

The Truth about diffusion (in liquids)

Aleksandar Donev

Courant Institute, *New York University*
&
Eric Vanden-Eijnden, *Courant*
Pep Español, UNED, Madrid, Spain

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

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

where $\chi \succeq \mathbf{0}$ is a diffusion tensor.

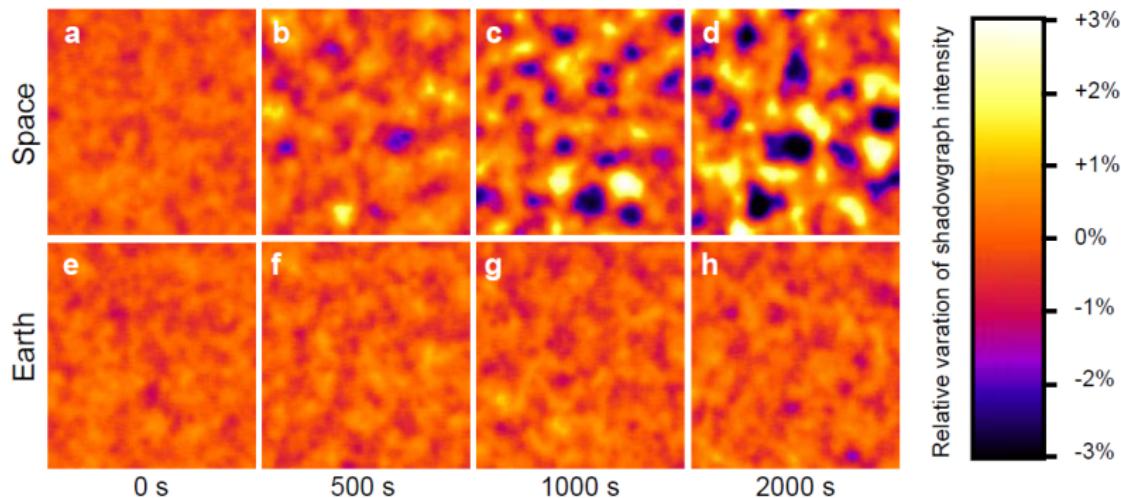
- But there is well-known hints that the **microscopic** origin of Fickian diffusion is **different in liquids** from that in gases or solids, and that **thermal velocity fluctuations** play a key role [1, 2].
- The **Stokes-Einstein relation** connects mass diffusion to **momentum diffusion** (viscosity 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** [3].

Giant Nonequilibrium Fluctuations



Experimental results by A. Vailati *et al.* from a microgravity environment [3] showing the enhancement of concentration fluctuations in space (box scale is 5mm on the side, 1mm thick).

Fluctuations become macroscopically large at macroscopic scales!

They cannot be neglected as a microscopic phenomenon.

Hydrodynamic Correlations

- The mesoscopic model we develop here 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 the **effects of caging**:
 - ① The **Schmidt number is very large** (unlike gases) and particles remain trapped in their cage while fast molecular collisions (interactions) diffuse momentum and energy.
 - ② The breaking and movement of cages requires **collective (hydrodynamic) rearrangement** and thus the assumption of independent Brownian walkers is not appropriate.

This is well-appreciated in the colloidal literature and is described as hydrodynamic “interactions” (really, **hydrodynamic correlations**), but we will see that the same applies to molecular diffusion.

Fluctuating Hydrodynamics

- The thermal velocity fluctuations are described by the (unsteady) **fluctuating Stokes equation**,

$$\rho \partial_t \mathbf{v} + \nabla \pi = \eta \nabla^2 \mathbf{v} + \sqrt{2\eta k_B T} \nabla \cdot \mathcal{W}, \quad \text{and} \quad \nabla \cdot \mathbf{v} = 0. \quad (1)$$

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

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

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

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

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

where the smoothing kernel σ filters out features at scales below a **molecular cutoff scale** σ .

Resolved (Full) Dynamics

- **Lagrangian** description of a **passive tracer** diffusing in the fluid,

$$\dot{\mathbf{q}} = \mathbf{u}(\mathbf{q}, t) + \sqrt{2\chi_0} \mathcal{W}_{\mathbf{q}}, \quad (2)$$

where $\mathcal{W}_{\mathbf{q}}(t)$ is a collection of white-noise processes (independent among tracers).

