Brownian dynamics of colloids in quasi two-dimensional confinement

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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.
  An example are colloids confined to diffuse on a planar liquid-liquid interface. This has been studied before by Johannes Bleibel, Alvaro Domínguez, and collaborators [1].
- 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.
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

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

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

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

$$M_{ij}(\mathbf{Q}) \equiv M_{ij}(\mathbf{q}_i, \mathbf{q}_j) = \mathcal{R}(\mathbf{q}_i, \mathbf{q}_j),$$

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

The self-diffusion coefficient of a single isolated particle is

$$\chi(r) = (k_B T) \mathcal{R}(r, r).$$
Rotne-Prager-Yamakawa Tensor

To a leading-order approximation, strictly valid only for dilute suspensions, for spherical colloids of radius $a$ we have the Rotne-Prager-Yamakawa tensor

$$\mathcal{R}(r_1, r_2) = \mathcal{R}(r_1 - r_2) = \int \delta_a (r_1 - r') G(r', r'') \delta_a (r_2 - r'') \, dr' \, dr'',$$

where $G$ is the Green’s function for Stokes flow, and $\delta_a$ denotes a surface delta function on a sphere of radius $a$.

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

$$\mathcal{R}(r \gg a) \rightarrow G(r) = \frac{1}{8\pi r} \left( I + \frac{r \otimes r}{r^2} \right). \quad (2)$$

For 3D bulk suspensions,

$$\mathcal{R}(r) = \frac{1}{6\pi \eta a} \left( \frac{3a}{4r} + \frac{a^3}{2r^3} \right) I + \left( \frac{3a}{4r} - \frac{3a^3}{2r^3} \right) \frac{r \otimes r}{r^2}, \quad r > 2a$$
As explained a long time ago by Martin Maxey in the context of the **Force Coupling Method** (FCM), and also in the context of the immersed boundary method by us, one can replace the surface delta function \( \delta_a \) by a **smooth Gaussian kernel** with standard deviation \( \sigma = a/\sqrt{\pi} \) to give \( \chi = k_B T / (6\pi \eta a) \) [2].

This gives the **FCM kernel** that is just as good as RPY:

\[
\mathcal{R}(r) = f(r) I + g(r) \frac{r \otimes r}{r^2},
\]

where

\[
\begin{bmatrix}
  f(r) \\
  g(r)
\end{bmatrix} = \frac{1}{8\pi \eta r} \left( 1 + \begin{bmatrix}
  2 \\
  -6
\end{bmatrix} \frac{a^2}{\pi r^2} \right) \text{erf} \left( \frac{r \sqrt{\pi}}{2a} \right) - \frac{1}{8\pi \eta r} \begin{bmatrix}
  2 \\
  -6
\end{bmatrix} \frac{a}{\pi r} \exp \left( -\frac{\pi r^2}{4a^2} \right).
\]

The main advantage of FCM is that it allows for **very efficient** (linear time!) BD using the fluctuating FCM method [3, 4].
An important property of the 3D RPY and FCM kernel is that they are divergence free,
\[ \nabla \cdot \mathcal{R}_{3D}(\mathbf{r}) = 0, \]
which follows from the fact the 3D flow is incompressible, \( \nabla \cdot \mathcal{G}(\mathbf{r}) = 0 \), and implies that
\[ \partial_Q \cdot \mathbf{M} = 0. \]
This has very important physical consequences on collective diffusion.

The same applies for t2D systems as well,
\[ \nabla \cdot \mathcal{R}_{t2D}(\mathbf{r}) = 0, \]
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 \( q = (x, y) \) 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,
  \[ \nabla_{(x,y)} \cdot R_{q2D}(r) \neq 0, \]
  which means that there will be a nonzero \( \partial Q \cdot M \), and the diffusive dynamics will be very different from either 3D or t2D.
- Following Bleibel et al., to start take the Oseen tensor as the hydrodynamic kernel,
  \[ f(r \gg a) \approx g(r \gg a) \approx \frac{1}{8\pi \eta r}, \]
  which gives something that in the far field looks like a repulsive Coulomb force,
  \[ \frac{dq_i}{dt} = k_B T (\partial Q \cdot M)_i + \cdots = \sum_{j \neq i} \frac{k_B T}{8\pi \eta r} \cdot \frac{q_i - q_j}{\|q_i - q_j\|^2} + \cdots \]
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 $\mathbf{q}_i(t)$,

$$c(r,t) = \sum_{i=1}^{N} \delta(\mathbf{q}_i(t) - r),$$  \hspace{1cm} (3)

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

$$\partial_t c(r,t) = \nabla \cdot (\chi(r) \nabla c(r,t)) - \nabla \cdot (\mathbf{w}(r,t) c(r,t)) + \left( k_B T \right) \nabla \cdot \left( c(r,t) \int \mathcal{R}(r,r') \nabla' c(r',t) \, dr' \right).$$  \hspace{1cm} (4)

The Fickian term $\nabla \cdot (\chi(r) \nabla c(r,t))$ is not the whole story.

