Fluctuating hydrodynamics and coarse-graining

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- **Pep Español**, UNED, Madrid (Theory of Coarse-Graining)
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- **Alejandro Garcia**, San Jose State University (physics and applications)
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1. Augmented Langevin Equations

2. Diffusion without Hydrodynamics

3. Discrete Fluctuating Hydrodynamics

4. Diffusion with Hydrodynamics: TCG

5. Diffusion with Hydrodynamics: FHD

6. Diffusion with Hydrodynamics: BD-HI

7. FHD and Colloidal Suspensions

8. Renormalization in Electrolytes
At thermodynamic equilibrium, start from microscopic configuration and then define **coarse-grained** degrees of freedom \( x = X(z) \) to get a coarse-grained “Hamiltonian” or free energy

\[
H(x) = -(k_B T) \ln \int_z \delta [X(z) - x] c_{eq}(z) dz,
\]

where \( c_{eq}(z) dz \) is the equilibrium measure (ensemble) for the microscopic dynamics.

The equilibrium distribution for the coarse variables is the **Gibbs distribution** (similarly, **Einstein distribution** for closed system)

\[
P_{eq}(x) = Z^{-1} \exp \left[ -\frac{H(x)}{k_B T} \right], \tag{1}
\]

and any reasonable coarse-grained dynamics must preserve this distribution as an invariant measure.
Important: Since \( z \) is finite-dimensional, assume \( X \) is also finite-dimensional.

A reasonable postulate for the coarse-grained dynamics for isothermal systems is the augmented Ito Langevin equation:

\[
\frac{dx}{dt} = -N \cdot \frac{\partial H}{\partial x} + (2k_B T)^{1/2} B \cdot \mathcal{W}(t) + (k_B T) \frac{\partial}{\partial x} \cdot N^*,
\]

where \( \mathcal{W}(t) \) is a vector of independent white-noise processes.

The fluctuation-dissipation balance condition is

\[
BB^* = \frac{1}{2} (N + N^*) = M \succeq 0.
\]

In this picture \( L = \frac{1}{2} (N^* - N) \) is the “conservative” part and \( M \) is the “dissipative” part of the dynamics,

\[
\frac{dH}{dt} = \frac{\partial H}{\partial x} \cdot N \cdot \frac{\partial H}{\partial x} = \text{Re} \left( \frac{\partial H}{\partial x} \cdot M \cdot \frac{\partial H}{\partial x} \right) \leq 0.
\]
This can be justified to some extent via projection operator formalism(s) and the assumption of separation of time-scales, i.e., Markovianity of the CG dynamics (upcoming book on Theory of Coarse Graining by Pep Español).

The Mori-Zwanzig formalism gives explicit expressions for \( N(x) \) as a sum of a “drift” term, which is the projection of the microscopic Poisson bracket onto the constrained manifold \( X(z) = x \), and a “friction” term, which is the integral of the autocorrelation function of the projected microscopic dynamics (Green-Kubo formulas).

For closed systems with strict energy conservation, see GENERIC formalism described in Ottinger’s book “Beyond Equilibrium Thermodynamics”.

The microscopic dynamics is time-reversible at equilibrium with momentum inversion, and therefore so must be the coarse-grained dynamics.
The coarse-grained variables will transform differently under time-reversal,

\[ \tilde{x}_k = \epsilon_k x_k, \]

where the parity \( \epsilon_k = 1 \) for positional variables and \( \epsilon_k = -1 \) for velocity variables.

If the free-energy is time-reversal invariant, \( \tilde{H}(\tilde{x}) = H(x) \), and the mobility satisfies the reciprocal relations

\[ \tilde{N}_{kj}(\tilde{x}) = N_{kj}(x) = \epsilon_k \epsilon_j N^\star_{jk}(x), \quad (3) \]

then the time-reversed evolution is

\[ \frac{d\tilde{x}}{dt} = -\tilde{N} \cdot \frac{\partial \tilde{H}}{\partial \tilde{x}} + (2k_B T)^{1/2} \tilde{B} \cdot \mathcal{W}(t) + (k_B T) \frac{\partial}{\partial \tilde{x}} \cdot \tilde{N}^\star, \quad (4) \]

Therefore, the reversed evolution has exactly the same form as the forward evolution (2), that is, the process is time reversible at equilibrium (obeys detailed balance w.r.t. to the Gibbs distribution).
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Uncorrelated Brownian Walkers

- **Fluctuating hydrodynamics** (FHD) is a coarse-grained description of mass, momentum and energy transport in fluids (gases and liquids).
- Consider **diffusion** of colloidal particles immersed in a viscous liquid; assume the particles are **uncorrelated Brownian walkers**.
- The positions of the $N$ particles $Q(t) = \{ q_1(t), \ldots, q_N(t) \}$ follow the Ito SDEs
  \[ dQ = (2\chi)^{1/2} dB, \]  
  \[ (5) \]
  where $B(t)$ is a collection of independent Brownian motions.
- We are interested in describing a spatially coarse-grained **fluctuating empirical concentration field**,
  \[ c_\xi(r, t) = \sum_{i=1}^{N} \delta_\sigma(q_i(t) - r), \]
  \[ (6) \]
  where $\delta_\sigma$ is a smoothing kernel with support $\sim \sigma$ that converges to a delta function as $\sigma \rightarrow 0$. 

\[ A. \text{ Donev (CIMS)} \]
Consider first the limit $\sigma \to 0$, which corresponds to no coarse graining (no loss of information except particle numbering).

Dean obtained an SPDE for $c(r, t) = \sum \delta(q_i(t) - r)$, using straightforward Ito calculus and formal properties of the Dirac delta function,

$$\partial_t c = \chi \nabla^2 c + \nabla \cdot \left( \sqrt{2\chi c} \mathcal{W}_c(r, t) \right), \quad (7)$$

where $\mathcal{W}_c(r, t)$ denotes a spatio-temporal white-noise vector field.

This is a typical example of a fluctuating hydrodynamics equation, which is deceptively simple, yet extremely subtle from both a physical and mathematical perspective.

The term $\sqrt{2\chi c} \mathcal{W}_c$ can be thought of as a stochastic mass flux, in addition to the “deterministic” dissipative flux $\chi \nabla c$. 
Formal Langevin SPDEs

- This formally looks like a coarse-grained purely dissipative Langevin equation (products imply a contraction over spatial position)

\[ \partial_t c = -\mathcal{M} [c(\cdot, t)] \cdot \frac{\delta \mathcal{F}}{\delta c(\cdot, t)} + (2k_B T \mathcal{M} [c(\cdot, t)])^{\frac{1}{2}} \cdot \mathcal{W}_c(\cdot, t), \quad (8) \]

where \( \mathcal{M} [c(\cdot)] \) is a positive-semidefinite mobility functional defined by its action on a scalar field \( f(\mathbf{r}) \),

\[ \int d\mathbf{r}' \mathcal{M} [c(\cdot); \mathbf{r}, \mathbf{r}'] f(\mathbf{r}') \equiv - (k_B T)^{-1} \nabla \cdot (\chi c(\mathbf{r}) \nabla f(\mathbf{r})). \]

- Here \( \mathcal{F} \) is the ideal gas free energy functional (in the Grand Canonical ensemble with reservoir concentration \( c_0 \))

\[ \mathcal{F} [c (\cdot)] = k_B T \int c(\mathbf{r}) (\ln (c(\mathbf{r})/c_0) - 1) d\mathbf{r} \]

associated with a corresponding formal Gibbs-Boltzmann distribution that has no clear mathematical meaning.
What is it useful for?

