Computational modeling of diffusive mixing: from giant fluctuations to Fick's law

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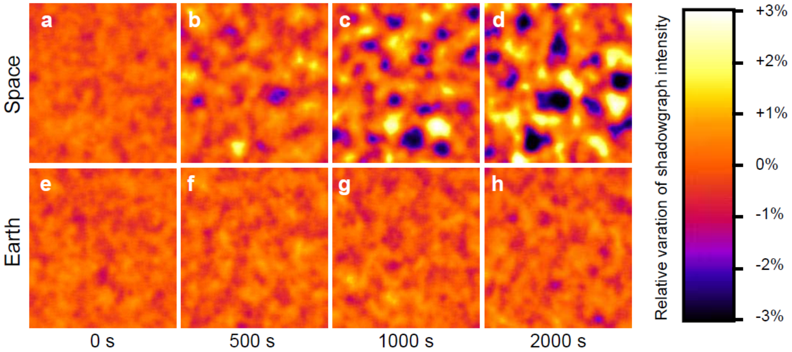
Diffusion in Liquids

- 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.

Giant Fluctuations in Simulations

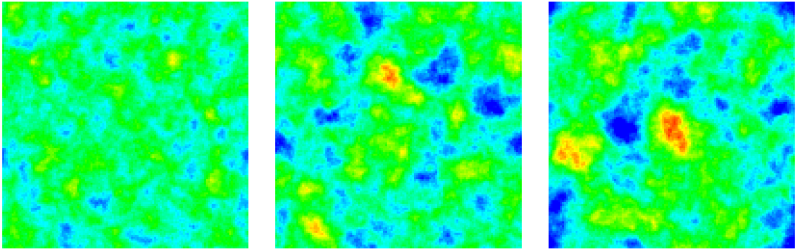


Figure: Computer simulations of microgravity experiments.

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 (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,

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

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

- **Lagrangian** description of a **passive tracer** diffusing in the fluid [2],

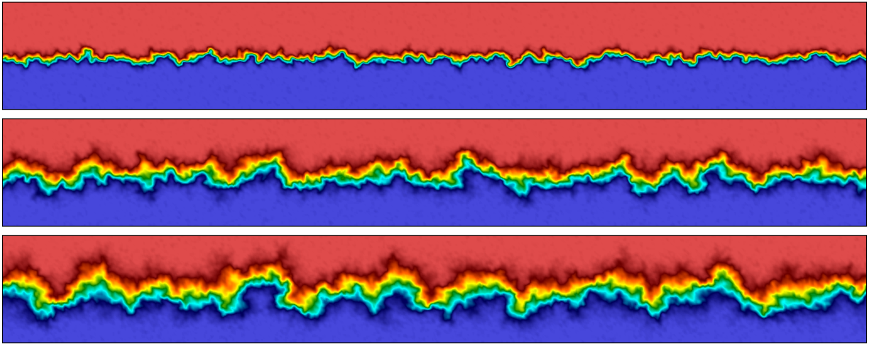
$$\frac{d\mathbf{q}}{dt} = \mathbf{u}(\mathbf{q}, t) + \sqrt{2\chi_0}\, \boldsymbol{\mathcal{W}}_{\mathbf{q}}, \tag{3}$$

  where $\boldsymbol{\mathcal{W}}_{\mathbf{q}}(t)$ are independent white-noise processes.

- For isothermal mixtures of fluids with **unequal densities** (gravity), the incompressible approximation needs to be replaced with a **low Mach approximation** [3],

$$\boldsymbol{\nabla} \cdot \mathbf{v} = \rho^{-1} \left(\frac{\partial \rho}{\partial c} \right)_{P,T} (D_t c).$$

Fractal Fronts in Diffusive Mixing



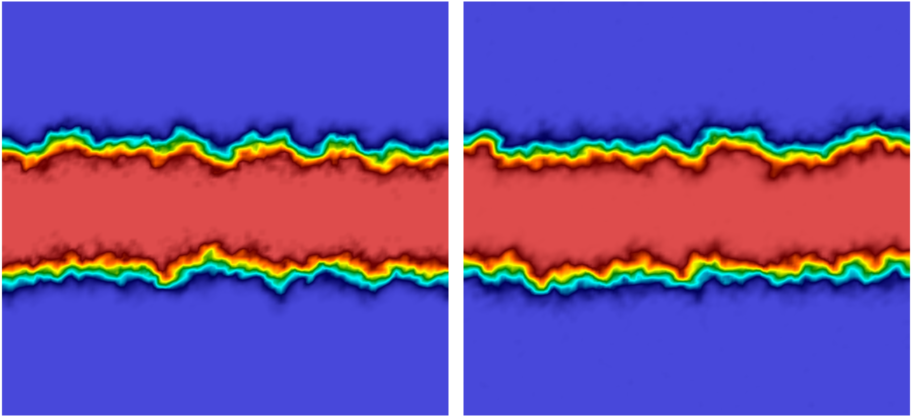
Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of **thermal fluctuations** [4]. These **giant fluctuations** have been studied experimentally [1] and with hard-disk molecular dynamics [3].

