Theory of anomalous collective diffusion in colloidal monolayers on a spherical interface

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A planar colloidal monolayer exhibits anomalous collective diffusion due to the hydrodynamic interactions. We investigate how this behavior is affected by the curvature of the monolayer when it resides on the interface of a spherical droplet. It is found that the characteristic times of the dynamics still exhibit the same anomalous scaling as in the planar case. The spatial distribution, however, shows a difference due to the relevance of the radius of the droplet. Since for the droplet this is both a global magnitude, i.e., pertaining the spatial extent of the spherical surface, and a local one, i.e., the radius of curvature, the question remains open as to which of these two features actually dominates in the case of a generically curved interface.

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I. INTRODUCTION

The hydrodynamic interactions between the particles of a colloid, which are mediated by flows in the embedding ambient fluid, are very relevant for the dynamics of the colloid, see, e.g., Ref. [1]. The presence of near boundaries, like an interface, affect these interactions, and additionally introduce a new player with which the particles interact hydrodynamically. The theoretical study of these effects has a long history, see, e.g., Refs. [2–4] for the case of a planar interface between two coexisting fluids. More recently, one has considered the case when the interface has a richer rheological behavior, namely surface viscosity [5–8], elasticity [9], ultra–low surface tension [10], bending rigidity [11, 12], or when it is curved [13–15]. All these works study the case of a single particle and are primarily concerned with self–diffusion, i.e., the random motion of a tagged particle. Our goal is, however, the collective diffusion, that describes the decay of density perturbations. This is an intrinsically many–body problem, for which the hydrodynamic interaction between the particles (but modified by the presence of the interface) is most relevant. These are two distinct, albeit related concepts [1, 16].

Most works addressing the influence of the hydrodynamic interactions on the collective diffusion have dealt with the case of colloids in bulk, i.e., three–dimensionsal (3D) distributions of particles [16–18]. Recent investigations have considered confined configurations [19], e.g., two–dimensional (2D) distributions inside a fluid also confined to 2D, either between plates [20, 21] or as a film [22]. A particularly interesting case is a colloidal monolayer, produced when the particles are constrained to re-side on a fluid–fluid interface, see, e.g., Ref. [21]. It is a partially confined system in that the particle distribution is confined to a 2D manifold, but the ambient fluid is unconfined in 3D. Recent theoretical investigations, confirmed experimentally [25, 26], predicted that both the short–time [27] and the long–time [28] coefficient of collective diffusion for a planar monolayer diverge, i.e., the diffusive decay of a density perturbation in the monolayer can be described as anomalous due to the hydrodynamic interactions. This feature is specific to the configuration of partial confinement and is a direct consequence of the “dimensional mismatch” between the 2D colloidal sub–system and the 3D embedding fluid (see the discussion after Eq. (10)). Numerical simulations [29] suggest that this mismatch does not have, however, any dramatic effect on the coefficient of self–diffusion, which remains finite.

One may wonder how robust the anomalous collective diffusion is, and so recent works have explored this phenomenology when the simplifying assumptions of the original theoretical model are relaxed: one has considered the influence of the direct particle–particle interaction, e.g., as capillary monopoles [28], as hard spheres [30], or as Lennard–Jones particles [29]. One has also addressed the effect of the finite time it takes for the ambient flow to respond to the evolution of the colloidal monolayer [31], or the possibility, beyond the perfect confinement to a plane, that the particles move slightly in and out of the plane [29, 32]. Along the line of these investigations, the present work addresses how the role of the hydrodynamic interactions is affected when the monolayer is curved rather than perfectly flat.

