Diffusion in liquids: DDFT with hydrodynamic interactions and (giant) fluctuations

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

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

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
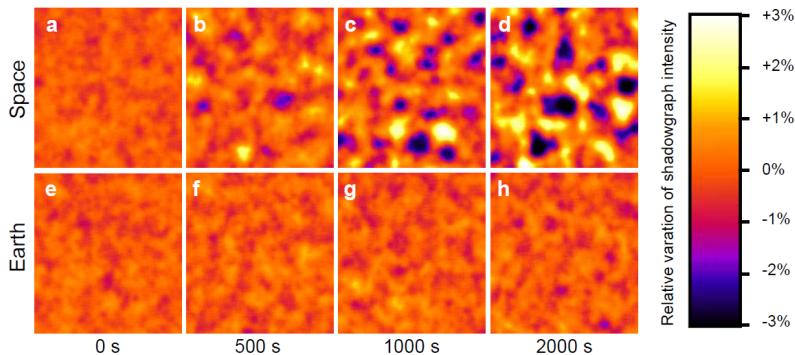
Experimental results by A. Vailati *et al.* from a microgravity environment [3] showing the enhancement of concentration fluctuations in space (box scale is 5mm on the side, 1mm thick).
Fluctuations become macrosopically large at macroscopic scales!
They cannot be neglected as a microscopic phenomenon.

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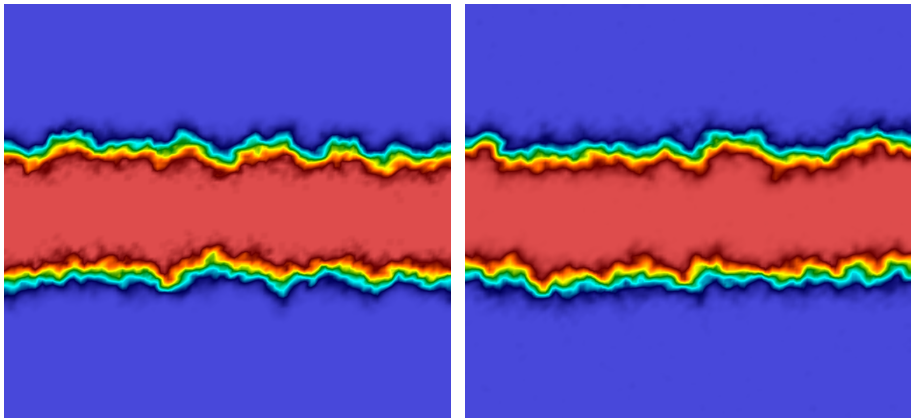
Snapshots of concentration in a miscible mixture showing the development of a *rough* diffusive interface due to the effect of **thermal fluctuations**. These **giant fluctuations** have been studied experimentally [3] and with hard-disk molecular dynamics [4].

Uncorrelated Brownian Walkers

- Consider **diffusion** of colloidal particles immersed in a viscous liquid; assume the particles are **uncorrelated Brownian walkers**.

- The positions of the N particles $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t)\}$ follow the Ito SDEs

$$d\mathbf{Q} = (2\chi)^{\frac{1}{2}} \, d\boldsymbol{\mathcal{B}}, \tag{1}$$

where $\boldsymbol{\mathcal{B}}(t)$ is a collection of independent Brownian motions.

- We are interested in describing a spatially coarse-grained **fluctuating empirical concentration field**,

$$c_\xi(\mathbf{r}, t) = \sum_{i=1}^{N} \delta_\xi(\mathbf{q}_i(t) - \mathbf{r}), \tag{2}$$

where δ_ξ is a smoothing kernel with support $\sim \xi$ that converges to a delta function as $\xi \to 0$.

"Coarse Graining" ala Dean

- Consider first the limit $\xi \to 0$, which corresponds to **no coarse graining** (no loss of information except particle numbering).

- Dean obtained an (**ill-defined**!) SPDE for $c\left(\mathbf{r}, t\right) = \sum \delta\left(\mathbf{q}_i\left(t\right) - \mathbf{r}\right)$, using straightforward Ito calculus and properties of the Dirac delta function,

$$\partial_t c = \chi \boldsymbol{\nabla}^2 c + \boldsymbol{\nabla} \cdot \left(\sqrt{2\chi c}\, \boldsymbol{\mathcal{W}}_c\right), \tag{3}$$

  where $\boldsymbol{\mathcal{W}}_c\left(\mathbf{r}, t\right)$ denotes a spatio-temporal **white**-**noise** vector field.

