Multiscale Methods for Hydrodynamics of Complex Fluids

Aleksandar Donev[1]
Lawrence Postdoctoral Fellow
Lawrence Livermore National Laboratory
Collaborators:
Berni J. Alder, *LLNL*
Alejandro Garcia, *San Jose State University*
John Bell, *LBL*

UT Austin, January 2009

---

[1] This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (LLNL-PRES-408395).

Outline

1. Introduction
2. Particle Methods
3. Coarse Graining of the Solvent
4. Continuum Solvent
5. Bead-Solvent Coupling
6. Hybrid Particle-Continuum Method

Micro- and nano-hydrodynamics

- Flows of fluids (gases and liquids) through micro- (μm) and nano-scale (nm) structures has become technologically important, e.g., **micro-fluidics, microelectromechanical systems (MEMS).**
- **Biologically-relevant** flows also occur at micro- and nano- scales.
- The flows of interest often include **suspended particles**: colloids, polymers (e.g., DNA), blood cells, bacteria: **complex fluids**.
- Essential distinguishing feature from “ordinary” CFD: **thermal fluctuations**!

Example: DNA Filtering

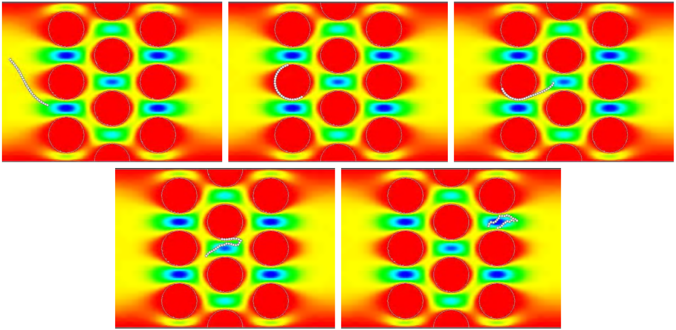


Figure: From the work of David Trebotich (LLNL)

Example: Droplet Formation

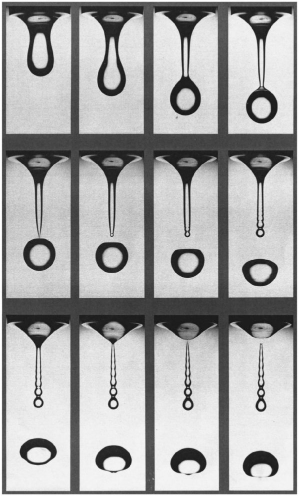
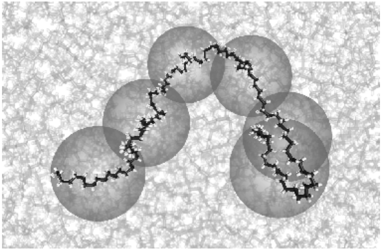


Figure: From Jens Eggers, Reviews of Modern Physics, 69, 1997

Polymer chains



Johan Padding, Cambridge

- I consider modeling of a polymer chain in a flowing solution, for example, DNA in a micro-array.
- The detailed structure of the polymer chain is usually **coarse-grained** to a model of spherical **beads**:

Bead-Link	The beads are free joints between inextensible links
Bead-Spring	Kuhn segments of the chain are point particles (beads) connected by non-linear elastic springs (FENE, worm-like, etc.)

The issue: **How to couple the polymer model with the surrounding fluid model?**

The Vision: Particle/Continuum Hybrid

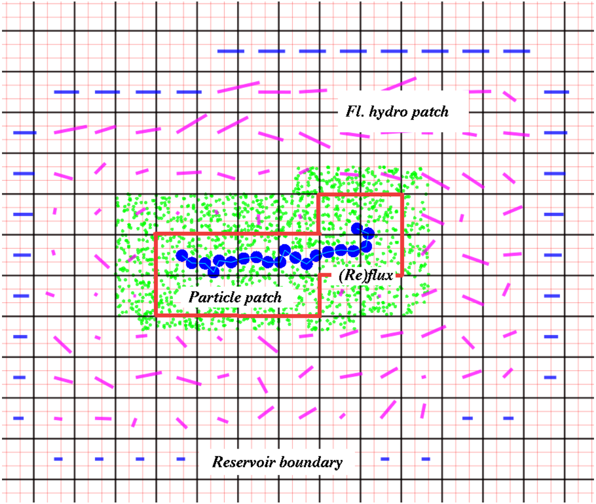


Figure: Hybrid method for a polymer chain.

