Multiscale Methods for Hydrodynamics of Complex Fluids

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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)
Introduction

Example: Droplet Formation

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

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:

Johan Padding, Cambridge

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?
Figure: Hybrid method for a polymer chain.
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)**

\[ m \ddot{r}_i = \sum_j f_{ij}(r_{ij}) \]

- Standard (time-driven) molecular dynamics:
  All of the particles are displaced *synchronously* in small *time steps* \( \Delta t \), 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**. 
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.

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).

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).
In order to examine the time-scales involved, we focus on a fundamental problem:

*A single bead of size \( a \) and density \( \rho' \) suspended in a stationary fluid with density \( \rho \) and viscosity \( \eta \) (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 \( \mu m \) (colloids, DNA), while typical atomistic sizes are \( 1\text{Å} = 0.1 nm \).
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 \( \eta \) 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 \( D \approx kT/(a\eta) \).
Coarse Graining of the Solvent

Estimates from Molecular Theory

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

  \[ \lambda \sim \frac{R}{\phi} , \]

  For typical liquids, $\phi \approx 1$, $R \approx 1\text{Å} = 0.1\text{nm}$.

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

\[
t_{coll} \sim 10^{-15} \text{s} = 1 \text{fs}
\]

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.

The sound speed \( c \sim \sqrt{C} \cdot \sqrt{\frac{kT}{m}} \), giving an estimate for the sound time

\[
t_{sonic} \sim \begin{cases} 
1 \text{ns} \text{ for } a \sim \mu \text{m} \\
1 \text{ps} \text{ for } a \sim \text{nm}
\end{cases}
\]

, with gap \( \frac{t_{sonic}}{t_{coll}} \sim \frac{a}{\sqrt{C} \lambda} \sim 10^2 - 10^5 \)
The viscosity of the particle fluid can be estimated to be

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

giving **viscous time** estimates

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

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

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

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, \( \mathbf{R} = \{ \mathbf{r}_1, \ldots, \mathbf{r}_N \} \), \( \mathbf{U} \) is the unperturbed velocity field at the bead centers, \( \mathbf{F} \) are the bead-bead interaction forces, and \( d\mathbf{W}_i = \sqrt{dt} \cdot \mathcal{N}_i \) are independent Wiener process increments (white noise).

- **Typical assumption for the diffusion tensor** is that it depends only on the configuration:

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

where \( \mathbf{\Omega}_{ij} \) is the **Oseen tensor**, with additional **complex corrections** for flow in bounded domains (channels).
Formally, we consider the continuum field of conserved quantities

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

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

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

where the flux is broken into a hyperbolic, diffusive, and a stochastic flux.
The flux expressions assumed in the **compressible** Navier-Stokes(-Fourier) (NS) equations:

\[
H = \begin{bmatrix}
\rho v \\
\rho vv^T + P\delta \\
(e + P)v
\end{bmatrix}
\quad \text{and} \quad
D = \begin{bmatrix}
0 \\
\tau \\
\tau \cdot v + \kappa \nabla T
\end{bmatrix}.
\]

Here the **primary variables** are density \( \rho \), velocity \( v \), and temperature \( T \), determined from:

\[
j = \rho v \quad \text{and} \quad e = c_v \rho T + \frac{\rho v^2}{2}
\]

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

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

\[
S = \begin{bmatrix}
0 \\
\sigma \\
\sigma \cdot \mathbf{v} + \zeta
\end{bmatrix},
\]

and solved the linearized NS equations in Fourier space to obtain the local fluctuations in the density, momentum and energy.

- By comparing to statistical mechanics, they obtained a fluctuation-dissipation theorem:

\[
\langle \sigma_{ij}(r, t)\sigma_{kl}(r', t') \rangle = 2\eta kT \delta_{ijkl} \delta(r - r') \delta(t - t')
\]
\[
\langle \zeta_i(r, t)\zeta_i(r', t') \rangle = 2\kappa kT \delta_{ij} \delta(r - r') \delta(t - t')
\]

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

\[ \nabla \cdot \mathbf{v} = 0 \]

\[ \rho_0 \mathbf{v}_t = -\nabla P - \rho_0 (\mathbf{v} \cdot \nabla)\mathbf{v} + \eta \nabla^2 \mathbf{v}, \]

where now the pressure \( P(r, t) \) is the Lagrange multiplier 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 $a \gg 1\text{nm}$
- Density and temperature thermal fluctuations need to also be small. Estimates from statistical mechanics
  \[
  \left( \frac{\delta \rho}{\rho} \right)^2 \approx \frac{1}{CN_s} \quad \text{and} \quad \left( \frac{\delta T}{T} \right)^2 \approx \frac{1}{N_s} = \frac{R^3}{\phi a^3} \ll 1,
  \]
  give $a \gg 1\text{nm}$.
- Conclusion: Unless the compressibility is very (unrealistically!) small, an incompressible/isothermal formulation is applicable only when $a \gg 1\text{nm}$. 
Bead-Solvent Coupling

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 $v_{rel} = 0$ 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.
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:

\[ m \dot{\mathbf{v}} = [F(R) - \gamma \mathbf{v}] \, dt + \sqrt{2\gamma kT} \, dW \]

- **Point beads** with artificial friction coefficients \( \gamma \approx 6\pi a \eta \) based on asymptotic Stokes law
- Point beads exerting (smeared) \( \delta \)-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)!
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**.
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
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 $\Phi_H$.

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 $\Delta t$ and collisions are processed (including virtual particles!), giving the total particle flux $\Phi_p$.

4. The hydro solution is overwritten in the particle patch based on the particle state $u_p$.

5. The hydro solution is corrected based on the more accurate flux, $u_H \leftarrow u_H - \Phi_H + \Phi_p$. 
Back to the Brownian Bead

(MNG) (MNG)
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 boyant bead ($M=8m$) hybrid

VACF $C(t)$

- Incompressible theory
- Particle ($L=1$)
- Hybrid ($L=1, 3^3$)
- Deterministic hybrid
- Hybrid ($L=1, 4^3$)

Time ($t$)

Small Bead (~10 particles)
Medium boyant bead (M=60m) hybrid

- Incompressible theory
- Particle (L=1)
- Hybrid (L=1, 3^3)
- Deterministic hybrid
- Hybrid (L=3, 4^3)
Large bovant hard bead ($D=0.5$, $M=1000m$) for $L=1.25$
Large boyant hard bead \((D=0.5, M=1000m)\) for \(L=2\)
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**).
Stochastic Event-Driven Molecular Dynamics.

Stochastic Hard-Sphere Dynamics for Hydrodynamics of Non-Ideal Fluids.

J. B. Bell, A. Garcia, and S. A. Williams.

R. Delgado-Buscalioni and G. De Fabritiis.
Embedding molecular dynamics within fluctuating hydrodynamics in multiscale simulations of liquids.

P. Español.
Stochastic differential equations for non-linear hydrodynamics.

S. A. Williams, J. B. Bell, and A. L. Garcia.
Algorithm Refinement for Fluctuating Hydrodynamics.