- This is a typical example of a fluctuating hydrodynamics equation, which is deceptively simply, yet extremely subtle from both a physical and mathematical perspective.

- The term $\sqrt{2\chi c}\, \boldsymbol{\mathcal{W}}_c$ can be thought of as a **stochastic mass flux**, in addition to the "deterministic" **Fickian flux** $\chi \boldsymbol{\nabla} c$.

Brownian Dynamics

- The Ito equations of **Brownian Dynamics** (BD) for the (correlated) positions of the N particles $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t)\}$ are

$$d\mathbf{Q} = -\mathbf{M}\left(\partial_{\mathbf{Q}} U\right) dt + (2k_B T \mathbf{M})^{\frac{1}{2}} d\boldsymbol{\mathcal{B}} + k_B T \left(\partial_{\mathbf{Q}} \cdot \mathbf{M}\right) dt, \qquad (4)$$

where $\boldsymbol{\mathcal{B}}(t)$ is a collection of independent Brownian motions, $U(\mathbf{Q})$ is a conservative interaction potential.

- Here $\mathbf{M}(\mathbf{Q}) \succeq \mathbf{0}$ is a symmetric positive semidefinite **mobility** block **matrix** for the collection of particles, and introduces **correlations** among the walkers.

- The Fokker-Planck equation (FPE) for the probability density $P(\mathbf{Q}, t)$ corresponding to (4) is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \mathbf{Q}} \cdot \left\{ \mathbf{M} \left[\frac{\partial U}{\partial \mathbf{Q}} P + (k_B T) \frac{\partial P}{\partial \mathbf{Q}} \right] \right\}, \qquad (5)$$

and is in detailed-balance (i.e., is time reversible) with respect to the **Gibbs-Boltzmann distribution** $\sim \exp\left(-U(\mathbf{Q})/k_B T\right)$.

Hydrodynamic "Interactions"

- Let's start from the (low-density) **pairwise approximation**

$$\forall (i,j): \quad \mathbf{M}_{ij} \left(\mathbf{q}_i, \mathbf{q}_j \right) = \frac{\mathcal{R} \left(\mathbf{q}_i, \mathbf{q}_j \right)}{k_B T} = \frac{1}{k_B T} \sum_k \phi_k \left(\mathbf{q}_i \right) \phi_k \left(\mathbf{q}_j \right),$$

- Here $\mathcal{R} \left(\mathbf{r}, \mathbf{r}' \right)$ is a **symmetric positive-definite kernel** that is **divergence-free**, and can be diagonalized in an (infinite dimensional) set of divergence-free basis functions $\phi_k \left(\mathbf{r} \right)$.

- For the **Rotne-Prager-Yamakawa tensor** mobility, $\mathcal{R}(\mathbf{r}', \mathbf{r}'') \equiv \mathcal{R}(\mathbf{r}' - \mathbf{r}'' \equiv \mathbf{r})$,

$$\mathcal{R}(\mathbf{r}) = \chi \begin{cases} \left(\dfrac{3\sigma}{4r} + \dfrac{\sigma^3}{2r^3} \right) \mathbf{I} + \left(\dfrac{3\sigma}{4r} - \dfrac{3\sigma^3}{2r^3} \right) \dfrac{\mathbf{r} \otimes \mathbf{r}}{r^2}, & r > 2\sigma \\ \left(1 - \dfrac{9r}{32\sigma} \right) \mathbf{I} + \left(\dfrac{3r}{32\sigma} \right) \dfrac{\mathbf{r} \otimes \mathbf{r}}{r^2}, & r \leq 2\sigma \end{cases} \quad (6)$$

where σ is the radius of the colloidal particles and the **diffusion coefficient** χ follows the Stokes-Einstein formula $\chi = k_B T / (6\pi\eta\sigma)$.

