The Truth about diffusion (in liquids)

Aleksandar Donev

Courant Institute, *New York University*
&
Eric Vanden-Eijnden, *Courant*
Thomas G. Fai, *Courant*

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

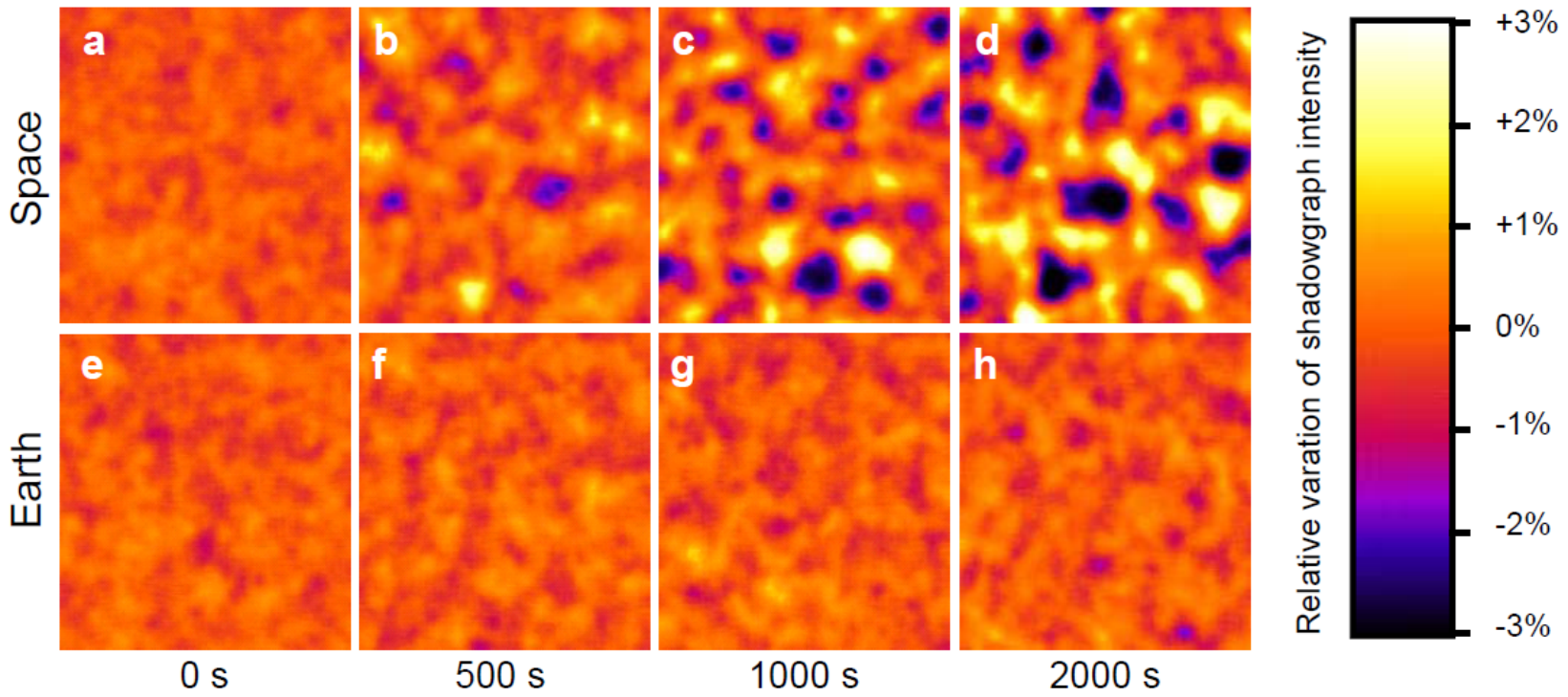
$$\partial_t c = \boldsymbol{\nabla} \cdot [\boldsymbol{\chi}(\mathbf{r}) \boldsymbol{\nabla} c],$$

  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.

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**,

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

  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.

Resolved (Full) Dynamics

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

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

  where $\boldsymbol{\mathcal{W}}_{\mathbf{q}}(t)$ is a collection of white-noise processes (independent among tracers).
  In this case σ is the typical size of the tracers.

