

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

Alvaro Domínguez*

Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Apdo. 1065, 41080 Sevilla, Spain



(Received 9 November 2017; published 12 February 2018)

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 to 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.

DOI: [10.1103/PhysRevE.97.022607](https://doi.org/10.1103/PhysRevE.97.022607)

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], ultralow 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

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-dimensional (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 [20–22] or as a film [23]. A particularly interesting case is a colloidal monolayer, produced when the particles are constrained to reside on a fluid-fluid interface (see, e.g., Ref. [24]). 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 subsystem 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 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

*dominguez@us.es

¹For 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 [1].

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 results. On the minus side, this configuration is very simple and some questions regarding the influence of curvature on the hydrodynamic interactions remain open. In Sec. II, we introduce and solve the simplest model that exhibits the phenomenology of interest, namely, the interplay between the intrinsic dynamics of the colloid and the hydrodynamic interactions mediated by the ambient fluids. The discussion of the results and the conclusions are presented in Sec. III.

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 η_1 and η_2 represent the dynamic viscosities of the fluids outside and inside of the droplet, respectively. We take spherical coordinates (r, θ, ϕ) with origin at the center of the droplet, so that \mathbf{e}_r denotes the unit vector normal to the particle monolayer dwelling on the fluid interface; consequently, the dyadic $\mathcal{I} - \mathbf{e}_r \mathbf{e}_r$ denotes the projector onto the plane tangent to it (with \mathcal{I} the unit tensor), and

$$\nabla_{\parallel} := (\mathcal{I} - \mathbf{e}_r \mathbf{e}_r) \cdot \nabla|_{r=R} = \frac{\mathbf{e}_{\theta}}{R} \frac{\partial}{\partial \theta} + \frac{\mathbf{e}_{\phi}}{R \sin \theta} \frac{\partial}{\partial \phi} \quad (1)$$

is the nabla operator on the spherical surface.

The areal number density of particles in the monolayer is described by the field $\varrho(\mathbf{r} = R\mathbf{e}_r(\theta, \phi), t)$ defined on the spherical interface. It obeys the continuity equation on static curved surfaces [38],

$$\frac{\partial \varrho}{\partial t} = -\nabla_{\parallel} \cdot (\varrho \mathbf{v}_{\parallel}). \quad (2)$$

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 time scales such that the overdamped approximation holds [1]. The flow of the monolayer is driven by the gradient of the chemical potential $\mu(\varrho)$ (the ‘‘thermodynamic’’ force) [16,26], and by the drag by the ambient flow $\mathbf{u}(\mathbf{r})$ induced in the surrounding fluids,

$$\mathbf{v}_{\parallel} = -\Gamma \nabla_{\parallel} \mu + \mathbf{u}(\mathbf{r} \in \text{monolayer}), \quad (3)$$

where Γ is the mobility. With the ideal gas approximation,

$$\mu = -kT \ln \varrho \quad (4)$$

(here, k is Boltzmann’s constant and T is the temperature of the system), 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 $\mathbf{u}(\mathbf{r})$ driven by the dynamics in the monolayer has to be determined. Unlike the monolayer fields $\varrho(\mathbf{r} = R\mathbf{e}_r)$ and $\mathbf{v}_{\parallel}(\mathbf{r} = R\mathbf{e}_r)$, the field $\mathbf{u}(\mathbf{r})$ 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),

$$\eta \nabla^2 \mathbf{u} - \nabla p = 0, \quad \nabla \cdot \mathbf{u} = 0, \quad (5)$$

where p is the pressure field enforcing the incompressibility constraint, and the viscosity η takes the value η_1 or η_2 , depending on where the equations are considered, i.e., outside or inside of the spherical interface. These equations have to be complemented by the appropriate boundary conditions. Thus, the velocity is assumed to vanish at infinity (i.e., no externally driven flows),

$$\mathbf{u}(\mathbf{r}) \rightarrow 0 \quad \text{as} \quad |\mathbf{r}| \rightarrow \infty, \quad (6)$$

