of side *a*
  - On average, *M* SRD particles with mass m_f are placed in each cell of volume Δx^3
- Two simulations steps
  - Particle streaming
    - particles move according to Forward Euler $\boldsymbol{v}_\iota\tau$
  - Velocity update (coarse-grained collision)
    - Apply rotation about randomly chosen axis to fluctuating part of the velocity



$$\mathbf{v}_i(t+\tau) = \mathbf{u}(\xi_i(t+\tau)) + \omega(\xi_i(t+\tau))(\mathbf{v}_i(t) - \mathbf{u}(\xi_i(t+\tau)))$$

- Can also have $U(r_{coll}-r_{SRD})$

$$m_f \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i$$

$$\frac{dr_i}{dt} = \mathbf{v}_i$$

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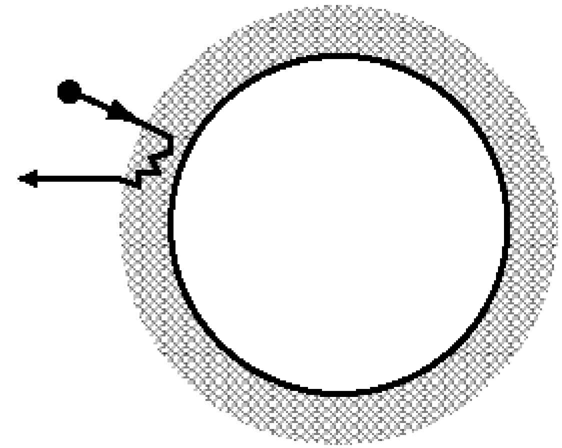
Coupling to Colloids

- To avoid finite size effects $a < R_c/2$
- Srd particles collide with colloids
  - Solvent coarse-grained so assume no-slip via stochastic rule
    - SRD particle receives a new random velocity magnitude

$$P(v_n) \propto v_n \exp(-\beta v_n^2)$$

$$P(v_t) \propto \exp(-\beta v_t^2)$$

    - Difference in new and old velocity is momentum transferred to colloid
- Can have generalized slip conditions or pair-interaction, $U(r_{coll}-r_{SRD})$



Selecting Parameters for LJ System

- Dynamics of interest

$$D_{coll} = \frac{1}{6\pi R_{coll}}\left(\frac{k_B T}{\rho_f \nu_f}\right), \quad \nu_r = {}^{\nu_{bulk}}\!/\!_{\nu_f}$$

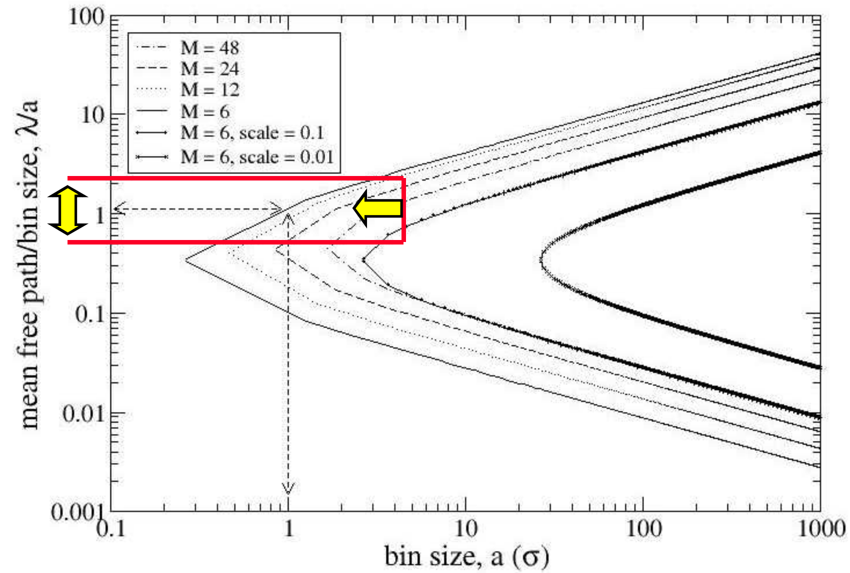
$$Pe = \frac{\tau_D}{t_s} = \frac{4R_{coll}^{\ 2} / D_{coll}}{2R_{coll} / u_s} = 12\pi u_s R_{coll}^{\ 2}\left(\frac{\rho_f \nu_f}{k_B T}\right)$$