The curvature of the interface can affect the diffusive dynamics and alter Fick’s law for Brownian diffusion qualitatively [33–35]. Even when this change is neglected, the analytical study of diffusion on a curved manifold poses its own mathematical problems, which one can try to manage by means of specific tools from the realm of differential geometry, see, e.g., Refs. [36, 37]. For the problem at hand, the issue is further complicated because

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For instance, a collection of independent, noninteracting particles (ideal gas) is a physical realization of an ensemble of isolated particles, so that the coefficient of collective diffusion coincides trivially with the coefficient of self–diffusion.
the determination of the hydrodynamic interactions requires solving the hydrodynamic equations for the ambient flow together with the boundary conditions imposed by a curved manifold. Thus, in this work we consider the simplest configuration of a perfectly spherical interface supporting the monolayer. This case is of actual relevance for the interpretation of experimental results, since the assembly of a monolayer at the surface of a spherical droplet is a quite common and relatively easy procedure. Furthermore, this case is amenable to a mathematical analysis allowing for the derivation of analytical solutions. A boundary condition on the normal component of the velocity vanishes (impenetrable interface),

\[ (I-e_r e_r) \cdot \mathbf{u}(r) = 0 \quad \text{as} \quad |r| \to \infty, \]

while, at the interface \( r = R e_r \), the normal component of the velocity vanishes (impenetrable interface),

\[ e_r \cdot \mathbf{u}(r = R^+ e_r) = e_r \cdot \mathbf{u}(r = R^- e_r) = 0, \]

the tangential component is continuous,

\[ (I-e_r e_r) \cdot \mathbf{u}(r = R^+ e_r) = (I-e_r e_r) \cdot \mathbf{u}(r = R^- e_r), \]

and the viscous stress \( \sigma = \eta [\nabla \mathbf{u} + (\nabla \mathbf{u})^\top] \) has a discontinuity in the tangential component,

\[ (I-e_r e_r) \cdot \{\sigma(r = R^+ e_r) - \sigma(r = R^- e_r)\} \cdot e_r = \eta \nabla \cdot \mathbf{u}. \]

This expresses a force balance condition, like Eq. 7, but localized at the interface. It describes the shear flow driven by the Brownian motion in the monolayer. A boundary condition on the normal component of the stress is not necessary to solve the problem; it only plays a role in order to determine the local forces necessary to maintain the surface of the droplet undeformed in spite of the presence of the particles and the ambient fluid. In real experiments, this constraint is usually achieved by the surface tension due to its large value in typical systems.

The model just presented provides a coarse-grained description of the large scale evolution of the particle distribution. It includes implicitly the microscopic details pertaining the shape and size of the particles as well as their

\[ \mu = \frac{v}{kT} \ln \delta, \]

\[ \eta \nabla^2 \mathbf{u} - \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0, \]

where \( \Gamma \) is the mobility. With the ideal gas approximation, the first term in Eq. 3 yields Fick’s law of Brownian diffusion on the interface with the surface diffusivity \( D = \Gamma kT \) \( [33] \). (Notice that, because the spherical interface is assumed impenetrable, the component of the ambient flow \( \mathbf{u} \) normal to it vanishes, see Eq. 7 below, so that the field \( \mathbf{v}_\parallel \) constructed according to this prescription is indeed tangential.)

To provide a complete model, the ambient flow \( \mathbf{u}(r) \) driven by the dynamics in the monolayer has to be determined. Unlike the monolayer fields \( \phi(r = Re_r) \) and \( \mathbf{v}_\parallel(r = Re_r) \), the field \( \mathbf{u}(r) \) is defined everywhere in space. For colloids, it is a good approximation \( 1 \) to use the Stokes equations describing creeping flow (small Reynolds and Mach numbers),

\[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla \mathbf{p} + \frac{1}{\rho} \nabla \cdot \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_r}{\partial t} = \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_\phi}{\partial t} = \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_z}{\partial t} = \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \delta \mathbf{E} \]

(2)

\[ \frac{\partial \mathbf{e}_r}{\partial t} = \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_\phi}{\partial t} = \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_z}{\partial t} = \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \delta \mathbf{E} \]