while, at the interface $\mathbf{r} = R\mathbf{e}_r$, the normal component of the velocity vanishes (impenetrable interface),

$$\mathbf{e}_r \cdot \mathbf{u}(\mathbf{r} = R^-\mathbf{e}_r) = \mathbf{e}_r \cdot \mathbf{u}(\mathbf{r} = R^+\mathbf{e}_r) = 0, \quad (7)$$

the tangential component is continuous,

$$(\mathcal{I} - \mathbf{e}_r \mathbf{e}_r) \cdot \mathbf{u}(\mathbf{r} = R^+\mathbf{e}_r) = (\mathcal{I} - \mathbf{e}_r \mathbf{e}_r) \cdot \mathbf{u}(\mathbf{r} = R^-\mathbf{e}_r), \quad (8)$$

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

$$(\mathcal{I} - \mathbf{e}_r \mathbf{e}_r) \cdot \{\sigma(\mathbf{r} = R^+\mathbf{e}_r) - \sigma(\mathbf{r} = R^-\mathbf{e}_r)\} \cdot \mathbf{e}_r = \varrho \nabla_{\parallel} \mu. \quad (9)$$

This expresses a force balance condition, like Eq. (5) 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 interfaces.²

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 to the shape and size of the particles as well as their 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 come in with a number of simplifications [26]. First, the model leaves complex rheological properties of the interface out of consideration; it behaves simply as a passive constraint on the particles forcing them to remain attached to it. Second, the model also neglects possible modifications of Fick’s law altogether due to the curvature of the monolayer. Third, the direct interaction between the particles—electric and dispersion forces, hard-core effects, etc., are disregarded. The only possible interparticle forces are transmitted by the ambient fluid, and this hydrodynamic interaction is finally modeled 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

²See, e.g., Ref. [39, Supplemental Material] for a detailed discussion of the case of small capillary number.

Eq. (9)], an approach valid for a sufficiently dilute monolayer and which can be actually termed mean-field-like.³

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 [40]) to a scale-dependent diffusion coefficient (e.g., by changes in the local curvature on the microscopic scale of the monolayer [35]). 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 [34]. 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 $\mu(\varrho)$ 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 (10) below. Similarly, short-distance corrections to the hydrodynamic interaction due to near neighbors could be incorporated as a density-dependent renormalization of the value of the model rheological parameters, like the mobility Γ [41,42].

Linearization

Equations (2)–(9) determine completely the evolution of the particle number density ϱ in the surface of the droplet. In order to proceed further, let us assume small deviations from a homogeneous state, $\varrho(\mathbf{r}) = \varrho_0 + \delta\varrho(\mathbf{r})$ with $|\delta\varrho| \rightarrow 0$, and linearize Eq. (2) (all the other equations are already linear):

$$\frac{\partial \delta\varrho}{\partial t} \approx D \nabla_{\parallel}^2 \delta\varrho - \varrho_0 \nabla_{\parallel} \cdot \mathbf{u}. \quad (10)$$

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 $\nabla_{\parallel} \cdot \mathbf{u}(\mathbf{r} \in \text{monolayer}) \neq 0$. 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 $Y_{\ell}^m(\theta, \phi)$ (see Appendix A; the

superscript * denotes complex conjugation):

$$\rho_{\ell}^m := \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\phi Y_{\ell}^{m*}(\theta, \phi) \delta\varrho(\theta, \phi). \quad (11)$$

Therefore, Eqs. (5)–(10) lead to (see Appendix A)

$$\frac{\partial \rho_{\ell}^m}{\partial t} = -D_{\ell} \frac{\ell(\ell+1)}{R^2} \rho_{\ell}^m, \quad (12)$$

with an effective, ℓ -dependent diffusion coefficient

$$D_{\ell} := D \left[1 + \frac{R}{(\ell+1/2)L_{\text{hydro}}} \right], \quad (13)$$

