Multiscale Problems in Fluctuating Hydrodynamics

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[1]Informal talk

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Outline

1. Local Angular Momentum Conservation
2. Two-Component Mixture
3. Giant Fluctuations in Diffusive Mixing
4. Low Mach Number Limit
5. Chemical Reactions
6. Direct Fluid-Particle Coupling

Compressible Fluctuating Hydrodynamics

$$
\begin{aligned}
D_t\rho &= -\,\rho\boldsymbol{\nabla}\cdot\mathbf{v}\\
\rho\left(D_t\mathbf{v}\right) &= -\,\boldsymbol{\nabla}P+\boldsymbol{\nabla}\cdot\left(\eta\overline{\boldsymbol{\nabla}}\mathbf{v}+\boldsymbol{\Sigma}\right)\\
\rho c_v\left(D_t T\right) &= -\,P\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right)+\boldsymbol{\nabla}\cdot\left(\kappa\boldsymbol{\nabla}T+\boldsymbol{\Xi}\right)+\left(\eta\overline{\boldsymbol{\nabla}}\mathbf{v}+\boldsymbol{\Sigma}\right):\boldsymbol{\nabla}\mathbf{v}
\end{aligned}
$$

where the variables are the **density** ρ, **velocity** $\mathbf{v}$, and **temperature** T fields,

$$
\begin{aligned}
D_t\square &= \partial_t\square+\mathbf{v}\cdot\boldsymbol{\nabla}\left(\square\right)\\
\overline{\boldsymbol{\nabla}}\mathbf{v} &= \left(\boldsymbol{\nabla}\mathbf{v}+\boldsymbol{\nabla}\mathbf{v}^T\right)-2\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right)\mathbf{I}/3
\end{aligned}
$$

and capital Greek letters denote stochastic fluxes:

$$
\boldsymbol{\Sigma}=\sqrt{2\eta k_B T}\,\mathcal{W}.
$$

$$
\langle\mathcal{W}_{ij}(\mathbf{r},t)\mathcal{W}^{\star}_{kl}(\mathbf{r}',t')\rangle=\left(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}-2\delta_{ij}\delta_{kl}/3\right)\delta(t-t')\delta(\mathbf{r}-\mathbf{r}').
$$

Incompressible Velocity Equation

An **incompressible limit** $c_T^2 = \partial P / \partial \rho \to \infty$ (isothermal speed of sound) presumably leads to

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \boldsymbol{\nabla} \mathbf{v} = -\boldsymbol{\nabla} \pi + \nu \boldsymbol{\nabla}^2 \mathbf{v} + \boldsymbol{\nabla} \cdot \left(\sqrt{2 \nu \rho^{-1} \, k_B T} \, \boldsymbol{\mathcal{W}} \right)$$

$$\text{s.t.} \boldsymbol{\nabla} \cdot \mathbf{v} = 0,$$

where where the **kinematic viscosity** $\nu = \eta / \rho$, and π is determined from incompressibility.
We assume that $\boldsymbol{\mathcal{W}}$ can be modeled as spatio-temporal **white noise** (a delta-correlated Gaussian random field)

$$\langle \mathcal{W}_{ij}(\mathbf{r}, t) \mathcal{W}_{kl}^{\star}(\mathbf{r}', t') \rangle = \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) \delta(t - t') \delta(\mathbf{r} - \mathbf{r}').$$

Can one justify this limit more rigorously, at least formally?
In principle one can just write this sort of equation. But knowing where it came from seems important in some cases...

Angular Momentum

Starting from the general momentum conservation law

$$\partial_t \left(\rho \mathbf{v}\right) = -\boldsymbol{\nabla} \cdot \boldsymbol{\sigma} + \mathbf{f},$$

where $\boldsymbol{\sigma}$ is the stress tensor and $\mathbf{f}$ is an external force density, it is not hard to derive a law of motion for the *external angular momentum density* $\mathbf{w} = \mathbf{r} \times (\rho \mathbf{v})$,

$$\partial_t \mathbf{w} = -\boldsymbol{\nabla} \cdot (\mathbf{r} \times \boldsymbol{\sigma}) + \mathbf{r} \times \mathbf{f} + \boldsymbol{\sigma}_a, \tag{1}$$

where the vector dual of the antisymmetric part of the stress tensor $\boldsymbol{\sigma}^a = \left(\boldsymbol{\sigma} - \boldsymbol{\sigma}^T\right)/2$ is

$$\boldsymbol{\sigma}_a = \left(\boldsymbol{\sigma}^a_{yz}, \boldsymbol{\sigma}^a_{zx}, \boldsymbol{\sigma}^a_{xy}\right).$$

This shows that the angular momentum obeys a *local* conservation law if and only if $\boldsymbol{\sigma}_a = \mathbf{0}$, that is, if the stress tensor is symmetric.