(3)

\[ \frac{\partial \mathbf{e}_r}{\partial t} = \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_r \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_\phi}{\partial t} = \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_\phi \cdot \nabla) \delta \mathbf{E} \]

\[ \frac{\partial \mathbf{e}_z}{\partial t} = \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \mathbf{p} - \frac{1}{\rho} (\mathbf{e}_z \cdot \nabla) \delta \mathbf{E} \]

(4)

**II. THEORETICAL MODEL**

We consider a collection of colloidal particles trapped at the fluid interface of a spherical droplet at rest. The radius of the droplet will be denoted by \( R \), while \( \eta_1 \) and \( \eta_2 \) represent the dynamic viscosities of the fluids outside and inside of the droplet, respectively. We take spherical coordinates \((r, \theta, \phi)\) with origin at the center of the droplet, so that \( e_r \) denotes the unit vector normal to the particle monolayer dwelling on the fluid interface; consequently, the dyadic \( I - e_r e_r \) denotes the projector onto the plane tangent to it (with \( I \) the unit tensor), and

\[ \nabla_\parallel := (I - e_r e_r) \cdot \nabla|_{r=R} = e_\theta \frac{\partial}{R} \frac{\partial}{\partial \theta} + e_\phi \frac{\partial}{R \sin \theta} \frac{\partial}{\partial \phi}, \]

is the nabla operator on the spherical surface.

The areal number density of particles in the monolayer is described by the field \( \phi(r = Re_r, \theta, \phi, t) \) defined on the spherical surface. It obeys the continuity equation on static curved surfaces \( [33] \),

\[ \frac{\partial \phi}{\partial t} = -\nabla_\parallel \cdot (\phi \mathbf{v}_\parallel). \]

Here \( \mathbf{v}_\parallel \) is the velocity field of the monolayer, defined likewise on the spherical interface and tangential to it. We restrict ourselves to long scales such that the overdamped approximation holds \( 1 \). The flow of the monolayer is driven by the gradient of the chemical potential \( \mu(\phi) \) (the “thermodynamic” force) \( [10] [26] \), and by the drag by the ambient flow \( \mathbf{u}(r) \) induced in the surrounding fluids,

\[ \mathbf{v}_\parallel = -\Gamma \nabla_\parallel \mu + \mathbf{u}(r \in \text{monolayer}), \]

where \( \Gamma \) is the mobility. With the ideal gas approximation,

\[ \mu = -kT \ln \delta \]
interactions — with each other and with the fluids and the interface. But it considers both the simplest intrinsic dynamics of the colloid (free Brownian motion) and the simplest form of hydrodynamic interactions (macroscopic drag), which can be actually termed mean–field-like. An approach valid for a sufficiently dilute monolayer and is mediated by the force acting on the monolayer (see Eq. (9)), the particle number density $\rho$ of the particle number density $[41, 42]$. The model rheological parameters, like the mobility $\Gamma$, as a density–dependent renormalization of the value of the potential $\mu$ modelled in the point–particle approximation: each particle is passively dragged (see Eq. (3)) by the ambient flow $\mathbf{u}$ created by the force acting on the monolayer (see Eq. (9)), an approach valid for a sufficiently dilute monolayer and which can be actually termed mean–field–like.

All these approximations could be relaxed at the expense of mathematical simplicity. Rheological properties of the interface can be incorporated in different ways; for instance, surface viscosity would appear as an additional term (Boussinesq–Scriven) in Eq. (9). The interfacial curvature can alter Fick’s law in several ways: from a simple renormalization of the diffusion coefficient (e.g., by thermally activated fluctuations in the interfacial curvature) to a scale–dependent diffusion coefficient (e.g., by changes in the local curvature on the microscopic scale of the monolayer). In the extreme case, even the form of Fick’s law could cease to be valid, with changes depending on the precise microscopic physics ruling the system. The direct interactions are negligible in the dilute limit but they can be easily incorporated into the model through the density dependence of the chemical potential $\mu(\rho)$ in Eq. (3). This shows up eventually as a density–dependent diffusion coefficient, which however does not affect the anomalous diffusion phenomenology described by the linearized equation below. Similarly, short–distance corrections to the hydrodynamic interaction due to near–neighbours could be incorporated as a density–dependent renormalization of the value of the model rheological parameters, like the mobility $\Gamma$.

