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Investigating Colloidal Systems via Inertial and Noninertial Fast Lubrication Dynamics

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Outline

- Topic: Colloidal Systems
- Methods: Inertial and Noninertial FLD
- Systems Investigated and Results
- Considerations
- Summary
- Acknowlegements

Colloidal Simulations

- Explicit solvent methods too expensive for large systems at moderate concentration with large colloids, even for relatively simple monodisperse systems
- What is the best methodology to characterize the mobility and shear response?
- Implicit solvent methods Investigated:
  - **Inertial vs. Inertialess Fast Lubrication Dynamics (FLD)**
  - Stochastic Rotation Dynamics (SRD)
  - Dissipative Particle Dynamics (DPD)

Inertial Fast Lubrication Dynamics

- Inertial Langevin Equation: $m\mathbf{a} = \mathbf{F}_{HS}+\mathbf{F}_{hydro}$
- $\mathbf{F}_{HS}$ - hard sphere interactions:
  - steep integrated colloid potential (Everaers)
- $\mathbf{F}_{hydro}$ - hydrodynamic forces:
  - solvent viscosity η, temperature T, particle size d, volume fraction ϕ
  - $\mathbf{F}_{hydro} = R\mathbf{v} + \mathbf{F}_{stoch}$
  - full resistance tensor R characterizes dissipative forces: $R\mathbf{v}=\mathbf{F}_{iso\text{-}drag}+\mathbf{F}_{lub}$
  - $\mathbf{F}_{iso\text{-}drag} = 3\pi\eta d v f(\phi)$
    - f(ϕ) is a function of the volume fraction of the system – Higdon et al. determined this for monodisperse system
  - $\mathbf{F}_{lub} \sim \mathbf{v}_{ij}/h_{ij}$
    - Depends on relative particle velocities $\mathbf{v}_{ij}$, surface separation h_{ij}
  - $\mathbf{F}_{stoch}$
    - Stochastic thermal forces from solvent coupled to dissipative forces through fluctuation/dissipation theorem

- This equation can resolve the full dynamical range of particle motion - early time ballistic -> cage dynamics -> late time diffusion (if any)

Inertialess Langevin Equation

- Assumes inertial timescales much smaller than other timescales of interest (diffusive, structural relaxation, shearing, etc.)
- $0 = m\mathbf{a} = \mathbf{F}_{HS} + \mathbf{F}_{hydro} = \mathbf{F}_{HS} + \mathbf{F}_{stoch} + R\mathbf{v}$
- $\mathbf{v} = -R^{-1}(\mathbf{F}_{coll} + \mathbf{F}_{stoch})$
- Requires inversion of the resistance tensor (costly)
- Potentially allows larger timesteps than inertial langevin equation
  - Not always realizable
- Inertial timescales cannot be resolved with this method – motion is diffusive even at earliest times – difficulty describing motion inside regions where diffusion does not occur