Angular Momentum Equation

- In principle, molecules store internal angular momentum in internal degrees of freedom, and the complete set of variables should include a *molecular spin angular velocity* $\boldsymbol{\Omega}(\mathbf{r}, t)$,

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \boldsymbol{\nabla} \mathbf{v} = \nu \boldsymbol{\nabla}^2 \mathbf{v} - 2\nu_r \boldsymbol{\nabla} \times \left(\frac{\boldsymbol{\nabla} \times \mathbf{v}}{2} - \boldsymbol{\Omega} \right) + \mathbf{f}_{\mathbf{v}}$$

$$I \left(\partial_t \boldsymbol{\Omega} + \mathbf{v} \cdot \boldsymbol{\nabla} \boldsymbol{\Omega} \right) = \zeta \boldsymbol{\nabla}^2 \boldsymbol{\Omega} + 4\nu_r \left(\frac{\boldsymbol{\nabla} \times \mathbf{v}}{2} - \boldsymbol{\Omega} \right) + \mathbf{f}_{\boldsymbol{\Omega}},$$

  where ν_r is a rotational viscosity and ζ is a spin viscosity.

- In the limit $\nu_r \to \infty$, it seems that

$$\boldsymbol{\Omega} \approx \frac{\boldsymbol{\nabla} \times \mathbf{v}}{2} = \text{fluid angular velocity},$$

  and we get the usual velocity equation [note that $\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{v}) = -\boldsymbol{\nabla}^2 \mathbf{v}$].

contd.

- Fluctuation-dissipation balance gives the form of the stochastic forcing, I conjecture it to be

$$\mathbf{f}_{\boldsymbol{\Omega}} = \boldsymbol{\nabla} \cdot \left(\sqrt{2\zeta\rho^{-1}\, k_B T}\, \boldsymbol{\mathcal{W}}_A \right) + 2\sqrt{2\nu_r \rho^{-1} k_B T}\, \boldsymbol{\mathcal{W}}_B$$

- Total angular momentum density $\rho\left(\mathbf{r} \times \mathbf{v} + I\boldsymbol{\Omega}\right)$ should be locally conserved, implying

$$\mathbf{f}_{\mathbf{v}} = \boldsymbol{\nabla} \cdot \left(\sqrt{2\nu\rho^{-1}\, k_B T}\, \boldsymbol{\mathcal{W}} \right) - \boldsymbol{\nabla} \times \left(\sqrt{2\nu_r \rho^{-1} k_B T}\, \boldsymbol{\mathcal{W}}_B \right),$$

  where $\boldsymbol{\mathcal{W}}$ is a symmetric stochastic stress tensor.

- What happens in the limit $\nu_r \rightarrow \infty$? Does the stochastic stress become symmetric?
- Can you actually see any effect of antisymmetry of the stochastic stress tensor if you cannot see $\boldsymbol{\Omega}$?

Binary Fluid Mixtures

- Each species has its own velocity $\mathbf{v}_1$ and $\mathbf{v}_2$.
- Primitive variables are now the total density $\rho = \rho_1 + \rho_2$, the concentration $c = \rho_1/\rho$, the center-of-mass velocity $\mathbf{v} = c\mathbf{v}_1 + (1-c)\mathbf{v}_2$, *and* the inter-species velocity $\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$.
- The continuity equations are as usual

$$\partial_t \rho_1 = -\boldsymbol{\nabla} \cdot (\rho_1 \mathbf{v}_1) \text{ and } \partial_t \rho_2 = -\boldsymbol{\nabla} \cdot (\rho_2 \mathbf{v}_2) . \tag{2}$$