### A. Linearization

Equations (2)–(9) determine completely the evolution of the particle number density $\rho$ in the surface of the droplet. In order to proceed further, let us assume small deviations from a homogeneous state, $\rho(\mathbf{r}) = \rho_0 + \delta \rho(\mathbf{r})$ with $|\delta \rho| \to 0$, and linearize Eq. (2) (all the other equations are already linear):

$$\frac{\partial \delta \rho}{\partial t} \approx D \nabla^2 \delta \rho - \rho_0 \nabla \cdot \mathbf{u},$$

(10)

This equation still captures the effect both of diffusion by Brownian motion and of the hydrodynamic interactions between different parts of the monolayer. Notice that, although $\mathbf{u}(\mathbf{r})$ as a 3D field represents an incompressible flow, see Eq. (5), its restriction to the 2D monolayer will be compressible in general, so that $\nabla \cdot \mathbf{u}(\mathbf{r} \in \text{monolayer}) \neq 0$. Together with the long-range decay of the velocity field given by Eq. (5), this “dimensional mismatch” is the ultimate origin of the anomalous diffusion.

The departure from previous works dealing with this physical problem is that the monolayer is now a curved manifold. In this particular case, the mathematical problem can be addressed by expanding the fields defined on the spherical surface in spherical harmonics $Y_{lm}^m(\theta, \phi)$ (see App. A) the superscript * denotes complex conjugation:

$$\rho_l^m := \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \ Y_{lm}^m(\theta, \phi) \delta \rho(\theta, \phi).$$

(11)

Therefore, equations (5)–(10) lead to (see App. A)

$$\frac{\partial \rho_{l}^{m}}{\partial t} = -D_{l} \frac{\ell (\ell + 1)}{R^2} \rho_{l}^{m},$$

(12)

with an effective, $\ell$–dependent diffusion coefficient

$$D_{l} := D \left[1 + \frac{R}{(\ell + 1/2) L_{\text{hydro}}} \right],$$

(13)

expressed in terms of the characteristic length

$$L_{\text{hydro}} := \frac{4 \eta_{+} D}{kT \rho_0},$$

(14)

which was introduced in Ref. [28], where $\eta_{+} := (\eta_1 + \eta_2)/2$ is the average viscosity. (See App. B for a comparison with the equation for a planar monolayer). The solution of Eq. (12) is straightforward,

$$\rho_{l}^{m}(t) = \rho_{l}^{m}(0) e^{-t/\tau_{l}},$$

(15)

where we have defined the time scales

$$\tau_{l} := \frac{R^2}{\ell (\ell + 1) D_{l}} = \tau_{l}^{(\text{norm})} \left[1 + \frac{R}{(\ell + 1/2) L_{\text{hydro}}} \right]^{-1},$$

(16)

$$\tau_{l}^{(\text{norm})} := \frac{R^2}{\ell (\ell + 1) D}.$$  

(17)

In the absence of hydrodynamic interactions, i.e., normal diffusion, it would be $\tau_{l} = \tau_{l}^{(\text{norm})}$ (notice that $R^2/D$ is a more detailed discussion.
the characteristic time for Brownian motion over the size of the spherical surface).