expressed in terms of the characteristic length

$$L_{\text{hydro}} := \frac{4\eta_+ D}{kT\varrho_0}, \quad (14)$$

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

$$\rho_{\ell}^m(t) = \rho_{\ell}^m(0) e^{-t/\tau_{\ell}}, \quad (15)$$

where we have defined the time scales

$$\tau_{\ell} := \frac{R^2}{\ell(\ell+1)D_{\ell}} = \tau_{\ell}^{(\text{norm})} \left[1 + \frac{R}{(\ell+1/2)L_{\text{hydro}}} \right]^{-1}, \quad (16)$$

$$\tau_{\ell}^{(\text{norm})} := \frac{R^2}{\ell(\ell+1)D}. \quad (17)$$

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

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

$$\begin{aligned} \delta\varrho(\theta, \phi, t) &= \int_0^{\pi} d\theta' \sin \theta' \int_0^{2\pi} d\phi' \delta\varrho(\theta', \phi', 0) G(\theta, \phi; \theta', \phi'; t). \end{aligned} \quad (18)$$

From the solution (15), one can obtain (see Appendix C)

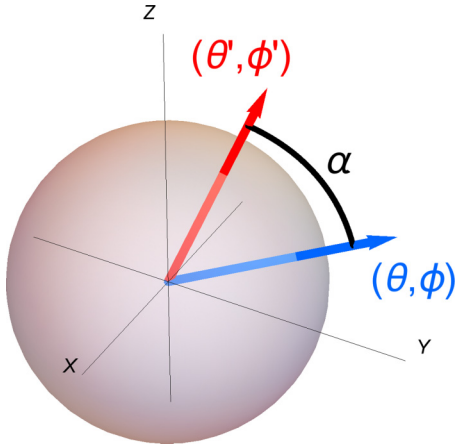
$$G(\theta, \phi; \theta', \phi'; t) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{4\pi} P_{\ell}(\cos \alpha) e^{-t/\tau_{\ell}}, \quad (19)$$

where α is the angle between the directions given by the pairs (θ, ϕ) and (θ', ϕ') (see Fig. 1).

III. DISCUSSION

The effect of the hydrodynamic interactions is already patent in a comparative plot of the Green's function, which formally represents the diffusion of an initially concentrated distribution, $\delta\varrho(\theta, \phi, t=0) = (\sin \theta)^{-1} \delta(\theta) \delta(\phi)$ (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.

³More precisely, the ambient flow is the superposition of the velocity fields created by the force acting on each particle *as if* isolated, and each one of them experiences this flow *as if* it were created by distant sources, e.g., like an externally imposed flow. See, e.g., Ref. [26, Appendix A] and Ref. [28, Supplemental Material] for a more detailed discussion.

FIG. 1. Definition of the angle α used in Eq. (19).

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 ℓ , so that the effect of the hydrodynamic interactions is unnoticeable. In the opposite limit $R \gg L_{\text{hydro}}$, however, it is

$$\frac{\tau_\ell}{\tau_\ell^{\text{norm}}} \approx \left(\ell + \frac{1}{2} \right) \frac{L_{\text{hydro}}}{R}, \quad (20)$$

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) and (17)] justifies the denomination of “anomalous diffusion” (“superdiffusion,” to be more precise). Also common is the meaning of the scale L_{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

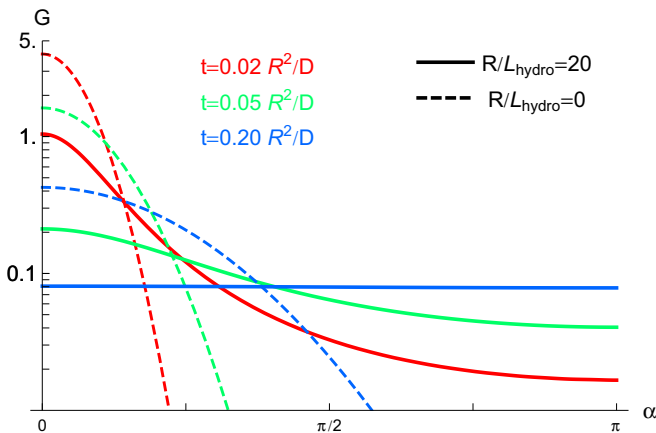


FIG. 2. Plot of the Green’s function, Eq. (19), at different times when the hydrodynamic interactions are considered (thick lines) or not (dashed lines). The vertical axis is in logarithmic scale.