In this case σ is the typical size of the tracers.

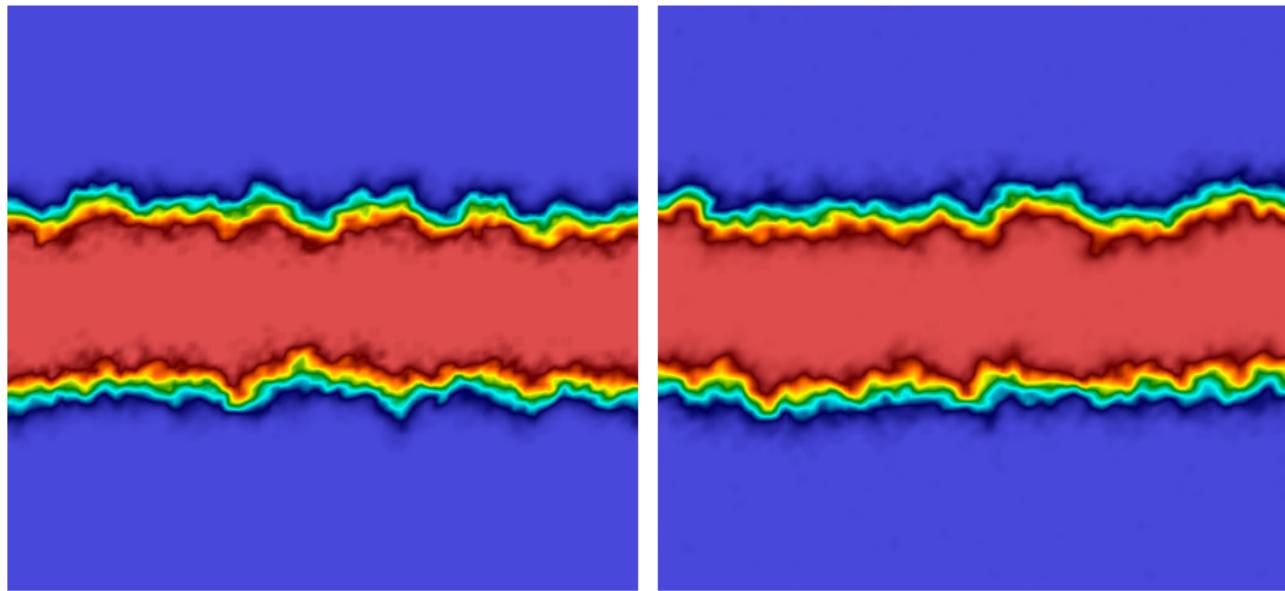
- **Eulerian** description of the **concentration** $c(\mathbf{r}, t)$ with an (additive noise) fluctuating advection-diffusion equation,

$$\partial_t c = -\mathbf{u} \cdot \nabla c + \chi_0 \nabla^2 c, \quad (3)$$

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

- The two descriptions are **equivalent**. When $\chi_0 = 0$, $c(\mathbf{q}(t), t) = c(\mathbf{q}(0), 0)$ or, due to reversibility, $c(\mathbf{q}(0), t) = c(\mathbf{q}(t), 0)$.

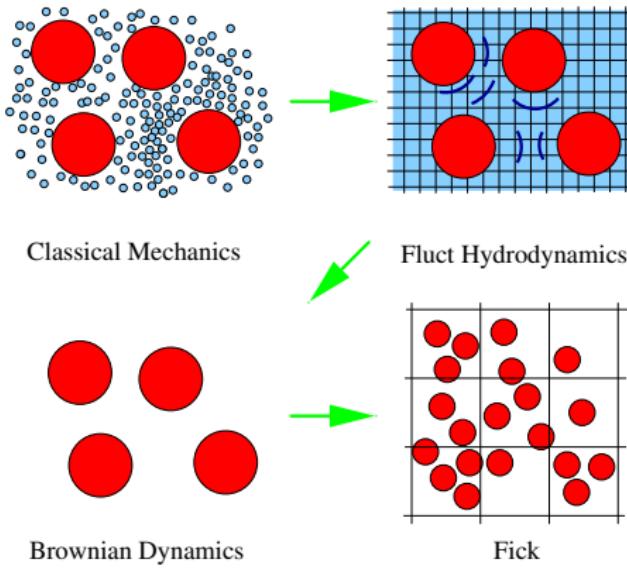
Fractal Fronts in Diffusive Mixing



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 [3] and with hard-disk molecular dynamics [4].