The Green function $G$ of Eq. (10) is defined by the relationship

$$\delta \rho(\theta, \phi, t) = \int_0^\pi d\theta' \sin \theta' \int_0^{2\pi} d\phi' \delta(\theta', \phi', 0) G(\theta, \phi; \theta', \phi'; t)$$

From the solution [15], one can obtain (see App. C)

$$G(\theta, \phi; \theta', \phi'; t) = \sum_{\ell=0}^\infty \frac{2\ell + 1}{4\pi} P_\ell(\cos \alpha) e^{-t/\tau_\ell}$$

where $\alpha$ is the angle between the directions given by the pairs $(\theta, \phi)$ and $(\theta', \phi')$, see Fig. 1.

III. DISCUSSION

The effect of the hydrodynamic interactions is already patent in a comparative plot of the Green function, which formally represents the diffusion of an initially concentrated distribution, $\delta \rho(\theta, \phi, t = 0) = (\sin \theta)^{-1} \delta(\theta) \delta(\phi)$, see Fig. 2. Qualitatively, one observes that the decay in time toward the equilibrium, homogeneous distribution is faster and the spread in space is broader when the hydrodynamic interaction is accounted for.

To be more precise, in the limit $R \ll L_{\text{hydro}}$, the time scale defined by Eq. (16) behaves as $\tau_\ell \approx \tau_\ell^{(\text{norm})}$ for any value of $\ell$, so that the effect of the hydrodynamic interactions is unnoticeable. In the opposite limit $R \gg L_{\text{hydro}}$, however, it is

$$\frac{\tau_\ell}{\tau_\ell^{(\text{norm})}} \approx \left( \ell + \frac{1}{2} \right) \frac{L_{\text{hydro}}}{R^2}$$

so that the characteristic times are drastically reduced for the many large-scale modes satisfying $\ell \lesssim R/L_{\text{hydro}}$. This “acceleration” of the dynamical evolution induced by the hydrodynamic interactions is a feature shared with the phenomenology in a planar monolayer; the scaling $\tau_\ell \sim 1/\ell$, rather than $\tau_\ell \sim 1/\ell^2$ (see Eqs. (16, 17)) justifies the denomination of “anomalous diffusion” (”superdiffusion”, to be more precise). Also common is the meaning of the scale $L_{\text{hydro}}$ as a crossover length for the observation of anomalous diffusion.

Differences arise, however, between both cases (planar and spherical monolayer) regarding the spatial structure. A useful diagnostic tool is the average of the Legendre polynomials,

$$\langle P_\ell(\cos \theta) \rangle = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi P_\ell(\cos \theta) G(\theta, \phi; 0, 0, t),$$

which provide a measure of how the density distribution initially concentrated at the pole of the sphere spreads over its surface. By using the orthonormality properties of the Legendre polynomials, it follows from Eq. (19) that

$$\langle P_\ell(\cos \theta) \rangle = e^{-t/\tau_{\ell}}.$$  

(22)

Particularly interesting is the quantity [37]

$$\langle R^2 \sin^2 \theta \rangle = \frac{2}{3} R^2 \left[ \langle P_0(\cos \theta) \rangle - \langle P_2(\cos \theta) \rangle \right]$$

$$= \frac{2}{3} R^2 \left[ 1 - e^{-t/\tau_2} \right],$$

(23)

closely related to the second moment of the density distribution. It provides a measurement of the lateral extension of the diffusing cloud ($R \sin \theta$ is the size projected onto the equatorial plane $\theta = \pi/2$). In the case of normal diffusion in the plane, the second moment grows linearly in time. This is at variance with the behavior when the hydrodynamic interactions are considered: for an unbounded planar monolayer, the Green function exhibits a tail $\propto r^{-3}$ with in-plane distance $r$ regardless of the value of the characteristic length $L_{\text{hydro}}$ (see App. B). This is

FIG. 1. Definition of the angle $\alpha$ used in Eq. (19).