- Postulated *approximate* momentum conservation equations

$$\begin{aligned} \partial_t (\rho_1 \mathbf{v}_1) + \dots &= -\boldsymbol{\nabla} P_1 + \boldsymbol{\nabla} \cdot \left[\frac{\rho_1}{\rho} \left(\eta \overline{\boldsymbol{\nabla}} \mathbf{v} + \boldsymbol{\Sigma} \right) \right] - \xi \mathbf{v}_{12} + \boldsymbol{\Theta} \\ \partial_t (\rho_2 \mathbf{v}_2) + \dots &= -\boldsymbol{\nabla} P_2 + \boldsymbol{\nabla} \cdot \left[\frac{\rho_2}{\rho} \left(\eta \overline{\boldsymbol{\nabla}} \mathbf{v} + \boldsymbol{\Sigma} \right) \right] + \xi \mathbf{v}_{12} - \boldsymbol{\Theta}, \end{aligned}$$

where $P_1 = \rho_1 k_B T/m$ and similarly for P_2, ξ is a friction coefficient, and

$$\boldsymbol{\Theta} = \sqrt{2\xi k_B T}\, \boldsymbol{\mathcal{W}}^{(c)}.$$

Contd.

- Kinetic theory suggests that the friction coefficient is [1]

$$\xi = c\,(1-c)\,\frac{\rho c_T}{\chi},$$

where $c_T = k_B T/m$ is the isothermal speed of sound.

- The equations can be written in terms of concentration $c = \rho_1/\rho$ and

$$\mathbf{u}_{12} = c(1-c)\mathbf{v}_{12}. \tag{3}$$

- Some approximations lead to the postulated **two-fluid** equations

$$\begin{aligned} \rho\left(\partial_t c + \mathbf{v}\cdot\boldsymbol{\nabla} c\right) &= -\boldsymbol{\nabla}\cdot\left[\rho\mathbf{u}_{12}\right], \\ \partial_t \mathbf{u}_{12} + \mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{u}_{12} &= -c_T^2\boldsymbol{\nabla} c - c_T^2\chi^{-1}\mathbf{u}_{12} + \rho^{-1}\boldsymbol{\Theta}, \end{aligned} \tag{4}$$

Overdamped Limit

- If the friction coefficient $c_T^2 \chi^{-1}$ is large, the friction term quickly damps the relative velocity

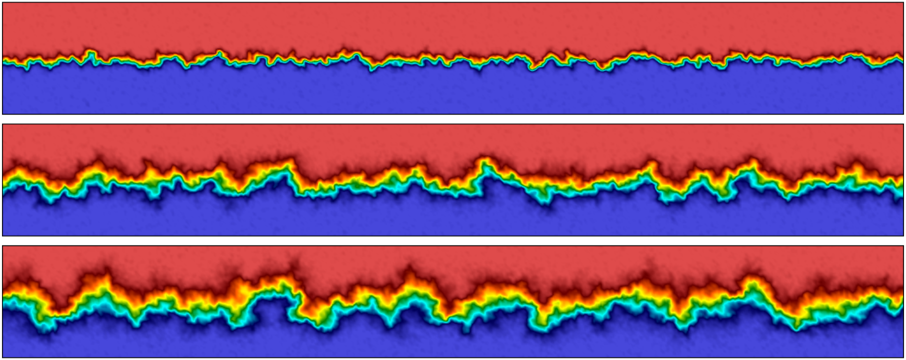
$$\mathbf{u}_{12} \approx -\chi \boldsymbol{\nabla} c + \frac{\chi}{\rho c_T^2} \boldsymbol{\Theta}.$$

- The concentration equation then becomes a stochastic Fick's law

$$\partial_t c + \mathbf{v} \cdot \boldsymbol{\nabla} c = \chi \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot \left(\sqrt{2m\chi\rho^{-1} \, c(1-c)} \, \boldsymbol{\mathcal{W}}^{(c)} \right).$$