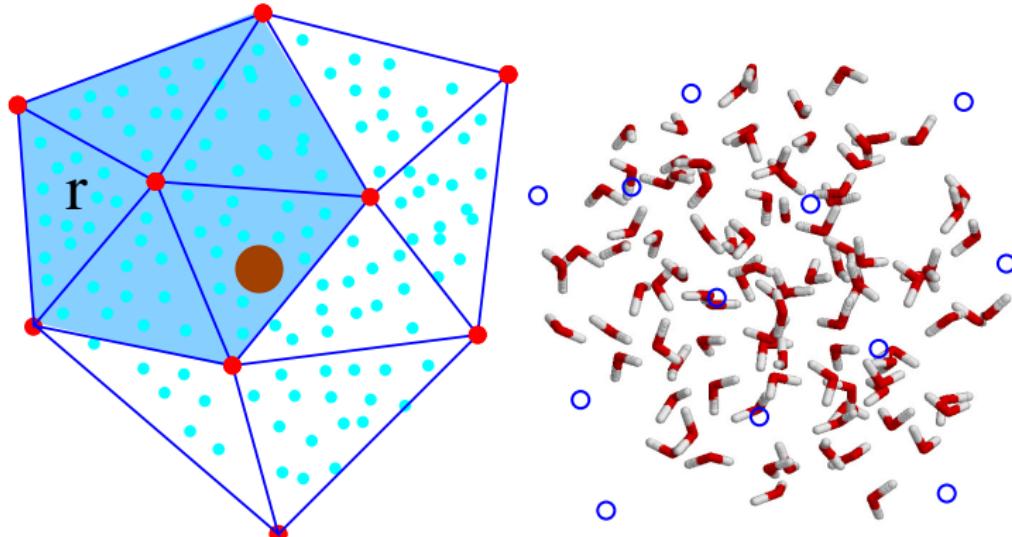
Coarse Graining Brownian Motion

- The proper way to interpret fluctuating hydrodynamics is via the **theory of coarse-graining** (here I follow Pep Espanol) [5].
- The first step is to define a discrete set of **relevant variables**, which are **mesoscopic observables** that **evolve slowly**



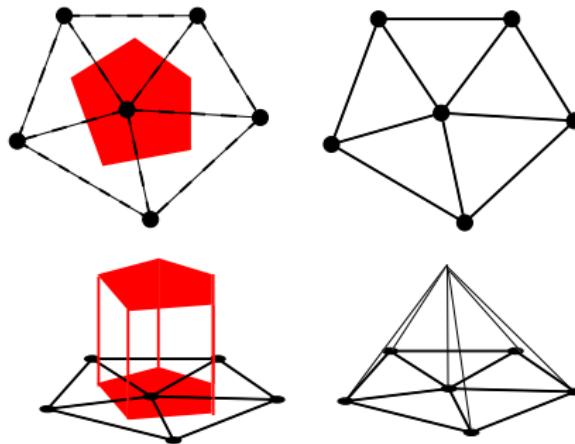
Fluctuating Hydrodynamics Level

- Relevant variables for **subgrid (nanoscopic) particles** associated to a **grid node μ** are:
 - **discrete mass $\rho_\mu(t)$ and momentum density $\mathbf{g}_\mu(t)$** (including the suspended particle!)
 - **position of the particle** (since momentum of particle is not slow!)