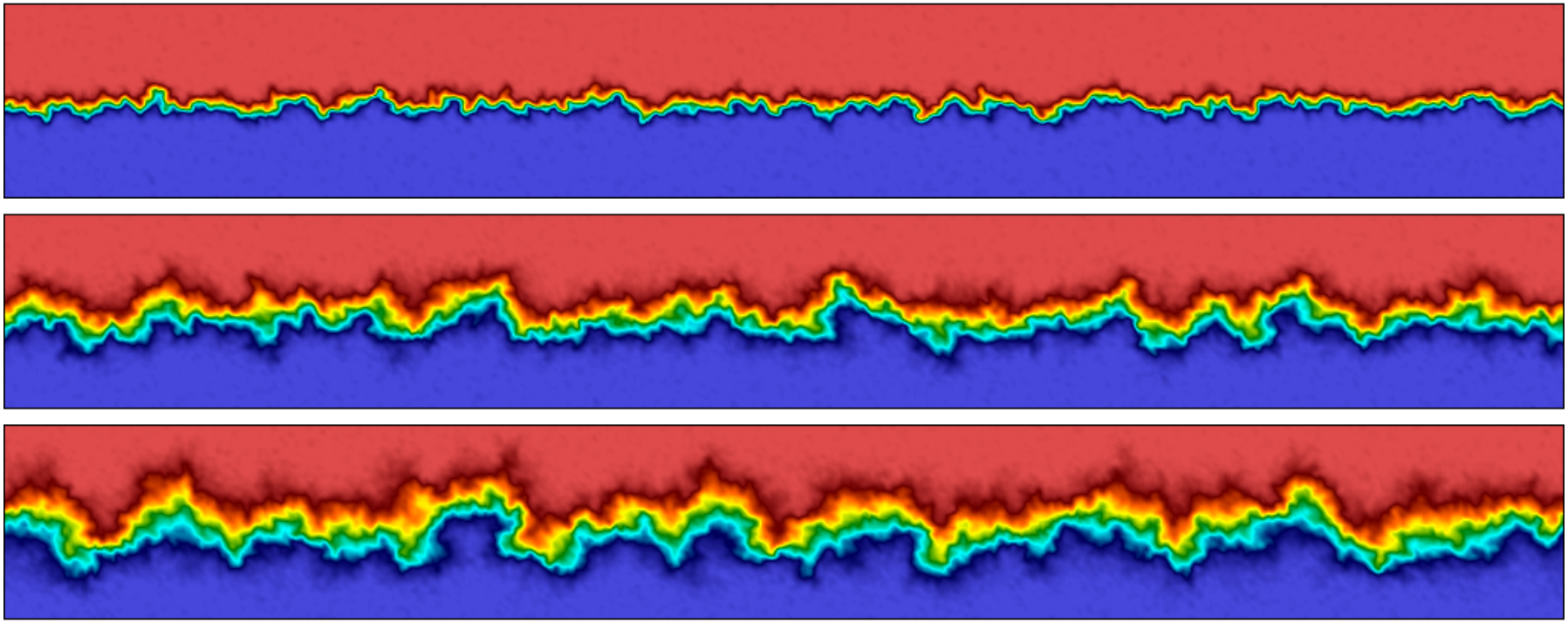
- **Eulerian** description of the **concentration** $c(\mathbf{r}, t)$ with an (additive noise) fluctuating advection-diffusion equation,

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

  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** [2]. These **giant fluctuations** have been studied experimentally [1] and with hard-disk molecular dynamics [3].

Our Goal: **Computational modeling of diffusive mixing in liquids in the presence of thermal fluctuations**.

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),

$$\partial_t c = -\mathbf{w} \odot \boldsymbol{\nabla} c + \chi_0 \boldsymbol{\nabla}^2 c, \tag{4}$$

  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**,

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

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

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

Stokes-Einstein Relation

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

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

  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.