\[
\frac{\partial t}{c} = \chi \nabla^2 c + \nabla \cdot \left( \sqrt{2 \chi c} \mathcal{W}_c \right)
\] (9)

- In principle, the Dean equation is **not really useful**, since it is a **mathematically ill-defined** tautology, a mere rewriting of the original equations for the particles. But...
- The ensemble average \( \bar{c} = \langle c \rangle \) follows **Fick’s law**, 
  \[
  \frac{\partial t}{\bar{c}} = \nabla \cdot (\chi \nabla \bar{c}) = \chi \nabla^2 \bar{c},
  \]
  which is also the **law of large numbers (LLN)** in the limit of **large coarse-graining scale**.
- The **central limit theorem** describing small Gaussian fluctuations \( \delta c = c - \bar{c} \) can be obtained by linearizing, 
  \[
  \frac{\partial t}{(\delta c)} = \chi \nabla^2 (\delta c) + \nabla \cdot \left( \sqrt{2 \chi \bar{c}} \mathcal{W}_c \right).
  \]
  Note that this equation of **linearized fluctuating hydrodynamics** is **mathematically well-defined**.
Furthermore, and more surprisingly, the Dean equation correctly predicts the **large deviation** behavior of the particle model (help from Eric Vanden-Eijnden, originates with Varadhan).

Define the empirical measure

\[ c_N(r, t) = \frac{1}{N} \sum_{i=1}^{N} \delta(r - q_i(t)), \]

which converges weakly to the solution of the deterministic diffusion equation \( \bar{c}(r, t) \) (LLN) with initial condition being the initial probability distribution of particle positions.

For a “reasonable” **test function** \( \phi(r) \), the empirical value

\[ \phi_N(t) = \frac{1}{N} \sum_{i=1}^{N} \phi(q_i(t)) = \int dr \phi(r) c_N(r, t) \]

converges as \( N \) increases to \( \bar{\phi} = \int dr \phi(r) \bar{c}(r, t) \).
**Large Deviation Theory** (LDT) tells us that

\[
\lim_{N \to \infty} N \ln P(\phi_N(t) \geq a) = \inf_{c} S_t[c] =
\]

\[
\inf_{c} \int dr \ c(r, t) (\ln (c(r, t)/\bar{c}(r, t)) - 1),
\]

where the infimum is taken over all (reasonable) functions (*not distributions!*) that satisfy \( \int dr \ c(r, t) = 1 \) and

\[
\int dr \ \phi(r) \ c(r, t) \geq a.
\]

**The path action functional** is formally given by Dean’s dynamics,

\[
S_T[c] = \frac{1}{4} \int_0^T dt \int dr \ (\partial_t c - \chi \nabla^2 c) (\nabla \cdot c \nabla)^{-1} (\partial_t c - \chi \nabla^2 c)
\]

\[
+ \int dr \ c(r, 0) (\ln (c(r, 0)/\bar{c}(r, 0)) - 1).
\]
All this suggests the nonlinear FHD is informative and maybe useful.

In particular, upon spatially discretizing the (formal) SPDE, the resulting system of SODEs can be seen as a spatial coarse-graining of the particle system, which has the right properties.

Numerically solving the discretized Dean equation with weak noise gives results in agreement with all three mathematically well-defined weak-noise limit theorems: LLN, CLT, and LDT. No need to perform linearizations manually, or to discretize stochastic path integrals!

I will show some examples where the nonlinearity gives a known physical effect, after a suitable smoothing / cutoff in Fourier space at molecular scales.
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Consider **diffusion of a (nano)colloidal particles in a liquid**. The first step is to define a discrete set of **relevant variables**, which are **mesoscopic observables** that **evolve slowly**.
The proper way to interpret fluctuating hydrodynamics is via the theory of coarse-graining (here I follow Pep Español) [1].

Introduce a triangulation and define Petrov-Galerkin finite-element (FE) functions on this grid such as the “tent” function $\psi_\mu(r)$. 
Define an orthogonal set of FE basis functions,

\[ \| \delta_\mu \psi_\nu \| = \delta_\mu \nu, \]  

where \( \| f \| \equiv \int d f(r) \). Here \( \delta_\mu(r) \) is a discrete Dirac delta function.

The discrete concentration field \( c_\mu \) at a node \( \mu \) at position \( r_\mu \) is defined as

\[ \hat{c}_\mu(t) = \sum_i^{N_B} \delta_\mu(q_i(t)) \]

where \( \delta_\mu(r) \) is a function localized around \( r_\mu \) satisfying

\[ \sum_\mu \mathcal{V}_\mu \delta_\mu(r) = 1 \ \forall r \ \Rightarrow \ \sum_\mu \mathcal{V}_\mu \hat{c}_\mu = N_B. \]

Continuum fields which are interpolated from discrete “fields” denoted here with bar:

\[ \bar{c}(r) = \psi_\mu(r)c_\mu \]
\[
\frac{dc}{dt} = -M \frac{\partial F}{\partial c} + (2k_B T)^{1/2} M^{1/2} \mathcal{W}(t) + (k_B T) \frac{\partial}{\partial x} \cdot M \quad (14)
\]

**Dissipative matrix** in TCG is given by the Green-Kubo integral (this derivation comes from Pep Español):

\[
M_{\mu\nu}(c) = \int dr \int dr' \nabla \delta_\nu(r) \nabla \delta_\mu(r') \times \int_0^T dt \langle \hat{J}_r(0) \hat{J}_r(t) \rangle^c , \quad (15)
\]

Current \( \hat{J}_r(z) \equiv \sum_i \delta(r - q_i)u_i \) where \( u_i = \dot{q}_i \). \( \quad (16) \)
A reasonable approximation

- Assume that the positions of the Brownian particles evolve in a much slower scale than the velocities (definitely true in liquids!):

\[
\hat{J}_\mathbf{r}(t) = \sum_i \mathbf{u}_i(t) \delta(\mathbf{r} - \mathbf{q}_i(t)) \approx \sum_i \mathbf{r}_i(t) \delta(\mathbf{r} - \mathbf{q}_i).
\] (17)

- This gives the conditional average

\[
\left\langle \hat{J}_\mathbf{r}(0) \hat{J}_{\mathbf{r}'}(t) \right\rangle^c = \left\langle \sum_i \mathbf{u}_i(0) \delta(\mathbf{r} - \mathbf{q}_i(0)) \sum_j \mathbf{u}_j(t) \delta(\mathbf{r}' - \mathbf{q}_j(t)) \right\rangle^c
\]

\[
= \sum_i \left\langle \mathbf{u}_i(0) \delta(\mathbf{r} - \mathbf{q}_i(0)) \mathbf{u}_i(t) \delta(\mathbf{r}' - \mathbf{q}_i(t)) \right\rangle^c
\]

\[
+ \sum_{i \neq j} \left\langle \mathbf{u}_i(0) \delta(\mathbf{r} - \mathbf{q}_i(0)) \mathbf{u}_j(t) \delta(\mathbf{r}' - \mathbf{q}_j(t)) \right\rangle^c.
\] (18)
An unreasonable approximation

