Coupling a nano-particle with fluctuating hydrodynamics

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Levels of Coarse-Graining

Figure: From Pep Español, “Statistical Mechanics of Coarse-Graining”.

[Diagram showing levels of coarse-graining from thermodynamics to classical mechanics]
Key is the **velocity autocorrelation function** (VACF) for the immersed particle

\[ C(t) = \langle \mathbf{V}(t_0) \cdot \mathbf{V}(t_0 + t) \rangle \]

From equipartition theorem \( C(0) = \langle V^2 \rangle = d \frac{k_B T}{M} \) for a compressible fluid, but for an incompressible fluid the kinetic energy of the particle that is **less than equipartition**.

Hydrodynamic persistence (conservation) gives a **long-time power-law tail** \( C(t) \sim (k_B T / M)(t/t_{\text{visc}})^{-3/2} \).

Diffusion coefficient is given by the **integral of the VACF** and is hard to compute in MD even for a single nanocolloidal particle.
Brownian Bead

- Classical picture for the following dissipation process: Push a sphere suspended in a liquid with initial velocity $V_{th} \approx \sqrt{k_B T / M}$ 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.
  - **Thermal fluctuations** get similarly dissipated, but their constant presence pushes the particle diffusively over a **diffusion time** $t_{diff} \approx a^2 / D$, where
    
    $$D \sim k_B T / (a \eta) \quad \text{(Stokes-Einstein relation)}.$$
The mean collision time is $t_{\text{coll}} \approx \lambda/V_{\text{th}} \sim \eta/(\rho c^2)$,

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

- **The sound time**

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

- It is often said that sound waves do not contribute to the long-time diffusive dynamics because their contribution to the VACF integrates to zero.
Estimates contd...

- **Viscous time** estimates

  \[ t_{visc} \sim \begin{cases} 
  1 \mu s & \text{for } a \sim \mu m \\
  1 \text{ps} & \text{for } a \sim \text{nm} 
  \end{cases} \]

  with gap \[ \frac{t_{visc}}{t_{sonic}} \sim 1 - 10^3 \]

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

  \[ t_{diff} \sim \begin{cases} 
  1 \text{s} & \text{for } a \sim \mu m \\
  1 \text{ns} & \text{for } a \sim \text{nm} 
  \end{cases} \]

  with gap \[ \frac{t_{diff}}{t_{visc}} \sim 10^3 - 10^6 \]

  which can now reach **macroscopic timescales**!

- In practice the **Schmidt number** is very large,

  \[ Sc = \frac{\nu}{D} = \frac{t_{diff}}{t_{visc}} \gg 1, \]

  which means the diffusive dynamics is **overdamped**.
Brownian Dynamics

- Overdamped equations of **Brownian Dynamics** (BD) for the particle positions $\mathbf{R}(t)$ are
  \[
  \frac{d\mathbf{R}}{dt} = \mathbf{M}\mathbf{F} + \left(2k_B T \mathbf{M}\right)^{\frac{1}{2}} \mathbf{W}(t) + k_B T (\partial_{\mathbf{R}} \cdot \mathbf{M}),
  \]
  where $\mathbf{M} = \mathbf{M}(\mathbf{R})$ is the symmetric positive semidefinite (SPD) hydrodynamic mobility matrix.

- Hydrodynamic mobility matrix is given by Green-Kubo formula
  \[
  (k_B T) \mathbf{M}_{ij} = \int_0^\tau dt \langle \mathbf{V}_i(0) \cdot \mathbf{V}_j(t) \rangle^\text{eq}.
  \]

- The upper bound $\tau$ must satisfy
  \[
  \tau \gg \frac{r_{ij}^2}{\nu} \sim \frac{L^2}{\nu} \gg t_{\text{visc}},
  \]
  so that the whole VACF power law tail is included in the integral. 
  **Therefore computing hydrodynamic interactions is infeasible with MD.**
Since computing the hydrodynamic mobility is so difficult in MD, usually $\mathcal{M}$ is modeled by the Rotne-Prager mobility [1],

$$\mathcal{M}_{ij} \approx \eta^{-1} \left( I + \frac{a^2}{6} \nabla_\mathbf{r}^2 \right) \left( I + \frac{a^2}{6} \nabla_{\mathbf{r}'}^2 \right) G(\mathbf{r} - \mathbf{r}') \bigg|_{\mathbf{r}'=\mathbf{q}_i}^{\mathbf{r}=\mathbf{q}_j}.$$

where $G$ is the Green’s function for the Stokes problem (Oseen tensor for infinite domain).

This is not only an approximate closure neglecting a number of effects, but also requires an estimate of the effective hydrodynamic radius $a$ as input.