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

Molecular Dynamics Simulations

- We performed event-driven **hard disk simulations** of diffusive mixing with about 1.25 million disks.
- The two species had equal molecular diameter but potentially different molecular masses, with density ratio $R = m_2/m_1 = 1$, 2 or 4.
- In order to convert the particle data to hydrodynamic data, we employed finite-volume averaging over a grid of 128^2 hydrodynamic cells 10×10 molecular diameters (about 76 disks per hydrodynamic cell).
- We also performed fluctuating low Mach number **finite-volume simulations** using the same grid of hydrodynamic cells, at only a small fraction of the computational cost [3].
- Quantitative statistical comparison between the molecular dynamics and fluctuating hydrodynamics was excellent once the values of the **bare diffusion** and **viscosity** were adjusted based on the level of coarse-graining.

Hard-Disk Simulations



MD vs. Fluct Hydro

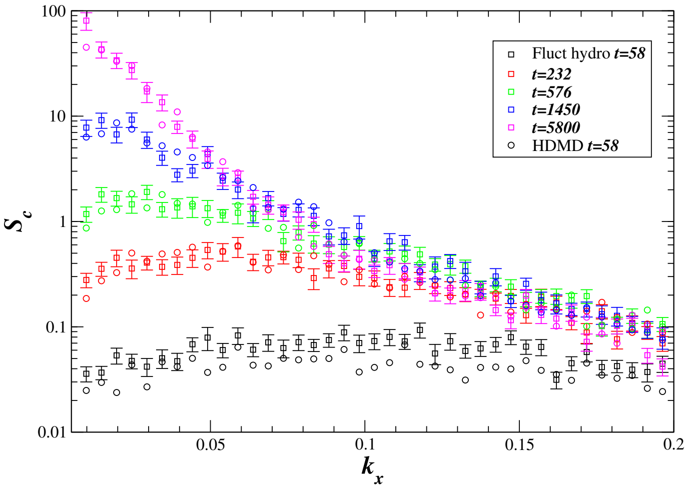


Figure: Discrete spatial spectrum of the interface fluctuations for mass ratio $R = 4$ at several points in time, for fluctuating hydrodynamics (squares with error bars) and HDMD (circles, error bars comparable to those for squares).

Linearized Fluctuating Hydrodynamics

- When macroscopic gradients are present, steady-state thermal fluctuations become **long-range correlated**.
- Consider a **binary mixture** of fluids and consider **concentration fluctuations** around a steady state $c_0(\mathbf{r})$,

$$c(\mathbf{r}, t) = c_0(\mathbf{r}) + \delta c(\mathbf{r}, t).$$

- The concentration fluctuations are **advected by the random velocities**,

$$\partial_t (\delta c) + \mathbf{v} \cdot \boldsymbol{\nabla} c_0 = \chi \boldsymbol{\nabla}^2 (\delta c) + \sqrt{2\chi c_0} \left(\boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{W}}_c \right).$$

- Note that here χ is the deterministic (Fickian) diffusion coefficient which is, as we will see shortly, (much) *larger* than the bare χ_0.

Back of the Envelope

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

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

  where $g = \bar{c}_x$ 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,

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

- 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).

Nonlinear Fluctuating Hydrodynamics

- 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.

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 [5]

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

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**,

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

  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

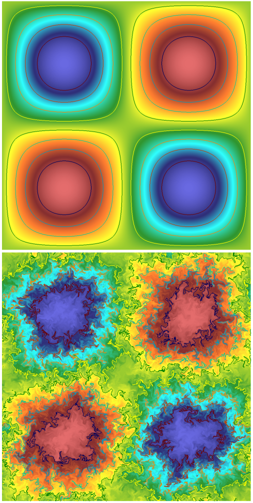
$$\chi(\mathbf{r}) = \frac{k_B T}{\eta} \int \boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}') \, \mathbf{G}(\mathbf{r}', \mathbf{r}'') \, \boldsymbol{\sigma}^T(\mathbf{r}, \mathbf{r}'') \, d\mathbf{r}' d\mathbf{r}'', \qquad (6)$$

  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.