Now assume incorrectly that the velocities of different particles are uncorrelated (ignore hydrodynamics!),

$$\langle \hat{J}_r (0) \hat{J}_{r'}(t) \rangle^c \simeq \delta(r - r') \sum_i \langle u_i (0) u_i(t) \delta(r - q_i(t)) \rangle^c$$  \hspace{1cm} (19)$$

$$\simeq \delta(r - r') \sum_i \langle u_i (0) u_i(t) \rangle^c \langle \delta(r - q_i) \rangle^c.$$  \hspace{1cm} (20)$$

Finally we get the approximate dissipative matrix

$$M_{\mu\nu}(c) \simeq \int dr \int dr' \nabla \delta_\nu(r) \nabla \delta_\mu(r')$$

$$\times \delta(r - r') \left( \sum_i \delta(r - q_i) \right)^c \chi(c)$$  \hspace{1cm} (21)$$

where the self-diffusion coefficient is

$$\chi(c) = \int_0^T dt \langle u_i (0) u_i(t) \rangle^c \approx \chi = \int_0^\infty dt \langle u_i (0) u_i(t) \rangle^{eq}.$$
Approximate but still not closed expression:

\[ M_{\mu\nu}(c) \approx \chi \int d\mathbf{r} \nabla \delta_{\nu}(\mathbf{r}) \nabla \delta_{\mu}(\mathbf{r}) \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle^c, \quad (22) \]

Close using “linear for spiky approximation” [1]:

\[ \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle^c \approx \sum_{\mu} \psi_{\mu}(\mathbf{r}) c_{\mu}. \]

Finally we get a dissipative matrix which is proportional to the concentration

\[ M_{\mu\nu}(c) = \chi \sum_{\sigma} \| \nabla \delta_{\nu} \nabla \delta_{\mu} \psi_{\sigma} \| c_{\sigma} \quad (23) \]

which turns out to be a Petrov-Galerkin FEM discretization of the covariance of Dean’s noise, \( \nabla \cdot c(\mathbf{r}) \nabla \) [2].
Caveats

- Note: We can easily generate $(2k_B T)^{1/2} M^{1/2} \mathcal{W}(t)$ by generating stochastic Gaussian fluxes on each face of the grid [2].
- Now the caveats! First, for $M$ to be SPD we require that

$$
\bar{c}(r) = \sum_\sigma c_\sigma \psi_\sigma(r) > 0 \quad \forall r,
$$

which is not obviously true.
- Things will be OK (for a physicist ;-) if the coarse-graining cells are large enough to contain many particles.
- The difficulties with the continuum equation (is $c$ “smooth” and non-negative?) re-surface in the discrete setting!
Somewhat embarrassingly, we have *not* been able to derive a reasonable approximation of the **discrete free energy function** $F(c)$.

Specifically, we have not been able to obtain an expression for the large deviation functional for the discrete concentration field because of the logarithmic highly nonlinear term in $c \ln c$.

Therefore **we cannot yet get a simple discretization of the diffusion term** $\chi \nabla^2 c$ from TCG, sigh...

Fundamental issue with discrete approach: Discrete operators don’t satisfy continuum identities like the chain rule, so the cancellation $\nabla \cdot (c \nabla \ln c) = \nabla^2 c$ doesn’t work discretely!

But let me show now another more relevant example where we have worked it all out [1].
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Relevant variables for **subgrid (nanoscopic) particles** associated to a **grid node** $\mu$ are:

- **discrete mass** $\rho_\mu(t)$ and **momentum density** $g_\mu(t)$ (including the suspended particle!)
- **position of the particle** (since momentum of particle is not slow!)
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 [1],

\[ \hat{q}(z = \{q, p\}) = q_0, \tag{24} \]

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

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

where \( i = 0 \) labels the nanoparticle. Note that both mass and momentum densities include the nanoparticle!
Mori-Zwanzig Procedure

- One can use the **(Mori-)Zwanzig formalism** with a **Markovian assumption** (due to separation of timescales) to derive a system of SDEs for the (discrete) coarse-grained variables [1].

- Introduce a *regularized* Dirac delta kernel

\[
\Delta(r, r') \equiv \delta_\mu(r) \psi_\mu(r') = \Delta(r', r) \quad \Rightarrow \\
\int dr' \Delta(r, r') \delta_\mu(r') = \delta_\mu(r) \\
\int dr' \Delta(r, r') \psi_\mu(r') = \psi_\mu(r).
\]

- For brevity, I will drop some terms in the free energy due to fact that the nanoparticle itself changes the equation of state of the fluid since it introduces a local density inhomogeneity. I will also set the bulk viscosity of the fluid to zero.
After making a number of approximations and using the linear for spiky closure, we get the **closed system of SODEs** [1]:

\[
\begin{align*}
\frac{dq}{dt} &= \bar{v}(q) + \frac{\chi_0}{k_B T} F^{\text{ext}} + \sqrt{2k_B T \chi_0} \mathcal{W}_q(t) \\
\frac{d\rho_\mu}{dt} &= \|\bar{\rho} \bar{v} \cdot \nabla \delta_\mu\| \\
\frac{dg_\mu}{dt} &= \|\bar{g} \bar{v} \cdot \nabla \delta_\mu\| - \|\delta_\mu \nabla P\| + k_B T \nabla \delta_\mu(q) + \delta_\mu(q) F^{\text{ext}} \\
&\quad + \eta \|\delta_\mu \nabla^2 \bar{v}\| + \frac{\eta}{3} \|\delta_\mu \nabla (\nabla \cdot \bar{v})\| + \text{noise}
\end{align*}
\]

The pressure equation of state is *modeled* by

\[
P(r) \simeq \frac{c^2}{2 \rho_{eq}} (\bar{\rho}(r)^2 - \rho_{eq}^2) .
\] (25)
Final Continuum Equations

The same equations can be obtained from a Petrov-Galerkin FEM discretization of the (isothermal) Landau-Lifshitz FHD SPDEs (+ colloid):

\[
\frac{d}{dt} q = \int dr \Delta(r, q) v(r, t) + \frac{\chi_0}{k_B T} F^{\text{ext}} + \sqrt{2k_B T \chi_0} \mathcal{W}_q(t)
\]

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

\[
\partial_t g(r, t) = -\nabla \cdot (g v) - \nabla P(r) - k_B T \nabla \left( \Delta(r, q) \right) + F^{\text{ext}} \Delta(r, q)
\]

\[
+ \eta \nabla^2 v + \left( \frac{\eta}{3} \right) \nabla \left( \nabla \cdot v \right)
\]

\[
+ \nabla \cdot \left( \sqrt{2\eta k_B T} \tilde{\mathcal{W}} - \sqrt{\frac{2\eta k_B T}{3}} \text{Tr} (\tilde{\mathcal{W}}) I \right)
\]

where \( v = g / \rho \), the stochastic stress is the symmetric tensor field \( \tilde{\mathcal{W}} = (\mathcal{W} + \mathcal{W}^T) / \sqrt{2} \), and the pressure is given by

\[
P(r) = \left( \frac{c^2}{2\rho_{\text{eq}}} \right) (\rho(r)^2 - \rho_{\text{eq}}^2).
\]
The TCG discrete equations are exactly the same as obtained from a Petrov-Galerkin finite-element discretization of fluctuating hydrodynamic SPDEs, using the same dual set of basis functions as used for coarse graining.

This provides a link between continuum $\rightarrow$ discrete (top-down) and discrete $\rightarrow$ continuum (bottom-up) approaches, “derives” FHD, gives a way to discretize SPDEs, and relates the transport coefficients to the microscopic dynamics.