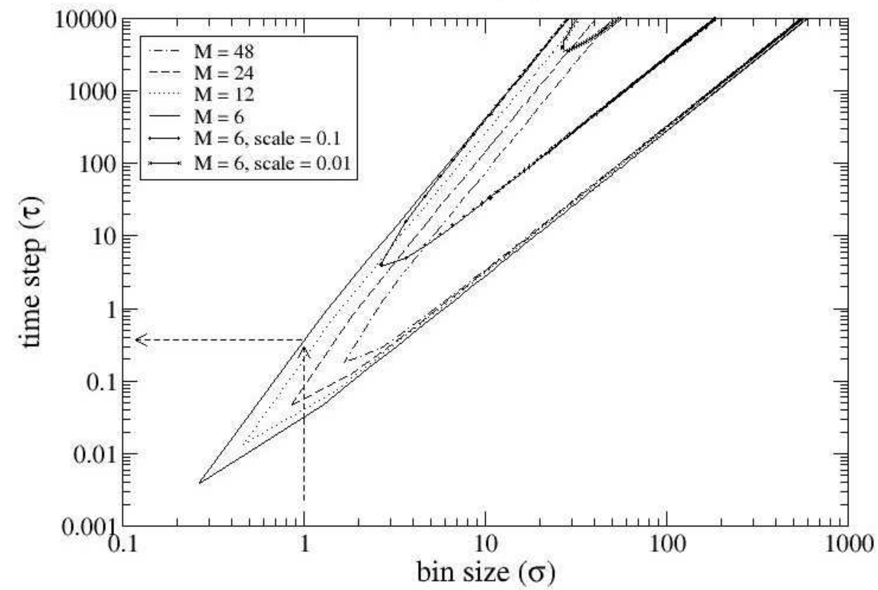
- Physical parameters: $\rho_f, \nu_f, kT, P, R_{coll}$
- Computational parameters

$$\nu_f = \frac{\Delta x^2}{18\Delta t}\left(1 - \frac{1-e^{-M}}{M}\right) + \frac{k_B T \Delta t}{4\rho_f \Delta x^3}\frac{M(M+2)}{M-1}$$

$$\lambda = \Delta t\sqrt{{}^{Mk_B T}\!/\!_{\rho_f \Delta x^3}}, \quad \lambda > 0.5\Delta x, \quad \lambda << R_{coll}$$

$$\rho_f = {}^{Mm_f}\!/\!_{\Delta x^3}, \quad \frac{P}{k_B T} = \frac{M}{\Delta x^3}, \quad \Delta x < {}^{R_{coll}}\!/\!_{2}$$

