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 $c(r, t)$,

$$\partial_t c = \nabla \cdot [\chi(r) \nabla c].$$

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 $\eta$) and the molecular diameter $\sigma$,

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

Macroscopic diffusive fluxes in liquids are known to be accompanied by long-ranged nonequilibrium **giant fluctuations** [3].
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.
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].
The thermal velocity fluctuations are described by the (unsteady) fluctuating Stokes equation,

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

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

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

The solution of this SPDE is a white-in-space distribution (very far from smooth!), so we cannot advect with it in a non-linear setting.
Define a **smooth advection velocity** field, $\nabla \cdot u = 0$,

$$u(r, t) = \int \sigma(r, r') v(r', t) \, dr' \equiv \sigma \ast v,$$

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

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

$$\partial_t c + u \cdot \nabla c = \chi_0 \nabla^2 c,$$

where $\chi_0$ is the **bare diffusion coefficient**.
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

$$\chi \nu = \text{const.}$$
Adiabatic mode elimination gives the following limiting Ito stochastic advection-diffusion equation,

$$\partial_t c + \mathbf{w} \cdot \nabla c = \chi_0 \nabla^2 c + \nabla \cdot [\chi (\mathbf{r}) \nabla c].$$  \hspace{1cm} (3)

The enhanced or fluctuation-induced diffusion is

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

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,

$$\langle \mathbf{w} (\mathbf{r}, t) \otimes \mathbf{w} (\mathbf{r}', t') \rangle = 2 \delta (t - t') \int_0^\infty \langle \mathbf{u} (\mathbf{r}, t) \otimes \mathbf{u} (\mathbf{r}', t + t') \rangle dt'.$$
An explicit calculation for **Stokes flow** gives the explicit result

\[
\chi(r) = \frac{k_B T}{\eta} \int \sigma(r, r') G(r', r'') \sigma^T(r, r'') \, dr' \, dr'',
\]

where \(G\) is the Green’s function for steady Stokes flow.

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

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

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.**
The Physics of Diffusion

Importance of Hydrodynamics

\[ \partial_t c = \chi \nabla^2 c - \mathbf{w} \cdot \nabla c \]

- For hydrodynamically uncorrelated walkers, Dean derived a different (formal) SPDE [5],
  \[ \partial_t c = \chi \nabla^2 c + \nabla \cdot \left( \sqrt{2\chi c} \mathbf{W}_c \right). \]

- 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.
Figure: The decay of a single-mode initial condition, as obtained from a Lagrangian simulation with $2048^2$ tracers.
The ensemble mean of concentration follows Fick’s deterministic law,
\[
\partial_t \langle c \rangle = \nabla \cdot (\chi_{\text{eff}} \nabla \langle c \rangle) = \nabla \cdot [ (\chi_0 + \chi) \nabla \langle c \rangle ],
\]
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 ($\chi_0$) is irreversible and dissipative, but diffusion by advection ($\chi$) 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 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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