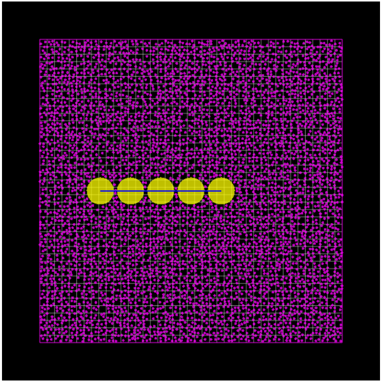
Particle Methods for Complex Fluids

- The most direct and accurate way to simulate the interaction between the **solvent** (fluid) and **solute** (beads, chain) is to use a particle scheme for both: **Molecular Dynamics (MD)**

$$m\ddot{\mathbf{r}}_i = \sum_j \mathbf{f}_{ij}(\mathbf{r}_{ij})$$

- Standard (time-driven) molecular dynamics:
  All of the particles are displaced *synchronously* in small *time steps* Δt, calculating positions and forces on each particle at every time step.
- The stiff repulsion among beads demands small time steps, and chain-chain crossings are a problem.
- For hard spheres, one can use **asynchronous event-driven MD**.
  "*Asynchronous Event-Driven Particle Algorithms*", by A. Donev, to appear in SIMULATION, 2008, **cs.OH/0703096**.

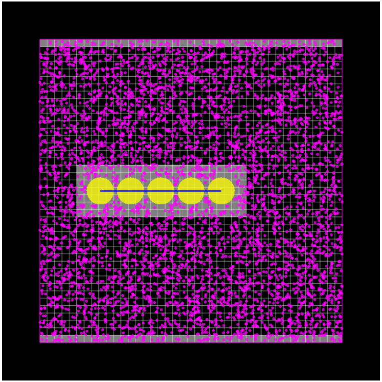
Event-Driven (Hard-Sphere) MD



- **Tethered** (square-well) hard-sphere chain polymers are the simplest but useful model.
- Most of the computation is "wasted" on the *unimportant solvent particles*!
- Over longer times it is **hydrodynamics** (*local momentum* and energy **conservation**) and **fluctuations** (Brownian motion) that matter.

(MNG)
"*Stochastic Event-Driven Molecular Dynamics*" [1],
A. Donev, A. L. Garcia and B. J. Alder,
J. Comp. Phys., 227(4):2644-2665, 2008

Direct Simulation Monte Carlo (DSMC)



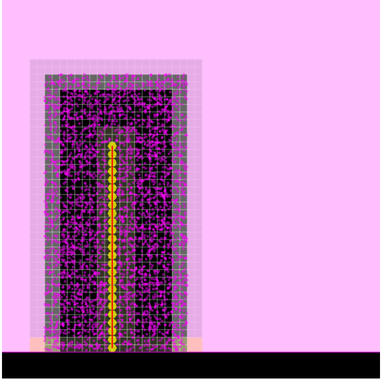
(MNG)

- **Stochastic conservative collisions** of randomly chosen nearby solvent particles, as in Direct Simulation Monte Carlo (DSMC).
- Solute particles still interact with **both** solvent and other solute particles as hard spheres.
- Binary DSMC collisions can be replaced with **multiparticle collisions** (MPCD/SRD).

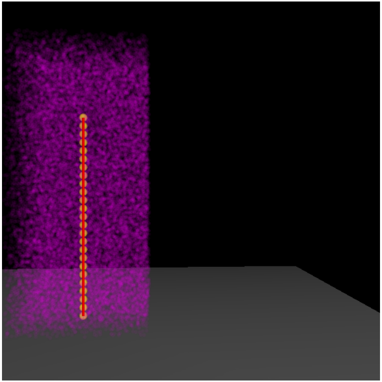
No fluid structure: Viscous fluid that is really an ideal gas! [2]

"*Stochastic Hard-Sphere Dynamics for Hydrodynamics of Non-Ideal Fluids*", by A. Donev, A. L. Garcia and B. J. Alder, **Phys. Rev. Lett. 101:075902 (2008)** [arXiv:0803.0359]

Tethered Polymer in Shear Flow



(MNG)



(MNG)

- We implement **open (stochastic) boundary conditions**: *Reservoir particles* are inserted every timestep in the boundary cells with appropriately biased velocities (local Maxwellian or Chapman-Enskog distributions).