Lagrangian Overdamped Dynamics

- In the Lagrangian description, the overdamped limit in the Stratonovich interpretation is

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

  where $\boldsymbol{\mathcal{B}}_{\mathbf{q}}(t)$ are **independent** Brownian motions (one per tracer).
- The *single* realization of the random field $\sum_k \phi_k \circ d\mathcal{B}_k$ affects *all* of the walkers and induces **correlations between the tracers**.
- In the Ito interpretation the Lagrangian description reverts to the well-known **Brownian dynamics** for the positions of the N tracers (Brownian walkers) $\mathbf{Q} = \{\mathbf{q}_1, \ldots, \mathbf{q}_N\}$,

$$d\mathbf{Q} = \left(2k_B T\, \mathbf{M}(\mathbf{Q})\right)^{\frac{1}{2}} d\boldsymbol{\mathcal{B}} + \left(\partial_{\mathbf{Q}} \cdot \mathbf{M}(\mathbf{Q})\right) dt + \sqrt{2\chi_0}\, d\boldsymbol{\mathcal{B}}_{\mathbf{Q}}, \tag{8}$$

  where the **mobility matrix** has the form

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

The Truth is in the Hydrodynamic Correlations

- In fact, we could have started from the equations of Brownian dynamics with the *assumption*

$$\mathbf{M}_{ij}\left(\mathbf{q}_i, \mathbf{q}_j\right) = \frac{\mathcal{R}\left(\mathbf{q}_i, \mathbf{q}_j\right)}{2k_B T} = \frac{1}{2k_B T}\sum_k \phi_k\left(\mathbf{q}_i\right)\phi_k\left(\mathbf{q}_j\right), \qquad (9)$$

  where $\mathcal{R}\left(\mathbf{r}, \mathbf{r}'\right)$ is a **symmetric positive-definite kernel** that is divergence-free, $\boldsymbol{\nabla} \cdot \mathcal{R}\left(\mathbf{r}, \mathbf{r}'\right) = 0$.
- The **Rotne-Prager-Yamakawa tensor** widely used for dilute colloidal suspensions satisfies these properties; in the far field it is the **Oseen tensor**

$$\mathcal{R}\left(\mathbf{r}', \mathbf{r}''\right) \approx \frac{1}{8\pi r}\left(\mathbf{1} + \hat{\mathbf{r}} \otimes \hat{\mathbf{r}}\right) + O\left(\left(\frac{\sigma}{r}\right)^3\right) \text{ where } \mathbf{r} = \mathbf{r}' - \mathbf{r}''. \quad (10)$$

The Truth contd.

- From (8,9) one can derive a closed **linear equation** for the empirical concentration $c(\mathbf{r},t)=\sum_{i=1}^{N}\delta(\mathbf{q}_i(t)-\mathbf{r})$ which is *exactly* the same as the one we derived taking the overdamped limit of our Eulerian description (fluctuating hydrodynamics).
- Strangely, if one assumes **uncorrelated walkers** the equation for $c(\mathbf{r},t)$ is seemingly closed but **nonlinear**!
- In both cases (hydrodynamically correlated and uncorrelated walkers) the mean obeys Fick's law but the fluctuations are completely different.
- This shows the subtle but crucial importance of the **incompressible hydrodynamic correlations** among the trajectories of the tracers.

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 [5]** with random forcing,

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

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

   using a staggered **finite-volume** fluctuating hydrodynamics solver [2], and compute $\mathbf{u}^n = \boldsymbol{\sigma} \star \mathbf{v}^n$ by filtering.

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

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

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 [5]** with random forcing

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

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

   using a **spectral** (FFT-based) algorithm.
2. **Filter** the velocity with a Gaussian filter (in Fourier space),

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

3. Use a **non-uniform FFT** [6] to evaluate $\mathbf{u}^n = \mathbf{w}^n(\mathbf{q}^n)$, and **move the tracers**,

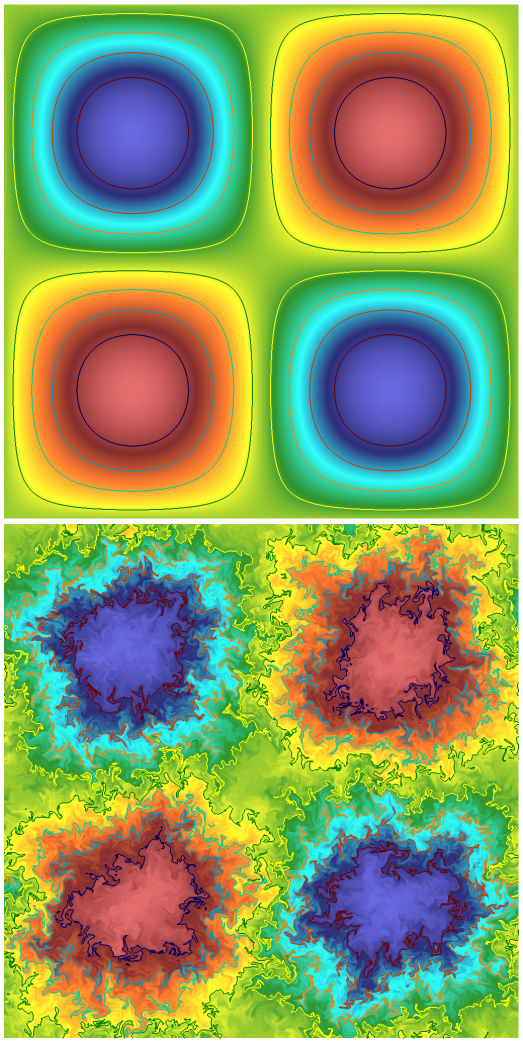
$$\mathbf{q}^{n+1} = \mathbf{q} + \mathbf{u}^n \Delta t.$$

