Hydrodynamic fluctuations in quasi-two dimensional diffusion

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Outline

1. Diffusion in bulk 2D and 3D
2. Diffusion in Quasi2D
3. Brownian Dynamics in Q2D
4. Numerical Results

Quick Intro

- Bulk colloidal suspensions in three dimensions (3D) have been studied for a long time.
- We consider colloids that are confined by some strong potential to remain on a plane [1].
  An example are colloids confined to diffuse on a **planar liquid-liuid interface**. This has been studied before by Johannes Bleibel, Alvaro Domínguez, and collaborators.
- In the limit of strong confining potential, the diffusive dynamics of the colloids is restricted to the plane: **quasi two-dimensions** (**q2D**).
- Note that the fluid flow around the colloids, mediating **hydrodynamic interactions** among the particles, is still three dimensional.
- If we consider colloids in a very thin film, we have 2D fluid flow: **true two-dimensions** (**t2D**).
- **The goal of this talk will be to study the surprising differences between 3D, t2D and q2D suspensions.**

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 $c(\mathbf{r}, t)$,
$$\partial_t c = \boldsymbol{\nabla} \cdot [\chi(\mathbf{r}; c) \boldsymbol{\nabla} c],$$
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 [2].
- The **Stokes-Einstein relation** connects mass diffusion to **momentum diffusion** (viscosity η) for **dilute solutions in 3D**,
$$\chi \approx \frac{k_B T}{6\pi\sigma\eta},$$
where σ is the tracer (hydrodynamic) diameter.

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.

Inertial 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,
$c(\mathbf{q}(0), t) = c(\mathbf{q}(t), 0)$.

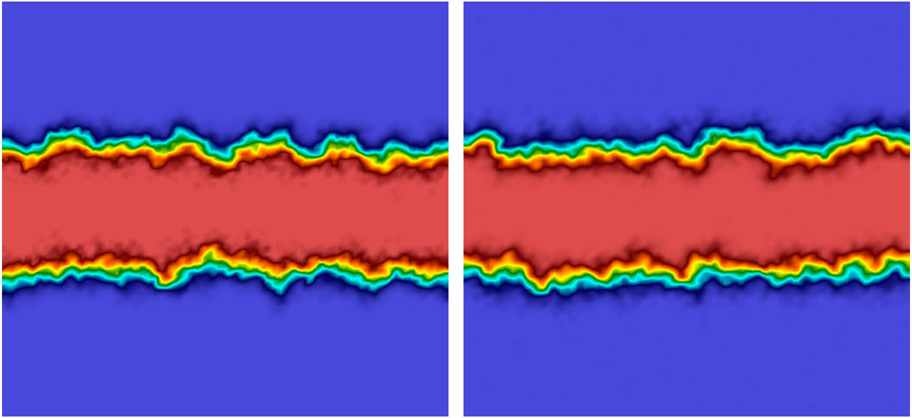
Fluctuating Hydrodynamics SPDEs

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

$$\mathbf{u}\left(\mathbf{r}, t\right) = \int \boldsymbol{\sigma}\left(\mathbf{r}, \mathbf{r}'\right) \mathbf{v}\left(\mathbf{r}', t\right) d\mathbf{r}' \equiv \boldsymbol{\sigma} \star \mathbf{v}$$

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

Fractal Fronts in Diffusive Mixing in 2D



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.

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 **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
$$\chi\left(\mathbf{r}\right)=\frac{k_{B}T}{\eta}\int\boldsymbol{\sigma}\left(\mathbf{r}-\mathbf{r}'\right)\mathbb{G}\left(\mathbf{r}'-\mathbf{r}''\right)\boldsymbol{\sigma}^{T}\left(\mathbf{r}-\mathbf{r}''\right)d\mathbf{r}'d\mathbf{r}'', \qquad (6)$$
where $\mathbb{G}$ 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 $S_c=\nu/\chi_{\text{eff}}=\nu/\left(\chi_0+\chi\right)\gg 1$.
- 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.

Relation to Brownian Dynamics

- If we take an **overdamped** limit of the **Lagrangian equation** we get the the Ito equations of **Brownian Dynamics** (BD) for the (correlated) positions of the N particles $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t)\}$,

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

  where $\boldsymbol{\mathcal{B}}(t)$ is a vector of Brownian motions, and $\mathbf{F}(\mathbf{Q})$ are forces.