The Need for Coarse-Graining

- In order to examine the time-scales involved, we focus on a fundamental problem:
  A single bead of size a and density ρ' *suspended in a stationary fluid with density* ρ and viscosity η (**Brownian walker**).
- By increasing the size of the bead obviously the **number of solvent particles** increases as $N \sim a^3$. But this is not the biggest problem (we have large supercomputers).
- The real issue is that a wide **separation of timescales occurs**: The *gap between the timescales of microscopic and macroscopic* processes widens as the bead becomes much bigger than the solvent particles (water molecules).
- Typical bead sizes are *nm* (nano-colloids, short polymers) or μm (colloids, DNA), while typical atomistic sizes are $1\text{Å} = 0.1nm$.

Estimates from Fluid Dynamics

- Classical picture for the following dissipation process: *Push a sphere suspended in a liquid with initial velocity* $V_{th} \approx \sqrt{kT/M}$, $M \approx \rho' a^3$, *and watch how the velocity decays:*
  - **Sound waves** are generated from the sudden compression of the fluid and they take away a fraction of the kinetic energy during a **sonic time** $t_{sonic} \approx a/c$, where c is the (adiabatic) sound speed.
  - **Viscous dissipation** then takes over and slows the particle *non-exponentially* over a **viscous time** $t_{visc} \approx \rho a^2/\eta$, where η is the shear viscosity. Note that the classical **Langevin time** scale $t_{Lang} \approx m/\eta a$ applies only to unrealistically dense beads!
  - **Thermal fluctuations** get similarly dissipated, but their constant presence pushes the particle diffusively over a **diffusion time** $t_{diff} \approx a^2/D$, where $D \sim kT/(a\eta)$.

Estimates from Molecular Theory

- For a typical particle fluid with particle size R, mass m, at temperature kT, and density (volume fraction) ϕ, we have the mean-free path

  $$\lambda \sim \frac{R}{\phi},$$

  For typical liquids, $\phi \approx 1$, $R \approx 1\text{Å} = 0.1nm$.
- The **equation of state** (EOS) of the fluid, $p = PV/NkT = p(\phi, T)$, determines the **incompressibility** $C \sim dp/d\phi$ and the speed of sound $c \sim \sqrt{C}$.

Timescale estimates.

- The mean collision time, i.e., the **MD time-scale**, is $t_{coll} \approx \lambda / v_{th}$, where the thermal velocity is $v_{th} \approx \sqrt{\frac{kT}{m}}$, for water

$$t_{coll} \sim 10^{-15} s = 1 fs$$

- Coarse-grained fluids such as the DSMC, the Stochastic Hard-Sphere, or Dissipative Particle Dynamics fluids increase the MD timescale artificially by not resolving the full atomistic structure structure.
- The sound speed $c \sim \sqrt{C} \cdot \sqrt{kT/m}$, giving an estimate for the **sound time**

$$t_{sonic} \sim \begin{cases} 1 ns \text{ for } a \sim \mu m \\ 1 ps \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{sonic}}{t_{coll}} \sim \frac{a}{\sqrt{C}\lambda} \sim 10^2 - 10^5$$

Estimates contd...

- The viscosity of the particle fluid can be estimated to be

$$\eta \sim \frac{\phi\lambda}{R^3}\sqrt{mkT}$$

giving **viscous time** estimates

$$t_{visc} \sim \begin{cases} 1\mu s \text{ for } a \sim \mu m \\ 1ps \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{visc}}{t_{sonic}} \sim \sqrt{C}\frac{a}{\lambda} \sim 1 - 10^3$$

- Finally, the **diffusion time** can be estimated to be

$$t_{diff} \sim \begin{cases} 1s \text{ for } a \sim \mu m \\ 1ns \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{diff}}{t_{visc}} \sim \frac{a}{\phi R} \sim 10^3 - 10^6$$

which can now reach **macroscopic timescales**!

Levels of Coarse-Graining

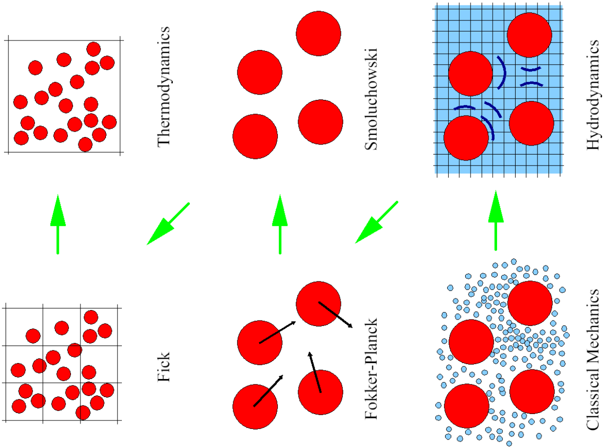


Figure: From Pep Español, "Statistical Mechanics of Coarse-Graining"