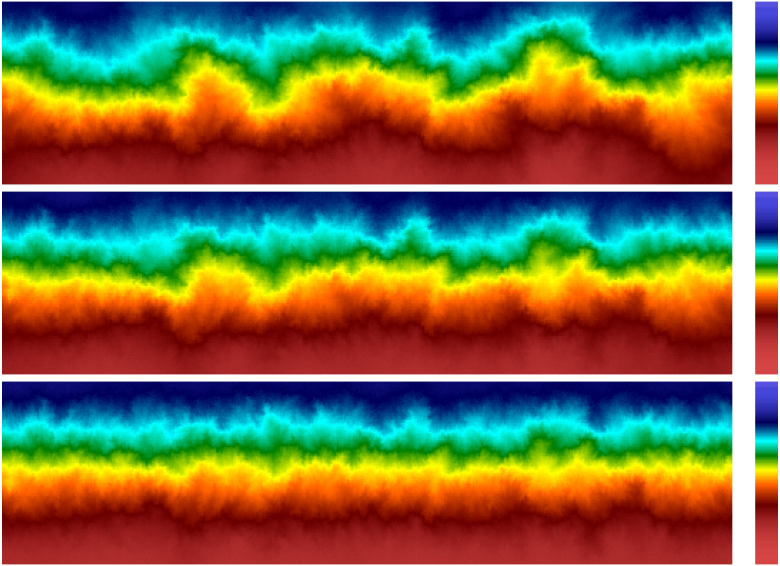
- The $c(1-c)$ should somehow ensure that $0 \leq c \leq 1$ strictly.
- Note that diffusion arose out of advection by fast velocity fluctuations, but there is double-counting via **v** fluctuations.

Fractal Fronts in Diffusive Mixing



Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface between two miscible fluids in zero gravity [2, 3, 4]. A similar pattern is seen over a broad range of Schmidt numbers and is affected strongly by nonzero gravity.

Animation: Diffusive Mixing in Gravity



Diffusion by Velocity Fluctuations

- In liquids diffusion of mass is much slower than diffusion of momentum, $\chi \ll \nu$, leading to a Schmidt number

$$S_c = \frac{\nu}{\chi} \sim 10^3.$$

- Model equations for giant fluctuations in diffusive mixing are

$$\begin{aligned} \partial_t \mathbf{v} =& \mathcal{P} \left[\nu \boldsymbol{\nabla}^2 \mathbf{v} + \boldsymbol{\nabla} \cdot \left(\sqrt{2\nu\rho^{-1} k_B T} \, \boldsymbol{\mathcal{W}} \right) \right] \\ \partial_t c =& - \mathbf{v} \cdot \boldsymbol{\nabla} c + \chi \boldsymbol{\nabla}^2 c, \end{aligned}$$

  where $\mathcal{P}$ is the orthogonal projection onto the space of divergence-free velocity fields, $\mathcal{P} = \mathbf{I} - \mathcal{G} \left(\mathcal{D} \mathcal{G} \right)^{-1} \mathcal{D}$ in real space, where $\mathcal{D} \square \equiv \boldsymbol{\nabla} \cdot \square$ denotes the divergence operator and $\mathcal{G} \equiv \boldsymbol{\nabla}$ the gradient operator.

- Conjecture: There exists some limiting dynamics for c in the limit $S_c \to \infty$ in the scaling

$$\nu = \chi S_c, \quad \chi(\chi + \nu) \approx \chi\nu = \text{const}$$

contd.

- The coupled *linearized velocity*-concentration system in one dimension is:

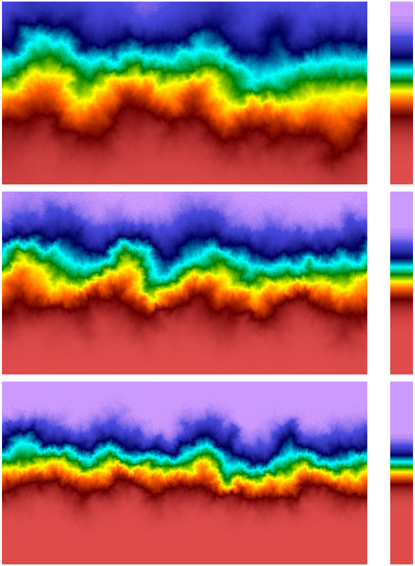
$$\begin{aligned} v_t &= \nu v_{xx} + \sqrt{2\nu}\, W_x && (5) \\ c_t &= \chi c_{xx} - v \bar{c}_x, && (6) \end{aligned}$$

  where $g = \bar{c}_x$ is the imposed background concentration gradient.
- Concentration fluctuations become long-ranged and are enhanced by the gradient

$$\langle \hat{c}\hat{c}^\star \rangle \sim \frac{(\bar{c}_x)^2}{\chi(\chi+\nu)k^4}.$$

- In the simpler linearized case it can be shown that the limiting dynamics exists and the term $v\bar{c}_x$ becomes a stochastic forcing for the concentration (Eric Vanden-Eijnden). General case is still an **open question**.