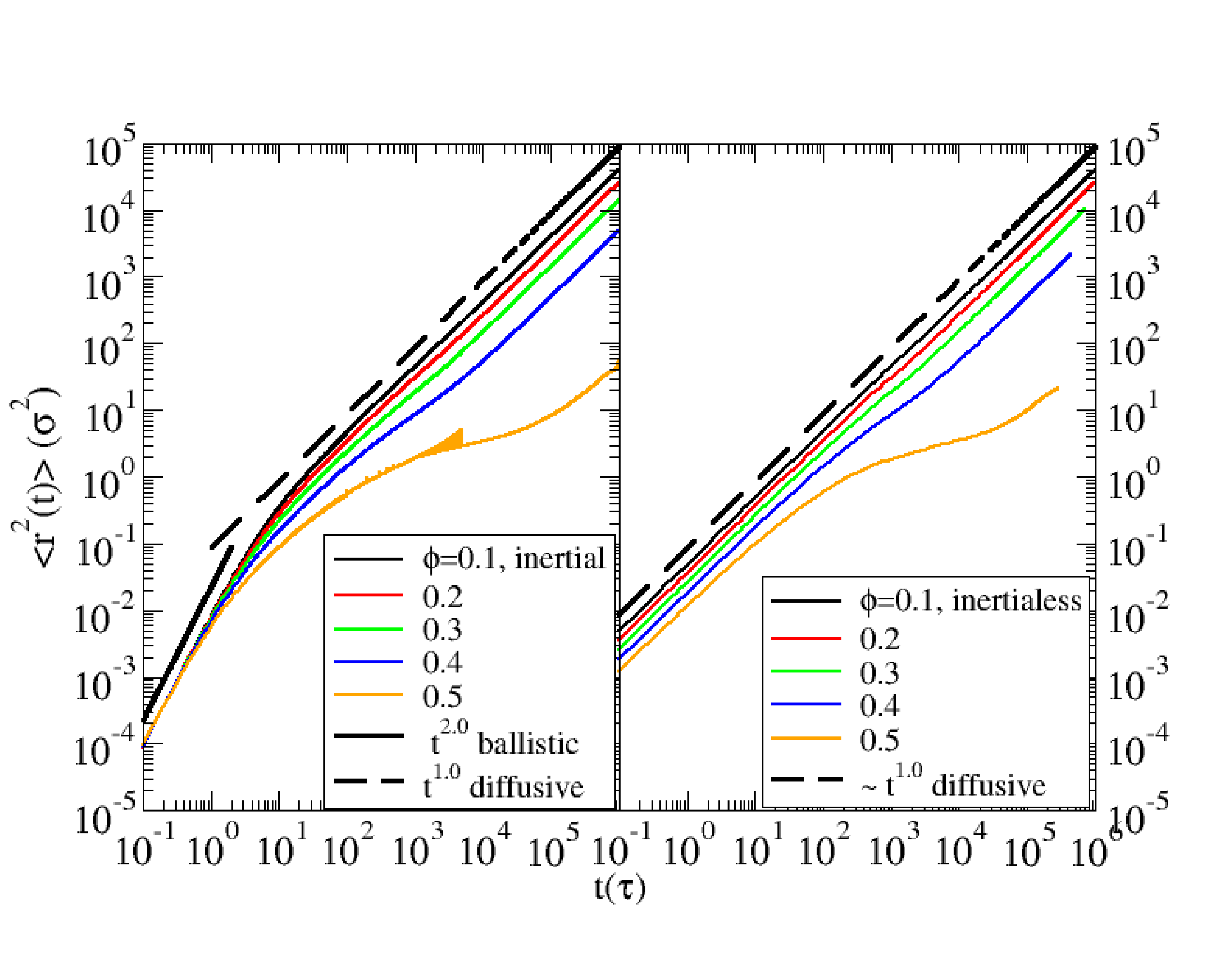
Issues

- Early results indicated difference between noninertial and inertial Langevin equation solutions to mid to late time dynamics (diffusion) in a colloid – resolved
- Telescoped inertial Langevin equations are an alternate method for providing late time information for systems where the inertial Langevin equation cannot achieve the necessary time scales

Model System 1

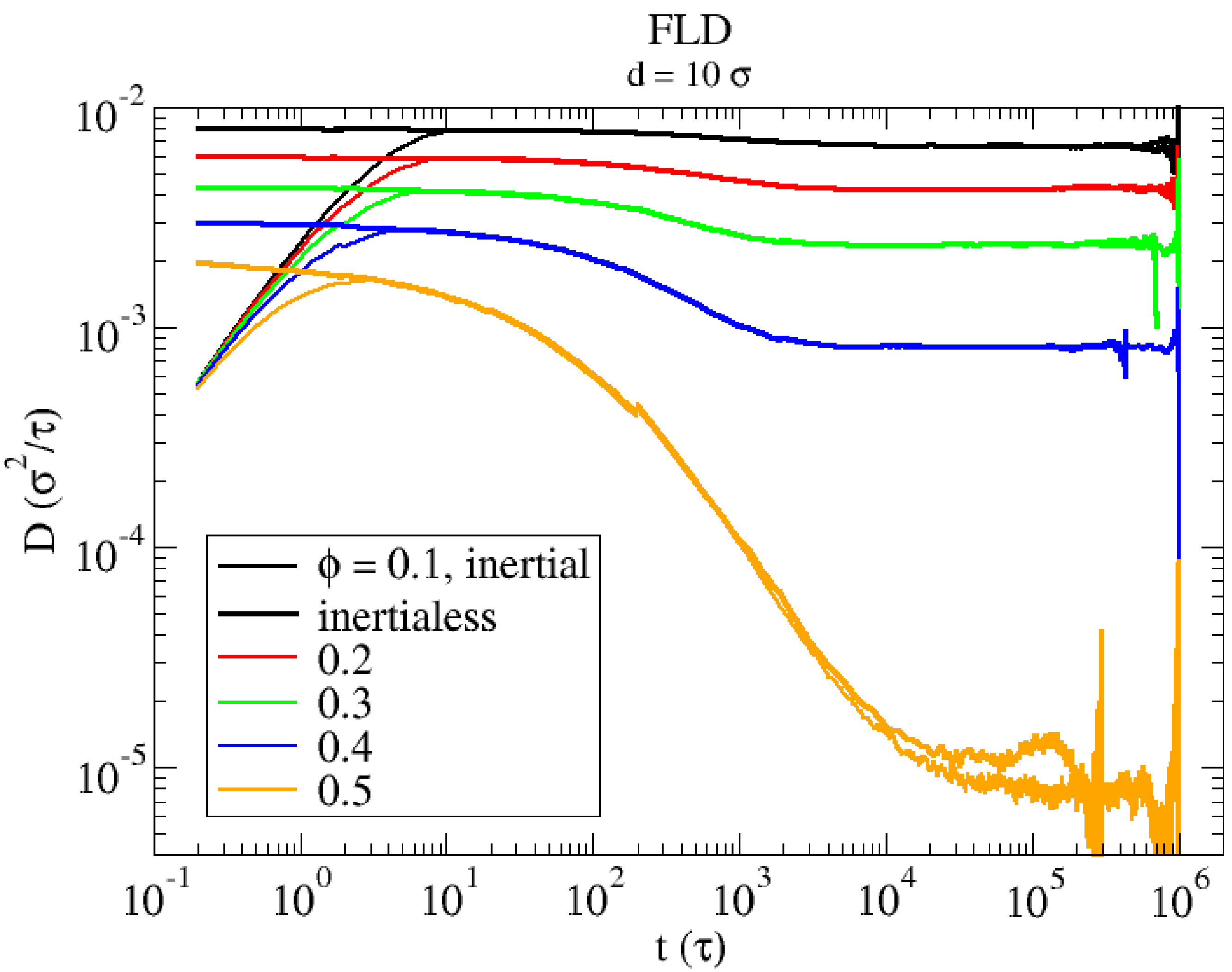
- 2048 colloids
- LJ-like system (length in σ, time in τ, mass in m)
- d = 10σ
- implicit solvent with η=1.01 m/στ
- kT=1
- Hard sphere colloid potential (Everaers)
  - H = $4\pi^2$ (Hammaker constant)
  - $\sigma_{coll} = \sigma = 0.1d$ (width of potential)
  - cutoff at minimum ($30^{-1/6}\sigma_{coll}$) for repulsive interactions only
- ϕ = 0.1 - 0.5
- Explicit and Implicit Langevin equations used to solve for particle motion