- Here $\mathbf{M}(\mathbf{Q}) \succeq \mathbf{0}$ is a symmetric positive semidefinite (SPD) **mobility matrix**, *assumed* here to have a far-field **pairwise approximation**

$$\mathbf{M}_{ij}(\mathbf{Q}) \equiv \mathbf{M}_{ij}\left(\mathbf{q}_i, \mathbf{q}_j\right) = \boldsymbol{\mathcal{R}}\left(\mathbf{q}_i - \mathbf{q}_j\right),$$

  where $\boldsymbol{\mathcal{R}}$ is the **hydrodynamic kernel**.

- The self-diffusion tensor of a single isolated particle is

$$\chi = (k_B T)\, \boldsymbol{\mathcal{R}}(\mathbf{0}).$$

Rotne-Prager-Yamakawa Tensor

- In our model the hydrodynamic kernel is

$$\boldsymbol{\mathcal{R}}\left(\mathbf{r}_1-\mathbf{r}_2\right)=\int \boldsymbol{\sigma}\left(\mathbf{r}_1-\mathbf{r}'\right)\mathbb{G}\left(\mathbf{r}'-\mathbf{r}''\right)\boldsymbol{\sigma}\left(\mathbf{r}_2-\mathbf{r}''\right)d\mathbf{r}'d\mathbf{r}''.$$

- Observe that in the far-field, $r \gg a$, the RPY tensor becomes the **long-ranged** Oseen tensor

$$\boldsymbol{\mathcal{R}}\left(r \gg a\right)\to\mathbb{G}\left(\mathbf{r}\right)=\frac{1}{8\pi r}\left(\mathbf{I}+\frac{\mathbf{r}\otimes\mathbf{r}}{r^2}\right). \tag{7}$$

- For **3D bulk** suspensions, if $\boldsymbol{\sigma}\left(\mathbf{r}\right)=\boldsymbol{\delta}\left(r-a\right)$ is a surface delta function, we get the widely-used **Rotne-Prager-Yamakawa tensor**

$$\boldsymbol{\mathcal{R}}\left(\mathbf{r}\right)=\frac{1}{6\pi\eta a}\left(\frac{3a}{4r}+\frac{a^3}{2r^3}\right)\mathbf{I}+\left(\frac{3a}{4r}-\frac{3a^3}{2r^3}\right)\frac{\mathbf{r}\otimes\mathbf{r}}{r^2},\quad r>2a.$$

Force Coupling Tensor

- Replace the surface delta function δ_a by a **smooth Gaussian kernel** with standard deviation $\sigma = a/\sqrt{\pi}$ to give $\chi = k_B T / (6\pi\eta a)$.
- This gives the **FCM kernel** that **is just as good as RPY**:

$$\mathcal{R}(\mathbf{r}) = f(r)\,\mathbf{I} + g(r)\,\frac{\mathbf{r}\otimes\mathbf{r}}{r^2}, \quad \text{where}$$

$$\begin{bmatrix} f(r) \\ g(r) \end{bmatrix} = \frac{1}{8\pi\eta r}\left(1 + \begin{bmatrix} 2 \\ -6 \end{bmatrix} \frac{a^2}{\pi\, r^2}\right) \operatorname{erf}\left(\frac{r\sqrt{\pi}}{2a}\right).$$

$$-\frac{1}{8\pi\eta r}\begin{bmatrix} 2 \\ -6 \end{bmatrix} \frac{a}{\pi\, r} \exp\left(-\frac{\pi\, r^2}{4a^2}\right).$$

- The use of **FHD** (fluctuating hydrodynamics) with Gaussian kernels allows for **very efficient (linear time!) BD**, even for the RPY kernel [4].

Divergence of the mobility

$$d\mathbf{Q} = \mathbf{M} \cdot \mathbf{F}(\mathbf{Q})\, dt + (2k_B T\, \mathbf{M})^{\frac{1}{2}}\, d\boldsymbol{\mathcal{B}} + k_B T\, (\partial_{\mathbf{Q}} \cdot \mathbf{M})\, dt.$$

- An important property of the **3D RPY and FCM** kernel is that they **are divergence free**,
$$\boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{R}}_{3D}(\mathbf{r}) = 0,$$
which follows from the fact the 3D flow is incompressible, $\boldsymbol{\nabla} \cdot \mathbb{G}(\mathbf{r}) = 0$, and implies that
$$\partial_{\mathbf{Q}} \cdot \mathbf{M} = 0.$$
This has important consequences on **collective diffusion**.
- The same applies for **t2D** systems as well,
$$\boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{R}}_{t2D}(\mathbf{r}) = 0,$$
but there are still some important differences between t2D and 3D diffusion related to **giant fluctuations**.