The TCG gives generalized Green-Kubo formulas for the dissipative coefficients.

But a key artifact is that the discrete delta function or kernel $\Delta (r, q)$ is attached to the grid (artificial!) rather than to the particle cage (physical) $\sigma (r - q)$. 
Renormalization of Diffusion Coefficient

- The bare diffusion coefficient depends on the grid resolution as
  is not a material constant,

\[ \chi_0 = \frac{1}{d} \int_0^\tau dt \langle \delta \hat{u}(0) \cdot \delta \hat{u}(t) \rangle^{eq} \]  

where the particle excess velocity over the fluid is

\[ \delta \hat{u} = \hat{u} - \langle \hat{u} \rangle^q \hat{\rho} \hat{g} \approx \hat{u} - \bar{v}(q). \]

- The actual dressed or renormalized diffusion coefficient
  \( \chi = \chi_0 + \Delta \chi \) should be grid-independent,

\[ \chi = \frac{1}{d} \int_0^\tau dt \langle \hat{u}(0) \cdot \hat{u}(t) \rangle^{eq} \approx \chi_0 + \frac{1}{d} \int_0^\tau dt \langle \bar{v}(q(0)) \cdot \bar{v}(q(t)) \rangle^{eq} \]

\[ \approx \chi_0 + \frac{1}{d} \int_0^\infty dt \psi_\mu(q) \langle v_\mu(0) \cdot v_\mu'(t) \rangle_q^{eq} \psi_\mu'(q) \]
We will understand this better by switching to an SPDE-based FHD description instead of the fully discrete one; the SPDEs are a useful device to guide physics and discretizations/TCG.

In-between the microscopic and macroscopic lies a whole continuum of scales: The free energy and transport coefficients (mobility) must depend on the coarse-graining scale in nonlinear FHD (but not in linearized FHD).

Even for interacting Brownian walkers, as coarse-graining scale becomes macroscopic, the LLN is Fick’s law but with renormalized free energy (proven by Varadhan):

\[ \partial_t c = \chi \nabla^2 \Pi(c) = \chi \nabla \cdot \left( \frac{d\Pi(c)}{dc} \nabla c \right), \]

where \( \Pi(c) = c \left( \frac{df}{dc} \right) - f \) is the osmotic pressure, where \( f(c) \) is the macroscopic free-energy density at thermodynamic equilibrium.
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There is a common belief that diffusion in all sorts of materials, including gases, liquids and solids, is described by random walks and **Fick’s law** for the **concentration** of labeled (tracer) particles $c(r, t)$,

$$\partial_t c = \nabla \cdot [\chi \nabla c],$$

where $\chi \succeq 0$ is a diffusion tensor.

But there is well-known hints that the **microscopic** origin of Fickian diffusion is **different in liquids** from that in gases or solids, and that **thermal velocity fluctuations** play a key role [3].

The **Stokes-Einstein relation** connects mass diffusion to **momentum diffusion** (viscosity $\eta$),

$$\chi \approx \frac{k_B T}{6\pi \sigma \eta},$$

where $\sigma$ is a molecular diameter; which shows that diffusion and hydrodynamics (viscosity) are intimately linked.
The mesoscopic model we develop next applies, to a certain degree of accuracy, to two seemingly very different situations:

1. Molecular diffusion in binary fluid mixtures, notably, diffusion of tagged particles (e.g., fluorescently-labeled molecules in a FRAP experiment).
2. Diffusion of colloidal particles at low concentrations.

The microscopic mechanism of molecular diffusion in liquids is different from that in either gases or solids due to caging:

1. In liquids molecules are caged (trapped) for long periods of time as they collide with neighbors: **Momentum and heat diffuse much faster than does mass.**
2. The breaking and movement of cages requires collective (hydrodynamic) rearrangement and thus the assumption of independent Brownian walkers is not appropriate.
Based on the TCG justification, after an incompressible approximation, we can *postulate* the FHD equations describing *diffusion of tracer particles in a liquid*:

\[
\rho \partial_t \mathbf{v} + \nabla \pi = \eta \nabla^2 \mathbf{v} + \sqrt{\eta k_B T} \nabla \cdot (\mathbf{W} + \mathbf{W}^T), \quad \text{and} \quad \nabla \cdot \mathbf{v} = 0.
\]

\[
\mathbf{u}(r, t) = \int \sigma (r - r') \mathbf{v}(r', t) \, dr' \equiv \sigma \star \mathbf{v}
\]

\[
\partial_t c = -\mathbf{u} \cdot \nabla c + \chi_0 \nabla^2 c + \nabla \cdot \left( \sqrt{2\chi_0 c} \mathbf{W}_c \right)
\]

where \( \chi_0 \) is a *bare diffusion coefficient*. 
Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of *thermal fluctuations*. These *giant fluctuations* have been studied experimentally and with hard-disk molecular dynamics.
When macroscopic gradients are present, steady-state thermal fluctuations become \textbf{long-range correlated}.

Consider \textit{concentration fluctuations} around a steady state \( c_0(r) \),

\[
c(r, t) = c_0(r) + \delta c(r, t).
\]

The concentration fluctuations are \textbf{advected by the random velocities},

\[
\partial_t (\delta c) + \mathbf{v} \cdot \nabla c_0 = \chi \nabla^2 (\delta c) + \sqrt{2\chi c_0} (\nabla \cdot \mathbf{W}_c).
\]

Note that here \( \chi \) is the macroscopic (renormalized) diffusion coefficient, not the bare \( \chi_0 \)!

Also note we don’t need the smoothed velocity \( \mathbf{u} \) in linearized FHD.
The coupled *linearized velocity*-concentration system in one dimension:

\[ \nu_t = \nu \nu_{xx} + \sqrt{2} \nu W_x \]
\[ c_t = \chi c_{xx} - \nu \bar{c}_x, \]

where \( \bar{c}_x \) is the imposed background concentration gradient.

The linearized system can be easily solved in Fourier space to give a power-law divergence for the spectrum of the concentration fluctuations as a function of wavenumber \( k \),

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

Concentration fluctuations become long-ranged and are enhanced as the square of the gradient, to values much larger than equilibrium fluctuations. In real life the divergence is suppressed by surface tension, gravity, or boundaries (usually in that order).
Experimental results by A. Vailati et al. (Nature Comm. 2011) from a microgravity environment, showing the enhancement of concentration fluctuations in space (box scale is 5mm on the side, 1mm thick). **Fluctuations become macrosopically large at macroscopic scales!** They cannot be neglected as a microscopic phenomenon.
In order to avoid linearization, we will exploit time-scale separation to write an effective diffusion equation for concentration by eliminating the fluid velocity.

In liquids $\chi \ll \nu$, leading to a very large Schmidt number

$$S_c = \frac{\nu}{\chi} \sim 10^3 - 10^4.$$  

This extreme stiffness solving the concentration/tracer equation numerically challenging.

There exists a limiting (overdamped) dynamics for $c$ in the limit $S_c \to \infty$ in the scaling

$$\chi \nu = \text{const.}$$
Adiabatic mode elimination gives the following limiting **stochastic advection-diffusion equation** (reminiscent of the Kraichnan’s model in turbulence),

\[
\partial_t c = -w \odot \nabla c + \chi_0 \nabla^2 c, \tag{27}
\]

where \( \odot \) denotes a Stratonovich dot product.