Animation: Changing Schmidt Number



Binary Mixture Compressible Equations

$$\begin{aligned} D_t\rho &= -\rho\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right) \\ \rho\left(D_t\mathbf{v}\right) &= -\boldsymbol{\nabla}P+\boldsymbol{\nabla}\cdot\left(\eta\overline{\boldsymbol{\nabla}}\mathbf{v}+\boldsymbol{\Sigma}\right) \\ \rho c_v\left(D_t T\right) &= -P\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right)+\boldsymbol{\nabla}\cdot\left(\kappa\boldsymbol{\nabla}T+\boldsymbol{\Xi}\right)+\left(\eta\overline{\boldsymbol{\nabla}}\mathbf{v}+\boldsymbol{\Sigma}\right):\boldsymbol{\nabla}\mathbf{v} \\ \rho\left(D_t c\right) &= \boldsymbol{\nabla}\cdot\left[\rho\chi\left(\boldsymbol{\nabla}c\right)+\boldsymbol{\Psi}\right], \end{aligned} \tag{7}$$

The pressure $P(\rho, c, T)$ can be decomposed into a *thermodynamic* portion P_0 and a kinematic portion $\left(\mathrm{Ma}^2\right)\pi$.
If $c_T^2 = \partial P/\partial\rho \to \infty$ the fluctuations of the thermodynamic pressure are fast, leading to the **equation of state (EOS) constraint**

$$P(\rho, c, T) = P_0 = \mathbf{const}$$

Low Mach Number Approximation

- The density is not an independent variable anymore but rather determined from the constraint.
- By differentiating the EOS constraint and using the continuity equation we get

$$\rho\boldsymbol{\nabla}\cdot\mathbf{v}=\left(\frac{\partial\rho}{\partial c}\right)_{P,T}(D_{t}c)+\left(\frac{\partial\rho}{\partial T}\right)_{P,c}(D_{t}T),$$

  which is a generalization of the incompressibility constraint.
- In the stochastic setting this is a strange sort of *stochastic constraint*

$$\rho\boldsymbol{\nabla}\cdot\mathbf{v}=-\boldsymbol{\nabla}\cdot\left[\rho\chi\left(\boldsymbol{\nabla}c\right)+\boldsymbol{\Psi}+\dots\right].$$

- By linearizing around equilibrium and using Fourier transforms this can be shown to lead to a velocity **v** which is "white" in time (has nonzero power at infinite wavefrequencies).

Chemical Langevin Equation

- Consider a single reaction with stochiometric coefficients are $\boldsymbol{\nu} = \boldsymbol{\vartheta}^{-} - \boldsymbol{\vartheta}^{+}$ (negative for reactants)

$$\left(\vartheta_1^{+}, \ldots, \vartheta_n^{+}\right) \leftrightarrow \left(\vartheta_1^{-}, \ldots, \vartheta_n^{-}\right).$$

- The contribution to the mass balance from the reaction is

$$\left(\partial_t \rho_j\right)_{\text{react}} = \nu_j m_j \left[-\left(\beta P r\right) \tilde{\mathcal{A}} + \left(\beta P r\right)^{\frac{1}{2}} \left(2\frac{\tilde{\mathcal{A}}}{\mathcal{A}}\right)^{\frac{1}{2}} \check{\mathcal{W}}(r, t)\right], \tag{8}$$

where the reaction *affinity*

$$\tilde{\mathcal{A}} = \exp\left(\sum_k \tilde{\mu}_k^{-}\right) - \exp\left(\sum_k \tilde{\mu}_k^{+}\right) = \left(\prod_k e^{\tilde{\mu}_k^{+}} - \prod_k e^{\tilde{\mu}_k^{-}}\right),$$

$$\mathcal{A} = \sum_k \tilde{\mu}_k^{-} - \sum_k \tilde{\mu}_k^{+} = \beta \sum_k \nu_k m_k \mu_k.$$

Here $\tilde{\mu}_k^{\pm} = \beta \vartheta_k^{\pm} m_k \mu_k$ are related to the chemical potentials μ_k.