Results: Mean Square Displacement



- Both methods agree well for late time values but early time behavior is distinct
- Inertial resolves ballistic regime
- Inertialess gives "artificial" value for early time "diffusion"crossing over at late times to value that agrees with inertial
- For this case, a larger timestep CANNOT be used with inertialess simulations – system becomes unstable

Results: Diffusivities



D(t) is slope of msd

Good agreement between inertial and inertialess solutions for all ϕ at times from early time diffusion to late time diffusion

Inertialess FLD does not resolve ballistic particle motion while inertial FLD does

Effect of Lubrication Forces

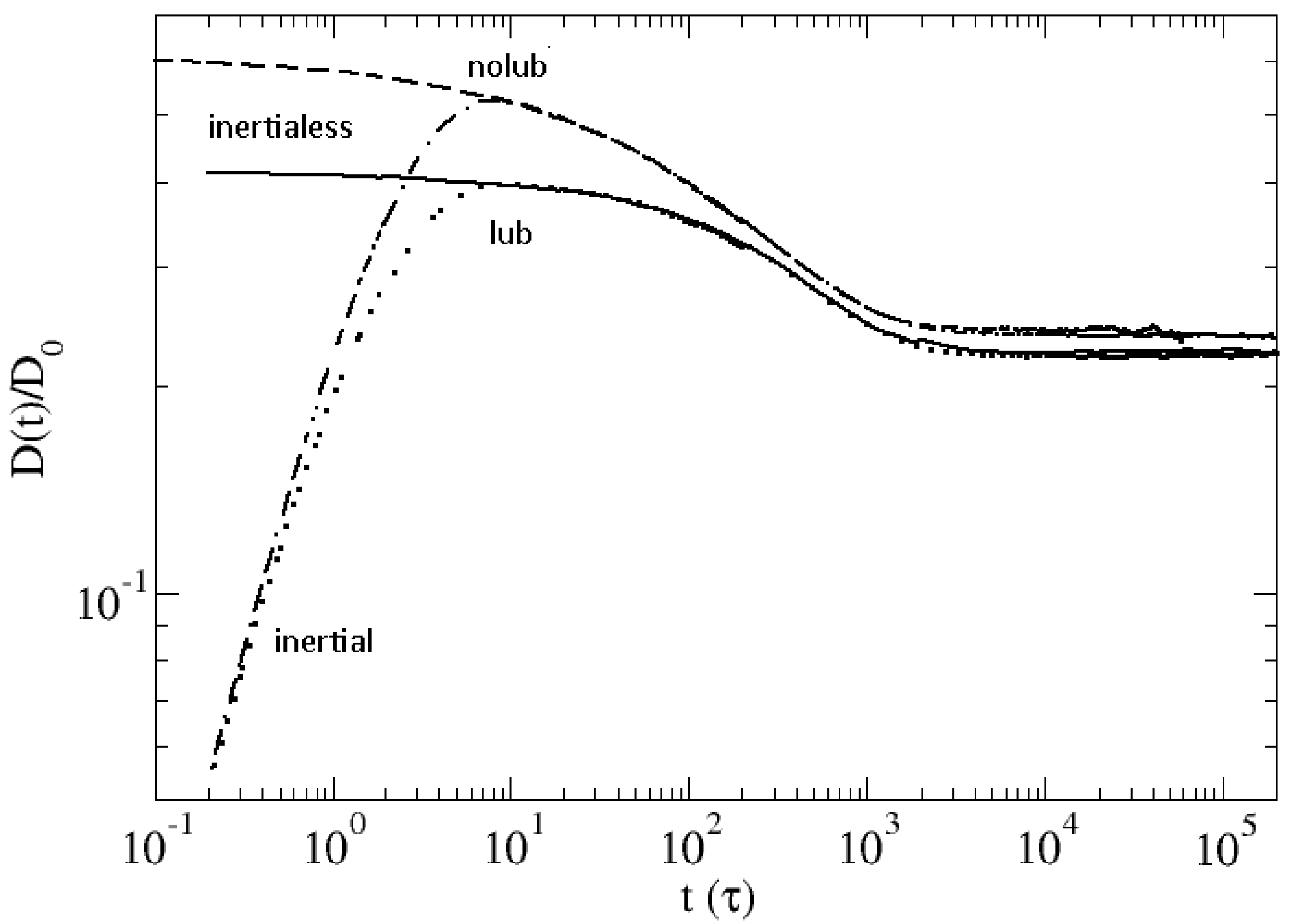


FIG. 4: Diffusivities vs. t for $\phi = 0.3$ for inertialess FLD with lubrication (solid) and without (dot) and inertial FLD with lubrication (dash) and without (dash-dot).

- For both inertial and noninertial FLD, lubrication forces reduce early time dynamics but have minor impact (~10%) on late time dynamics