Our goal will be to split the integral into a short-time piece, computed by feasible MD via Green-Kubo integrals, and a long-time contribution, computed by fluctuating hydrodynamics coupled to an immersed particle.
“Old” approach: Particle/Continuum Hybrid

Figure: Hybrid method for a polymer chain.
VACF using a hybrid

- Split the domain into a particle and a continuum (hydro) subdomains [2].
- Particle solver is a coarse-grained fluid model (Isotropic DSMC).
- Hydro solver is a simple explicit (fluctuating) compressible fluctuating hydrodynamics code.
- Time scales are limited by the MD part despite increased efficiency.
Large Bead (~1000 particles)

![Graph showing MC(t) / k_B T against t / t_{visc}]

- **Stoch. hybrid (L=2)**
- **Det. hybrid (L=2)**
- **Stoch. hybrid (L=3)**
- **Det. hybrid (L=3)**
- **Particle (L=2)**
- **Theory**

Legend:
- Red line: Stoch. hybrid (L=2)
- Green line: Stoch. hybrid (L=3)
- Black line: Particle (L=2)
- Magenta line: Theory
Figure: **Coarse-Graining a Nanoparticle**: Schematic representation of a nanoparticle (left) surrounded by molecules of a simple liquid solvent (in blue). The shaded area around node $\mu$ located at $r_\mu$ is the support of the finite element function $\psi_\mu(r)$ and defines the hydrodynamic cell (right).
Define an orthogonal set of basis functions,

\[ \| \delta_\mu \psi_\nu \| = \delta_{\mu \nu}, \tag{3} \]

where \( f \| \equiv \int d r f(r) \).

Continuum fields which are interpolated from discrete "fields":

\[ \bar{\rho}(r) = \psi_\mu(r) \rho_\mu \tag{4} \]

Introduce a regularized Dirac delta function

\[ \Delta(r, r') \equiv \delta_\mu(r) \psi_\mu(r') = \Delta(r', r) \tag{5} \]

Note the exact properties

\[ \int d r \delta_\mu(r) = 1, \quad \int d r \ r \delta_\mu(r) = \rho_\mu \tag{6} \]

\[ \int d r' \Delta(r, r') \delta_\mu(r') = \delta_\mu(r) \]
Slow variables

- Key to the Theory of Coarse-Graining is the proper selection of the relevant or slow variables.
- We assume that the nanoparticle is smaller than hydrodynamic cells and accordingly choose the coarse-grained variables [3],

\[ \hat{R}(z = \{q, p\}) = q_0, \]  

(7)

- We define the mass and momentum densities of the hydrodynamic node \( \mu \) according to

\[
\hat{\rho}_\mu(z) = \sum_{i=0}^{N} m_i \delta_{\mu}(q_i), \quad \text{discrete of} \quad \hat{\rho}_r(z) = \sum_{i=0}^{N} m_i \delta(q_i - r) \\
\hat{g}_\mu(z) = \sum_{i=0}^{N} p_i \delta_{\mu}(q_i), \quad \text{discrete of} \quad \hat{g}_r(z) = \sum_{i=0}^{N} p_i \delta(q_i - r)
\]

where \( i = 0 \) labels the nanoparticle. Note that both mass and momentum densities include the nanoparticle!
\[
\frac{d\mathbf{R}}{dt} = \mathbf{\bar{v}}(\mathbf{R}) - \frac{D_0}{k_B T} \frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{D_0}{k_B T} \mathbf{F}^{\text{ext}} + \sqrt{2k_B T D_0} \mathcal{W}(t)
\]

\[
\frac{d\rho_\mu}{dt} = \|\bar{\rho} \mathbf{\bar{v}} \cdot \nabla \delta_\mu\|
\]

\[
\frac{dg_\mu}{dt} = \|g \mathbf{\bar{v}} \cdot \nabla \delta_\mu\| + k_B T \nabla \delta_\mu(\mathbf{R}) - \|\delta_\mu \nabla P\| + \delta_\mu(\mathbf{R}) \mathbf{F}^{\text{ext}}
\]

\[
+ \eta \|\delta_\mu \nabla^2 \mathbf{\bar{v}}\| + \left(\frac{\eta}{3} + \zeta\right) \|\delta_\mu \nabla (\nabla \cdot \mathbf{\bar{v}})\| + \frac{d\mathbf{\bar{g}}_\mu}{dt}
\]

(8)

The pressure equation of state is modeled by

\[
P(\mathbf{r}) \simeq \frac{c^2}{2\rho_{eq}} (\bar{\rho}(\mathbf{r})^2 - \rho_{eq}^2) + m_0 \frac{(c_0^2 - c^2)}{\rho_{eq}} \Delta(\mathbf{R}, \mathbf{r}) \bar{\rho}(\mathbf{r}),
\]