Nonlinear Fluctuations

- For ideal gas mixtures,

  $$e^{\beta \nu_k m_k \mu_k} = C_k \left(m_k k_B T \right)^{-\frac{3\nu_k}{2}} \left(\frac{\rho_k}{m_k} \right)^{\nu_k},$$

  giving the more familiar stochastic law-of-mass action form

  $$\left(\beta P r \right) \tilde{\mathcal{A}} = k^+ \prod_k^{\text{reac}} \left(\frac{\rho_k}{m_k} \right)^{\vartheta_k^+} - k^- \prod_k^{\text{prod}} \left(\frac{\rho_k}{m_k} \right)^{\vartheta_k^-},$$

  where $k^{\pm}$ are the more familiar forward/reverse reaction rates.
- Near chemical equilibrium, both $\mathcal{A}$ and $\tilde{\mathcal{A}}$ are close to zero, and

  $$2\frac{\tilde{\mathcal{A}}}{\mathcal{A}} \approx \exp\left(\sum_k \tilde{\mu}_k^+ \right) + \exp\left(\sum_k \tilde{\mu}_k^- \right),$$

  which is the more common form of the chemical Langevin equation. This form *separates the forward and reverse reactions* and their noises.

Kramers Picture

- The two forms are not, however, equivalent far from equilibrium, which is where most chemical reactions operate.
- One can actually derive the nonlinear equation from a simpler linear equation in a stiff limit.
- Ala Kramers, think of reaction as a diffusion along a reaction coordinate $0 \leq \gamma \leq 1$.
- Denote the probability that reaction complex is in state γ at point $(\mathbf{r}, t)$ with $c(\gamma, \mathbf{r}, t)$.
  Drop $(\mathbf{r}, t)$ for now for notational simplicity.
- The chemical potential is related to the *enthalpy* $h(\gamma)$ which has the familiar "energy barrier" form,

$$\mu(\gamma) = \frac{k_B T}{m_{\text{rc}}} \ln c(\gamma) + h(\gamma),$$

where $m_{\text{rc}} = \sum_k \vartheta_k^+ m_k = \sum_k \vartheta_k^- m_k$ is the reaction complex mass.

Stiff Limits

- The diffusion along γ follows the postulated stochastic diffusion equation

$$\left(D_t c\right)_{\text{react}} = -\frac{\partial}{\partial\gamma}\xi\left[\frac{\partial c}{\partial\gamma} + \frac{m_{\text{rc}}}{k_B T}\frac{\partial h}{\partial\gamma}\right] + \frac{\partial}{\partial\gamma}\left(\sqrt{2m\xi\rho^{-1}c}\,\mathcal{W}\right).$$

- If the reaction barrier is much larger than $k_B T$, most complexes are in the product ($\gamma = 1$) or the reactant state ($\gamma = 0$).
- In this way Bedeaux *et al.* obtain the *nonlinear* mass reaction law [5]. For the fluctuations, they linearized the equations first.
- It is an **open question** to see if one can do the nonlinear analysis and thus resolve the ambiguity in the nonlinear Langevin equation.

Fluid-Structure Coupling

- Consider a blob (Brownian particle) of size a with position $\mathbf{q}(t)$ and velocity $\mathbf{u} = \dot{\mathbf{q}}$, and the velocity field for the fluid is $\mathbf{v}(\mathbf{r}, t)$.
- We do not care about the fine details of the flow around a particle, which is nothing like a hard sphere with stick boundaries in reality anyway.
- Take an **Immersed Boundary Method** (IBM) approach and describe the fluid-blob interaction using a localized smooth **kernel** $\delta_a(\Delta\mathbf{r})$ with compact support of size a (integrates to unity).
- Often presented as an interpolation function for point Lagrangian particles but here a is a **physical size** of the blob [6].