Results: Validation

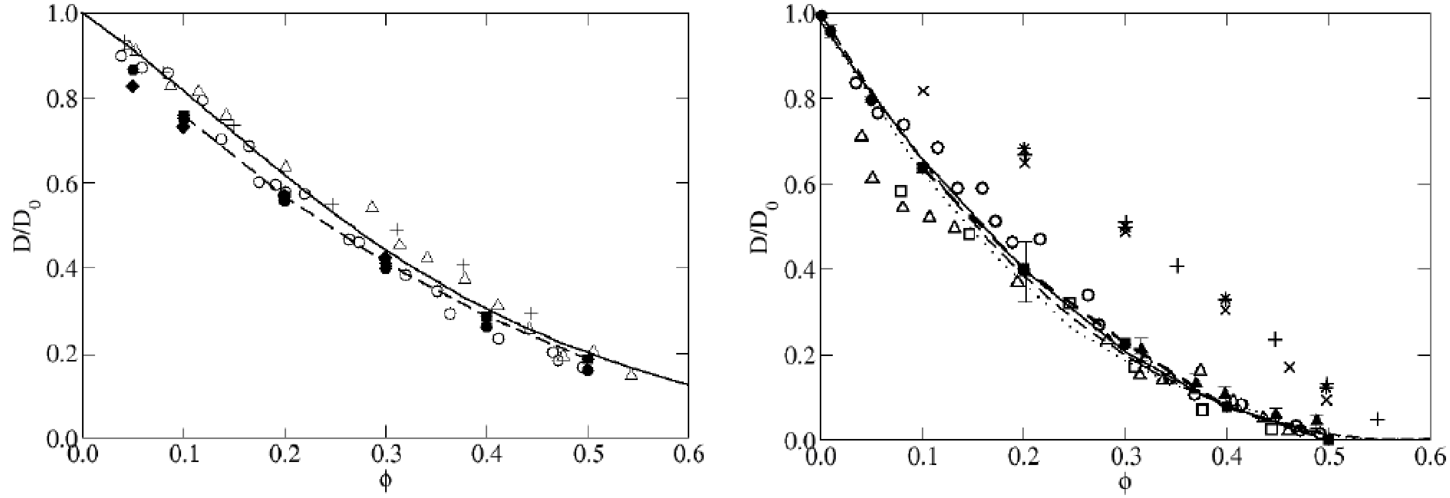
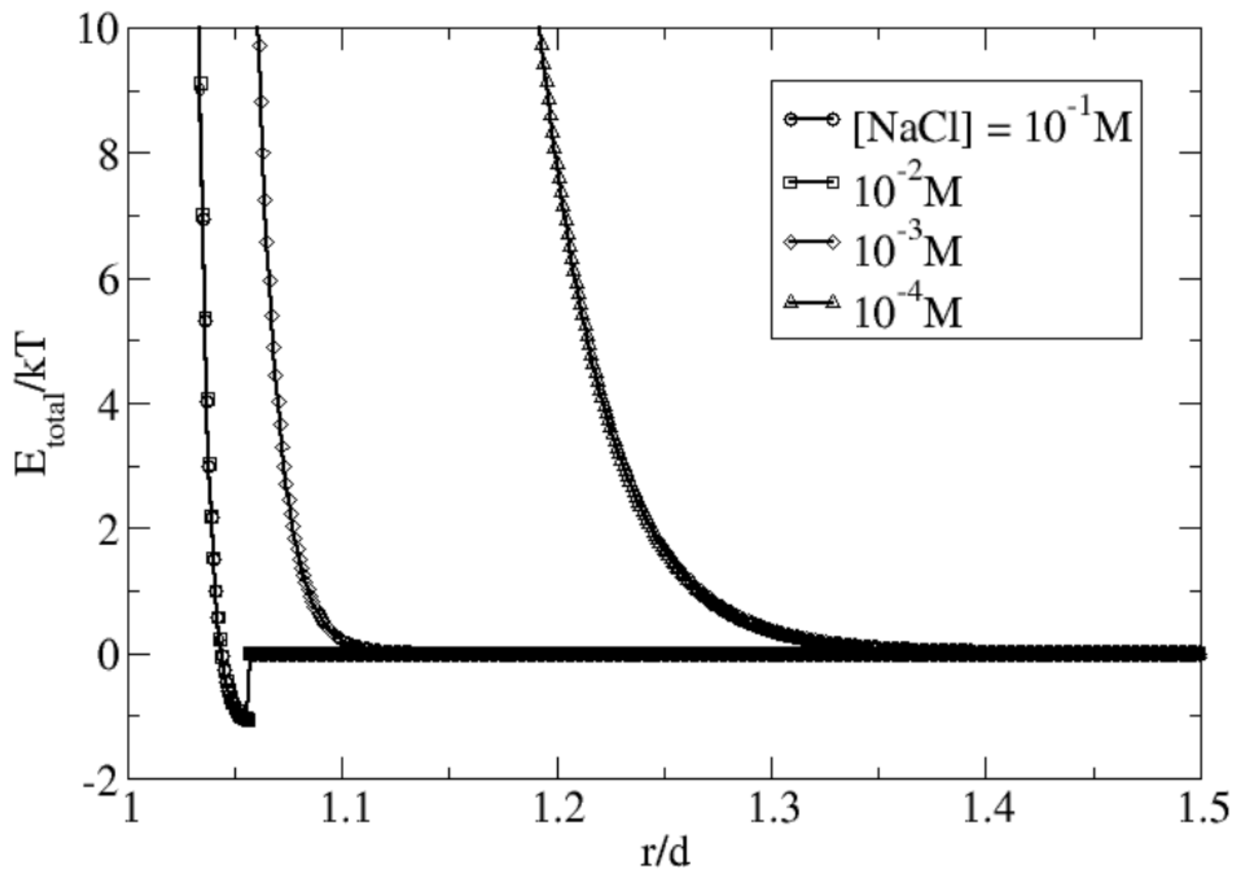


FIG. 2: a) LEFT: Early time diffusivities vs ϕ for FLD simulations: inertial (solid circle), noninertial (solid square - dash line), Higdon et al. (solid diamond), theoretical predictions by Tokuyama (solid line), and experimental results by Ottewill (open triangle), van Veluwen (+), and van Megen (open circle). b) RIGHT: Late time diffusivities vs ϕ for simulations: FLD inertial (solid circle), FLD noninertial (solid square - dash line), SD - Foss/Brady (solid triangle), BD - Foss/Brady (+), BD - Cichocki (x), BD - Schaertl (*), theoretical prections: Schweizer (dot line), Tokuyama (dash line), quadratic fit (solid line), and experimental results: Ottewill (open triangle), van Veluwen (open square), and van Megen (open circle).

