The Truth about diffusion (in liquids)

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Diffusion in Liquids

- There is a common belief that diffusion in gases, liquids and solids is described by **Fick's law** for the concentration $c(\mathbf{r}, t)$,

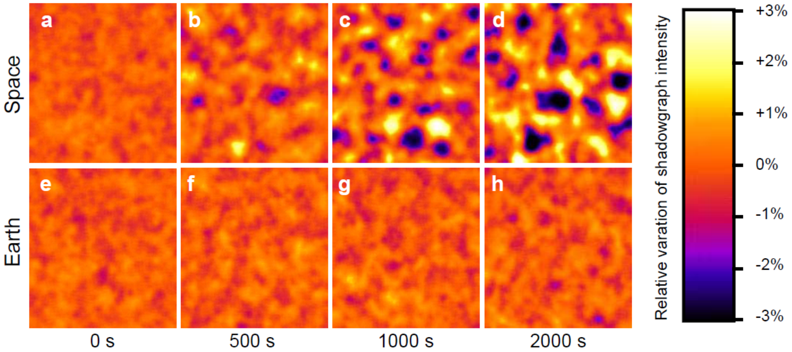
$$\partial_t c = \boldsymbol{\nabla} \cdot [\chi(\mathbf{r}) \boldsymbol{\nabla} c].$$

- 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].
  Berni Alder's discovery of the long-time VACF tail was the first indication Brownian motion in liquids is a bit more subtle than Einstein thought!
- The **Stokes-Einstein relation** connects mass diffusion to **momentum diffusion** (viscosity η) and the molecular diameter σ,

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

- Macroscopic diffusive fluxes in liquids are known to be accompanied by long-ranged nonequilibrium **giant fluctuations** [3].

Giant Nonequilibrium Fluctuations

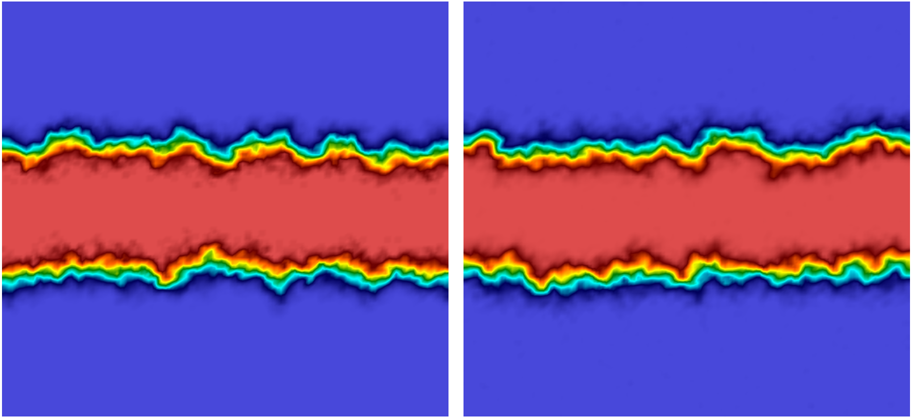


Experimental results by A. Vailati *et al.* from a microgravity environment [3] showing the enhancement of concentration fluctuations in space (box scale is 5mm on the side, 1mm thick).

Fluctuations become macrosopically large at macroscopic scales!

They cannot be neglected as a microscopic phenomenon.

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].

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**,

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

The solution of this SPDE is a white-in-space distribution (very far from smooth!), so we **cannot advect** with it in a non-linear setting.

Resolved (Full) Dynamics

- 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.

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

$$\partial_t c + \mathbf{u} \cdot \boldsymbol{\nabla} c = \chi_0 \boldsymbol{\nabla}^2 c, \qquad (2)$$

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

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

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

Eulerian Overdamped Dynamics

- Adiabatic mode elimination gives the following limiting Ito **stochastic advection-diffusion equation**,

$$\partial_t c + \mathbf{w} \cdot \boldsymbol{\nabla} c = \chi_0 \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot \left[\chi\left(\mathbf{r}\right) \boldsymbol{\nabla} c \right]. \quad (3)$$

- The enhanced or **fluctuation-induced diffusion** is

$$\chi\left(\mathbf{r}\right) = \int_0^\infty \langle \mathbf{u}\left(\mathbf{r}, t\right) \otimes \mathbf{u}\left(\mathbf{r}, t + t'\right) \rangle dt'.$$

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

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

Stokes-Einstein Relation

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

$$\chi(\mathbf{r}) = \frac{k_B T}{\eta} \int \boldsymbol{\sigma}(\mathbf{r}, \mathbf{r}') \, \mathbf{G}(\mathbf{r}', \mathbf{r}'') \, \boldsymbol{\sigma}^T(\mathbf{r}, \mathbf{r}'') \, d\mathbf{r}' d\mathbf{r}'', \quad (4)$$

  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.

Importance of Hydrodynamics

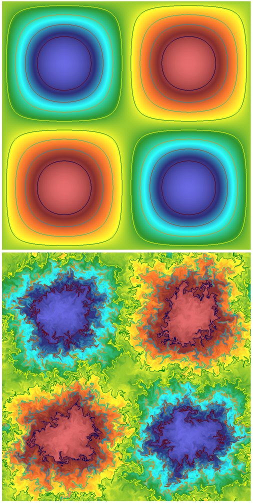
$$\partial_t c = \chi \boldsymbol{\nabla}^2 c - \mathbf{w} \cdot \boldsymbol{\nabla} c$$

- For hydrodynamically **uncorrelated walkers**, Dean derived a different (formal) SPDE [5],

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

- In both cases (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** and in MD.

Is Diffusion Irreversible?



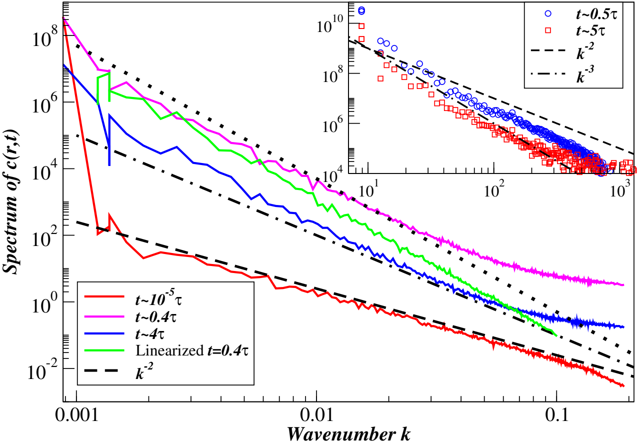


Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with 2048^2 tracers.

Effective Dissipation

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

$$\partial_t \langle c \rangle = \boldsymbol{\nabla} \cdot \left(\chi_{\text{eff}} \boldsymbol{\nabla} \langle c \rangle \right) = \boldsymbol{\nabla} \cdot \left[\left(\chi_0 + \chi \right) \boldsymbol{\nabla} \langle c \rangle \right], \tag{5}$$

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 gives rise to **giant fluctuations**.

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.
- 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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