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 Irreversible?



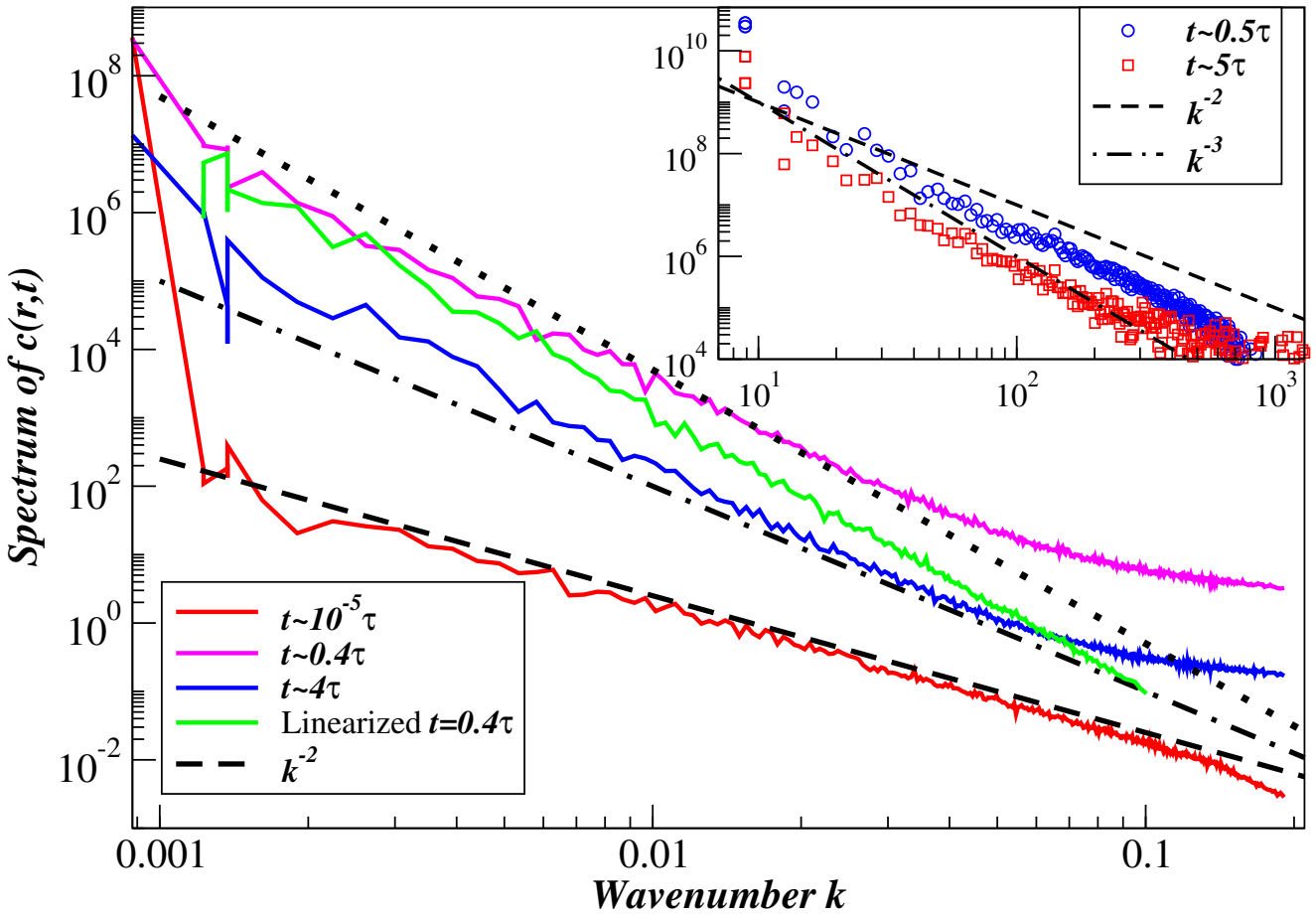


Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with 2048^2 tracers.