The advection velocity \( w(\mathbf{r}, t) \) is **white in time**, with covariance proportional to a Green-Kubo integral of the velocity auto-correlation,

\[
\langle w(\mathbf{r}, t) \otimes w(\mathbf{r}', t') \rangle = 2 \delta(t - t') \int_0^\infty \langle u(\mathbf{r}, t) \otimes u(\mathbf{r}', t + t') \rangle dt'.
\]

In the Ito interpretation, there is **enhanced diffusion**,

\[
\partial_t c = -w \cdot \nabla c + \chi_0 \nabla^2 c + \nabla \cdot [\Delta \chi \nabla c] \tag{28}
\]

where \( \Delta \chi(\mathbf{r}) \) is an **analag of eddy diffusivity** in turbulence.
Enhanced Diffusivity

- Introduce an (infinite dimensional) set of basis functions $\phi_k(r)$,

$$
(k_B T)^{-1} \int_0^\infty \langle u(r, t) \otimes u(r', t + t') \rangle dt' = \mathcal{R}(r, r').
$$

$$
= \sum_k \phi_k(r) \otimes \phi_k(r').
$$

- For periodic boundaries $\phi_k$ can be Fourier modes but in general they depend on the boundary conditions for the velocity.

- The notation $w \odot \nabla c$ is a short-hand for $\sum_k (\phi_k \cdot \nabla c) \circ dB_k/dt$, where $B_k(t)$ are independent Brownian motions (Wiener processes).

- Similarly, $w \cdot \nabla c$ is shorthand notation for $\sum_k (\phi_k \cdot \nabla c) dB_k/dt$.

- The enhanced or fluctuation-induced diffusion is

$$
\Delta \chi(r) = \int_0^\infty \langle u(r, t) \otimes u(r, t + t') \rangle dt' = (k_B T) \mathcal{R}(r, r).
$$
Stokes-Einstein Relation

- An explicit calculation for **Stokes flow** gives the explicit result

\[
\Delta \chi (r) = \frac{k_B T}{\eta} \int \sigma (r - r') G (r', r'') \sigma (r - r'') \, dr' \, dr'',
\]  

(29)

where \( G \) is the Green’s function for steady Stokes flow.

- For an appropriate filter \( \sigma \), this gives **Stokes-Einstein formula** for the diffusion coefficient in a finite domain of length \( L \) of a sphere of radius \( \sigma \),

\[
\chi = \frac{k_B T}{\eta} \left\{ \begin{array}{ll}
(4\pi)^{-1} \ln \frac{L}{\sigma} & \text{if } d = 2 \\
(6\pi \sigma)^{-1} \left( 1 - \frac{\sqrt{2} \sigma}{L} \right) & \text{if } d = 3.
\end{array} \right.
\]

- The limiting dynamics is a good approximation if the effective Schmidt number \( S_c = \nu / \chi_{\text{eff}} = \nu / (\chi_0 + \chi) \gg 1 \).

- In liquids it seems \( \chi_0 \ll \chi \): **Diffusion in liquids is dominated by advection by thermal velocity fluctuations, and is more similar to eddy diffusion in turbulence than to Fickian diffusion.**
If we take an \textit{overdamped} limit of the \textbf{Lagrangian equation}

\[ dq = u(q, t) \, dt + \sqrt{2 \chi_0} \, dB_q, \]  

we get a system of instantaneously \textit{correlated} Brownian motions:

\[ dq = \sum_k \phi_k(q) \circ dB_k + \sqrt{2 \chi_0} \, dB_q, \]  

where $B_q(t)$ are \textbf{independent} Brownian motions (one per tracer).

This is \textbf{equivalent to} the well-known equations of \textbf{Brownian dynamics with hydrodynamic interactions} for diffusion of colloids!
1. Augmented Langevin Equations
2. Diffusion without Hydrodynamics
3. Discrete Fluctuating Hydrodynamics
4. Diffusion with Hydrodynamics: TCG
5. Diffusion with Hydrodynamics: FHD
6. Diffusion with Hydrodynamics: BD-HI
7. FHD and Colloidal Suspensions
8. Renormalization in Electrolytes
Brownian HydroDynamics

- The Ito equations of **Brownian Dynamics** (BD) for the (correlated) positions of the \( N \) particles \( Q(t) = \{q_1(t), \ldots, q_N(t)\} \) are

\[
dQ = -M(\partial_Q U) \, dt + (2k_B T M)^{1/2} \, dB + k_B T (\partial_Q \cdot M) \, dt, \quad (32)
\]

where \( U(\mathbf{Q}) \) is a conservative interaction potential.

- Here \( M(\mathbf{Q}) \succeq 0 \) is a symmetric positive semidefinite **mobility matrix** that captures **hydrodynamic correlations**.

- The Fokker-Planck equation (FPE) for the probability density \( P(\mathbf{Q}, t) \) corresponding to (32) is

\[
\frac{\partial P}{\partial t} = \frac{\partial}{\partial Q} \cdot \left\{ M \left[ \frac{\partial U}{\partial Q} P + (k_B T) \frac{\partial P}{\partial Q} \right] \right\}, \quad (33)
\]

and is in detailed-balance (i.e., is time reversible) with respect to the **Gibbs–Boltzmann distribution** \( \sim \exp \left( -U(\mathbf{Q}) / k_B T \right) \).
Hydrodynamic Correlations

The FHD equations we wrote earlier give a pairwise approximation to the mobility:

\[ \forall (i,j) : \quad M_{ij}(q_i, q_j) = R(q_i, q_j), \]

\[ = \eta^{-1} \int \sigma(q_i - r') G(r', r'') \sigma(q_j - r'') \, dr' \, dr''. \]

Here \( R(r, r') \) is a symmetric positive-definite divergence-free hydrodynamic kernel (div-free part is important!).

For bulk 3D commonly used is the Rotne-Prager-Yamakawa tensor,

\[
R(r) = \chi \left\{ \begin{array}{ll}
\left( \frac{3\sigma}{4r} + \frac{\sigma^3}{2r^3} \right) I + \left( \frac{3\sigma}{4r} - \frac{3\sigma^3}{2r^3} \right) \frac{r \otimes r}{r^2}, & r > 2\sigma \\
\left( 1 - \frac{9r}{32\sigma} \right) I + \left( \frac{3r}{32\sigma} \right) \frac{r \otimes r}{r^2}, & r \leq 2\sigma
\end{array} \right.
\]

for which \( \sigma(r) = \delta(r - a) \) and \( \chi = k_B T / (6\pi\eta\sigma) \).
We can use Ito calculus to obtain an equation for the **empirical** or instantaneous **concentration**

\[ c(r, t) = \sum_{i=1}^{N} \delta(q_i(t) - r). \]  

(35)

Following a similar procedure to Dean [4], with Eric Vanden-Eijnden we get the same **stochastic advection diffusion** equation as derived from the overdamped limit of the FHD equations,

\[ \partial_t c = -w \cdot \nabla c + \nabla \cdot [\Delta \chi(r) \nabla c]. \]  

(36)

This equation is **well-defined mathematically since linear** and \( w \) is smooth; advection is different from diffusion but random advection looks like diffusion!

One can use the same equation (36) to evolve a probability distribution for finding a particle at a given location; in this case \( c(r, t) \) is a function not a distribution.
Importance of Hydrodynamics

- For uncorrelated walkers, $M_{ij} = \delta_{ij} (k_B T)^{-1} \chi I$, the noise is very different, $\nabla \cdot (\sqrt{2\chi c} \mathcal{W}_c)$.