diagnostic tool is the average of the Legendre polynomials,

$$\langle P_\ell(\cos \theta) \rangle = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi P_\ell(\cos \theta) G(\theta, \phi; 0, 0, t), \quad (21)$$

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

$$\langle P_\ell(\cos \theta) \rangle = e^{-t/\tau_\ell}. \quad (22)$$

Particularly interesting is the quantity [37]

$$\begin{aligned} \langle R^2 \sin^2 \theta \rangle &= \frac{2}{3} R^2 [\langle P_0(\cos \theta) \rangle - \langle P_2(\cos \theta) \rangle] \\ &= \frac{2}{3} R^2 [1 - e^{-t/\tau_2}], \end{aligned} \quad (23)$$

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’s function exhibits a tail $\propto r^{-3}$ with in-plane distance r regardless of the value of the characteristic length L_{hydro} (see Appendix B). This is 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 buildup 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]:

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

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 of 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 $R \rightarrow \infty$. Since R quantifies both the local curvature of the interface and its global extension, there remains the ambiguity whether $R \rightarrow \infty$ 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_{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 to 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?

ACKNOWLEDGMENTS

The author acknowledges support by the Ministerio de Economía y Competitividad del Gobierno de España through Grant No. FIS2017-87117-P (partially financed by the European Regional Development Fund).

APPENDIX A: SPHERICAL HARMONICS

We use the standard definition of the spherical harmonics,

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

in terms of the associated Legendre functions of the first kind, $P_\ell^{|m|}$, with ℓ 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

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

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 $\nabla_s \sigma \leftrightarrow \varrho \nabla_{\parallel} \mu$. The solution to Eq. (5) 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. [44]; in our notation, it is

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

in terms of the average viscosity $\eta_+ := (\eta_1 + \eta_2)/2$. The use of Eq. (A2) renders expression $\nabla_{\parallel} \cdot \mathbf{u}(\mathbf{r} = R\mathbf{e}_r)$ 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,

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

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

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

with the diffusion coefficient

$$D_k^{(\text{flat})} := D \left[1 + \frac{1}{L_{\text{hydro}} k} \right]. \quad (\text{B3})$$

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's function in the planar case, defined analogously to Eq. (18), can be obtained in the limit $r \gg L_{\text{hydro}}$ [26],

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

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

$$\langle r^2 \rangle = \int d^2\mathbf{r} r^2 G(r, t), \quad (\text{B5})$$

is undefined in an unbounded monolayer.

APPENDIX C: THE GREEN'S FUNCTION

The solution (15) and Eq. (11) allow one to write the time-evolved density field as

$$\begin{aligned} \delta\varrho(\theta, \phi, t) &= \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \rho_\ell^m(0) e^{-t/\tau_\ell} Y_\ell^m(\theta, \phi) \\ &= \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-t/\tau_\ell} Y_\ell^m(\theta, \phi) \int_0^\pi d\theta' \sin\theta' \\ &\quad \times \int_0^{2\pi} d\phi' Y_\ell^{m*}(\theta', \phi') \delta\varrho(\theta', \phi', 0). \end{aligned} \quad (\text{C1})$$

The comparison with Eq. (18) gives the expression

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

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

theorem [45],

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

where the angle α (see Fig. 1) satisfies

$$\cos \alpha = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi'). \quad (\text{C4})$$