Fluctuations come via the random velocity field $\mathbf{w}$ defined later on...
The **nonlinear nonlocal hydrodynamic** term can be rewritten as

\[
\nabla \cdot \left( c(r, t) \int R(r, r') \nabla' c(r', t) \, dr' \right) = \\
- \nabla \cdot \left( c(r, t) \int (\nabla' \cdot R(r, r')) \, c(r', t) \, dr' \right).
\]

For 3D and t2D, \( \nabla \cdot R(r, r') = \nabla' \cdot R(r, r') = 0 \), and (4) becomes a **linear** stochastic equation that can easily be solved numerically [6].

Importantly, in 3D/t2D, we get Fick’s law even with HIs [6]:

\[
\partial_t c^{(1)}(r, t) = \nabla \cdot \left( \chi(r) \nabla c^{(1)}(r, t) \right),
\]

for the single-particle distribution function \( c^{(1)}(r, t) = \langle c(r, t) \rangle \).

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 $\nabla \cdot \mathcal{R}(r) \neq 0$ and it is long-ranged, giving
  \[ \partial_t c^{(1)}(r, t) = \nabla \cdot \left( \chi(r) \nabla c^{(1)}(r, t) \right) + (k_B T) \nabla \cdot \left( \int \mathcal{R}(r, r') \nabla' c^{(2)}(r, r', t) \, dr' \right), \]
  which is not closed, is nonlocal, and nonlinear.

- For an ideal gas, the standard closure for the two-particle correlation function is
  \[ c^{(2)}(r, r', t) \approx c^{(1)}(r, t) c^{(1)}(r', t), \]
  giving the approximation
  \[ \partial_t c^{(1)}(r, t) = \nabla \cdot \left( \chi(r) \nabla c^{(1)}(r, t) \right). \]
Consider the case of a spatially uniform system with concentration $c(r, t) = c_0 + \delta c(r, t)$, where $\delta c \ll c_0$.

If we linearize (4) around the uniform state and ignore fluctuations:

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

This equation can trivially be solved in Fourier space,

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

where $D_c(k)$ is the short-time collective diffusion coefficient [1],

$$D_c(k) = \chi \left( 1 + \frac{1}{kL_h} \right) = \chi + (k_B T) \frac{c_0}{4\eta k}.$$  \hspace{1cm} (7)

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.
Numerical Results

Collective diffusion coefficient

Dynamic structure factor in q2D

\(a=1, \eta=1, \Delta t=0.2, L=560.5, \phi=1.0\)

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

Relaxation of density bump (instance)

Figure: Relaxation of a density bump ($\Delta c = 1/3c_0$) in a stripe periodic configuration (100K particles, $\phi \approx 1$).
Numerical Results

Relaxation of density bump (mean)

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

Relaxation of density bump width

Figure: Second moment (variance) of $y$ position of particles, $\langle y^2 \rangle - \langle y \rangle^2$. 
Figure: Mean square displacement of particles at equilibrium: **long time** self-diffusion coefficient $\chi$ is smaller than short-time $\chi_0 = k_B T / (6\pi \eta a)$. 

$$D_0 = \frac{1}{6\pi \eta a}$$

$L = 560.5$
If we color the particles red and green, \( c^{(1)} = c^{(1)}_R + c^{(1)}_G \), we expect:

\[
\frac{\partial}{\partial t} c^{(1)}_{R/G} (r, t) = \nabla \cdot \left( \chi \nabla c^{(1)}_{R/G} (r, t) \right) + (k_B T) \nabla \cdot \left( c^{(1)}_{R/G} (r, t) \int \mathcal{R} (r, r') \nabla' \left( c^{(1)}_R (r', t) + c^{(1)}_G (r', t) \right) dr' \right)
\]

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

\[
\frac{\partial}{\partial t} c^{(1)}_{R/G} (r, t) = \nabla \cdot \left( \chi \nabla c^{(1)}_{R/G} (r, t) \right).
\]

This means that diffusive mixing in q2D, on average, looks the same as for simple BD-noHl (uncorrelated Brownian walkers) and t2D. But the wrinkle is that \( \chi \) depends on \( c_0 \) (albeit weakly), and fluctuations are different.
Figure: Comparison of ensemble average to two-color theory.
Figure: Color diffusion in q2D (left) versus t2D (right) (100K particles, $\phi \approx 1$).
Figure: Comparison of ensemble average to ordinary Brownian motion.
(not so) Giant Fluctuations

Figure: Not-so-giant fluctuations in q2D compared to **linearized FHD theory**.
By combining the Fluctuating Immersed Boundary (FIB) method [7] with the Fluctuating Force Coupling Method (FCM) [3] 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 $\kappa = (k, k_z)$,

$$\hat{R}_k = \frac{1}{2\pi} \int_{k_z} dk_z \frac{1}{\eta k^2} \left( I - \frac{\kappa \otimes \kappa}{k^2} \right) \exp \left( -\frac{a^2 k^2}{\pi} \right).$$

$$= \frac{1}{\eta k^3} \left( c_2 (ka) k_T \otimes k_T + c_1 (ka) k \otimes k^T \right). \quad (8)$$

where both $c_1$ and $c_2$ decay exponentially $\sim \exp (-a^2 k^2)$ in Fourier space (pseudospectral methods).
Comparison to true 2D

- For small $k$ we have the 2D projection of the t2D or q2D Oseen tensor,
  \[ c_1(K = ka \ll 1) \approx \frac{1}{4} \] for q2D, and 0 for t2D, and
  \[ c_2(K = ka \ll 1) \approx \frac{1}{2} \] for q2D, and $\frac{1}{k}$ for t2D.