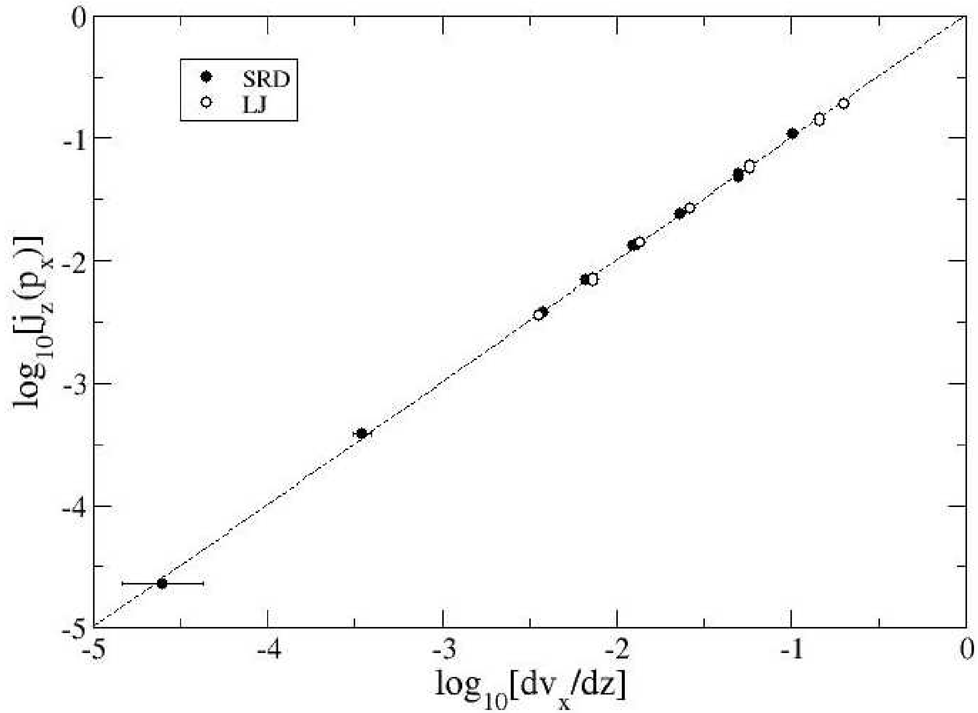




Comparison of Pure LJ and SRD Solvents

- **Solvent properties (LJ units)**
  - $\rho_f = 0.6$
  - $k_B T = 1.0$

- **Non-equilibrium low shear-rate (Muller-Plathe)**
  - **extrapolate to zero shear intercept**
    - $\nu_{meas,LJ} = 1.67$