Effective Dissipation

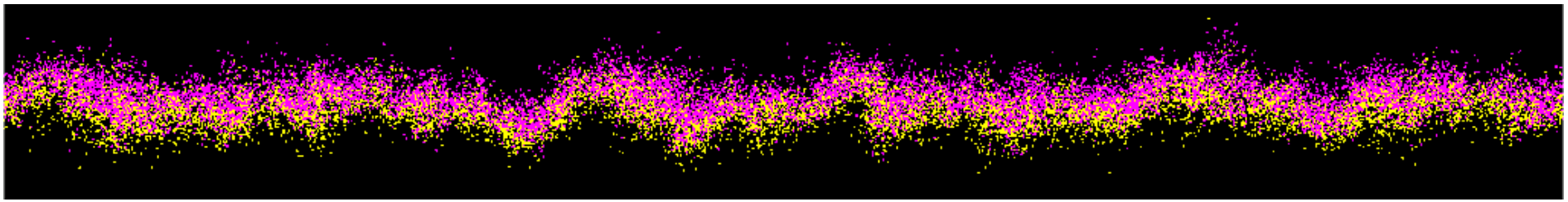
- The **ensemble mean** of concentration follows **Fick's deterministic law**,

$$\partial_t \langle c \rangle = \boldsymbol{\nabla} \cdot (\boldsymbol{\chi}_{\text{eff}} \boldsymbol{\nabla} \langle c \rangle) = \boldsymbol{\nabla} \cdot [(\chi_0 + \boldsymbol{\chi}) \boldsymbol{\nabla} \langle c \rangle] , \tag{11}$$

  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 ($\boldsymbol{\chi}$) 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". *Can we make this more precise?*

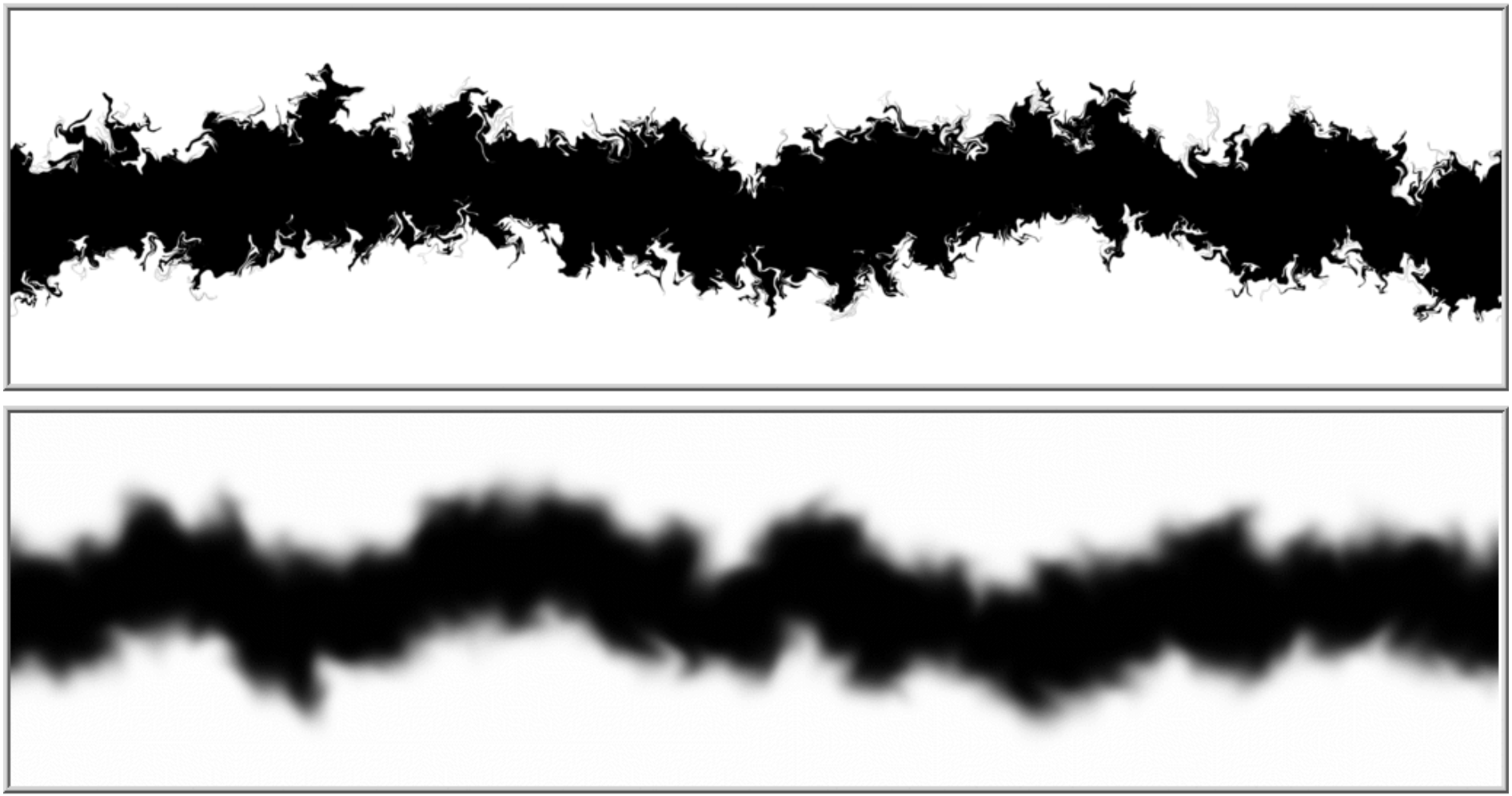
Virtual FREP Experiment ($\chi_0 = 0$)