- The short-time self diffusion coefficient $\chi_0 = f(k_B T/\eta)$,
  \[ f = \frac{1}{6\pi a} \cdot \frac{1}{1 + 4.41a/L} \approx \frac{1}{6\pi a} \] for q2D, and
  \[ f = \frac{1}{4\pi} \ln \left( \frac{L}{3.71a} \right) \] for t2D,
  and $L$ is the system size.
For an ideal gas we have the Ito BD equation:

$$dQ = (2k_B T M)^{1/2} dB + k_B T (\partial_Q \cdot M) \, dt,$$

(10)

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

$$\frac{dq_i}{dt} = w(q_i, t) + k_B T \left( a(q_i) + \sum_{j \neq i} b(q_i, q_j) \right),$$

(11)

where $a(r) = \nabla \cdot R(r, r) = \nabla \cdot \chi(r)$ and $b(r, r') = \nabla' \cdot R(r, r').$

For a translationally-invariant system $a = 0$, and for t2D $b = 0$.

Here $w(r, t)$ is a random velocity field that advects the particles. It is white in time and has a spatial covariance $\sim R$,

$$\langle w(r, t) \otimes w(r', t') \rangle = 2(k_B T) R(r, r') \delta(t - t').$$

(12)
The final BD equation is, with $\partial_i \delta_a (r) = \partial \delta_a (r) / \partial r_i$ [5],

$$
\frac{dq_i}{dt} = w(q_i, t) + \int \delta_a (q_i - r') \sum_j G (r', r'') \, dr' dr'' .
$$

(13)

$$
\left[ F_j \delta_a (q_j - r'') + (k_B T) (\partial \delta_a) (q_j - r'') \right] .
$$

For FCM the kernel $\delta_a$ is a Gaussian with $\sigma = a / \sqrt{\pi}$ [2],

$$
\hat{G}_k = \hat{R}_k \exp \left( \frac{a^2 k^2}{\pi} \right) = \frac{1}{\eta} \left[ g_k (k) k_- \otimes k_-^T + f_k (k) k \otimes k^T \right] .
$$
1. Evaluate particle forces $F^n = F(Q^n)$.

2. Compute in real space on a grid the fluid forcing

$$f(r) = \sum_i F_i \delta_a(q_i - r) + (k_B T) \sum_i (\partial \delta_a)(q_i - r).$$

and use the FFT to convert $f$ to Fourier space, $\hat{f}_k$.

3. Compute the fluid velocity resulting from fluid forcing $f$ in Fourier space as a convolution with the Green’s function,

$$\hat{v}_{k}^{\text{det}} = \hat{G}_k \hat{f}_k.$$
Brownian Dynamics in Q2D

BD-q2D algorithm (II)

1. Generate a random fluid velocity with covariance \((2k_B T) \hat{G}_k\) in Fourier space,

\[
\hat{v}_k^{\text{stoch}} = \sqrt{\frac{2k_B T}{\eta \Delta t}} \left( \sqrt{g_k(k)} k_{\perp} z_k^{(2)} + \sqrt{f_k(k)} k z_k^{(1)} \right).
\]

2. Use the FFT to compute \(v(r)\) from

\[
\hat{v}_k = \hat{v}_k^{\text{det}} + \hat{v}_k^{\text{stoch}}.
\]

3. Convolve \(v(r)\) with a Gaussian in real space to compute particle velocities,

\[
u_i = \int \delta_a(q_i - r) v(r) \, dr.
\]

4. Advance the particles,

\[
q_i^{n+1} = q_i^n + u_i \Delta t.
\]
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. **What is the long-time self diffusion coefficient in q2D?** Does Einstein’s relation \( \chi = (k_B T) \mu \) hold?

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?** Nontrivial to generalize the BD-q2D algorithm and new physics...
Johannes Bleibel, A Domínguez, F Günther, J Harting, and M Oettel.
Hydrodynamic interactions induce anomalous diffusion under partial confinement.

Localized force representations for particles sedimenting in Stokes flow.

Blaise Delmotte and Eric E Keaveny.
Simulating brownian suspensions with fluctuating hydrodynamics.

Rapid sampling of stochastic displacements in brownian dynamics simulations.
Software available at https://github.com/stochasticHydroTools/PSE.

A. Donev and E. Vanden-Eijnden.
Dynamic Density Functional Theory with hydrodynamic interactions and fluctuations.

A. Donev, T. G. Fai, and E. Vanden-Eijnden.
A reversible mesoscopic model of diffusion in liquids: from giant fluctuations to Fick’s law.

Brownian Dynamics without Green’s Functions.
Software available at https://github.com/stochasticHydroTools/FIB.