Quasi-2D suspensions

- For q2D, dynamics can be described by BD-HI with $\mathbf{q} = (x, y)$ being position in the plane.
- Now the hydrodynamic kernel is still the same RPY or FCM kernel, but now **the flow is not incompressible in the plane**,
$$\boldsymbol{\nabla}_{(x,y)} \cdot \boldsymbol{\mathcal{R}}_{q2D}(\mathbf{r}) \neq 0,$$
which means that there will be a nonzero $\partial_{\mathbf{Q}} \cdot \mathbf{M}$, and the diffusive dynamics will be **very different** from either 3D or t2D.
- To start take the **Oseen tensor** as the hydrodynamic kernel,
$$f\left(r \gg a\right) \approx g\left(r \gg a\right) \approx \frac{1}{8\pi\eta r},$$
which gives something that in the far field looks **like a repulsive Coulomb force**,
$$\frac{d\mathbf{q}_i}{dt} = \cdots + k_B T \left(\partial_{\mathbf{Q}} \cdot \mathbf{M}\right)_i = \cdots + \sum_{j \neq i} \frac{k_B T}{8\pi\eta r} \cdot \frac{\mathbf{q}_i - \mathbf{q}_j}{\left\|\mathbf{q}_i - \mathbf{q}_j\right\|^2} + \ldots$$

Diffusion Equation with HIs

- **For the majority of the rest of this talk we assume particles do not interact with a direct potential (ideal gas)**.
  Unphysical but steric repulsion does not change (short-time) collective diffusion that much.
- Define a concentration from the positions of the particles $\mathbf{q}_i(t)$,

$$c(\mathbf{r},t) = \sum_{i=1}^{N} \delta\left(\mathbf{q}_i(t) - \mathbf{r}\right), \tag{8}$$

  Ito's rule gives the following (formal) *closed* but **nonlinear** stochastic advection-diffusion equation for the concentration [5],

$$\partial_t c(\mathbf{r},t) = \boldsymbol{\nabla} \cdot \left(\chi(\mathbf{r}) \boldsymbol{\nabla} c(\mathbf{r},t)\right) - \boldsymbol{\nabla} \cdot \left(\mathbf{w}(\mathbf{r},t)\, c(\mathbf{r},t)\right) + (k_B T)\, \boldsymbol{\nabla} \cdot \left(c(\mathbf{r},t) \int \mathcal{R}(\mathbf{r},\mathbf{r}') \boldsymbol{\nabla}' c(\mathbf{r}',t)\, d\mathbf{r}' \right). \tag{9}$$

- Fluctuations come via the random velocity field $\mathbf{w}$ that comes from the fluctuating fluid velocity in FHD.

Nonlocal (Far-Field) HIs in 3D/t2D

- The **nonlinear nonlocal hydrodynamic** term can be rewritten as

$$\boldsymbol{\nabla} \cdot \left(c(\mathbf{r}, t) \int \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}') \boldsymbol{\nabla}' c(\mathbf{r}', t) \, d\mathbf{r}' \right) =$$

$$-\boldsymbol{\nabla} \cdot \left(c(\mathbf{r}, t) \int \left(\boldsymbol{\nabla}' \cdot \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}') \right) c(\mathbf{r}', t) \, d\mathbf{r}' \right).$$

- For 3D and t2D, $\boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}') = \boldsymbol{\nabla}' \cdot \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}') = 0$, and (9) becomes a **linear** stochastic equation that can easily be solved numerically.
- Importantly, in 3D/t2D, we get Fick's law even with HIs [2]:

$$\partial_t c^{(1)}(\mathbf{r}, t) = \boldsymbol{\nabla} \cdot \left(\chi(\mathbf{r}) \boldsymbol{\nabla} c^{(1)}(\mathbf{r}, t) \right),$$

  for the single-particle distribution function $c^{(1)}(\mathbf{r}, t) = \langle c(\mathbf{r}, t) \rangle$.
- But the story is not so simple if one looks at **giant fluctuations**, as I will show later and has been measured in 3D experiments.

Nonlocal (Far-Field) HIs in q2D

- The story is very different in q2D because now $\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{R}}(\mathbf{r})\neq 0$ and it is **long-ranged**, giving

$$\begin{aligned}\partial_t c^{(1)}(\mathbf{r},t) &= \boldsymbol{\nabla}\cdot\left(\chi(\mathbf{r})\boldsymbol{\nabla}c^{(1)}(\mathbf{r},t)\right)+ \qquad (10)\\ (k_B T) &\; \boldsymbol{\nabla}\cdot\left(\int\boldsymbol{\mathcal{R}}\left(\mathbf{r},\mathbf{r}'\right)\boldsymbol{\nabla}'c^{(2)}\left(\mathbf{r},\mathbf{r}',t\right)\,d\mathbf{r}'\right),\end{aligned}$$

  which is not closed, is nonlocal, and nonlinear.