Model System 2

- 2048 colloids
- PS-H_20 system
- d = 950nm (stabilized with SDS)
- $\eta = 10^{-3}$ Pa·s
- T=298.15K
- Hard sphere colloid potential (Everaers)
  - $H_{PS\text{-}H20}$ (Hammaker constant)
  - $\sigma_{coll} = \sigma = 0.1d$ (width of potential)
  - cutoff at minimum ($30^{-1/6}\sigma_{coll}$) for repulsive interactions only
- Yukawa electrostatic screening with [NaCl] = 10^{-4} M → 10^{-1} M
- $\phi = 0.1 - 0.4$
- Explicit and Implicit Langevin equations used to solve for particle motion

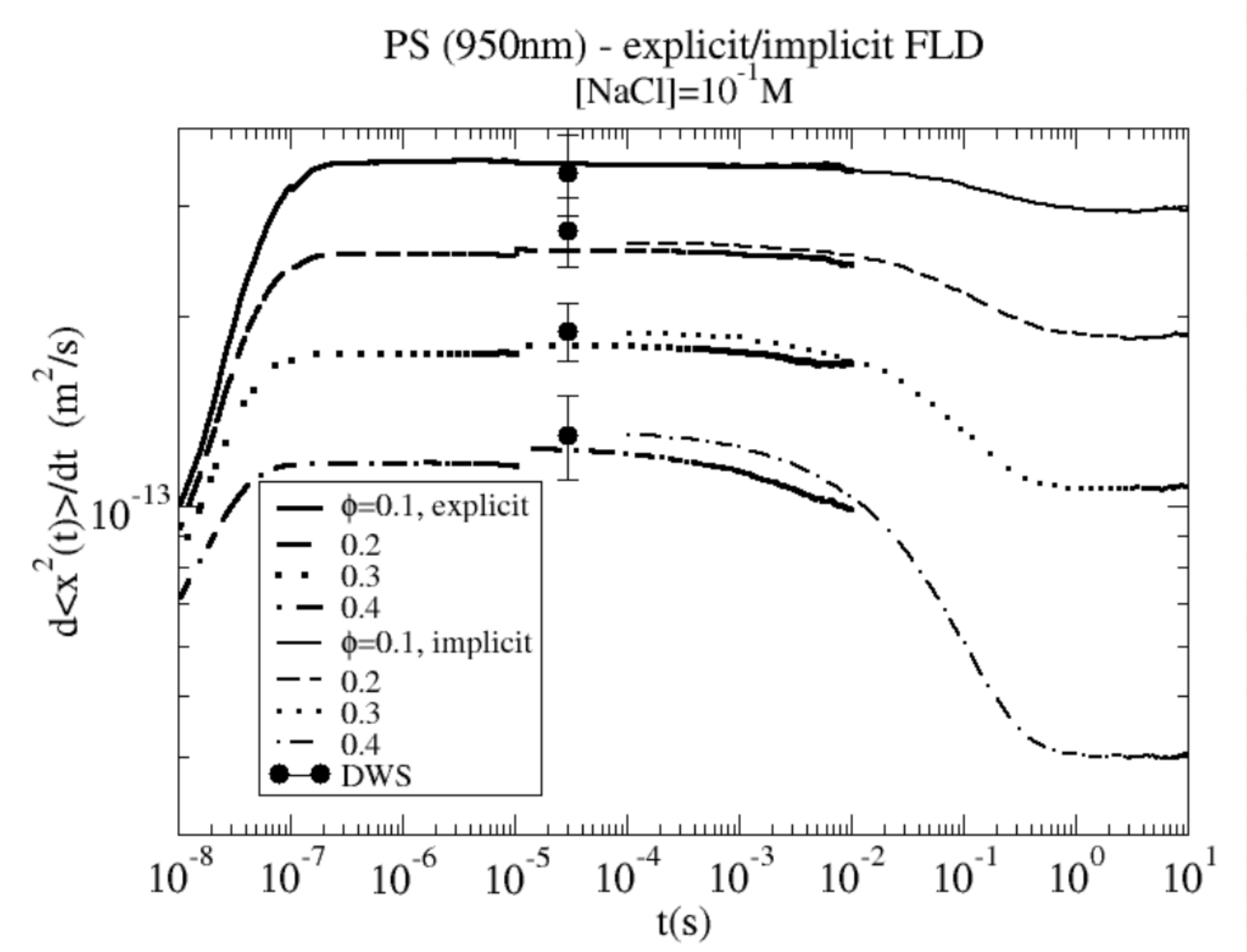
Interaction Potential



Interparticle Potential for 950 nm charged polystyrene in water

- At high salt concentrations hard sphere colloid potential dominates ([NaCl]=10^{-1}-10^{-2}M)
- At low salt concentration, yukawa electrostatic potential dominates (10^{-4}M)

Results: Diffusivities



- Actual System behaved most like $[NaCl]=10^{-1}M$ due to SDS – little electrostatic interaction but still repulsive
- Explicit FLD allows for resolution of particle mobility from early times (ballistic timescale ~ 10ns) to crossover from early to late time diffusivity
- Implicit FLD allows for resolution of particle mobilities from crossover to well into late time diffusivity range
- LARGE range of timescales