Local Averaging and Spreading Operators

- Define the local fluid velocity,

$$\mathbf{v}_{\mathbf{q}} = \left[\mathbf{J}\left(\mathbf{q}\right)\right]\mathbf{v} = \int \delta_a\left(\mathbf{q}-\mathbf{r}\right)\mathbf{v}\left(\mathbf{r},t\right)d\mathbf{r}.$$

- The **induced force density** in the fluid because of the particle is:

$$\mathbf{f} = -\boldsymbol{\lambda}\delta_a\left(\mathbf{q}-\mathbf{r}\right) = -\left[\mathbf{S}\left(\mathbf{q}\right)\right]\boldsymbol{\lambda},$$

  where $\boldsymbol{\lambda}$ is a fluid-particle force (note that this ensures **momentum conservation**).

- Crucial for **energy conservation** is that the *local averaging operator* $\mathbf{J}(\mathbf{q})$ and the *local spreading operator* $\mathbf{S}(\mathbf{q})$ are **adjoint**, $\mathbf{S} = \mathbf{J}^{\star}$.

Fluid-Particle Direct Coupling

- The equations of motion in our coupling approach are **postulated** (Pep Español is working on a derivation) to be

$$\begin{aligned} \rho\left(\partial_t \mathbf{v} + \mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v}\right) &= -\boldsymbol{\nabla}\pi + \nu\boldsymbol{\nabla}^2\mathbf{v} + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma} - \left[\mathbf{S}\left(\mathbf{q}\right)\right]\boldsymbol{\lambda} \\ m_e\dot{\mathbf{u}} = m_e\ddot{\mathbf{q}} &= \mathbf{F}\left(\mathbf{q}\right) + \boldsymbol{\lambda} \\ \text{s.t. } \boldsymbol{\nabla}\cdot\mathbf{v} &= 0, \end{aligned}$$

  where the fluid-particle force $\boldsymbol{\lambda}$ is a frictional + stochastic force

$$\boldsymbol{\lambda} = -\zeta\left[\mathbf{u} - \mathbf{J}\left(\mathbf{q}\right)\mathbf{v}\right] + \sqrt{2\zeta k_B T}\,\widetilde{\mathcal{W}},$$

  $\mathbf{F}\left(\mathbf{q}\right) = -\boldsymbol{\nabla}U\left(\mathbf{q}\right)$ is the applied force, and m_e is the **excess mass** of the particle.

- Dunweg and Ladd [7] (**arXiv:0803.2826v2**), and also Atzberger [8], have shown that this system satisfies fluctuation-dissipation balance, that is, preserves the invariant Gibbs distribution

$$P\left(\mathbf{v},\mathbf{u},\mathbf{q}\right) = Z^{-1}\exp\left\{-\beta\left[U\left(\mathbf{q}\right) + m_e\frac{u^2}{2} + \int\rho\frac{v^2}{2}\,d\mathbf{r}\right]\right\}.$$

Overdamped Limit #1

- If we take $\zeta \to \infty$, the particle velocity $\mathbf{u}$ becomes rapidly fluctuating around the local fluid velocity $[\mathbf{J}(\mathbf{q})]\,\mathbf{v}$.
- We *postulate* that the limiting equations are (can we derive them?)

$$\begin{aligned} \rho\left(\partial_t \mathbf{v} + \mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v}\right) &= -\boldsymbol{\nabla}\pi + \nu\boldsymbol{\nabla}^2\mathbf{v} + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma} - [\mathbf{S}(\mathbf{q})]\,\boldsymbol{\lambda} + \text{correction} \\ m_e\dot{\mathbf{u}} &= \mathbf{F}(\mathbf{q}) + \boldsymbol{\lambda} \\ \text{s.t. }\ \mathbf{u} = \dot{\mathbf{q}} &= [\mathbf{J}(\mathbf{q})]\,\mathbf{v} \text{ and } \boldsymbol{\nabla}\cdot\mathbf{v} = 0, \end{aligned}$$

  where $\boldsymbol{\lambda}$ is now a Lagrange multiplier that enforces the **no-slip condition $\mathbf{u} = \mathbf{v}_{\mathbf{q}}$**.
- The **fluctuationing stress** $\boldsymbol{\Sigma} = \sqrt{2\nu\rho^{-1}\,k_B T}\,\boldsymbol{\mathcal{W}}$ drives the Brownian motion.
- In the existing (stochastic) IBM approaches **inertial effects** are ignored, $m_e = 0$ and thus $\boldsymbol{\lambda} = -\mathbf{F}$.

contd.