- For an ideal gas, the standard closure for the two-particle correlation function is

$$c^{(2)}\left(\mathbf{r},\mathbf{r}',t\right)\approx c^{(1)}\left(\mathbf{r},t\right)c^{(1)}\left(\mathbf{r}',t\right),$$

  giving the approximation

$$\begin{aligned}\partial_t c^{(1)}(\mathbf{r},t) &= \boldsymbol{\nabla}\cdot\left(\chi(\mathbf{r})\boldsymbol{\nabla}c^{(1)}(\mathbf{r},t)\right). \qquad (11)\\ &+(k_B T)\,\boldsymbol{\nabla}\cdot\left(c^{(1)}(\mathbf{r},t)\int\boldsymbol{\mathcal{R}}\left(\mathbf{r},\mathbf{r}'\right)\boldsymbol{\nabla}'c^{(1)}\left(\mathbf{r}',t\right)\,d\mathbf{r}'\right)\end{aligned}$$

Dynamics of Density Fluctuations in q2D

- Consider the case of a spatially uniform system with concentration $c(\mathbf{r},t) = c_0 + \delta c(\mathbf{r},t)$, where $\delta c \ll c_0$.
- If we linearize (9) around the uniform state and ignore fluctuations:

$$\partial_t \delta c(\mathbf{r},t) = \chi \boldsymbol{\nabla}^2 \delta c(\mathbf{r},t) + (k_B T)\, \boldsymbol{\nabla} \cdot \left(c_0 \int \boldsymbol{\mathcal{R}}(\mathbf{r}-\mathbf{r}') \boldsymbol{\nabla}' \delta c(\mathbf{r}',t)\, d\mathbf{r}' \right).$$

- This equation can trivially be solved in Fourier space,

$$\frac{d}{dt}\left(\hat{\delta c}_{\mathbf{k}}\right) = -\left(\chi k^2 + (k_B T)\, c_0 \mathbf{k} \cdot \hat{\boldsymbol{\mathcal{R}}}_{\mathbf{k}} \cdot \mathbf{k}\right) \hat{\delta c}_{\mathbf{k}} = -\chi k^2 D_c(\mathbf{k})\, \hat{\delta c}_{\mathbf{k}},$$

where $D_c(\mathbf{k})$ is the **short-time collective diffusion coefficient**,

$$D_c(\mathbf{k}) = \chi \left(1 + \frac{1}{k L_h}\right) = \chi + (k_B T)\, \frac{c_0}{4\eta k}. \tag{12}$$

- For high packing densities $\phi = \pi c_0 a^2 \sim 1$, we have $L_h \sim a$: **strong collective diffusion effects at all length scales**.

Hydrodynamics in q2D

- By combining the Fluctuating Immersed Boundary (FIB) method with the Fluctuating Force Coupling Method (FCM) we obtain an **efficient** $O(N)$ **algorithm for q2D-BD**.
- The key idea behind both of these is to use **fluctuating hydrodynamics** to obtain the random displacements but I will present it here from a more algebraic perspective [4].
- The key is to go Fourier space, with $\boldsymbol{\kappa} = (\mathbf{k}, k_z)$,

$$\begin{aligned} \hat{\mathcal{R}}_{\mathbf{k}} &= \frac{1}{2\pi} \int_{k_z} \frac{dk_z}{\eta \kappa^2} \left(\mathbf{I} - \frac{\boldsymbol{\kappa} \otimes \boldsymbol{\kappa}}{\kappa^2} \right) \exp\left(-\frac{a^2 \kappa^2}{\pi} \right). \\ &= \frac{1}{\eta k^3} \left(c_2 (ka)\, \mathbf{k}_\perp \otimes \mathbf{k}_\perp^T + c_1 (ka)\, \mathbf{k} \otimes \mathbf{k}^T \right). \end{aligned} \tag{13}$$

where both c_1 and c_2 decay exponentially $\sim \exp\left(-a^2 k^2\right)$ in Fourier space (**pseudospectral methods**).

Comparison to true 2D

- For small k we have the 2D projection of the t2D or q2D Oseen tensor,

$$
\begin{aligned}
c_1 (K = ka \ll 1) &\approx \frac{1}{4} \text{ for q2D, and 0 for t2D, and} \\
c_2 (K = ka \ll 1) &\approx \frac{1}{2} \text{ for q2D, and } \frac{1}{k} \text{ for t2D.}
\end{aligned}
$$

- The short-time self diffusion coefficient $\chi_0 = f\ (k_B T/\eta)$,

$$
\begin{aligned}
f &= \frac{1}{6\pi a} \cdot \frac{1}{1 + 4.41 a/L} \approx \frac{1}{6\pi a} \quad \text{for q2D, and} \qquad (14) \\
f &= \frac{1}{4\pi} \ln \left(\frac{L}{3.71 a} \right) \quad \text{for t2D,}
\end{aligned}
$$

and L is the system size.