FIG. 2. Plot of the Green function, Eq. (19), at different times when the hydrodynamic interactions are considered (thick lines) or not (dashed lines). The vertical axis is in logarithmic scale.
ultimately a consequence of the long–ranged nature of the induced ambient flow and implies that the average $\langle r^2 \rangle$ is formally infinite. To make sense of this magnitude requires a regularization by means of a large–distance cutoff, e.g., as a finite size of the system or by relaxing the assumption of instantaneous build–up of the hydrodynamic interactions [31, 43]. This behavior is altered significantly, however, when the interface is spherical. In order to obtain a meaningful comparison, consider the short time expansion of Eq. (23), when the difference between the projected extension $R \sin \theta$ of the particle cloud and the “true” (geodesic) extension $r = R \theta$ is expected to be statistically irrelevant [37]:

$$\langle R^2 \sin^2 \theta \rangle \approx \frac{2R^2 t}{3\tau_2} = 4D_2 t \quad (t \to 0). \quad (24)$$

This average is well defined and actually behaves the same as in normal diffusion in a plane. The hydrodynamic interactions only show up in that the diffusion coefficient $D_2$ is renormalized, see Eq. (13). And so, when $R \ll L_{\text{hydro}}$, the hydrodynamic interactions are irrelevant, $D_2 \approx D$, and any mention to the radius $R$ drops from the expression (23). In the opposite limit $R \gg L_{\text{hydro}}$, the diffusion coefficient does depend on the parameter $R$: it is much larger, $D_2 = (2R/5L_{\text{hydro}})D \gg D$, but still finite, diverging formally only in the limit $R \to \infty$. Since $R$ quantifies both the local curvature of the interface and its global extension, there remains the ambiguity whether $R \to \infty$ should be better interpreted as either the flat interface limit or the unbounded interface limit.

In summary, the dramatic reduction of the diffusion times on scales above a certain characteristic length $L_{\text{hydro}}$ observed in a flat monolayer is preserved for a spherical monolayer. In this sense, the collective diffusion in the spherical configuration can be also qualified as anomalous. The radius of the spherical interface enters as a natural cutoff that renders the second moment (23) (and, actually, any other higher–order moment of the density distribution) finite. The spherical configuration, however, is very particular in that the radius is a quantity pertaining both the global structure of the surface, namely its finite size, and its local curvature, and it is not clear how to disentangle the influence of the respective features. Thus, there still remains unanswered the question about which feature is actually more determinant: could an unbounded, but locally curved surface disrupt the effect of the hydrodynamic interactions that leads to anomalous diffusion?

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**Appendix A: Spherical harmonics**

We use the standard definition of the spherical harmonics,

$$Y_\ell^m(\theta, \phi) := \sqrt{\frac{2\ell + 1}{4\pi} \frac{\ell - |m|}{\ell + |m|}} P_\ell^{|m|} (\cos \theta) e^{im\phi}, \quad (A1)$$

in terms of the associated Legendre functions of the first kind, $P_\ell^{|m|}$, with $\ell$ a positive integer and $m$ an integer such that $|m| \leq \ell$. These functions are a complete, orthonormal basis for functions defined on the surface of a sphere and verify

$$\nabla_\parallel^2 Y_\ell^m = -\frac{\ell(\ell + 1)}{R^2} Y_\ell^m. \quad (A2)$$

The linear boundary–value problem given by Eqs. [5–9] can be solved easily with the help of the spherical harmonics. This is precisely the same problem studied recently in Ref. [44]: our Eqs. [5–9] become equations (1-4) of Ref. [44] upon identifying $\nabla_r \sigma \leftrightarrow \nabla_\parallel \mu$. The solution to Eq. (6) can be written as an expansion in spherical harmonics, with different expansion coefficients inside and outside of the spherical interface. The boundary conditions (7–9) at the interface provide relationships between the coefficients inside and outside. Finally, the boundary condition (6) and the additional condition that the velocity field must be regular everywhere (in particular, at the origin $r = 0$ of the coordinate system) determine the value of these coefficients uniquely. We only need the velocity field evaluated at points of the monolayer, which is given by Eq. (12) in Ref. [14]: in our notation, it is