- The correction (I believe) arising from the adiabatic mode elimination is

$$\text{correction} = -\frac{(m - m_e)}{m} \boldsymbol{\nabla} \mathbf{S} \left(k_B T \right)$$

  and thus does not matter in the incompressible limit.

- It is perfectly reasonable to add an additional contribution

$$\dot{\mathbf{q}} = \left[\mathbf{J} \left(\mathbf{q} \right) \right] \mathbf{v} + \zeta^{-1} \mathbf{F} \left(\mathbf{q} \right) + \sqrt{2 \zeta^{-1} k_B T} \, \widetilde{\boldsymbol{\mathcal{W}}},$$

  although strictly in the limit $\zeta \to \infty$ this would vanish, so it is not exactly clear in what sense the above applies.

Overdamped Limit #2

- If we take $\eta \to \infty$, we get the asymptotic *Brownian dynamics* limit

$$\dot{\mathbf{q}}\left(t\right) = \mathbf{M}\mathbf{F}\left(\mathbf{q}\right) + \sqrt{2k_B T}\,\mathbf{M}^{1/2}\widetilde{\mathcal{W}} + k_B T\left(\boldsymbol{\nabla}_{\mathbf{q}} \cdot \mathbf{M}\right),$$

- Here the mobility depends on the fluid equation

$$\begin{aligned}\mathbf{M}\left(\mathbf{q}\right) &= \zeta^{-1} - \mathbf{J}\boldsymbol{\mathcal{L}}^{-1}\mathbf{S} \\ &= \zeta^{-1} + \nu^{-1}\int d\mathbf{r}' \int d\mathbf{r}\left[\mathbf{G}\left(\mathbf{r},\mathbf{r}'\right)\right]\delta_{\Delta a}\left(\mathbf{q}-\mathbf{r}'\right)\delta_{\Delta a}\left(\mathbf{q}-\mathbf{r}\right)\end{aligned}$$

  and where **G** is the Green's function for the Stokes equation (Oseen tensor) with $\nu = 1$.

- I stated lots of things that I can almost or I cannot formally prove...
- What to do in the full nonlinear setting (not a Stokes approximation)?

Open Questions

- Diffusion as an overdamped limit of inter-species velocity fluctuations (multicomponent mixtures are done *ad hoc* at present).
- Incompressible limit in the stochastic setting.
- Limiting dynamics for diffusive mixing for large Schmidt numbers.
- Fluctuating low Mach number equations.
- Local angular momentum conservation.
- Fluid-particle coupling in the overdamped limit.
- Fluctuations in nonlinear chemical reactions.

References/Questions?

E. Goldman and L. Sirovich.
Equations for gas mixtures.
Physics of Fluids, 10:1928, 1967.

A. Donev, A. L. Garcia, Anton de la Fuente, and J. B. Bell.
Enhancement of Diffusive Transport by Nonequilibrium Thermal Fluctuations.
J. of Statistical Mechanics: Theory and Experiment, 2011:P06014, 2011.

A. Vailati, R. Cerbino, S. Mazzoni, C. J. Takacs, D. S. Cannell, and M. Giglio.
Fractal fronts of diffusion in microgravity.
Nature Communications, 2:290, 2011.

F. Balboa Usabiaga, J. Bell, R. Delgado-Buscalioni, A. Donev, T. Fai, B. E. Griffith, and C. S. Peskin.
Staggered Schemes for Incompressible Fluctuating Hydrodynamics.
Submitted to J. Comp. Phys., 2011.

D. Bedeaux, I. Pagonabarraga, J.M.O. de Zárate, J.V Sengers, and S. Kjelstrup.
Mesoscopic non-equilibrium thermodynamics of non-isothermal reaction-diffusion.
Phys. Chem. Chem. Phys., 12(39):12780–12793, 2010.

F. Balboa Usabiaga, I. Pagonabarraga, and R. Delgado-Buscalioni.
Inertial coupling for point particle fluctuating hydrodynamics.
In preparation, 2011.

B. Dunweg and A.J.C. Ladd.
Lattice Boltzmann simulations of soft matter systems.
Adv. Comp. Sim. for Soft Matter Sciences III, pages 89–166, 2009.

P. J. Atzberger.
Stochastic Eulerian-Lagrangian Methods for Fluid-Structure Interactions with Thermal Fluctuations.
J. Comp. Phys., 230:2821–2837, 2011.