- In both cases (hydrodynamically correlated and uncorrelated walkers) the mean obeys Fick's law but the fluctuations are completely different.

- For uncorrelated walkers, out of equilibrium the fluctuations develop very weak long-ranged correlations.

- For hydrodynamically correlated walkers, out of equilibrium the fluctuations exhibit very strong “giant” fluctuations with a power-law spectrum truncated only by gravity or finite-size effects. These giant fluctuations have been confirmed experimentally.
Augmented Langevin Equations

Diffusion without Hydrodynamics

Discrete Fluctuating Hydrodynamics

Diffusion with Hydrodynamics: TCG

Diffusion with Hydrodynamics: FHD

Diffusion with Hydrodynamics: BD-HI

FHD and Colloidal Suspensions

Renormalization in Electrolytes
Now let’s consider **diffusion in colloidal suspensions of rigid particles** that are large enough that we can treat them as “macroscopic” in fluid dynamics (e.g., put a no-slip boundary condition on their surface).

But they are still mesoscopic and **Brownian motion is important**.

Methods such as Stokesian Dynamics have been developed in chemical engineering to simulate suspensions of rigid colloidal particles.

The bottleneck in all methods is generating the Brownian increments/velocities; no linear-scaling method existed before work in my group.

We have shown that using **linearized FHD** one can generate the Brownian motion piece with **linear scaling concurrently** with the deterministic motion [5]!
We consider a rigid body $\Omega$ immersed in a fluctuating fluid. In the fluid domain, we have the fluctuating Stokes equation

$$\rho \partial_t v + \nabla \pi = \eta \nabla^2 v + (2 k_B T \eta)^{\frac{1}{2}} \nabla \cdot Z \nabla \cdot v = 0,$$

with no-slip BCs on any walls, and the fluid stress tensor

$$\sigma = -\pi I + \eta (\nabla v + \nabla^T v) + (2 k_B T \eta)^{\frac{1}{2}} Z$$

consists of the usual viscous stress as well as a stochastic stress modeled by a symmetric white-noise tensor $Z(r, t)$, i.e., a Gaussian random field with mean zero and covariance

$$\langle Z_{ij}(r, t) Z_{kl}(r', t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \delta(r - r').$$
At the fluid-body interface the no-slip boundary condition is assumed to apply,

\[ \mathbf{v}(\mathbf{q}) = \mathbf{u} + \mathbf{\omega} \times \mathbf{q} - \ddot{\mathbf{u}}(\mathbf{q}) \text{ for all } \mathbf{q} \in \partial\Omega, \]  

(38)

with the inertial body dynamics

\[ m \frac{d\mathbf{u}}{dt} = \mathbf{F} - \int_{\partial\Omega} \lambda(\mathbf{q}) \, d\mathbf{q}, \]  

(39)

\[ I \frac{d\mathbf{\omega}}{dt} = \mathbf{\tau} - \int_{\partial\Omega} [\mathbf{q} \times \lambda(\mathbf{q})] \, d\mathbf{q}, \]  

(40)

where \( \lambda(\mathbf{q}) \) is the normal component of the stress on the outside of the surface of the body, i.e., the traction

\[ \lambda(\mathbf{q}) = \mathbf{\sigma} \cdot \mathbf{n}(\mathbf{q}). \]
Mobility Problem

From linearity, at zero Reynolds number and infinite Schmidt number the deterministic rigid-body motion is defined by a linear mapping $\mathbf{U} = \mathcal{N} \mathbf{F}$ via the **mobility problem**:

$$
\nabla \pi = \eta \nabla^2 \mathbf{v} \quad \text{and} \quad \nabla \cdot \mathbf{v} = 0 \quad + \text{BCs}
$$

$$
\mathbf{v}(\mathbf{q}) = \mathbf{u} + \mathbf{\omega} \times \mathbf{q} - \ddot{\mathbf{u}}(\mathbf{q}) \quad \text{for all } \mathbf{q} \in \partial \Omega,
$$

(41)

With **force and torque balance**

$$
\int_{\partial \Omega} \lambda(\mathbf{q}) \, d\mathbf{q} = \mathbf{F} \quad \text{and} \quad \int_{\partial \Omega} [\mathbf{q} \times \lambda(\mathbf{q})] \, d\mathbf{q} = \mathbf{\tau},
$$

(42)

where $\lambda(\mathbf{q}) = \sigma \cdot \mathbf{n}(\mathbf{q})$ with

$$
\sigma = -\pi \mathbf{I} + \eta \left( \nabla \mathbf{v} + \nabla^T \mathbf{v} \right).
$$

(43)
Consider a suspension of \( N_b \) rigid bodies with configuration \( Q = \{q, \theta\} \) consisting of positions and orientations (described using quaternions) immersed in a Stokes fluid.

By eliminating (not done carefully mathematically!) the fluid from the equations in the overdamped limit (infinite Schmidt number) we get the equations of Brownian Dynamics

\[
\frac{dQ(t)}{dt} = U = \mathbf{N} F + (2k_B T \mathbf{N})^{\frac{1}{2}} \mathbf{W}(t) + (k_B T) \partial Q \cdot \mathbf{N},
\]

where \( \mathbf{N}(Q) \) is the body mobility matrix, with “square root” given by fluctuation-dissipation balance

\[
\mathbf{N}^{\frac{1}{2}} \left( \mathbf{N}^{\frac{1}{2}} \right)^T = \mathbf{N}.
\]

\( U = \{u, \omega\} \) collects the linear and angular velocities

\( F(Q) = \{f, \tau\} \) collects the applied forces and torques.
First Kind Boundary Integral Formulation

- Let us first ignore the Brownian motion and compute $\mathbf{F}$. 
- We can write down an equivalent **first-kind boundary integral equation** for the surface traction $\lambda (\mathbf{q} \in \partial \Omega)$,

$$
\mathbf{v} (\mathbf{q}) = \mathbf{u} + \omega \times \mathbf{q} = \int_{\partial \Omega} \mathcal{G} (\mathbf{q}, \mathbf{q}') \lambda (\mathbf{q}') \, d\mathbf{q}' \quad \text{for all } \mathbf{q} \in \partial \Omega, \quad (44)
$$

along with the force and torque balance condition (39).

- Assume that the surface of the body is discretized in some manner and the **single-layer operator** is computed using some quadrature,

$$
\int_{\partial \Omega} \mathcal{G} (\mathbf{q}, \mathbf{q}') \lambda (\mathbf{q}') \, d\mathbf{q}' \equiv \mathbf{M} \lambda \rightarrow \mathbf{M} \lambda,
$$

where $\mathbf{M}$ is an SPD operator given by a kernel that decays like $r^{-1}$, discretized as an SPD mobility matrix $\mathbf{M}$. 

In matrix/operator notation the **mobility problem** is a **saddle-point** linear system for the tractions $\lambda$ and rigid-body motion $U$,

$$
\begin{bmatrix}
\mathcal{M} & -\mathcal{K} \\
-\mathcal{K}^T & 0
\end{bmatrix}
\begin{bmatrix}
\lambda \\
U
\end{bmatrix}
=
\begin{bmatrix}
0 \\
-F
\end{bmatrix},
$$

(45)

where $\mathcal{K}$ is a simple geometric matrix.