Eulerian Overdamped Dynamics

- We can use standard calculus to obtain an equation for the **empirical** or instantaneous **concentration**

$$c(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{q}_i(t) - \mathbf{r}). \qquad (7)$$

- Following a similar procedure to Dean now, we get the **stochastic advection diffusion** equation [5]

$$\partial_t c = \boldsymbol{\nabla} \cdot [\boldsymbol{\chi}(\mathbf{r}) \boldsymbol{\nabla} c] - \mathbf{w} \cdot \boldsymbol{\nabla} c, \qquad (8)$$

where the diffusion coefficient $\boldsymbol{\chi}(\mathbf{r}) = \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r})$ and the random velocity field $\mathbf{w}(\mathbf{r}, t)$ has covariance

$$\langle \mathbf{w}(\mathbf{r}, t) \otimes \mathbf{w}(\mathbf{r}', t') \rangle = 2\boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}') \delta(t - t'). \qquad (9)$$

- This equation is now well-defined mathematically since linear. One can use the same equation (8) to evolve a probability distribution for finding a particle at a given location.

Hydrodynamic Correlation Tensor

- A rather general formula for the hydrodynamic correlation tensor can be obtained by following a **fluctuating hydrodynamics** formalism [2]:

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

  where the smoothing kernel $\boldsymbol{\sigma}$ filters out features at scales below a **cutoff scale** σ (e.g., colloid size).

- The **effective diffusion coefficient** is

$$\boldsymbol{\chi}\left(\mathbf{r}\right) = \boldsymbol{\mathcal{R}}\left(\mathbf{r}, \mathbf{r}\right) = \frac{k_B T}{\eta} \int \boldsymbol{\sigma}\left(\mathbf{r}, \mathbf{r}'\right) \mathbf{G}\left(\mathbf{r}', \mathbf{r}''\right) \boldsymbol{\sigma}^T\left(\mathbf{r}, \mathbf{r}''\right) d\mathbf{r}' d\mathbf{r}'', \quad (10)$$

  where $\mathbf{G}$ 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,

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

Importance of Hydrodynamics

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

- For hydrodynamically **uncorrelated walkers**, $\mathbf{M}_{ij} = \delta_{ij}(k_B T)^{-1}\chi\mathbf{I}$, the noise is very different, $\boldsymbol{\nabla} \cdot \left(\sqrt{2\chi c}\,\boldsymbol{\mathcal{W}}_c\right)$.
- 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 simulations.
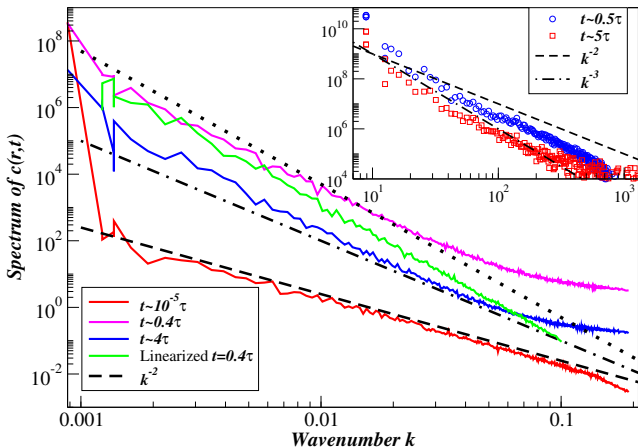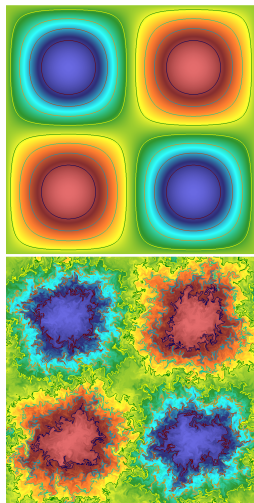
Is Diffusion Dissipative?

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

Conclusions

- Fluctuations are **not just a microscopic phenomenon**: giant fluctuations can reach macroscopic dimensions or certainly dimensions much larger than molecular.
- **Fluctuating hydrodynamics** and **Brownian dynamics** can both describe these effects and give the same equations in the end.
- **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 (?).

Chemically-Reactive Mixtures

- The species density equations for a mixture of N_{S} species are given by

$$\frac{\partial}{\partial t}\left(\rho_s\right) + \nabla \cdot \left(\rho_s \mathbf{v} + \mathbf{F}\right) = m_s \Omega_s, \qquad (s = 1, \ldots N_{\mathrm{S}}) \qquad (11)$$

where $\mathbf{F}$ are diffusive fluxes and Ω_s are chemical production rates.

