Multiscale models of diffusive mixing: from giant fluctuations to Fick's law

Aleksandar Donev

Courant Institute, *New York University*
&
Eric Vanden-Eijnden, *Courant Institute*
and others

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Diffusion in Liquids

- 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 $c(\mathbf{r}, t)$,

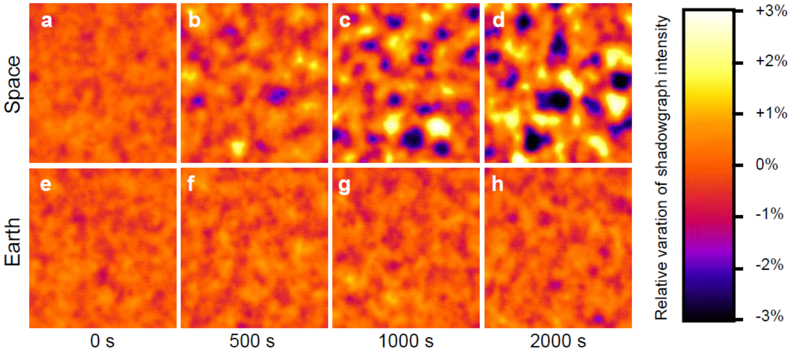
$$\partial_t c = \boldsymbol{\nabla} \cdot [\boldsymbol{\chi}(\mathbf{r}) \boldsymbol{\nabla} c],$$

  where $\boldsymbol{\chi} \succeq \mathbf{0}$ 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.
- The **Stokes-Einstein relation** connects mass diffusion to **momentum diffusion** (viscosity η),

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

  where σ is a molecular diameter.
- Macroscopic diffusive fluxes in liquids are known to be accompanied by long-ranged nonequilibrium **giant** concentration **fluctuations** [1].

Giant Nonequilibrium Fluctuations



Experimental results by A. Vailati *et al.* from a microgravity environment [1] 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.

Fluctuating Hydrodynamics

- The thermal velocity fluctuations are described by the (unsteady) **fluctuating Stokes equation**, $\boldsymbol{\nabla} \cdot \mathbf{v} = 0$,

$$\rho \partial_t \mathbf{v} + \boldsymbol{\nabla} \pi = \eta \boldsymbol{\nabla}^2 \mathbf{v} + \sqrt{2 \eta k_B T}\, \boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{W}} - \beta \rho c \, \mathbf{g}, \tag{1}$$

  where the thermal (stochastic) momentum flux is spatio-temporal **white noise**,

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

  The solution of this SPDE is a white-in-space distribution (very far from smooth!).

- Define a **smooth advection velocity** field, $\boldsymbol{\nabla} \cdot \mathbf{u} = 0$,

$$\mathbf{u}\,(\mathbf{r}, t) = \int \boldsymbol{\sigma}\,(\mathbf{r}, \mathbf{r}')\, \mathbf{v}\,(\mathbf{r}', t)\, d\mathbf{r}' \equiv \boldsymbol{\sigma} \star \mathbf{v},$$

  where the smoothing kernel $\boldsymbol{\sigma}$ filters out features at scales below a **molecular cutoff scale** σ (typical size of the tracers).

Resolved (Full) Dynamics

- **Eulerian** description of the **concentration** $c(\mathbf{r}, t)$ with an (additive noise) fluctuating advection-diffusion equation,

$$\partial_t c = -\mathbf{u} \cdot \boldsymbol{\nabla} c + \chi_0 \boldsymbol{\nabla}^2 c, \tag{2}$$

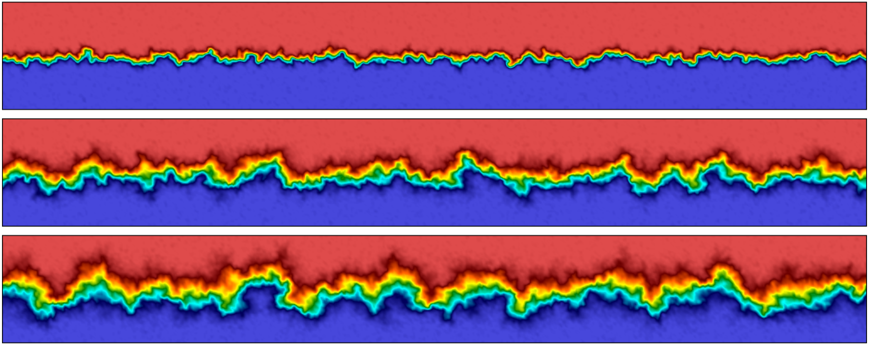
  where χ_0 is the **bare** or **molecular diffusion coefficient**.