Diffusion as random advection

- For an **ideal gas** we have the Ito BD equation:

$$d\mathbf{Q} = \left(2k_B T\,\mathbf{M}\right)^{\frac{1}{2}} d\boldsymbol{\mathcal{B}} + k_B T\left(\partial_{\mathbf{Q}} \cdot \mathbf{M}\right) dt, \qquad (15)$$

- Brownian motion of a particle in an ideal gas in q2D [5]:

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{w}\left(\mathbf{q}_i, t\right) + k_B T\left(\mathbf{a}\left(\mathbf{q}_i\right) + \sum_{j\neq i} \mathbf{b}\left(\mathbf{q}_i, \mathbf{q}_j\right)\right), \qquad (16)$$

  where $\mathbf{a}\left(\mathbf{r}\right) = \boldsymbol{\nabla} \cdot \boldsymbol{\mathcal{R}}\left(\mathbf{r}, \mathbf{r}\right) = \boldsymbol{\nabla} \cdot \chi\left(\mathbf{r}\right)$ and $\mathbf{b}(\mathbf{r}, \mathbf{r}') = \boldsymbol{\nabla}' \cdot \boldsymbol{\mathcal{R}}(\mathbf{r}, \mathbf{r}')$.

- For a translationally-invariant system $\mathbf{a} = 0$, and for t2D $\mathbf{b} = 0$.
- Here $\mathbf{w}\left(\mathbf{r}, t\right)$ is a **random fluid velocity that advects the particle**s,

$$\langle \mathbf{w}\left(\mathbf{r}, t\right) \otimes \mathbf{w}\left(\mathbf{r}', t'\right)\rangle = 2\left(k_B T\right) \boldsymbol{\mathcal{R}}\left(\mathbf{r}, \mathbf{r}'\right) \delta\left(t - t'\right). \qquad (17)$$

Efficient Brownian Dynamics in q2D

- The final BD equation is, with $\partial_i \delta_a(\mathbf{r}) = \partial \delta_a(\mathbf{r}) / \partial r_i$ [5],
$$\frac{d\mathbf{q}_i}{dt} = \mathbf{w}(\mathbf{q}_i, t) + \int \delta_a(\mathbf{q}_i - \mathbf{r}') \sum_j \mathbb{G}(\mathbf{r}', \mathbf{r}'') \, d\mathbf{r}' d\mathbf{r}'' \cdot \quad (18)$$
$$\left[\mathbf{F}_j \delta_a(\mathbf{q}_j - \mathbf{r}'') + (k_B T)(\partial \delta_a)(\mathbf{q}_j - \mathbf{r}'')\right].$$
- From (13) we get
$$\widehat{\mathbf{w}}_{\mathbf{k}} = \sqrt{\frac{2k_B T}{\eta k^3}} \left(\sqrt{c_2(ka)}\, \mathbf{k}_\perp \mathcal{Z}_{\mathbf{k}}^{(2)} + \sqrt{c_1(ka)}\, \mathbf{k} \mathcal{Z}_{\mathbf{k}}^{(1)} \right), \quad (19)$$
where $\mathcal{Z}_{\mathbf{k}}^{(1/2)}(t)$ are independent white noise processes – stochastic momentum flux in **fluctuating Stokes equation**.
- For FCM the kernel δ_a is a Gaussian with $\sigma = a/\sqrt{\pi}$,
$$\hat{\mathbb{G}}_{\mathbf{k}} = \hat{\mathcal{R}}_{\mathbf{k}} \exp\left(\frac{a^2 k^2}{\pi}\right) = \frac{1}{\eta}\left[g_k(k)\, \mathbf{k}_\perp \otimes \mathbf{k}_\perp^T + f_k(k)\, \mathbf{k} \otimes \mathbf{k}^T\right].$$

BD-q2D algorithm (I)

1. Evaluate particle forces $\mathbf{F}^n = \mathbf{F}(\mathbf{Q}^n)$.
2. Compute in real space on a grid the fluid forcing
$$\mathbf{f}(\mathbf{r}) = \sum_i \mathbf{F}_i \delta_a(\mathbf{q}_i - \mathbf{r}) + (k_B T) \sum_i (\partial \delta_a)(\mathbf{q}_i - \mathbf{r}).$$
and use the FFT to convert $\mathbf{f}$ to Fourier space, $\hat{\mathbf{f}}_{\mathbf{k}}$.
3. Compute the fluid velocity resulting from fluid forcing $\mathbf{f}$ in Fourier space as a convolution with the Green's function,
$$\hat{\mathbf{v}}_k^{\text{det}} = \hat{\mathbb{G}}_{\mathbf{k}} \hat{\mathbf{f}}_{\mathbf{k}}.$$