The **contour lines** become very **rough**, and eventually fill the whole plane, unless we put some bare diffusion to smooth things out.
But this generates **sub-molecular scale** features, compare to **hard-disk molecular dynamics** (1M disks):



We should perform **spatial coarse-graining** to study $c_\delta = \boldsymbol{\delta} \star c$, where $\delta > \sigma$ is a mesoscopic **measurement (observation) scale**.

Lagrangian Tracking of Interfaces



Spatial Coarse-Graining

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

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

  where $\boldsymbol{\delta}$ 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 $\mathbf{w}_\delta$ fixed.
- For the Ito equation (5), **without any approximations**, we obtain,

$$\partial_t \bar{c}_\delta = -\mathbf{w}_\delta \cdot \boldsymbol{\nabla} \bar{c}_\delta + \chi_0 \boldsymbol{\nabla}^2 \bar{c}_\delta + \boldsymbol{\nabla} \cdot \left[\boldsymbol{\chi}(\mathbf{r}) \boldsymbol{\nabla} \bar{c}_\delta \right], \tag{12}$$

  with an identical effective diffusion coefficient $\chi_{\text{eff}} = \chi_0 + \boldsymbol{\chi}$.
- We **postulate** that this gives a physically reasonable **coarse-grained model** for $c_\delta = \boldsymbol{\delta} \star c$.

Coarse-Grained Equations

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

$$\partial_t c_\delta \approx -\mathbf{w}_\delta \odot \boldsymbol{\nabla} c_\delta + \boldsymbol{\nabla} \cdot \left[\left(\chi_0 + \Delta \boldsymbol{\chi}_\delta \right) \boldsymbol{\nabla} c_\delta \right], \tag{13}$$

  where the **diffusion renormalization** $\Delta \boldsymbol{\chi}_\delta (\mathbf{r})$ [7, 8] is

$$\Delta \boldsymbol{\chi}_\delta = \boldsymbol{\chi} - \boldsymbol{\delta} \star \boldsymbol{\chi} \star \boldsymbol{\delta}^T. \tag{14}$$

- 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.