    - **Use to get SRD parameters**
    - **Measured SRD viscosity is as expected**



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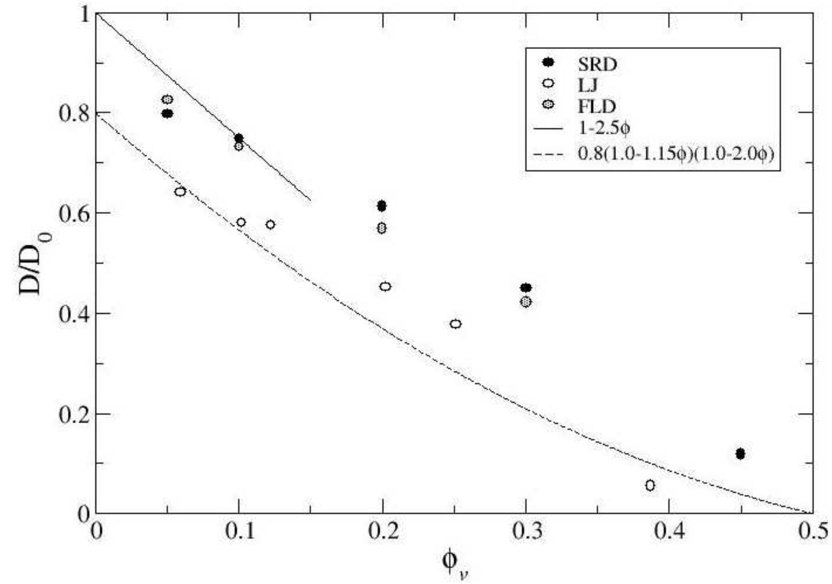
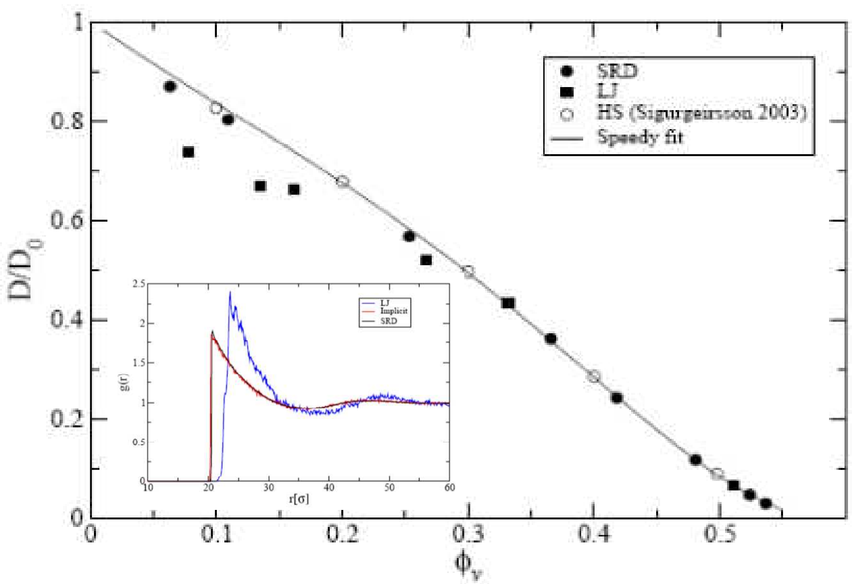
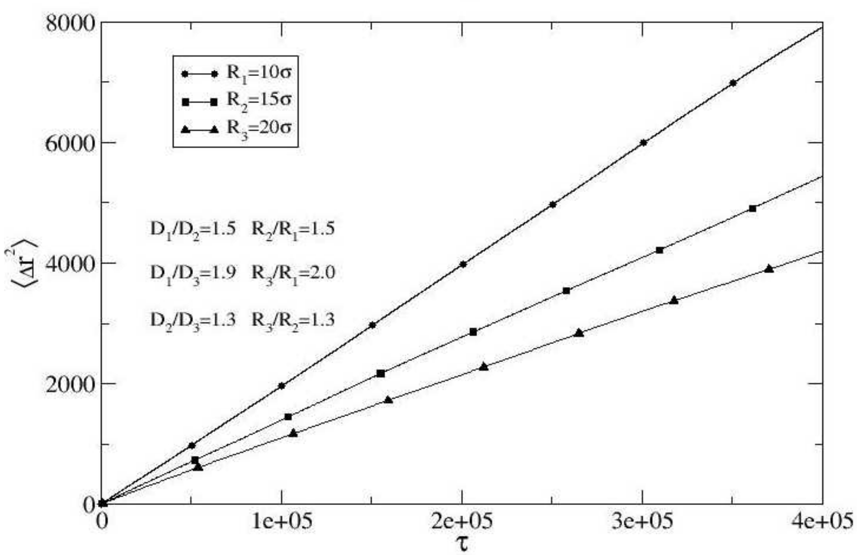
Equilibrium: Colloid Diffusion