BD-q2D algorithm (II)

1. Generate a random fluid velocity with covariance $(2k_B T)\,\hat{\mathbb{G}}_{\mathbf{k}}$ in Fourier space,
$$\hat{\mathbf{v}}_k^{\text{stoch}} = \sqrt{\frac{2k_B T}{\eta \Delta t}} \left(\sqrt{g_k(k)}\,\mathbf{k}_{\perp} \mathcal{Z}_{\mathbf{k}}^{(2)} + \sqrt{f_k(k)}\,\mathbf{k} \mathcal{Z}_{\mathbf{k}}^{(1)} \right).$$
2. Use the FFT to compute $\mathbf{v}(\mathbf{r})$ from
$$\hat{\mathbf{v}}_k = \hat{\mathbf{v}}_k^{\text{det}} + \hat{\mathbf{v}}_k^{\text{stoch}}.$$
3. Convolve $\mathbf{v}(\mathbf{r})$ with a Gaussian in real space to compute particle velocities,
$$\mathbf{u}_i = \int \delta_a(\mathbf{q}_i - \mathbf{r})\,\mathbf{v}(\mathbf{r})\,d\mathbf{r}.$$
4. Advance the particles,
$$\mathbf{q}_i^{n+1} = \mathbf{q}_i^n + \mathbf{u}_i \Delta t.$$

Collective diffusion coefficient

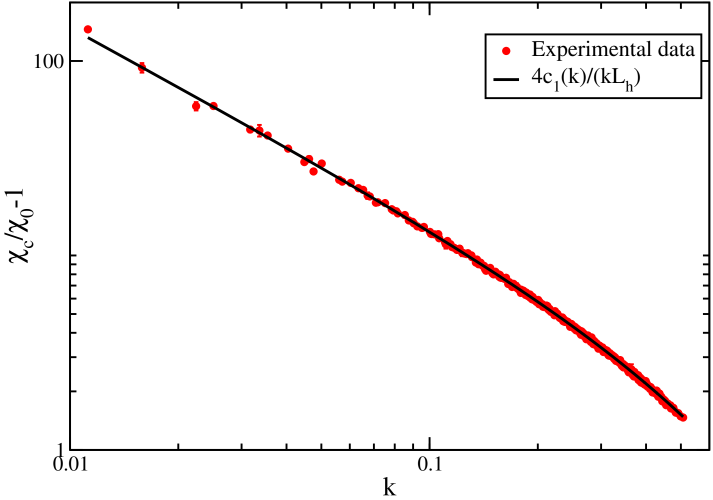


Figure: **Short time collective diffusion coefficient** in q2D obtained from the **dynamic structure factor** (autocorrelation function of the spatial FFT).

Relaxation of density bump (instance)

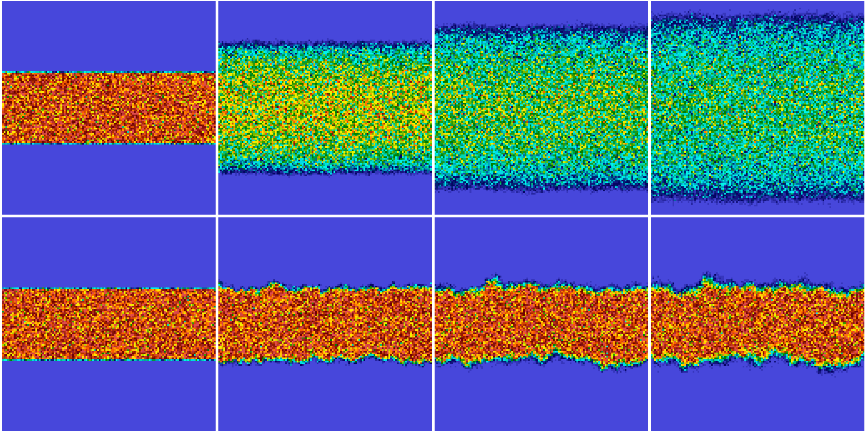


Figure: Expansion of clump in Quasi2D (top) and True2D (bottom). Compare fluctuations for classical diffusion **BD-noHI** to **True2D**.