Solve formally using Schur complements to get

$$
U = \mathcal{N} F = (\mathcal{K}^T \mathcal{M}^{-1} \mathcal{K})^{-1} F.
$$

How do we generate a Gaussian random vector with covariance $\mathcal{N}$?
Brownian motion

- FHD can help us generate a random “slip” velocity $\mathbf{u}$ with covariance given by the single-layer operator, $\langle \mathbf{u}\mathbf{u}^T \rangle \sim \mathbf{M}$ [5].
- This is because solving the steady Stokes equation with a stochastic stress tensor gives a velocity field whose covariance is the Green’s function $\mathbf{G}$.
- **Key idea:** Solve the mobility problem with random slip $\mathbf{u}$,

$$
\begin{bmatrix}
\mathbf{M} & -\mathbf{K} \\
-\mathbf{K}^T & 0
\end{bmatrix}
\begin{bmatrix}
\lambda \\
\mathbf{U}
\end{bmatrix}
= -
\begin{bmatrix}
\mathbf{u} = (2k_B T)^{1/2} \mathbf{M}^{1/2} \mathbf{W} \\
\mathbf{F}
\end{bmatrix},
$$

(46)

$$
\mathbf{U} = \mathbf{N}\mathbf{F} + (2k_B T)^{1/2} \mathbf{N}\mathbf{K}^T \mathbf{M}^{-1} \mathbf{M}^{1/2} \mathbf{W} = \mathbf{N}\mathbf{F} + (2k_B T)^{1/2} \mathbf{N}^{1/2} \mathbf{W},
$$

which defines a $\mathbf{N}^{1/2}$ with the correct covariance:

$$
\mathbf{N}^{1/2} \left( \mathbf{N}^{1/2} \right)^\dagger = \mathbf{N}\mathbf{K}^T \mathbf{M}^{-1} \mathbf{M}^{1/2} \left( \mathbf{M}^{1/2} \right)^\dagger \mathbf{M}^{-1} \mathbf{K}\mathbf{N}
= \mathbf{N} \left( \mathbf{K}^T \mathbf{M}^{-1} \mathbf{K} \right) \mathbf{N} = \mathbf{N} \mathbf{N}^{-1} \mathbf{N} = \mathbf{N}.
$$

(47)
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FHD and Colloidal Suspensions

Renormalization in Electrolytes

A. Donev (CIMS)
Electrolyte solutions are important for batteries, ion-selective membranes, biology, etc.

The conductivity of a dilute electrolyte depends strongly on the salt concentration $c$ (ionic strength) with a reduction $\sim \sqrt{c}$ (non-analytic!).

We have demonstrated that (one-loop) renormalization of the fluctuating Poisson-Nernst-Planck (PNP) equations reproduces all of the classical predictions of Debye-Hückel-Onsager theory with minimal effort [6].

We have also used numerical FHD to study the reaction+diffusion+gravity instability when (0.4mol/L) NaOH is placed on top of (1mol/L) of HCl in a Hele-Shaw cell ($L_x = L_y = 1.6$ cm, $L_z = 0.05$ cm).
Momentum fluctuations trigger the instability (GIF).
FHD for Electrolytes: Momentum

- Momentum equation in the Boussinesq (constant density) isothermal approximation for constant dielectric constant $\epsilon$:

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \pi = -\nabla \cdot (\rho \mathbf{v}\mathbf{v}^T) + \nabla \cdot (\eta \ddot{\mathbf{v}} + \Sigma) + \nabla \cdot (\epsilon \nabla \Phi) \nabla \Phi,$$

$$\nabla \cdot \mathbf{v} = 0,$$

where $\Phi (\mathbf{r}, t)$ is the electrostatic potential and $\nabla \cdot (\epsilon \nabla \Phi) \nabla \Phi$ is the Lorentz force.

- **Stochastic momentum flux** from FHD:

$$\Sigma = \sqrt{\eta k_B T} \left[ \mathbb{Z}^{\text{mom}} + (\mathbb{Z}^{\text{mom}})^T \right].$$

- The **electrophoretic** correction to conductivity $\sim \sqrt{c}$ is due to a coupling of charge and momentum fluctuations.
The mass density $\rho_s = w_s \rho$ of species $s$ for a mixture of $N_S$ species satisfies

$$\frac{\partial (\rho w_s)}{\partial t} = -\nabla \cdot (\rho w_s \mathbf{v}) - \nabla \cdot \mathbf{F}_s + m_s \Omega_s,$$

The dissipative and stochastic diffusive mass fluxes for a dilute species are as in Dean’s equation,

$$\mathbf{F}_s \approx -\rho D^0_s \left( \nabla w_s + \frac{m_s w_s z_s}{k_B T} \nabla \Phi \right) + \sqrt{2 \rho m_s w_s D^0_s} \mathbf{Z}^\text{mass}_s,$$

where $m_s$ is the molecular mass and the charge per unit mass is $z_s$, and $D^0_s$ is the bare self-diffusion coefficient.

For chemical reaction rates $\Omega_s$ we use the law of mass action; fluctuations can either be added using the chemical Langevin equation (CLE) or a master equation description (better).
The electric potential $\Phi(\mathbf{r}, t)$ satisfies the Poisson equation

$$- \nabla \cdot (\epsilon \nabla \Phi) = \sum_{s=1}^{N_s} \rho_s z_s. \quad (48)$$

A key mesoscopic length is the **Debye length**

$$\lambda_D \approx \left( \frac{\epsilon k_B T}{\sqrt{\sum_{s=1}^{N_s} \rho w_s m_s z_s^2}} \right)^{1/2}. \quad (49)$$

From now on we consider a **non-equilibrium steady state** under the action of an applied concentration gradient or electric field.

The fluctuations of the mass fractions $\delta w_i = w_i - \bar{w}_i$ from their average are $\bar{w}_i = \langle w_i \rangle$, and the fluctuations of the fluid velocity are $\delta \mathbf{v}$. 
The static structure factor matrix is

\[ S = \begin{pmatrix} S_{ww} & S_{wv} \\ S_{wv}^* & S_{vv} \end{pmatrix}, \]  

where each element is a cross correlation in Fourier space,

\[ S_{fg}(k) = \langle \delta \hat{f}(k) \delta \hat{g}(k)^* \rangle \]  

where \( \hat{f}(k) \) is the Fourier transform of \( f(r) \) and star denotes conjugate transpose.

By Plancherel's theorem,

\[ \langle (\delta f)(\delta g)^* \rangle = \frac{1}{(2\pi)^3} \int d\mathbf{k} \ S_{fg}(\mathbf{k}). \]  

Macroscopic gradient applied in the \( x \)-direction so only \( v_x \) is retained in the structure factors.
The FHD equations can be linearized around the macroscopic steady state and Fourier transformed to obtain for each wavenumber a linear SDE:

$$\partial_t \hat{U} = \mathcal{M}\hat{U} + \mathcal{N}\hat{Z},$$

(53)

where $\hat{U} = (\delta \hat{w}_1, \ldots, \delta \hat{w}_{N_{sp}}, \delta \hat{v}_x)^T$ and

$$[\mathcal{N}\mathcal{N}^*]_{ii} = \frac{2}{\rho} \left\{ \begin{array}{ll}
    k_i^2 D_0^0 m_i \bar{w}_i & i \leq N_{sp} \\
    k_{\perp i}^2 \nu k_B T & i = N_{sp} + 1
\end{array} \right.,$$

(54)

with $k_{\perp}^2 = k^2 - k_x^2 = k^2 \sin^2 \theta$, and $\theta$ is the angle between $\mathbf{k}$ and the $x$ axis.