Smoluchowski level: Brownian Dynamics

- When the bead **momenta are not of interest**, we can focus only on bead positions and use an **implicit solvent**.
- **Overdamped Brownian dynamics**:

$$d\mathbf{R} = \left[\mathbf{U} + \frac{\mathbf{D} \cdot \mathbf{F}(\mathbf{R})}{kT} + \frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{D}\right] dt + \sqrt{2}\mathbf{B} \cdot d\mathbf{W},$$

  where $\mathbf{R}$ is the vector containing bead positions, $\mathbf{R} = \{\mathbf{r}_1, ..., \mathbf{r}_N\}$, $\mathbf{U}$ is the unperturbed velocity field at the bead centers, $\mathbf{F}$ are the bead-bead interaction forces, and $dW_i = \sqrt{dt} \cdot \mathcal{N}_i$ are independent Wiener process increments (white noise).
- Typical assumption for the **diffusion tensor** is that it depends only on the configuration:

$$\mathbf{D} \equiv \mathbf{D}(\mathbf{R}) = \mathbf{B} \cdot \mathbf{B}^T, \text{ usually } \mathbf{D}_{ij} = k_B T[(6\pi\eta a)^{-1}\mathbf{I}\delta_{ij} + \mathbf{\Omega}_{ij}]$$

  where $\mathbf{\Omega}_{ij}$ is the **Oseen tensor**, with additional **complex corrections** for flow in bounded domains (channels).

The equations of hydrodynamics

- Formally, we consider the continuum field of **conserved quantities**

$$\mathbf{u}(\mathbf{r}) = \begin{bmatrix} \rho \\ \mathbf{j} \\ e \end{bmatrix} = \sum_i \begin{bmatrix} 1 \\ \mathbf{v}_i \\ v_i^2/2 \end{bmatrix} m_i \delta_\epsilon(\mathbf{r} - \mathbf{q}_i) = \sum_i \begin{bmatrix} m_i \\ \mathbf{p}_i \\ e_i \end{bmatrix} \delta_\epsilon(\mathbf{r} - \mathbf{q}_i),$$

  where $\epsilon \ll 1$ is a small coarse-graining parameter.

- Due to the **microscopic conservation** of mass, momentum and energy, the hydrodynamic field satisfies a conservation law

$$\mathbf{u}_t = -\boldsymbol{\nabla} \cdot \boldsymbol{\Phi} = -\boldsymbol{\nabla} \cdot (\mathbf{H} + \mathbf{D} + \mathbf{S}),$$

  where the flux is broken into a **hyperbolic, diffusive, and a stochastic flux**.

Navier-Stokes Equations

The flux expressions assumed in the **compressible Navier-Stokes(-Fourier)** (NS) equations:

$$\mathbf{H} = \left[\begin{array}{c} \rho \mathbf{v} \\ \rho \mathbf{v}\mathbf{v}^T + P\boldsymbol{\delta} \\ (e+P)\mathbf{v} \end{array} \right] \text{ and } \mathbf{D} = \left[\begin{array}{c} 0 \\ \boldsymbol{\tau} \\ \boldsymbol{\tau} \cdot \mathbf{v} + \kappa \boldsymbol{\nabla} T \end{array} \right].$$

Here the **primary variables** are density ρ, velocity $\mathbf{v}$, and temperature T, determined from:

$$\mathbf{j} = \rho \mathbf{v} \text{ and } e = c_v \rho T + \frac{\rho v^2}{2}$$

the **pressure** is determined from the equation of state $P = P(\rho, T)$, and the **viscous stress**

$$\boldsymbol{\tau} = 2\eta \left[\dot{\gamma} - \frac{\mathrm{Tr}(\dot{\gamma})}{3} \right], \text{ where the strain rate } \dot{\gamma} = \frac{1}{2}(\boldsymbol{\nabla}\mathbf{v} + \boldsymbol{\nabla}\mathbf{v}^T)$$

Stochastic Fluxes

- The NS equations do not include the influence of **thermal fluctuations**, which is essential at small scales!
- Landau and Lifshitz assumed stochastic stress and energy fluxes in the form of **uncorrelated (in time and space) Gaussian noise**

$$\mathbf{S} = \begin{bmatrix} 0 \\ \boldsymbol{\sigma} \\ \boldsymbol{\sigma} \cdot \mathbf{v} + \varsigma \end{bmatrix},$$

  and solved the **linearized NS equations** in Fouier space to obtain the local fluctuations in the density, momentum and energy.
- By comparing to statistical mechanics, they obtained a **fluctuation-dissipation theorem**:

$$\left\langle \boldsymbol{\sigma}_{ij}(\mathbf{r},t)\boldsymbol{\sigma}_{kl}(\mathbf{r}',t')\right\rangle = 2\eta kT\tilde{\boldsymbol{\delta}}_{ijkl}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
$$\left\langle \varsigma_{i}(\mathbf{r},t)\varsigma_{i}(\mathbf{r}',t')\right\rangle = 2\kappa kT\boldsymbol{\delta}_{ij}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

  giving the **Landau-Lifshitz Navier-Stokes** (LLNS) equations.