Irreversible vs. Reversible Dynamics

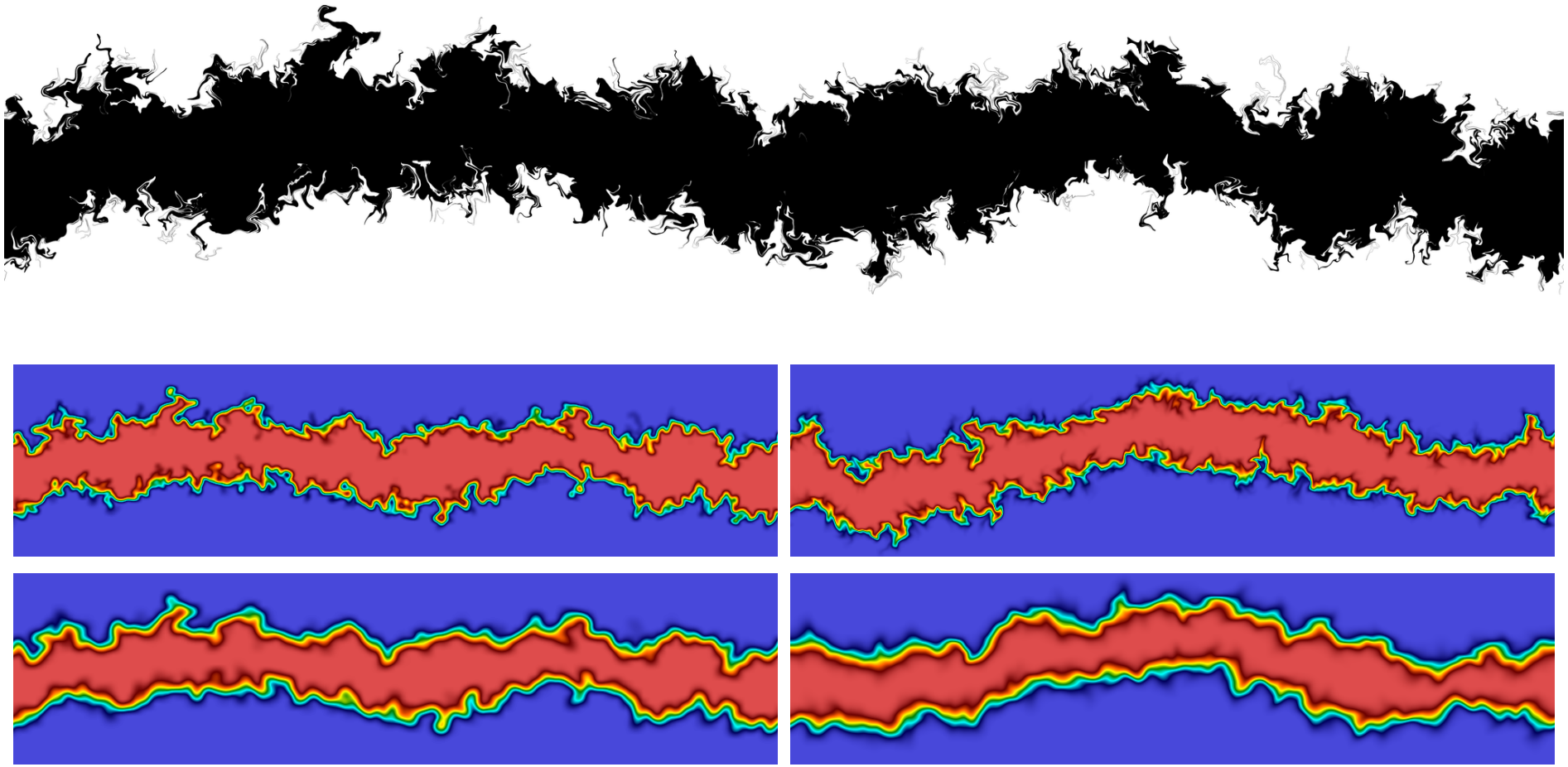


Figure: (*Top panel*) Diffusive mixing studied using the Lagrangian tracer algorithm. (*Bottom*) The spatially-coarse grained concentration c_δ obtained by blurring with a Gaussian filter of two different widths.

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.
- Due to **large separation of time scales** between mass and momentum diffusion we need to find the **limiting dynamics** to eliminate the stiffness.
- The **overdamped equation** is a stochastic advection-diffusion equation with a white-in-time velocity.
- 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 **reversible** (conservative) **rather than irreversible** (dissipative)!
- At **macroscopic scales**, however, one expects to recover **Fick's deterministic law**, in three, but not in two dimensions.

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