Relaxation of density bump (mean)

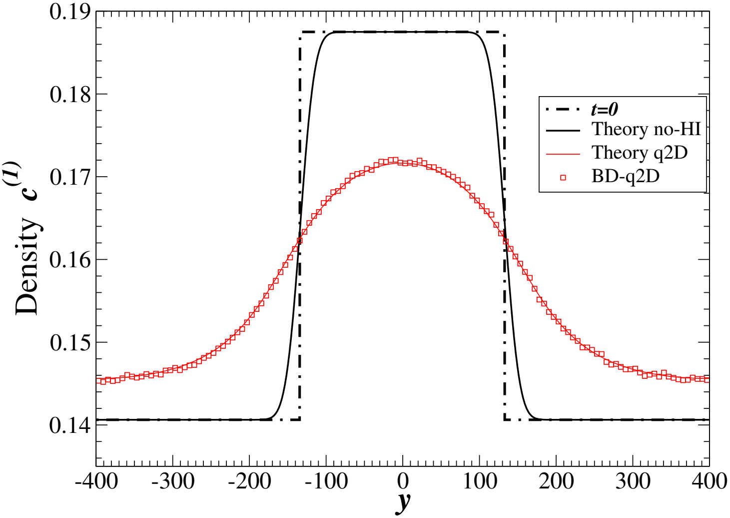


Figure: Comparison of ensemble average to (numerical) DDFT-HI.

Diffusion of tracers/color (theory)

- If we **color the particles** red and green, $c^{(1)} = c_R^{(1)} + c_G^{(1)}$, we expect:

$$\partial_t c_{R/G}^{(1)}(\mathbf{r},t) = \boldsymbol{\nabla}\cdot\left(\chi\boldsymbol{\nabla} c_{R/G}^{(1)}(\mathbf{r},t)\right) + (k_B T)$$

$$\boldsymbol{\nabla}\cdot\left(c_{R/G}^{(1)}(\mathbf{r},t)\int\mathcal{R}(\mathbf{r},\mathbf{r}')\,\boldsymbol{\nabla}'\left(c_R^{(1)}(\mathbf{r}',t)+c_G^{(1)}(\mathbf{r}',t)\right)\,d\mathbf{r}'\right)$$

- If we start the system with a uniform density, $c^{(1)} = c_R^{(1)} + c_G^{(1)} = c_0$, this will remain the case forever and we just get two uncoupled diffusion equations

$$\partial_t c_{R/G}^{(1)}(\mathbf{r},t) \;=\; \boldsymbol{\nabla}\cdot\left(\chi\boldsymbol{\nabla} c_{R/G}^{(1)}(\mathbf{r},t)\right).$$

- This means that **diffusive mixing** in q2D, is the same on average as for simple BD-noHI (uncorrelated Brownian walkers) and t2D. But the **fluctuations are different**.

Diffusive mixing (q2D vs t2D)

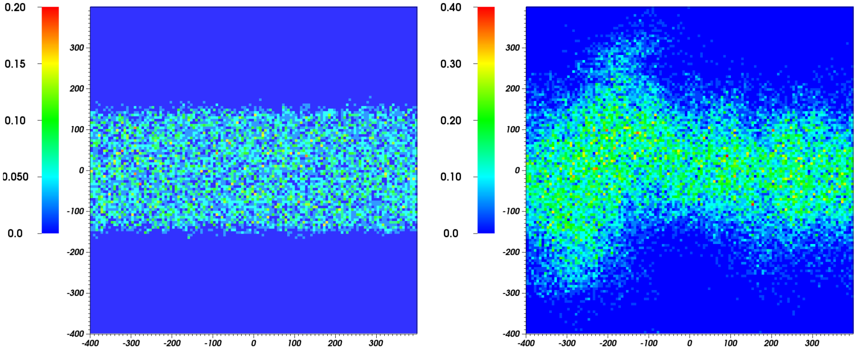


Figure: Color diffusion in q2D (left) versus t2D (right) (100K particles, $\phi \approx 1$).