Problems with the LLNS equations

- Numerically solving the *compressible* LLNS equations via explicit real-space methods has proven to be difficult (work by Alejandro Garcia and John Bell [3], as well as Rafael Delgado-Buscalioni *et al.* [4]): $\Delta t \ll \Delta x / c$. No one has even tried (semi) implicit methods or spectral methods yet, or compared carefully to fluctuating **Lattice-Boltzmann**!
- Adding stochastic fluxes to the non-linear NS equations (as derived in the mesoscopic limit by Pep Español [5]) produces **ill-behaved stochastic PDEs**: At small scales one gets **negative densities** and **temperatures**.
- Fluctuations at scales smaller than the atomistic correlation length and time should be renormalized to account for discreteness of matter (recall *ultra-violet catastrophe*).

Hydrodynamics at the nanoscale?

- It is not clear whether the Navier-Stokes equations apply at **nano-scales**. Berni Alder *et al.* have proposed **generalized hydrodynamics** for atomistic scales (wavelength and frequency-dependent viscosity), but this is intractable.
- The non-linear LLNS equations have an equilibrium correction to the temperature of order $1/N_s$ due to the term $\rho v^2 > 0$ for the **center-of-mass motion**.
- Conclusion: **It is necessary to perform systematic coarse graining of particle models to find a non-phenomenological form of the evolution equations for the hydrodynamic fields.**

Incompressible Navier-Stokes

- Under the assumption that the speed of sound is very large, $\delta P(\delta\rho, \delta T) \approx c^2 \delta\rho$, the energy equation decouples from the other two and the density becomes nearly constant, giving the **incompressible Navier-Stokes equations**

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{v} &= 0 \\ \rho_0 \mathbf{v}_t &= -\boldsymbol{\nabla} P - \rho_0 (\mathbf{v} \cdot \boldsymbol{\nabla}) \mathbf{v} + \eta \boldsymbol{\nabla}^2 \mathbf{v}, \end{aligned}$$

  where now the pressure $P(\mathbf{r}, t)$ is the Lagrange multipler for the incompressibility constraint.

- Physically, this means that very small changes in the density are sufficient to adjust the pressure arbitrarily and that temperature variations are negligible (isothermal).

When is incompressible/isothermal OK?

- For incompressibility assumption to apply, there must be separation of time scales $t_{visc} \gg t_{sonic}$, giving the constraint $a \gg 1nm$
- Density and temperature thermal fluctuations need to also be small. Estimates from statistical mechanics

  $$\left(\frac{\delta\rho}{\rho}\right)^2 \approx \frac{1}{CN_s} \text{ and } \left(\frac{\delta T}{T}\right)^2 \approx \frac{1}{N_s} = \frac{R^3}{\phi a^3} \ll 1,$$

  give $a \gg 1nm$.
- Conclusion: **Unless the compressibility is very (unrealistically!) small, an incompressible/isothermal formulation is applicable only when** $a \gg 1nm$.

Back to the Brownian Bead

- The **solvent** (fluid, liquid) can be modeled **implicitly** via analytical solutions (Brownian dynamics). But we want **reverse coupling** of the polymer motion on the flow (e.g., *drag reduction*)! We also need to resolve **shorter time scales** at nano systems.
- Macroscopically, the coupling between flow and moving bodies/structures/beads relies on:
  - **No-stick** boundary condition $\mathbf{v}_{rel} = 0$ at the surface of the bead.
  - Force on the bead is the integral of the stress tensor over the bead surface.
- The above two conditions are **questionable at nanoscales**, but even worse, they are very hard to implement numerically in an efficient and stable manner, even in the (phenomenological) Lattice-Boltzmann method.