- The mass fluxes take the form, excluding barodiffusion and thermodiffusion and with **no hydrodynamic correlations**,
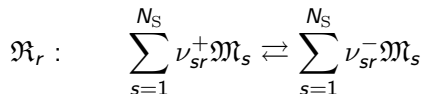
$$\mathbf{F} = \rho \mathrm{Diag}\left\{\rho_s/\rho\right\}\left[\boldsymbol{\chi}\boldsymbol{\Gamma}\boldsymbol{\nabla}\mathbf{x} + \sqrt{\frac{2}{n}}\,\boldsymbol{\chi}^{\frac{1}{2}}\mathcal{W}_F\left(\mathbf{r}, t\right)\right],$$

where n is the number density, and x_s is the mole fraction of species s.

- $\boldsymbol{\Gamma}$ is a matrix of thermodynamic factors, and $\boldsymbol{\chi}$ is an **SPD diffusion tensor** that can be related to the Maxwell-Stefan diffusion coefficients and Green-Kubo type formulas.

Chemistry

- Consider a system with N_R **elementary reactions** with reaction r

$$\mathfrak{R}_r : \qquad \sum_{s=1}^{N_S} \nu_{sr}^+ \mathfrak{M}_s \rightleftarrows \sum_{s=1}^{N_S} \nu_{sr}^- \mathfrak{M}_s$$

The **stoichiometric coefficients** are $\nu_{sr} = \nu_{sr}^- - \nu_{sr}^+$ and mass conservation requires that $\sum_s \nu_{sr} m_r = 0$.

- Define the dimensionless **chemical affinity**

$$\mathcal{A}_r = \sum_s \nu_{sr}^+ \hat{\mu}_s - \sum_s \nu_{sr}^- \hat{\mu}_s,$$

where $\hat{\mu}_s = m_s \mu_s / k_B T$ is the dimensionless **chemical potential per particle**.

- Also define the **thermodynamic driving force**

$$\hat{\mathcal{A}}_r = \exp\left(\sum_s \nu_{sr}^+ \hat{\mu}_s\right) - \exp\left(\sum_s \nu_{sr}^- \hat{\mu}_s\right) = \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} - \prod_s e^{\nu_{sr}^- \hat{\mu}_s}$$

Chemistry

- The mass production due to chemistry can take **one of two forms** [6]:

$$\Omega_s = \sum_r \nu_{sr} \left(\frac{P}{\tau_r k_B T} \right) \hat{\mathcal{A}}_r \text{ (deterministic LMA)} \qquad (12)$$

$$+ \sum_r \nu_{sr} \begin{cases} \left(2\frac{P}{\tau_r k_B T} \frac{\hat{\mathcal{A}}_r}{\bar{\mathcal{A}}_r} \right)^{\frac{1}{2}} \diamond \boldsymbol{\mathcal{Z}}(\mathbf{r}, t) & \text{log-mean eq. (LME)} \\ \left(\frac{P}{\tau_r k_B T} \prod_s e^{\nu_{sr}^+ \hat{\mu}_s} \right)^{\frac{1}{2}} \boldsymbol{\mathcal{Z}}(\mathbf{r}, t) & \text{chemical Langevin eq. (CLE)} \end{cases}$$

- The **LME** follows the correct structure of Langevin equations (GENERIC structure of Ottinger/Grmela). Is **time-reversible** (obeys detailed balance) **at thermodynamic equilibrium** wrt to the Einstein distribution.
- The **CLE** follows from a truncation of the Kramers-Moyal expansion at second order. No true thermodynamic equilibrium since it assumes **one-way reactions**.
- **Which one is correct? Neither!**

Poisson Noise

- The reason neither LME nor CLE are correct is that **there is no S(P)DE** that can correctly describe both the short-time (typical) and long-time (rare event) behavior of the master equation.

- This is related to the fact that the central limit theorem and large-deviation theory are not consistent with the same nonlinear S(P)DE.

- One must either use the **Chemical Master Equation (CME)** with SSA/Gillespie (microscopic rather than macroscopic), **or**

- One can use **Poisson noise** instead of **Gaussian noise** using **tau leaping**.
  This can be thought of as a **coarse-graining in time** of the original jump process described by the CME.

- Quite generally the appropriateness of assuming Gaussian white noise for the stochastic fluxes is questionable.

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