Structure factor is the solution of the continuous Lyapunov equation and easy to obtain using computer algebra,

$$\mathcal{M}\mathcal{S} + \mathcal{S}\mathcal{M}^* = -\mathcal{N}\mathcal{N}^*. $$

(55)
The fluctuations in the electric field can be expressed in terms of species fluctuations ($\nu = \sqrt{-1}$),

$$\delta \hat{E} = -\nu \mathbf{k} \delta \phi = -\frac{\nu \mathbf{k}}{\epsilon k^2} \delta \hat{q} = -\rho \frac{\nu \mathbf{k}}{\epsilon k^2} \sum_i z_i \delta \hat{w}_i. \quad (56)$$

At thermodynamic equilibrium $S_{wv}^{\text{eq}} = 0$ and $S_{wv}^{\text{eq}} = \sin^2(\theta) k_B T / \rho$ and

$$S_{w_i,w_i}^{\text{eq}} = \frac{1}{\rho} m_i \bar{w}_i - \left( \frac{1}{\epsilon k_B T} \right) \frac{\lambda^2}{1 + k^2 \lambda^2} (m_i z_i \bar{w}_i) (m_j z_j \bar{w}_j). \quad (57)$$
It is well-known that the colligative properties (e.g., vapor pressure, freezing point) of electrolyte solutions depend on their ionic strength.

Ionic interactions renormalize the Gibbs free energy by

\[
\Delta G = \frac{1}{2} \langle \delta q \delta \phi \rangle = \frac{\rho^2}{2\epsilon (2\pi)^3} \int \frac{z^T (S^{eq}_{ww} - \text{Diag} \{ m_i \bar{w}_i / \rho \}) z}{k^2} \, dk
\]

\[
= - \frac{k_B T}{8\pi \lambda^3}.
\]

This result leads directly to the limiting law of Debye and Hückel for point ions and shows an experimentally measurable effect of mesoscopic thermal charge fluctuations.

It is important to note that a broad range of wavenumbers contributes to the integral over \( k \), not just microscopic scales!
In perturbative (one-loop) renormalization theory we expand to quadratic order in fluctuations and then use the solution of the linearized FHD equations to obtain the quadratic terms.

This has been applied to many situations and is not rigorous but is simple to execute and leads to computable predictions of nonlinear (quadratic) FHD.

Here we expand the fluxes of the ions (giving the electric current) to quadratic order in the fluctuations:

\[
\bar{F}_i = \langle F_i(w, v) \rangle = F_i(\langle w \rangle, \langle v \rangle) + D^0_i \frac{eV_i}{k_B T} \langle \delta w_i \delta E \rangle + \langle \delta v \delta w_i \rangle \\
\equiv \bar{F}_i^0 + \bar{F}_i^{relx} + \bar{F}_i^{adv}
\] (58)

The term \( \bar{F}_i^{relx} \) is the relaxation correction and \( \bar{F}_i^{adv} \) the advection correction.
We can also **expand the linearized FHD equations** in powers of the applied field,

\[ \mathcal{M} = \mathcal{M}^{\text{eq}} + \mathcal{M}' + O(\mathcal{X}^2), \tag{59} \]

where \( \mathcal{X} \) is the applied thermodynamic force; \( \mathcal{M}^{\text{eq}} \) is \( O(\mathcal{X}^0) \) and \( \mathcal{M}' \) is \( O(\mathcal{X}^1) \).

Similarly, we can expand the structure factor as

\[ S = S^{\text{eq}} + S' + O(\mathcal{X}^2). \]

Nonequilibrium fluctuating hydrodynamics makes a **local equilibrium approximation**, which means that the noise covariance matrix \( \mathcal{N}\mathcal{N}^* \) is unchanged, giving the linear system

\[ \mathcal{M}^{\text{eq}}S' + S'(\mathcal{M}^{\text{eq}})^* = -\mathcal{M}'S^{\text{eq}} - S^{\text{eq}}(\mathcal{M}')^*. \tag{60} \]
Renormalization of conductivity

- Let’s consider an applied electric field $\mathbf{X} \equiv \mathbf{E}_{\text{ext}} = E_{\text{ext}} \mathbf{e}_x$.

- From the **linearized fluctuating PNP** equations in the presence of an applied field one can easily obtain

$$\mathcal{M'} = E_{\text{ext}} \left( \begin{array}{c|c} -\frac{\kappa \cos \theta}{k_B T} \text{Diag} \left( D_i^0 m_i z_i \right) & \mathbf{0} \\ \hline \sin^2(\theta) \mathbf{z}^T & 0 \end{array} \right). \quad (61)$$

- The conductivity gets renormalized by the fluctuations by two pieces: a relaxation and an advective contribution.

- The **advective flux correction** is due to the **non-equilibrium** contribution to the structure factor:

$$S'_{w_i,v} = \frac{\lambda^2 \sin^2 \theta}{1 + \lambda^2 k^2} \frac{m_i \bar{w}_i z_i}{\rho (D_i^0 + \nu)} E_{\text{ext}}. \quad (62)$$
Advective contribution

- The **advective flux correction** comes due to correlations of charge and velocity fluctuations:

\[
\bar{F}^{\text{adv}}_i = \langle \delta \mathbf{v} \delta w_i \rangle = \int_{k=0}^{\pi/a_i} dk \int_{-\pi/2}^{\pi/2} \cos(\theta) d\theta \ S'_{w_i,v}
\]

\[
\approx \left( \frac{1}{3\pi a_i} - \frac{1}{6\pi \lambda} \right) \frac{m_i \bar{w}_i z_i}{\eta} \ E_{\text{ext}}
\]

for Schmidt number \( Sc \gg 1 \) and \( \lambda \gg a \) (dilute solution).

- We have already seen the first piece \( \sim 1/a_i \) — this is the **renormalization of the diffusion coefficient** by the random advection!

- The second piece \( \sim 1/\lambda \) is called the **electrophoretic correction** and is \( \sim \sqrt{c} \); it was first obtained by Onsager and Fuoss by much more complicated means.
A similar calculation also gives the relaxation correction

\[ \bar{F}_{relx}^i = \frac{D_0^i m_i z_i}{k_B T} \langle \delta w_i \delta E \rangle = -\frac{(2 - \sqrt{2}) D_0^i m_i^2 z_i}{48\pi k_B T \rho \lambda^3} E_{ext}, \]  

which is in exact agreement with the result obtained by Onsager and Fuoss.

Fluctuating hydrodynamics is a powerful modeling tool at mesoscopic scales, as demonstrated here by the calculation of the thermodynamic and transport corrections for electrolytes.

The (fluctuating) PNP equations need to be corrected to order square root in the ionic strength, and are thus valid only for very dilute solutions.
In the analytical perturbative approach followed here, all corrections to the linearized fluctuating PNP equations appear additively, not multiplicatively as they should; to compute those we need **nonlinear computational FHD**.

The theoretical calculation here only works for rather dilute electrolytes. For realistic conditions we have $\lambda \sim a$ and we cannot really separate microscopic and electrostatic effects.

There are also too few ions per $\lambda^3$ volume, so we need to treat ions as **particles** using Brownian HydroDynamics – WIP.

The renormalization theory suggests that measuring conductivity can experimentally distinguish between bare and renormalized diffusion — awaiting results...
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