Point-Bead Approximations

- Lots of people make a point approximation for the beads (as in Brownian dynamics).
- The **coupling** between the solute and solvent is **phenomenological and approximate** for most methods in use:

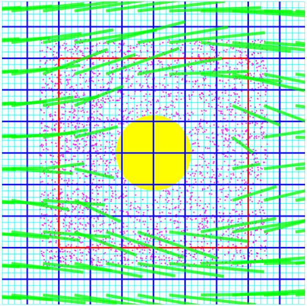
$$m d\dot{\mathbf{v}} = \left[\mathbf{F}(\mathbf{R}) - \gamma \mathbf{v}\right] dt + \sqrt{2\gamma kT}\, d\mathbf{W}$$

  - *Point beads* with artificial friction coefficients $\gamma \approx 6\pi a\eta$ based on asymptotic Stokes law
  - Point beads exerting (smeared) δ-function forces on the fluid
  - *Uncorrelated* fluctuating forces on the beads
- Such a **Langevin equation is physically inconsistent**, except at (unrealistic?) asymptotic time-scales (see Kramer, Peskin and Atzberger)!

The Immersed-Structure Method

- Beyond the wrong Langevin equation approach: **Immersed-structure method** of Kramer, Peskin and Atzberger for **incompressible fluctuating hydro**.
- The bead is in fact a **lump of fluid**: It moves with the volume-averaged velocity of the fluid and the force exerted on the bead is in fact exerted on the fluid.
- The method appears fully consistent, however, effects of sound waves and bead mass (inertial forces) are not taken into account: *separation of timescales is assumed*.
- Approximates the true mass and size into an **effective bead size** to match long-time behavior. This size is often *physically-meaningful*.

Complex Boundary Conditions using Particles



(MNG)

- Split the domain into a **particle** and a **hydro patch**, with timesteps $\Delta t_H = K \Delta t_P$.
- Hydro solver is a simple explicit MacCormack **(fluctuating) compressible LLNS** code and is *not aware* of particle patch.
- The method is based on Adaptive Mesh and Algorithm Refinement (AMAR) methodology for conservation laws and ensures **strict conservation** of mass, momentum, *and* energy [6].

Algorithm Refinement for Fluctuating Hydrodynamics, J. B. Bell and A. L. Garcia and S. A. Williams, SIAM Multiscale Modeling and Simulation, 6, 1256-1280, 2008

Freedom in Bead-Solvent Coupling

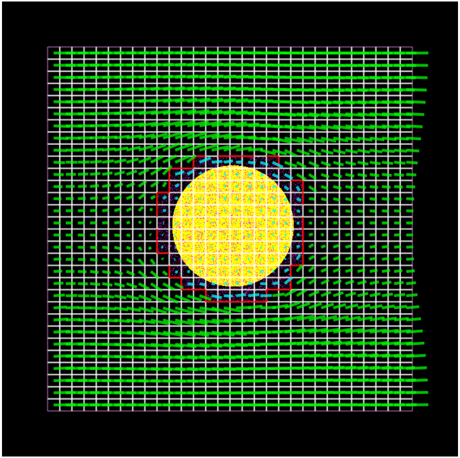


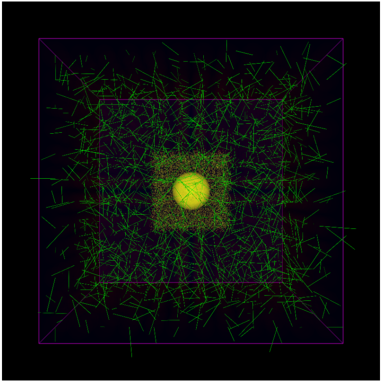
Figure: No event-driven handling at boundaries: **immersed bead**

Hydro-particle coupling

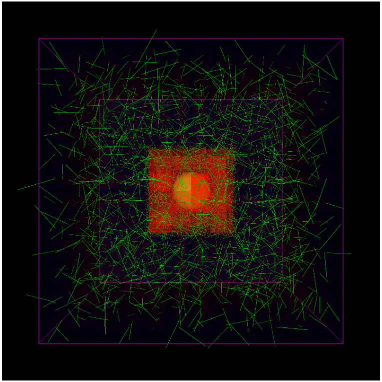
Steps of the coupling algorithm:

1. The hydro solution is computed everywhere, including the **particle patch**, giving an estimated total flux $\mathbf{\Phi}_H$.
2. **Reservoir particles** are *inserted* at the boundary of the particle patch based on *Chapman-Enskog distribution* from kinetic theory, accounting for *both* collisional and kinetic viscosities.
3. Reservoir particles are *propagated* by Δt and *collisions* are processed (including virtual particles!), giving the total particle flux $\mathbf{\Phi}_p$.
4. The hydro solution is overwritten in the particle patch based on the particle state $\mathbf{u}_p$.
5. The hydro solution is corrected based on the more accurate flux, $\mathbf{u}_H \leftarrow \mathbf{u}_H - \mathbf{\Phi}_H + \mathbf{\Phi}_p$.