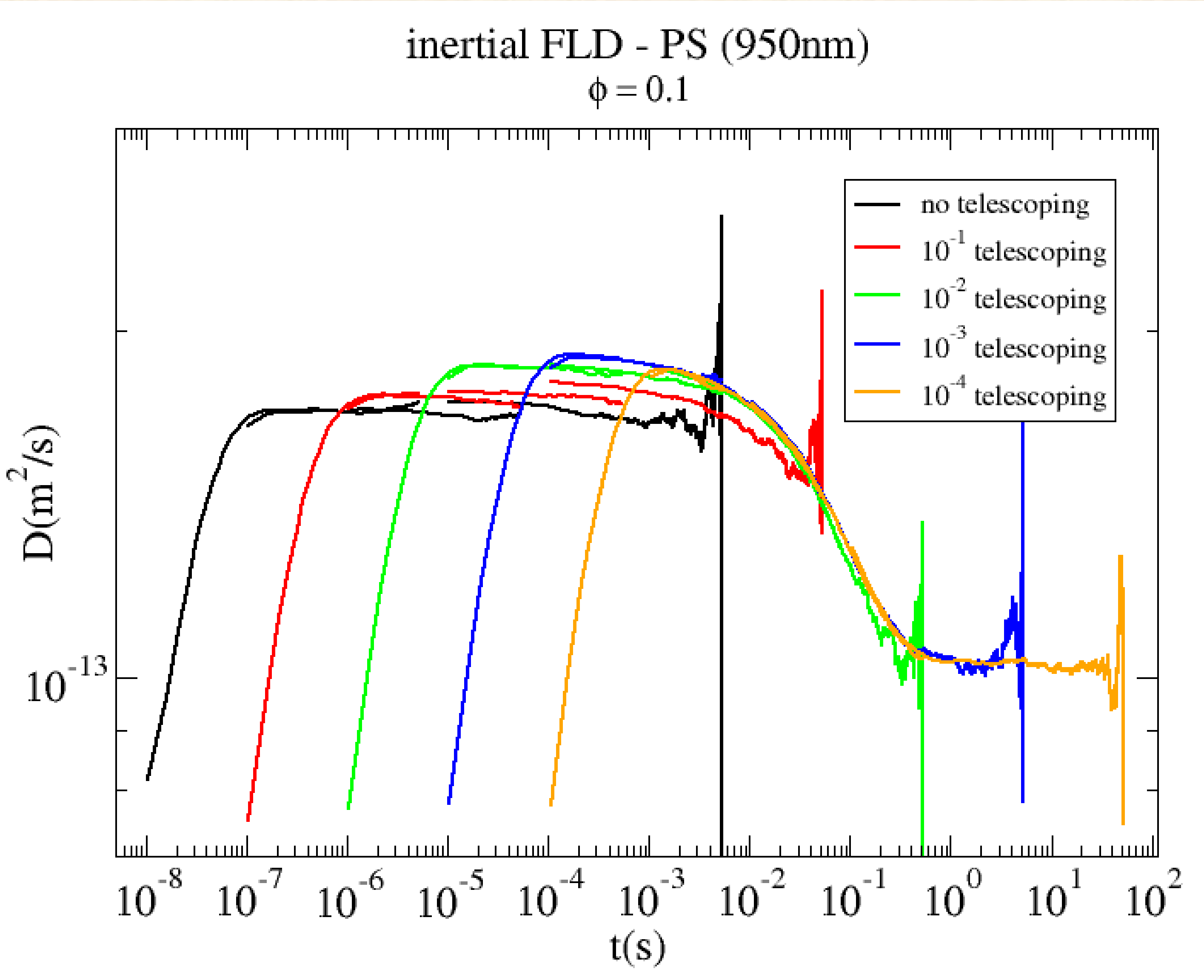
Alternative Method - Telescoping

- Dynamically similar: T, η, E_{pair} (colloid, Yukawa) scaled by $f < 1$
  - D unaffected in principle (D ~ T/η - unchanged)
  - Same range of potential explored by particles (E_{pair}/kT – unchanged)

- Larger simulation timestep available (similar to inertialess FLD)
- Inertial FLD is cheaper to run (no resistance matrix inversion)