Relevant Variables

- How to assign the molecules to the **coarse-grained nodes**?
- If one uses a nearest-node assignment, i.e., **Voronoi cells**, one gets divergent Green-Kubo transport coefficients.
- Instead, one can use the dual **Delaunay cells** to construct coarse-grained variables.



$$\mathbf{g}_\mu = \sum_{i=0}^N m_i \mathbf{v}_0 \delta_\mu(\mathbf{q}_i) \text{ follows a } \mathbf{conservation \ law}$$

Mori-Zwanzig Formalism

- 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.
- It turns out that these equations are *exactly* the same as obtained from a Petrov-Galerkin **finite-element discretization** of the fluctuating hydrodynamic SPDEs I wrote earlier, using **the same dual set of basis functions** as used for coarse graining.
 This provides a link between **continuum->discrete** and **discrete->continuum** approaches.
- The TCG gives generalized **Green-Kubo** formulas for the diffusion coefficients.
- A key difference with the phenomenological equations is that the discrete delta function or kernel is **attached to the grid** (artificial!) **rather than to the particle cage** (physical),

$$\sigma(\mathbf{r}, \mathbf{r}') \rightarrow \Delta(\mathbf{r}, \mathbf{r}') = \delta_\mu(\mathbf{r}) \delta_\mu^{-1}(\mathbf{r}').$$

Renormalization of Diffusion

- The **bare diffusion coefficient** concerns **near-field hydrodynamics** and can be computed using MD from

$$\chi_0 = \frac{1}{d} \int_0^{TMD} dt \langle \delta \hat{\mathbf{V}} \cdot \delta \hat{\mathbf{V}} \rangle_{\text{eq}},$$

where the particle **peculiar velocity** $\delta \hat{\mathbf{V}} = \hat{\mathbf{V}} - \bar{\mathbf{v}}(\hat{\mathbf{R}})$ is the velocity relative to the locally-interpolated fluid velocity.

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

- Observe that χ_0 is different from the macroscopic or **renormalized diffusion coefficient**

$$\chi = \frac{1}{d} \int_0^{\tau \gg TMD} dt \langle \hat{\mathbf{V}} \cdot \hat{\mathbf{V}} \rangle_{\text{eq}},$$

which is **independent of the grid resolution** but is essentially impossible to compute using MD since it includes **far-field hydrodynamics**.

Fluctuating Hydrodynamics SPDEs

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

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

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

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 $S_c \rightarrow \infty$ in the scaling

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

Eulerian Overdamped Dynamics

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

$$\partial_t c = -\mathbf{w} \odot \nabla c + \chi_0 \nabla^2 c, \quad (4)$$

where \odot denotes a Stratonovich dot product.

- 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**,

$$\partial_t c = -\mathbf{w} \cdot \nabla c + \chi_0 \nabla^2 c + \nabla \cdot [\chi(\mathbf{r}) \nabla c] \quad (5)$$

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

Enhanced Diffusivity

- Let us factorize the integral of the velocity correlation function in some (infinite dimensional) set of basis functions $\phi_k(\mathbf{r})$,

$$2 \int_0^\infty \langle \mathbf{u}(\mathbf{r}, t) \otimes \mathbf{u}(\mathbf{r}', t + t') \rangle dt' = \sum_k \phi_k(\mathbf{r}) \otimes \phi_k(\mathbf{r}').$$

For periodic boundaries ϕ_k can be Fourier modes but in general they **depend on the boundary conditions** for the velocity.

- The notation $\mathbf{w} \odot \nabla c$ is a short-hand for $\sum_k (\phi_k \cdot \nabla c) \circ d\mathcal{B}_k/dt$, where $\mathcal{B}_k(t)$ are independent Brownian motions (Wiener processes).
- Similarly, $\mathbf{w} \cdot \nabla c$ is shorthand notation for $\sum_k (\phi_k \cdot \nabla c) d\mathcal{B}_k/dt$.
- The enhanced or **fluctuation-induced diffusion** is

$$\chi(\mathbf{r}) = \int_0^\infty \langle \mathbf{u}(\mathbf{r}, t) \otimes \mathbf{u}(\mathbf{r}, t + t') \rangle dt' = \frac{1}{2} \sum_{k,k'} \phi_k(\mathbf{r}) \phi_{k'}(\mathbf{r}).$$

Stokes-Einstein Relation

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

$$\chi(\mathbf{r}) = \frac{k_B T}{\eta} \int \sigma(\mathbf{r}, \mathbf{r}') \mathbf{G}(\mathbf{r}', \mathbf{r}'') \sigma^T(\mathbf{r}, \mathbf{r}'') d\mathbf{r}' d\mathbf{r}'', \quad (6)$$

where \mathbf{G} is the Green's function for steady Stokes flow.