Back to the Brownian Bead



(MNG)

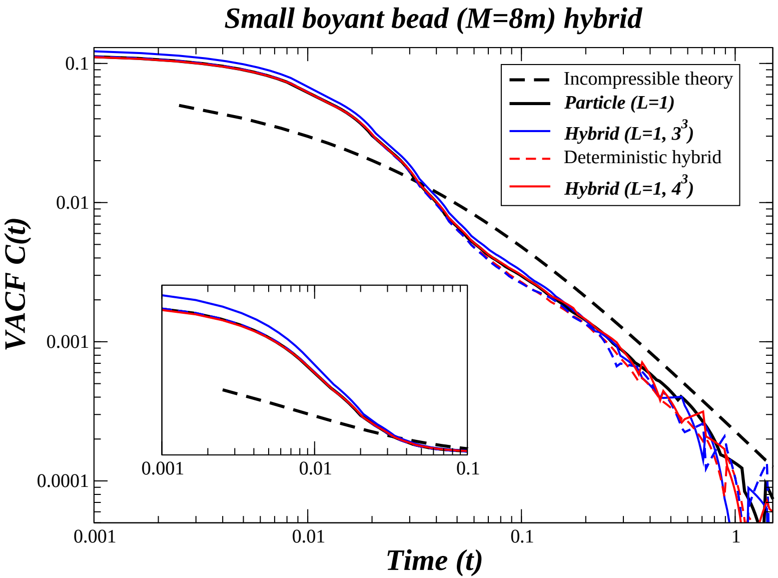


(MNG)

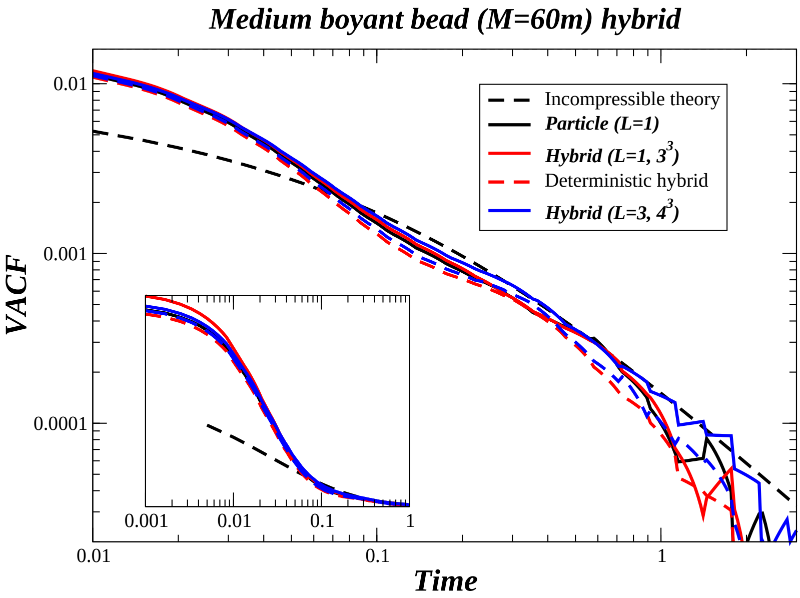
Velocity Autocorrelation Function

- We investigate the **velocity autocorrelation function** (VACF) for a Brownian bead
$$C(t) = \langle \mathbf{v}(t_0) \cdot \mathbf{v}(t_0 + t) \rangle$$
- From equipartition theorem $C(0) = kT/M$.
- For a **neutrally-boyant** particle, $\rho' = \rho$, incompressible hydrodynamic theory gives $C(0) = 2kT/3M$ because the momentum correlations decay instantly due to sound waves.
- Hydrodynamic persistence (conservation) gives a **long-time power-law tail** $C(t) \sim (kT/M)(t/t_{visc})^{-3/2}$ *not* reproduced in Brownian dynamics.