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

-
- [1] J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier Science, Amsterdam, 1996).
- [2] R. B. Jones, B. U. Felderhof, and J. M. Deutch, Diffusion of polymers along a fluid-fluid interface, *Macromolecules* **8**, 680 (1975).
- [3] K. Aderogba and J. R. Blake, Action of a force near the planar surface between two semi-infinite immiscible liquids at very low Reynolds numbers, *Bull. Austral. Math. Soc.* **18**, 345 (1978).
- [4] S. H. Lee and L. G. Leal, Motion of a sphere in the presence of a plane interface. Part 2. An exact solution in bipolar co-ordinates, *J. Fluid Mech.* **98**, 193 (1980).
- [5] P. G. Saffman and M. Delbrück, Brownian motion in biological membranes, *Proc. Natl. Acad. Sci. USA* **72**, 3111 (1975).
- [6] K. Danov, R. Aust, F. Durst, and U. Lange, Influence of the surface viscosity on the hydrodynamic resistance and surface diffusivity of a large Brownian particle, *J. Colloid Interface Sci.* **175**, 36 (1995).
- [7] J. Bławdziewicz, V. Cristini, and M. Loewenberg, Stokes flow in the presence of a planar interface covered with incompressible surfactant, *Phys. Fluids* **11**, 251 (1999).
- [8] B. U. Felderhof, Mobility of a particle immersed in a liquid film between two fluids, *J. Chem. Phys.* **124**, 124705 (2006).
- [9] B. U. Felderhof, Effect of surface tension and surface elasticity of a fluid-fluid interface on the motion of a particle immersed near the interface, *J. Chem. Phys.* **125**, 144718 (2006).
- [10] T. Bickel, Hindered mobility of a particle near a soft interface, *Phys. Rev. E* **75**, 041403 (2007).
- [11] T. Bickel, Brownian motion near a liquid-like membrane, *Eur. Phys. J. E* **20**, 379 (2006).
- [12] P. Vorobev, Role of membranes in hydrodynamic interaction of small particles, *Phys. Rev. E* **77**, 046306 (2008).
- [13] Y. O. Fuentes, S. Kim, and D. J. Jeffrey, Mobility functions for two unequal viscous drops in Stokes flow. II. Asymmetric motions, *Phys. Fluids* **1**, 61 (1989).
- [14] A. Daddi-Moussa-Ider, M. Lisicki, and S. Gekle, Hydrodynamic mobility of a solid particle near a spherical elastic membrane. II. Asymmetric motion, *Phys. Rev. E* **95**, 053117 (2017).
- [15] V. A. Shaik and A. M. Ardekani, Point force singularities outside a drop covered with an incompressible surfactant: Image systems and their applications, *Phys. Rev. Fluids* **2**, 113606 (2017).
- [16] G. K. Batchelor, Brownian diffusion of particles with hydrodynamic interaction, *J. Fluid Mech.* **74**, 1 (1976).
- [17] B. Cichocki and B. U. Felderhof, Diffusion of Brownian particles with hydrodynamic interaction and hard core repulsion, *J. Chem. Phys.* **94**, 556 (1991).
- [18] R. Verberg, I. M. de Schepper, and E. G. D. Cohen, Theory of long-time wave number dependent diffusion coefficients in concentrated neutral colloidal suspensions, *Europhys. Lett.* **48**, 397 (1999).
- [19] H. Diamant, Hydrodynamic interaction in confined geometries, *J. Phys. Soc. Jpn.* **78**, 041002 (2009).
- [20] R. Pesché and G. Nägele, Dynamical properties of wall-confined colloids, *Europhys. Lett.* **51**, 584 (2000).
- [21] B. Cui, H. Diamant, B. Lin, and S. A. Rice, Anomalous Hydrodynamic Interaction in a Quasi-Two-Dimensional Suspension, *Phys. Rev. Lett.* **92**, 258301 (2004).
- [22] Z. Chvoj, J. M. Lahtinen, and T. Ala-Nissila, Theory of collective diffusion in two-dimensional colloidal suspensions, *J. Stat. Mech.* (2004) P11005.
- [23] R. Di Leonardo, S. Keen, F. Ianni, J. Leach, M. J. Padgett, and G. Ruocco, Hydrodynamic interactions in two dimensions, *Phys. Rev. E* **78**, 031406 (2008).
- [24] B. P. Binks, Particles as surfactants—Similarities and differences, *Curr. Opin. Colloid Interface Sci.* **7**, 21 (2002).
- [25] B. Lin, B. Cui, X. Xu, R. Zangi, H. Diamant, and S. A. Rice, Divergence of the long-wavelength collective diffusion coefficient in quasi-one- and quasi-two-dimensional colloidal suspensions, *Phys. Rev. E* **89**, 022303 (2014).
- [26] J. Bleibel, A. Domínguez, and M. Oettel, 3D hydrodynamic interactions lead to divergences in 2D diffusion, *J. Phys.: Condens. Matter* **27**, 194113 (2015).
- [27] G. Nägele, M. Kollmann, R. Pesché, and A. J. Banchio, Dynamic properties, scaling and related freezing criteria of two- and three-dimensional colloidal dispersions, *Mol. Phys.* **100**, 2921 (2002).
- [28] J. Bleibel, A. Domínguez, F. Günther, J. Harting, and M. Oettel, Hydrodynamic interactions induce anomalous diffusion under partial confinement, *Soft Matter* **10**, 2945 (2014).
- [29] S. Panzuela, R. P. Peláez, and R. Delgado-Buscalioni, Collective colloid diffusion under soft two-dimensional confinement, *Phys. Rev. E* **95**, 012602 (2017).
- [30] B. D. Goddard, A. Nold, and S. Kalliadasis, Dynamical density functional theory with hydrodynamic interactions in confined geometries, *J. Chem. Phys.* **145**, 214106 (2016).
- [31] A. Domínguez, Signature of time-dependent hydrodynamic interactions on collective diffusion in colloidal monolayers, *Phys. Rev. E* **90**, 062314 (2014).
- [32] J. Bleibel, A. Domínguez, and M. Oettel, Onset of anomalous diffusion in colloids confined to quasimonolayers, *Phys. Rev. E* **95**, 032604 (2017).
- [33] H. Brenner and L. G. Leal, A micromechanical derivation of Fick's law for interfacial diffusion of surfactant molecules, *J. Colloid Interface Sci.* **65**, 191 (1978).
- [34] N. G. van Kampen, Brownian motion on a manifold, *J. Stat. Phys.* **44**, 1 (1986).
- [35] F. Debbasch and M. Moreau, Diffusion on a curved surface: A geometrical approach, *Physica A* **343**, 81 (2004).