- Here β is the solutal expansion coefficient, and $\mathbf{g}$ is the gravitational acceleration, and we have used the constant-coefficient Boussinesq approximation; one can do better using a **low Mach** approximation [2].
- In the physics literature often written imprecisely as the ill-defined but nevertheless useful

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

$$\partial_t c + \mathbf{v} \cdot \boldsymbol{\nabla} c = \chi_0 \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot \left(\sqrt{2\chi_0 c}\, \boldsymbol{\mathcal{W}}_c\right).$$

Diffusive Mixing



Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of **thermal fluctuations** [3]. These **giant fluctuations** have been studied experimentally [1] and with hard-disk molecular dynamics [2].

Separation of Time Scales

- 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.
- This means that $\chi \ll \nu$, leading to a **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 [4]

$$\chi \nu = \text{const.}$$

Eulerian Overdamped Dynamics

- Adiabatic mode elimination gives the following limiting **stochastic advection-diffusion equation** (reminiscent of the Kraichnan's model in turbulence),

$$\partial_t c = -\mathbf{w} \odot \boldsymbol{\nabla} c + \chi_0 \boldsymbol{\nabla}^2 c, \tag{3}$$

where $\odot$ denotes a Stratonovich dot product, and we ignored gravity [5, 6].

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

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

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

$$\partial_t c = -\mathbf{w} \cdot \boldsymbol{\nabla} c + \chi_0 \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot [\chi(\mathbf{r}) \boldsymbol{\nabla} c] \tag{4}$$

where $\chi(\mathbf{r})$ is an **analog of eddy diffusivity** in turbulence.

Stokes-Einstein Relation

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

$$\chi(\mathbf{r}) = \frac{k_B T}{\eta} \int \boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}') \, \mathbf{G}(\mathbf{r}', \mathbf{r}'') \, \boldsymbol{\sigma}^T(\mathbf{r}, \mathbf{r}'') \, d\mathbf{r}' d\mathbf{r}'', \qquad (5)$$

where **G** is the Green's function for steady Stokes flow.

- For an appropriate filter $\boldsymbol{\sigma}$, this gives **Stokes-Einstein formula** for the diffusion coefficient in a finite domain of length L,

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

- The limiting dynamics is a good approximation if the effective Schmidt number $S_c = \nu / \chi_{\text{eff}} = \nu / (\chi_0 + \chi) \gg 1$.
- The fact that for many liquids Stokes-Einstein holds as a good approximation implies that $\chi_0 \ll \chi$:
Diffusion in liquids is dominated by advection by thermal velocity fluctuations, and is more similar to eddy diffusion in turbulence than to standard Fickian diffusion.

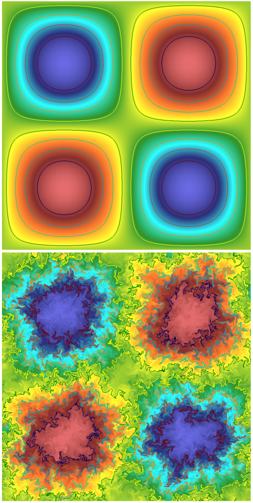
Effective Dissipation

- The **ensemble mean** of concentration follows **Fick's deterministic law**,

$$\partial_t \langle c \rangle = \boldsymbol{\nabla} \cdot (\chi_{\text{eff}} \boldsymbol{\nabla} \langle c \rangle) = \boldsymbol{\nabla} \cdot [(\chi_0 + \chi) \boldsymbol{\nabla} \langle c \rangle], \tag{6}$$

  which is well-known from stochastic homogenization theory.
- The physical behavior of diffusion by thermal velocity fluctuations is very different from classical Fickian diffusion:
  Standard diffusion (χ_0) is irreversible and dissipative, but diffusion by advection (χ) is reversible and conservative.
- Spectral power is not decaying as in simple diffusion but is transferred to smaller scales, like in the turbulent **energy cascade**.
- This transfer of power is **effectively irreversible** because power "disappears".