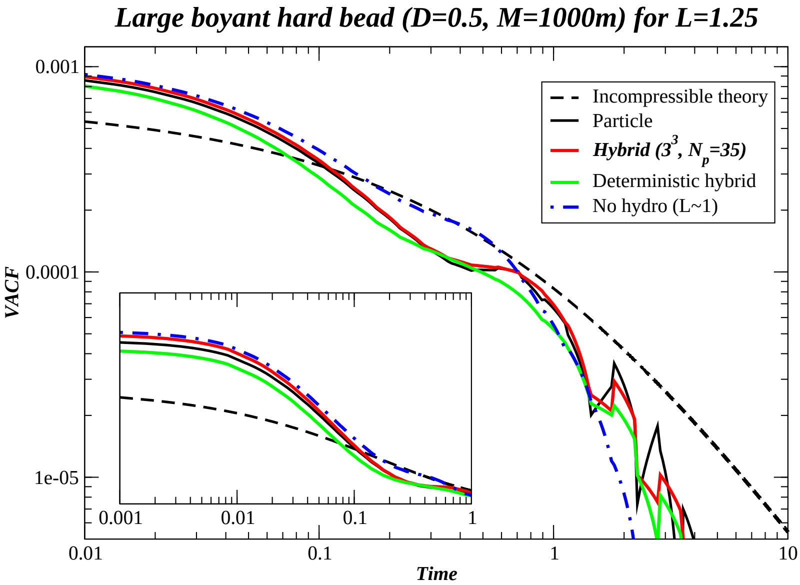
Small Bead (~10 particles)



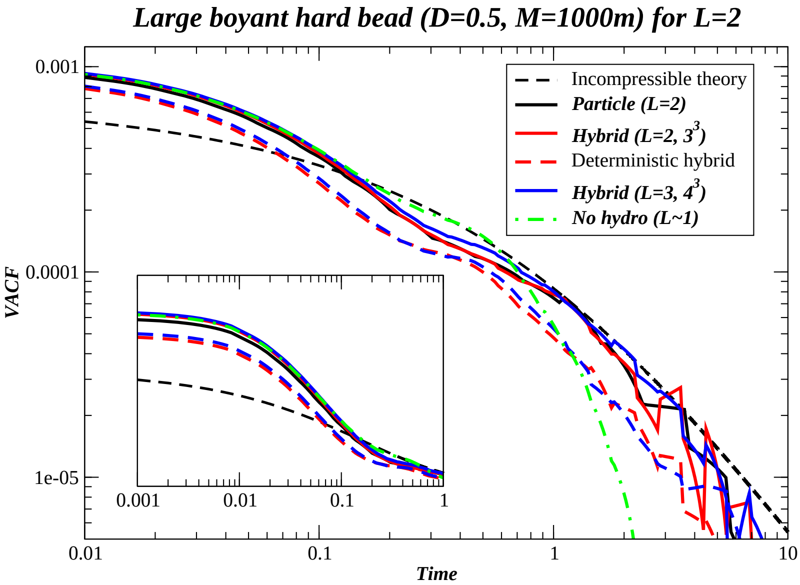
Medium Bead (~100 particles)



Large Bead in Small Box



Large Bead (˜1000 particles)



Future Directions

- New and better **numerical schemes** for fluctuating compressible hydro: resolving small wavelength fluctuations correctly with a large timestep (exponential integrators in Fourier space?).
- Theoretical work on the **equations of fluctuating hydrodynamics**: systematic coarse-graining and approximations.
- **Test, validate, and apply** the methodology for polymer problems.
- Couple our **non-ideal stochastic hard-sphere gas** to continuum hydrodynamics with *microscopic fidelity*.
- Ultimately we require an **Adaptive Mesh and Algorithm Refinement** (AMAR) framework that couples deterministic MD for the polymer chains (**micro**), a stochastic solvent (**micro-meso**), with compressible fluctuating Navier-Stokes (**meso**), and incompressible CFD (**macro**).

References/Questions?

A. Donev, A. L. Garcia, and B. J. Alder.
Stochastic Event-Driven Molecular Dynamics.
J. Comp. Phys., 227(4):2644–2665, 2008.

A. Donev, A. L. Garcia, and B. J. Alder.
Stochastic Hard-Sphere Dynamics for Hydrodynamics of Non-Ideal Fluids.
Phys. Rev. Lett, 101:075902, 2008.

J. B. Bell, A. Garcia, and S. A. Williams.
Numerical Methods for the Stochastic Landau-Lifshitz Navier-Stokes Equations.
Phys. Rev. E, 76:016708, 2007.

R. Delgado-Buscalioni and G. De Fabritiis.
Embedding molecular dynamics within fluctuating hydrodynamics in multiscale simulations of liquids.
Phys. Rev. E, 76(3):036709, 2007.

P. Español.
Stochastic differential equations for non-linear hydrodynamics.
Physica A, 248(1-2):77–96, 1998.

S. A. Williams, J. B. Bell, and A. L. Garcia.
Algorithm Refinement for Fluctuating Hydrodynamics.
SIAM Multiscale Modeling and Simulation, 6:1256–1280, 2008.