- **Diffusion as a function of volume fraction of d = 20σ colloids**
  - **Comparison to explicit LJ solvent results**
  - **Comparison to FLD**

- **MSD for three different sized colloids**



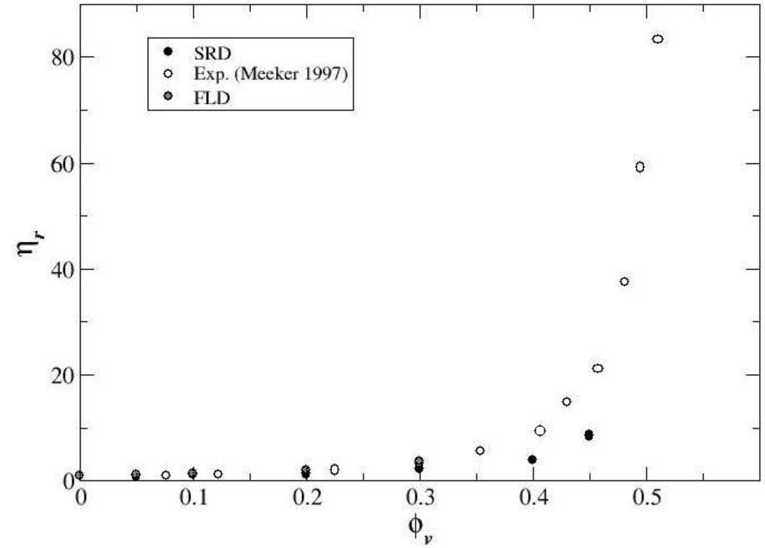


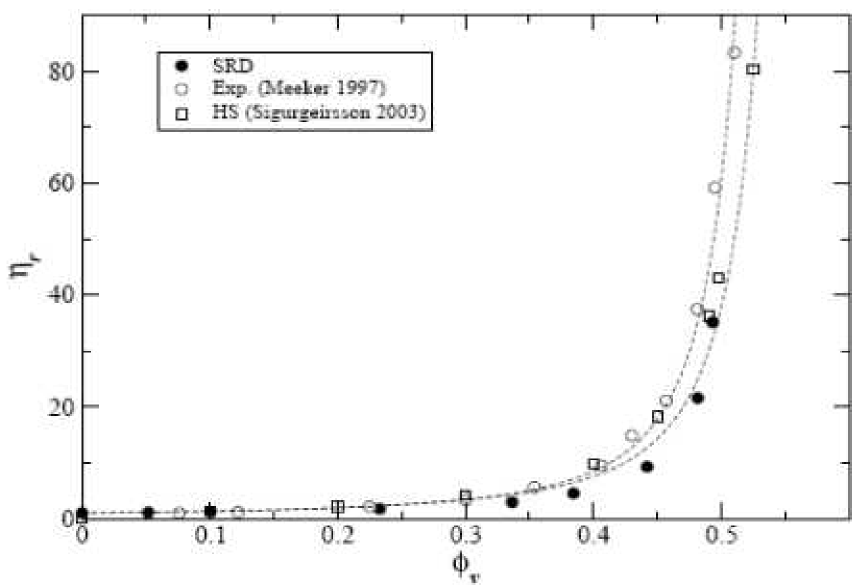


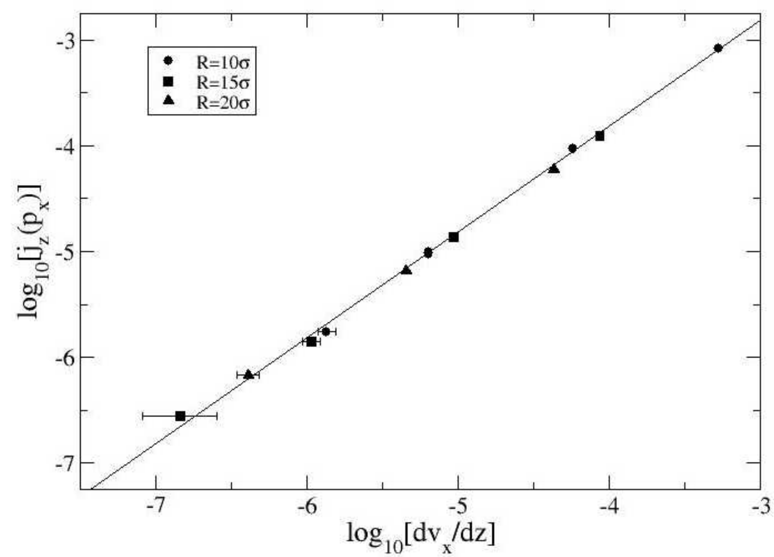
Non-equilibrium: Low Shear-rate Bulk Viscosity

- **Reduced viscosity as a function of volume fraction of d = 20σ colloids**
  - **Comparison to FLD**
  - **Comparison to Experimental results of Meeker (1997)**

- **Total momentum flux as a function of shear rate for suspensions of different**



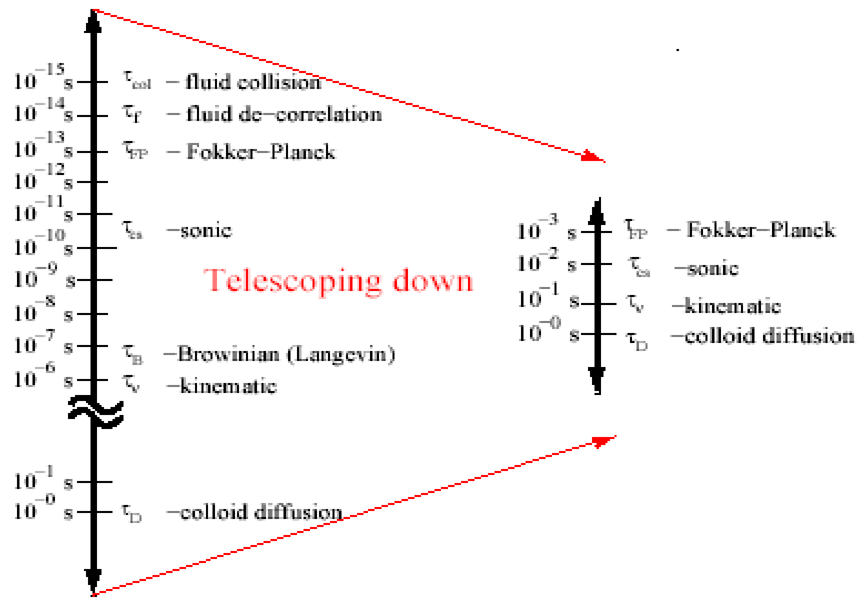




Summary and Outlook

- Validation with literature results almost complete
  - Some “punch-list” items being wrapped up
- Validation with NPFC Model systems ongoing
  - See Randy and Matt P.
- Extend Method for
  - Solvent removal: EISA
  - Phase separating, multi-component systems
  - Viscoelastic solvents

$$\tau_\nu = \frac{4R^2}{\nu_{sim}}$$



Time scales for 1 μm colloid in water.

From Padding and Louis (2006) cond-mat/0603391