- For an appropriate filter σ , this gives **Stokes-Einstein formula** for the diffusion coefficient in a finite domain of length L ,

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

- 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.

Relation to Brownian Dynamics

- If we take an **overdamped** limit of the **Lagrangian equation** we get the previous equation plus bare diffusion,

$$d\mathbf{q} = \sum_k \phi_k(\mathbf{q}) \circ d\mathcal{B}_k + \sqrt{2\chi_0} d\mathcal{B}_{\mathbf{q}}, \quad (7)$$

where $\mathcal{B}_{\mathbf{q}}(t)$ are **independent** Brownian motions (one per tracer).

- This is **equivalent** to the well-known **Brownian dynamics** where the mobility matrix has the form

$$\mathbf{M}_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \eta^{-1} \int \boldsymbol{\sigma}(\mathbf{q}_i, \mathbf{r}') \mathbf{G}(\mathbf{r}', \mathbf{r}'') \boldsymbol{\sigma}^T(\mathbf{q}_j, \mathbf{r}'') d\mathbf{r}' d\mathbf{r}''.$$

- Note that for $r \gg \sigma$ an isotropic+translational-invariant $\mathbf{M}_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \mathbf{M}_{ij}(\mathbf{q}_i - \mathbf{q}_j \equiv \mathbf{r})$ reverts to the **Oseen tensor**.
- The next-order corrections look *exactly* like the **RPY tensor**, but the behavior at short distances depends on the choice of the kernel $\boldsymbol{\sigma}$.

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,

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

$$\nabla \cdot \mathbf{v}^n = 0.$$

using a staggered **finite-volume** fluctuating hydrodynamics solver [6], and compute $\mathbf{u}^n = \sigma \star \mathbf{v}^n$ by filtering.

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

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

- ③ Take a **corrector step** for concentration,

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

Lagrangian Algorithm

The tracer Lagrangian dynamics can be efficiently simulated **without artificial dissipation** (implemented on GPUs):

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

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

$$\nabla \cdot \mathbf{v}^n = 0.$$

using a **spectral** (FFT-based) algorithm.

- ② **Filter** the velocity with a Gaussian filter (in Fourier space),

$$\mathbf{w}^n = \sigma \star \mathbf{v}^n.$$

- ③ Use a **non-uniform FFT** to evaluate $\mathbf{u}^n = \mathbf{w}^n(\mathbf{q}^n)$, and **move the tracers**,

$$\mathbf{q}^{n+1} = \mathbf{q} + \mathbf{u}^n \Delta t.$$

In non-periodic domains one would need to do a corrector step for tracers (Euler-Heun method for the Stratonovich SDE).

Numerical Issues

- ① All algorithms implemented on **GPUs** for periodic boundaries using **FFTs**. We do large simulations in **2D** here to study physics, **3D** is implemented but largest grid is $O(512^3)$.
- ② Eulerian algorithm also implemented in IBAMR library by Boyce Griffith, to be used for studying the effect of **boundary conditions** in experiments on giant fluctuations.
- ③ For Eulerian algorithm the difficulty is in the advection: we need essentially **non-dissipative advection** that is also **good with monotonicity preserving**.
- ④ Right now we use a strictly non-dissipative **centered advection**, for which we can calculate discrete diffusion enhancement operator exactly.
- ⑤ Also trying more sophisticated minimally-dissipative **semi-Lagrangian advection schemes** of John Bell implemented by Sandra May (unfinished).

Is Diffusion Dissipative?