$$\mathbf{u}(\mathbf{r} = \text{Re}_r(\theta, \phi)) = -\frac{kT \tau_+}{2\eta_+} \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} \frac{\rho_\ell^m}{2\ell + 1} \nabla_\parallel Y_\ell^m(\theta, \phi) \quad (A3)$$

in terms of the average viscosity $\eta_+ := (\eta_1 + \eta_2)/2$. The use of Eq. (A2) renders expression $\nabla_\parallel \cdot \mathbf{u}(\mathbf{r} = \text{Re}_r)$ in Eq. (10) into an expansion in spherical harmonics, from which Eq. (12) follows straightforwardly.

**Appendix B: The planar monolayer**

For an unbounded, planar monolayer, one introduces the 2D Fourier transform of a density perturbation,

$$\rho(\mathbf{k}) = \int d^2 r \ e^{-i \mathbf{k} \cdot \mathbf{r}} \delta(\mathbf{r}), \quad (B1)$$

where $\mathbf{r} = (x, y)$ is a point of the monolayer plane $z = 0$. This quantity obeys the dynamical equation [28]

$$\frac{\partial \rho(\mathbf{k})}{\partial t} = -D_k^{(\text{flat})} k^2 \rho(\mathbf{k}), \quad (B2)$$

with the diffusion coefficient

$$D_k^{(\text{flat})} := D \left[ 1 + \frac{1}{L_{\text{hydro}}^2 \overline{k}} \right]. \quad (B3)$$
The comparison with Eqs. (12) and (13) shows that for the small-scale modes ($\ell \gg 1$), they reduce to the planar case with the identification $k \leftrightarrow \ell/R$. The large-scale modes are sensitive to the curvature of the spherical interface and differences between both cases arise.

An analytic expression for the Green function in the planar case, defined analogously to Eq. (18), can be obtained in the limit $r \gg L_{\text{hydro}}$ [20],

$$G(r,t) \approx \frac{1}{2\pi} \left( \frac{L_{\text{hydro}}}{Dt} \right)^2 \left[ 1 + \left( \frac{rL_{\text{hydro}}}{Dt} \right)^2 \right]^{-3/2}.$$ (B4)

As a consequence of the slow $1/r^3$ asymptotic decay, the second moment of the Green function,

$$\langle \nu^2 \rangle = \int d^2r \, r^2 G(r,t),$$ (B5)

is undefined in an unbounded monolayer.

Appendix C: The Green function

The solution [15] allows one to write the time-evolved density field as

$$\delta \rho(\theta, \phi, t) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \rho_{\ell} m(0) \, e^{-t/\tau} Y_{\ell}^m(\theta, \phi)$$

$$\langle \nu^2 \rangle = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-t/\tau} Y_{\ell}^m(\theta, \phi) \times \int_{0}^{\pi} d\theta' \sin \theta' \int_{0}^{2\pi} d\phi' \, Y_{\ell}^m(\theta', \phi') \delta \rho(\theta', \phi', 0).$$  (C1)

In this manner, Eq. (C2) is simplified to Eq. (19).

$$G(\theta, \phi; \theta', \phi'; t) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-t/\tau} Y_{\ell}^m(\theta, \phi) Y_{\ell}^m(\theta', \phi').$$ (C2)

This can be simplified further by using the definition of the spherical harmonics, Eq. (A1), and by applying the addition theorem [15].

$$P_{\ell}(\cos \alpha) = P_{\ell}(\cos \theta) P_{\ell}(\cos \theta')$$

$$+ 2 \sum_{m=1}^{\ell} \frac{(\ell - m)!}{(\ell + m)!} P_{\ell}^m(\cos \theta) P_{\ell}^m(\cos \theta') \cos m(\phi - \phi'),$$  (C3)

where the angle $\alpha$ (see Fig. 1) satisfies

$$\cos \alpha = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi').$$ (C4)

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