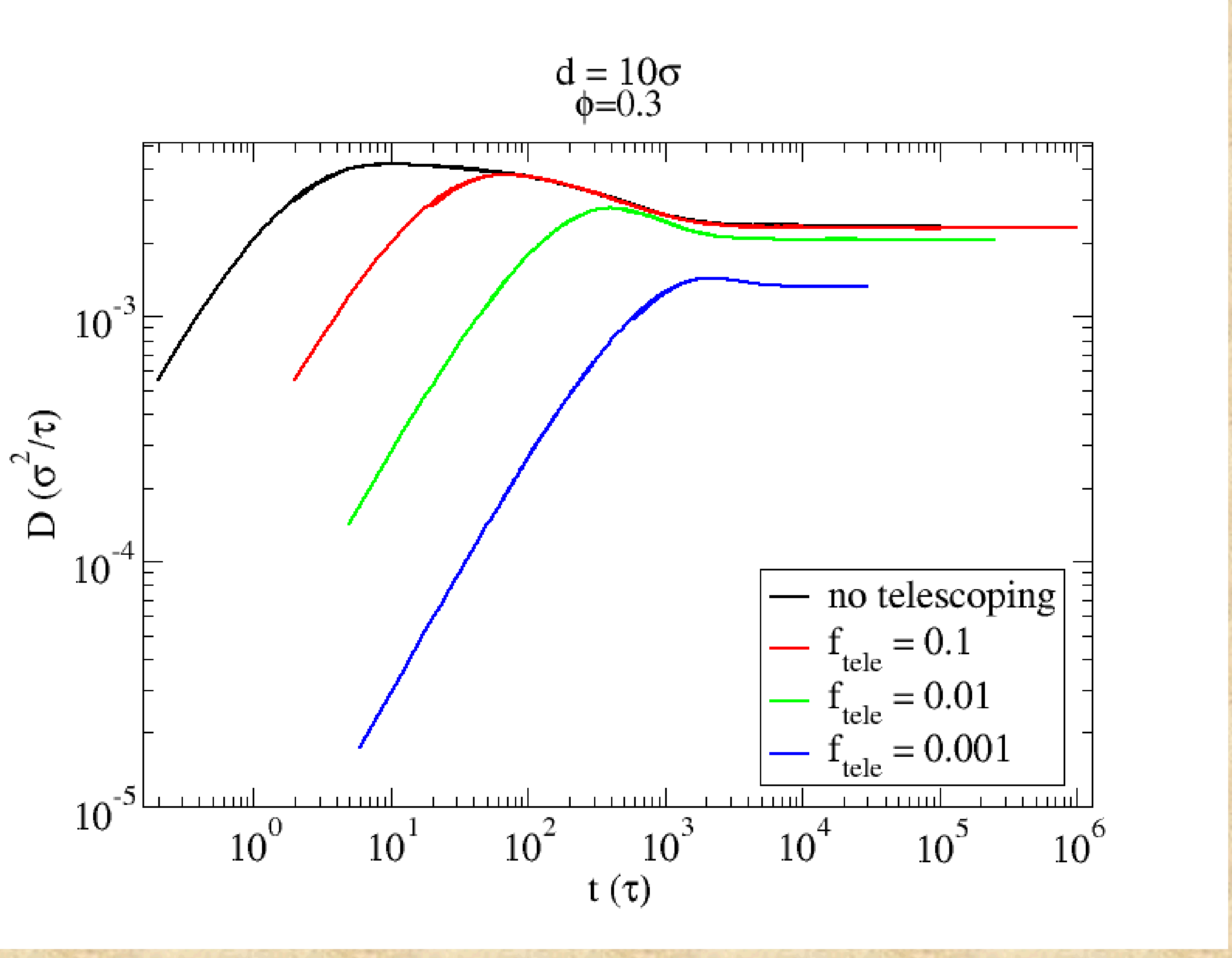
- Inertial timescales are pushed forward by 1/η
  - Momentum relaxation $\tau_B = 1/18(\rho_{coll}/\eta)d^2$
- Diffusive tiemscale is unaffected
  - Diffusive time $\tau_D = 3\pi\eta d^3/4kT$
- Care must be used in not pushing the two timescales together
  - System can move from diffusive inside cage of other particles to ballistic inside cage – this WILL affect both early and late time dynamics

Results: Diffusivities via Telescoping



- Large increase in timestep available using telescoping – comparable to inertialess
- Simulation is faster due to reduced cost of inertial simulation methodology
- Small affect on early time diffusivity that increases with telescoping factor (10-20%)
- Little or no adverse affects on late time dynamics

Limitations of Telescoping



- Telescoping works well for telescoping factors that maintain τB<τD
- Late time D affected adversely if condition is not met
- Particles are ballistic rather than diffusive in their cages

Summary

- Inertial and Noninertial FLD are useful implicit solvent methods for simulating particle mobility in colloidal suspensions - they compare well with experimental results for both early and late time behavior
- Implicit FLD potentially allows for larger timesteps by imposing diffusive motion at all timescales (inertial effects unresolved) – though the per-timestep cost is higher due to resistance matrix inversion
- Explicit FLD resolves all timescales but cannot be used to obtain late time mobilities for systems where there is a large difference between inertial and diffusive timescales
- Telescoped FLD is an alternative method for achieving late-time mobilities by scaling key system parameters while maintaining a dynamically similar system – it requires care in choosing an appropriate telescoping factor to avoid overlap of inertial and diffusive timescales

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