Diffusive mixing (no-HI, q2D, and t2D)

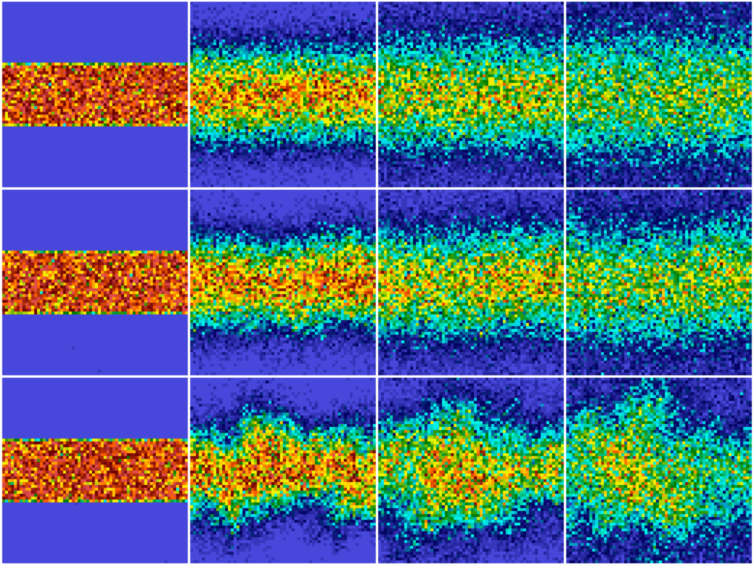
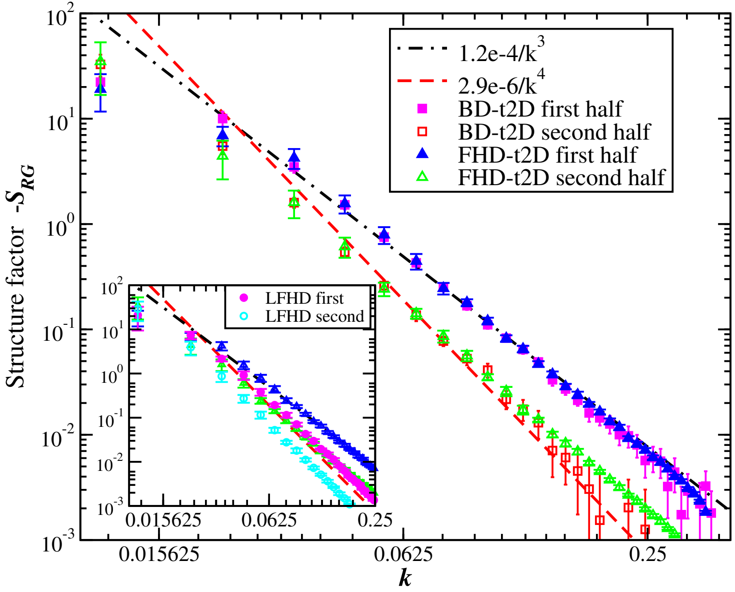
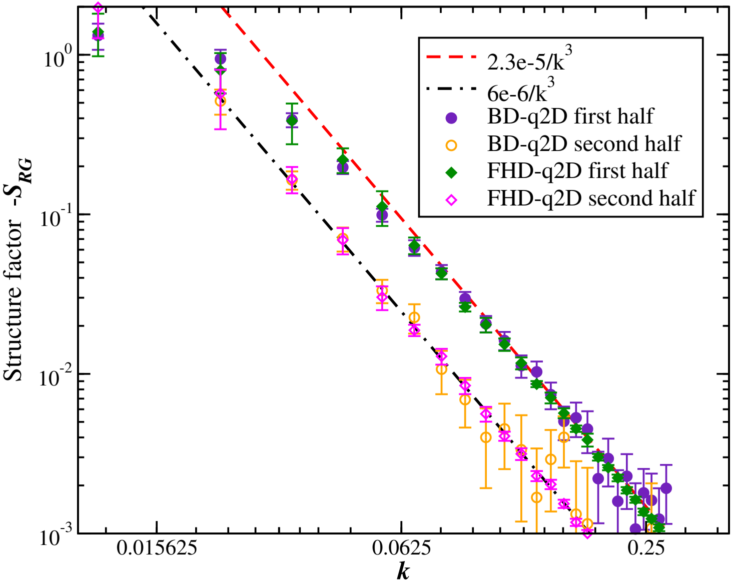


Figure: Diffusion of a perturbation of color (no-HI, q2D, and t2D)

Giant Color Fluctuations in t2D



Giant Color Fluctuations in q2D



Conclusions/questions

1. Diffusion is very strongly affected by **hydrodynamic correlations** and its nature depends heavily on the **geometry** of the fluid and the diffusion manifold.
2. In **true-2D** (diffusion in thin films) the mean obeys simple Fick's law at all scales but the fluctuations are giant.
3. In **quasi-2D** (diffusion on flat interfaces) the fluctuations are not giant but the mean does not obey Fick's law (at any scale?).
4. How are **lipid membranes** different: At what scales does the **Saffman kernel** work?
5. What is the **long-time collective diffusion coefficient** in q2D? Does a generalized Einstein-relation relating a "Fick" coefficient to collective mobility and isothermal compressibility hold?
6. How about diffusion of **colloids on a sphere**?

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