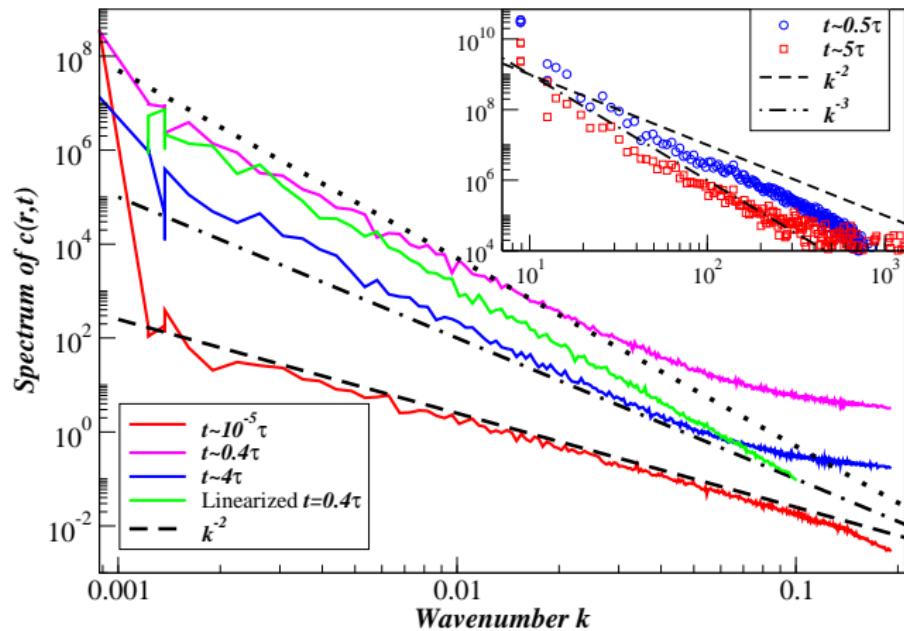
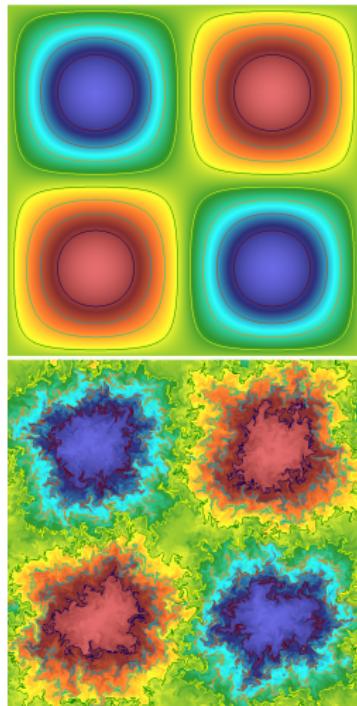


Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with 2048^2 tracers.

Effective Dissipation

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

$$\partial_t \langle c \rangle = \nabla \cdot (\chi_{\text{eff}} \nabla \langle c \rangle) = \nabla \cdot [(\chi_0 + \chi) \nabla \langle c \rangle], \quad (8)$$

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 dissipative, but diffusion by advection (χ) is 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”. *Can we make this more precise?*