(9)

and the gradient of the free energy is modeled by

\[
\frac{\partial \mathcal{F}}{\partial \mathbf{R}} \simeq m_0 \frac{(c_0^2 - c^2)}{\rho_{eq}} \int d\mathbf{r} \Delta(\mathbf{R}, \mathbf{r}) \nabla \bar{\rho}(\mathbf{r}).
\]

(10)
Final Continuum Equations

The same equations can be obtained from a Petrov-Galerkin discretization of the following system of the fluctuating hydrodynamics SPDEs

\[
\frac{d}{dt} R = \int d\mathbf{r} \Delta(\mathbf{r}, R) \mathbf{v}(\mathbf{r}) + \frac{D_0}{k_B T} \mathbf{F}^{\text{ext}} + \sqrt{2k_B T D_0} \mathbf{W}(t)
\]

\[
- \frac{D_0}{k_B T} \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \int d\mathbf{r} \Delta(R, \mathbf{r}) \nabla \rho(\mathbf{r})
\]

\[
\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{g}
\]

\[
\partial_t \mathbf{g}(\mathbf{r}, t) = -\nabla \cdot (\mathbf{g} \mathbf{v}) - k_B T \nabla \Delta(\mathbf{r}, R)
\]

\[
- \nabla P(\mathbf{r}) + \mathbf{F}^{\text{ext}} \Delta(\mathbf{r}, R)
\]

\[
+ \eta \nabla^2 \mathbf{v} + \left( \frac{\eta}{3} + \zeta \right) \nabla (\nabla \cdot \mathbf{v}) + \nabla \cdot \Sigma^\alpha\beta_r
\]  

(11)

where \( \mathbf{v} = \mathbf{g}/\rho \), and the pressure is given by

\[
P(\mathbf{r}) = \frac{c^2}{2 \rho_{\text{eq}}} (\rho(\mathbf{r})^2 - \rho_{\text{eq}}^2) + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \Delta(R, \mathbf{r}) \rho(\mathbf{r})
\]  

(12)
The scalar **bare diffusion coefficient is grid-dependent**, 

\[
D_0 = \frac{1}{d} \int_0^\tau dt \left\langle \delta \hat{V}(0) \cdot \delta \hat{V}(t) \right\rangle_{eq}
\]  

(13)

where the particle **excess velocity** over the fluid is 

\[
\delta \hat{V} = \hat{V} - \left\langle \hat{V} \right\rangle^{R,\rho,\hat{g}} \approx \hat{V} - \bar{v}(R).
\]

The crucial point is that now the integration time \( \tau \gg h^2/\nu \), where \( h \) is the grid spacing, is **accessible in MD**.

The true or **renormalized diffusion coefficient** [4] **should** be grid-independent,

\[
D = D_0 + \Delta D \approx D_0 + \frac{1}{d} \int_0^\tau dt \left\langle \vec{v}(R(0)) \cdot \vec{v}(R(t)) \right\rangle_{eq}
\]

\[
\approx D_0 + \frac{1}{d} \int_0^\infty dt \, \psi_\mu(R) \left\langle \mathbf{v}_\mu(0) \cdot \mathbf{v}_\mu'(t) \right\rangle_{eq}^R \psi_\mu'(R)
\]
Figure: VACF for a neutrally buoyant particle for $D_0 = 0$ and $c = c_0$, from coupling a finite-volume fluctuating hydrodynamic solver [5, 6].
Conclusions

- We considered the problem of modeling the Brownian motion of a solvated nanocolloidal particle over a range of time scales.
- Hydrodynamic scales are not accessible in direct MD so **coarse-grained models are necessary**.
- If one eliminates the solvent DOFs one obtains a *long-memory non-Markovian* SDE in the inertial case or a *long-ranged* overdamped SDE in the Brownian limit.
- If **fluctuating hydrodynamic variables** are retained in the description, one obtains a *large system of Markovian S(P)DEs*.
- A concurrent **hybrid coupling approach** couples MD directly to fluctuating hydrodynamics; **time scales are limited by the MD**.
- We derive coarse-grained equations by a combination of Mori-Zwanzig with physically-informed modeling.
- It remains to actually **try this in practice** and see what range of effects can be captured correctly and efficiently.
- It also remains to generalize this to a **denser suspension of colloids**.
Brownian Dynamics without Green’s Functions.
Software available at https://github.com/stochasticHydroTools/FIB.

A hybrid particle-continuum method for hydrodynamics of complex fluids.

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Coupling a nano-particle with isothermal fluctuating hydrodynamics: Coarse-graining from microscopic to mesoscopic dynamics.

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The Stokes-Einstein Relation at Moderate Schmidt Number.