- [36] J. Faraudo, Diffusion equation on curved surfaces. I. Theory and application to biological membranes, *J. Chem. Phys.* **116**, 5831 (2002).
- [37] P. Castro-Villarreal, Intrinsic and extrinsic measurement for Brownian motion, *J. Stat. Mech.: Theor. Exp.* (2014) P05017.
- [38] H. A. Stone, A simple derivation of the time-dependent convective-diffusion equation for surfactant transport along a deforming interface, *Phys. Fluids* **2**, 111 (1990).
- [39] A. Domínguez, P. Magaretti, M. N. Popescu, and S. Dietrich, Effective Interaction between Active Colloids and Fluid Interfaces Induced by Marangoni Flows, *Phys. Rev. Lett.* **116**, 078301 (2016).
- [40] E. Reister and U. Seifert, Lateral diffusion of a protein on a fluctuating membrane, *Europhys. Lett.* **71**, 859 (2005).
- [41] P. Nozières, A local coupling between sedimentation and convection: Application to the Beenakker-Mazur effect, *Physica A* **147**, 219 (1987).
- [42] B. U. Felderhof, Sedimentation and convective flow in suspensions of spherical particles, *Physica A* **153**, 217 (1988).
- [43] J. Bleibel, A. Domínguez, and M. Oettel, A dynamic DFT approach to generalized diffusion equations in a system with long-ranged and hydrodynamic interactions, *J. Phys.: Condens. Matter* **28**, 244021 (2016).
- [44] M. Schmitt and H. Stark, Marangoni flow at droplet interfaces: Three-dimensional solution and applications, *Phys. Fluids* **28**, 012106 (2016).
- [45] I. S. Gradshteyn and I. M. Ryzhik, in *Table of Integrals, Series, and Products*, 5th ed., edited by Alan Jeffrey (Academic, London, 1994).