Dissipation as Loss of Information

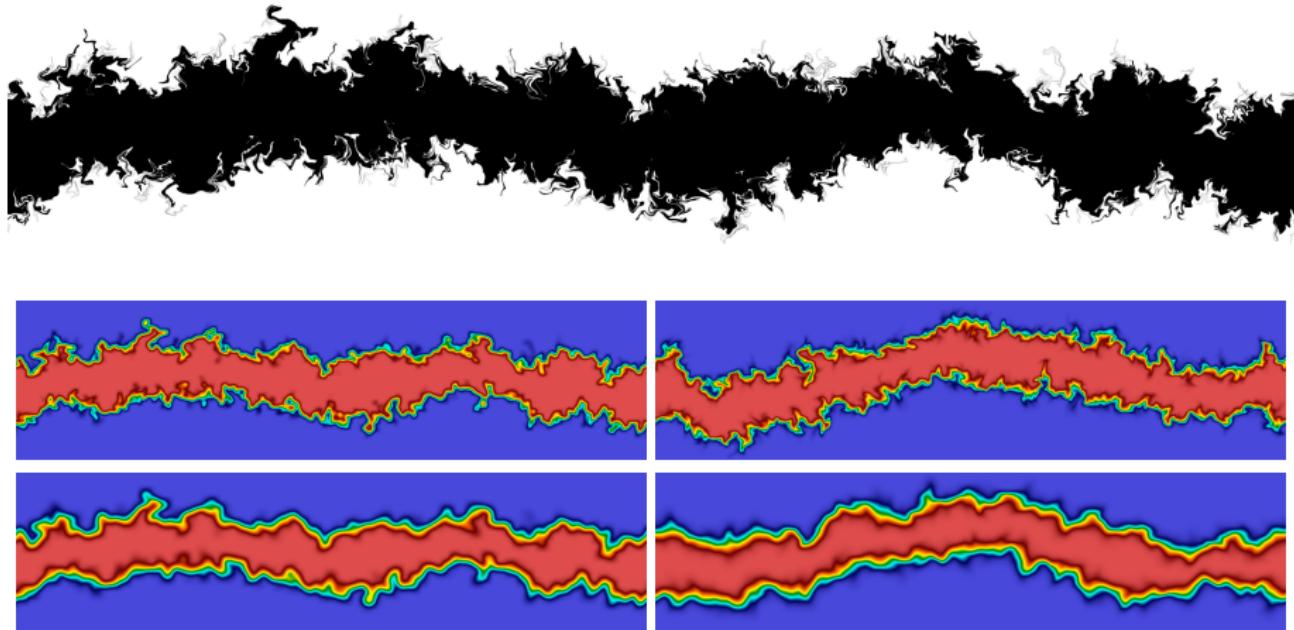


Figure: (Top panel) Diffusive mixing studied using the Lagrangian tracer algorithm. (Bottom) The spatially-coarse grained concentration c_δ obtained by blurring with a Gaussian filter of two different widths.

Spatial Coarse-Graining

- Split the velocity \mathbf{w} into a large-scale component \mathbf{w}_δ and a small-scale component $\tilde{\mathbf{w}}$,

$$\mathbf{w} = \delta \star \mathbf{w} + \tilde{\mathbf{w}} = \mathbf{w}_\delta + \tilde{\mathbf{w}} \text{ in law,}$$

where δ is a filter of **mesoscopic** width $\delta > \sigma$.

- Define $\bar{c}_\delta = \langle c \rangle_{\tilde{\mathbf{w}}}$ as the **conditional ensemble average** over the unresolved $\tilde{\mathbf{w}}$ keeping the resolved \mathbf{w}_δ fixed.
- For the Ito equation (5), **without any approximations**, we obtain,

$$\partial_t \bar{c}_\delta = -\mathbf{w}_\delta \cdot \nabla \bar{c}_\delta + \chi_0 \nabla^2 \bar{c}_\delta + \nabla \cdot [\chi(\mathbf{r}) \nabla \bar{c}_\delta], \quad (9)$$

with an identical effective diffusion coefficient $\chi_{\text{eff}} = \chi_0 + \chi$.

- We **postulate** that this gives a physically reasonable **coarse-grained model** for $c_\delta = \delta \star c$.

Coarse-Grained Equations

- In the Stratonovich interpretation the **coarse-grained equation** is

$$\partial_t c_\delta \approx -\mathbf{w}_\delta \odot \nabla c_\delta + \nabla \cdot [(\chi_0 + \Delta\chi_\delta) \nabla c_\delta], \quad (10)$$

where the **diffusion renormalization** $\Delta\chi_\delta(\mathbf{r})$ is

$$\Delta\chi_\delta = \chi - \delta * \chi * \delta^T. \quad (11)$$

- The coarse-grained equation has **true dissipation** (irreversibility) since $\Delta\chi_\delta > 0$.
- For $\delta \gg \sigma$ in three dimensions we get $\Delta\chi_\delta \approx \chi$ and so the coarse-grained equation becomes Fick's law with Stokes-Einstein's form for the diffusion coefficient. This hints that
In three dimensions (but not in two dimensions!) at macroscopic scales Fick's law applies. At mesoscopic scales fluctuating hydrodynamics with renormalized transport coefficients is a good model.

Conclusions

- Fluctuations are **not just a microscopic phenomenon**: giant fluctuations can reach macroscopic dimensions or certainly dimensions much larger than molecular.
- **Fluctuating hydrodynamics** describes these effects and can be **justified microscopically**.
- Due to **large separation of time scales** between mass and momentum diffusion in liquids we get an **overdamped** stochastic advection-diffusion equation.
- Diffusion in liquids is strongly affected and in fact dominated by **advection by velocity fluctuations**.
- This kind of “eddy” diffusion is very different from Fickian diffusion: it is **conservative rather than dissipative!**
- At **macroscopic scales**, however, one expects to recover **Fick's deterministic law**, in three, but not in two dimensions.
How to prove this? (law of large numbers, central limit theorem, large deviation theory)

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