Spectral power cascade



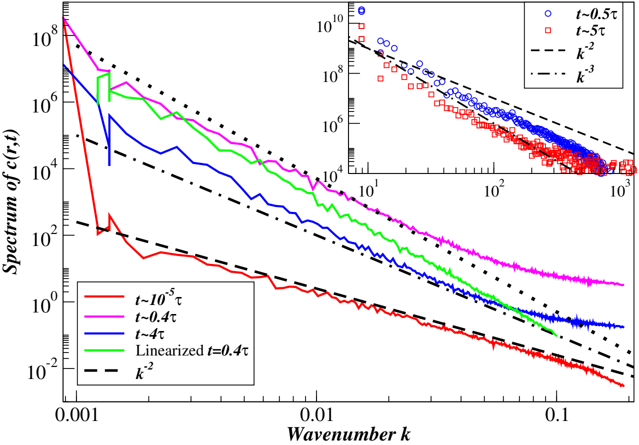


Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with 2048^2 tracers.

Linearized Fluctuating Hydrodynamics

- In experiments we observe the **coarse-grained concentration** $c_\delta = \boldsymbol{\delta} \star c$, where $\boldsymbol{\delta}$ is a filter of **mesoscopic** width $\delta \gg \sigma$.
- In **three dimensions**, we expect that the fluctuations in $c_\delta = \bar{c} + \delta c$, where $\bar{c} = \langle c \rangle$ is the solution of the *deterministic* Fick's law (LLN), are small and approximately Gaussian (CLT).
- At scales $\delta \gg \sigma$ we can therefore use **linearized fluctuating hydrodynamics**, assuming no macroscopic convection,

$$\partial_t \bar{c} = \chi_{\text{eff}} \boldsymbol{\nabla}^2 \bar{c}$$

$$\partial_t (\delta c) = -\mathbf{v} \cdot \boldsymbol{\nabla} \bar{c} + \chi_{\text{eff}} \boldsymbol{\nabla}^2 \delta c + \boldsymbol{\nabla} \cdot \left(\sqrt{2 \chi_{\text{eff}} \bar{c}}\, \boldsymbol{\mathcal{W}}_c \right)$$

$$\rho \partial_t \mathbf{v} + \boldsymbol{\nabla} \pi = \eta \boldsymbol{\nabla}^2 \mathbf{v} - \beta \rho (\delta c)\, \mathbf{g} + \sqrt{2 \eta k_B T}\, \boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{W}}.$$

  This system of SPDEs can easily be solved numerically once we take the **overdamped limit**.
- **One** numerical scheme can simulate **both** nonlinear (weakly 1st-order), or linearized equations (weakly 2nd-order) [7].

Multiscale Numerical Algorithm

The limiting dynamics can be efficiently simulated using the following **predictor-corrector algorithm** (implemented on GPUs):

1. Generate a random advection velocity by solving **steady Stokes** with random forcing,

$$\nabla \pi^{n+\frac{1}{2}} = \nu \left(\nabla^2 \mathbf{v}^n \right) + \Delta t^{-\frac{1}{2}} \nabla \cdot \left(\sqrt{2\nu\rho^{-1}\, k_B T}\, \mathcal{W}^n \right) - \rho\beta c^n \mathbf{g}$$
$$\nabla \cdot \mathbf{v}^n = 0.$$

   using a staggered **finite-volume** fluctuating hydrodynamics solver [3], and compute $\mathbf{u}^n = \boldsymbol{\sigma} \star \mathbf{v}^n$ by filtering.

2. Do a **predictor advection-diffusion solve** for concentration,

$$\frac{\tilde{c}^{n+1} - c^n}{\Delta t} = -\mathbf{u}^n \cdot \nabla c^n + \chi_0 \nabla^2 \left(\frac{c^n + \tilde{c}^{n+1}}{2} \right).$$

contd.

1. Solve a **corrector** steady Stokes system for **velocity**,

$$\nabla \pi^{n+\frac{1}{2}} = \eta \left(\nabla^2 \mathbf{v}^{n+\frac{1}{2}} \right) + \nabla \cdot \left(\sqrt{\frac{2\eta \, k_B T}{\Delta t \Delta V}} \mathbf{W}^n \right) - \rho\beta \left(\frac{c^n + \tilde{c}^{n+1}}{2} \right) \mathbf{g}$$

$$\nabla \cdot \mathbf{v}^{n+\frac{1}{2}} = 0,$$

and compute $\mathbf{u}^{n+\frac{1}{2}} = \boldsymbol{\sigma} \star \mathbf{v}^{n+\frac{1}{2}}$.