Is Diffusion Irreversible?



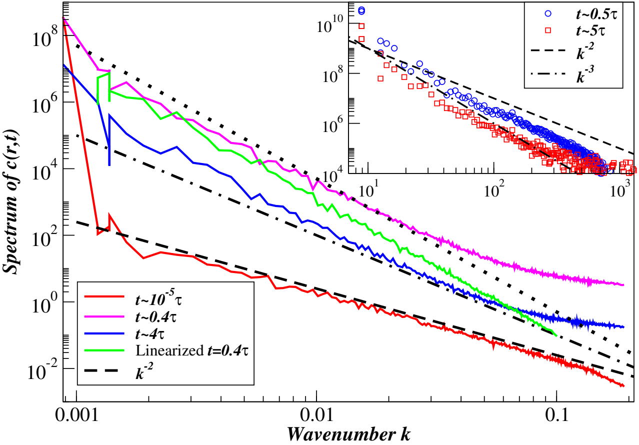


Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with 2048^2 tracers.

Effective Dissipation

- The **ensemble mean** of concentration follows **Fick's deterministic law**,
$$\partial_t \langle c \rangle = \boldsymbol{\nabla} \cdot \left(\chi_{\text{eff}} \boldsymbol{\nabla} \langle c \rangle \right) = \boldsymbol{\nabla} \cdot \left[\left(\chi_0 + \chi \right) \boldsymbol{\nabla} \langle c \rangle \right], \tag{7}$$
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". *Can we make this more precise?*

Spatial Coarse-Graining

Coarse-Grained Equations

- We **postulate** that a physically reasonable **coarse-grained model** for $c_\delta = \boldsymbol{\delta} \star c$ is the **coarse-grained equation** is

$$\partial_t c_\delta \approx -\mathbf{w}_\delta \odot \boldsymbol{\nabla} c_\delta + \boldsymbol{\nabla} \cdot \left[\left(\chi_0 + \Delta \boldsymbol{\chi}_\delta \right) \boldsymbol{\nabla} c_\delta \right], \quad (8)$$

where the **diffusion renormalization** $\Delta \boldsymbol{\chi}_\delta (\mathbf{r})$ [6, 7, 8] is

$$\Delta \boldsymbol{\chi}_\delta = \boldsymbol{\chi} - \boldsymbol{\delta} \star \boldsymbol{\chi} \star \boldsymbol{\delta}^T. \quad (9)$$

- 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

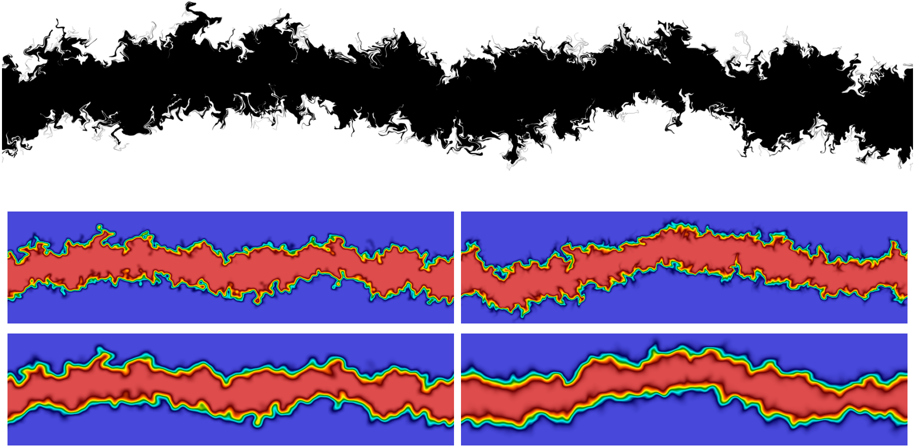


Figure: (*Top panel*) Diffusive mixing studied using the Lagrangian tracer algorithm. (*Bottom*) The spatially-coarse grained concentration c_δ obtained by blurring with a Gaussian filter of two different widths.

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 (overdamped) dynamics** to eliminate the stiffness.
- 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.
- How to generalize this to realistic **non-ideal binary mixtures** and to **multispecies mixtures**?

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