2. Take a **corrector** step for **concentration**,

$$\frac{c^{n+1} - c^n}{\Delta t} = -\mathbf{u}^{n+\frac{1}{2}} \cdot \nabla \left(\frac{c^n + \tilde{c}^{n+1}}{2} \right) + \chi_0 \nabla^2 \left(\frac{c^n + c^{n+1}}{2} \right).$$

This overdamped integrator provides a speedup of $O(\mathrm{Sc})$ over direct integration of the original inertial equations.

Breakdown of timescale separation

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

$$\begin{aligned} v_t &= \nu v_{xx} + \alpha c + \sqrt{2\nu}\, W_x \\ c_t &= \chi c_{xx} - h v, \end{aligned}$$

  where $h = \bar{c}_x = \text{const.}$ is the imposed background concentration gradient and $\alpha > 0$.
- 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, consistent with experimental measurements of giant fluctuations.
- But the time-evolution operator $\exp(\mathbf{L}t)$, where

$$\mathbf{L} = \begin{bmatrix} -\nu k^2 & \alpha \\ -h & -\chi k^2 \end{bmatrix},$$

  shows **two decay rates** that are **not separated** at small wavenumbers k for realistic values of ν and χ even though $\nu \gg \chi$!

Where does overdamped apply?

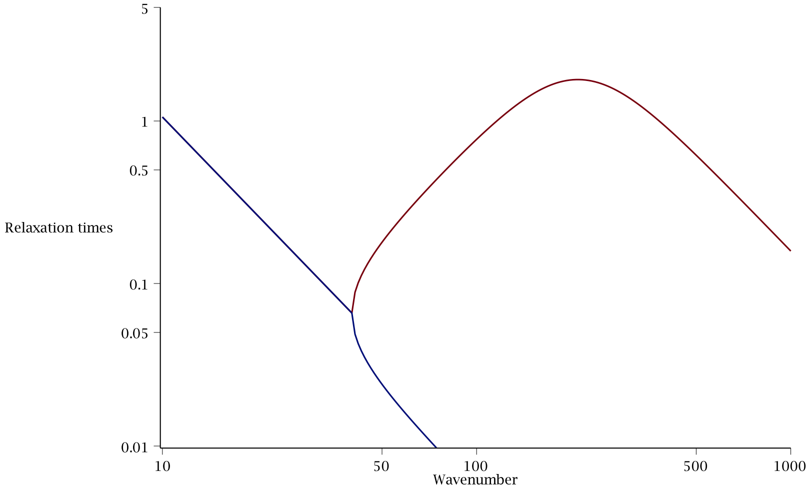


Figure: The overdamped limit is only good for wavenumbers above 50cm^{-1}. At even larger scales **fluid inertia cannot be neglected** when there is gravity

(Infinitely) Manyscale dynamics

- The deceptively simple **fluctuating hydrodynamics** equations describing diffusion in liquids proved to be a **grand challenge** in multiscale modeling: **manyscale multiphysics** dynamics.
- Firstly, there **several broad ranges of time scales** which are often **well-separated** from each other for different physical processes.
- Secondly, **different physics** arises at different length scales (and thus time scales):
  1. At microscopic scales $\sim \sigma$ **nonlinear overdamped** dynamics.
  2. At mesoscopic scales $L_g \gg \delta \gg \sigma$ **linearized overdamped** dynamics. Note this includes information from the microscopic scales (effective diffusion).
  3. At macroscopic scales $l \sim L_g$ **linearized inertial** dynamics.
  4. At human scales **nonlinear deterministic** dynamics is needed to describe various fluid instabilities (convection, turbulence). Fluctuations probably affect the dynamics near instabilities, critical points, etc.

Manyscale asymptotics

- It is interesting to note that all of these regimes are encoded in the (problematic) system of SPDEs,

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

$$\partial_t c + \mathbf{v}\cdot\boldsymbol{\nabla}c = \chi_0\boldsymbol{\nabla}^2 c + \boldsymbol{\nabla}\cdot\left(\sqrt{2\chi_0 c}\boldsymbol{\mathcal{W}}_c\right).$$

- Numerical methods of fluctuating hydrodynamics attempt to directly solve these equations but cannot accomplish this over the required range of space and time scales.
- (Stochastic) Asymptotic multiscale analysis is required to obtain effective dynamics in different regimes.
- **Can a single numerical method do everything? If not...**
- **How do we patch different regimes when there is a continuous transition between them?**

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