Spherical Brownian diffusion of particles on liquid-liquid interfaces of Pickering emulsions

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Abstract. We investigate the Brownian diffusion of particles that are confined in liquid/liquid interface in Pickering emulsions. These particles are subject to a spherical diffusion. Using the Green’s function techniques, we exactly derive the diffusion laws.

1. Introduction

Pickering emulsions are emulsions that are stabilized by solid particles [1, 2]. In fact, the solid particles form a spherical shell and impede coalescence when two droplets approach each other. Pickering emulsifiers irreversibly adsorb at the oil–water interface and require a much higher energy for desorption (≈ 10⁵ – 10⁶k_BT) as compared to the conventional surfactants (≈ 7 k_BT). The emulsifier-free character of Pickering emulsions makes them attractive regarding applications where the surfactants have detrimental effects, in particular, when contacted with living matter for health and body care applications [3-4].

Pickering emulsions have been the focus of considerable research in the past decade due to their properties such as high stability with respect to the coalescence, as well as due to advances in nanotechnology that allows us to create and characterize the nano-scale structures in new ways. In fact, the colloidal assembly of solid particles within Pickering emulsions can be used as templates for advanced materials such as Janus colloids, composite particles, and colloidosomes by analogy with liposomes. In addition to increasing possibilities for practical applications, Pickering emulsions also provide a new and convenient experimental model system for investigating spherical diffusion, i.e. Brownian motion of solid particles at the liquid-liquid interfaces [5-7].

Diffusion on the sphere is a problem that arises in several contexts. Diffusion is an important mode of transport of biological substances (lipids and proteins) on the cell walls which are curved surfaces. Spherical diffusion also crops up in surface smoothening in computer graphics and global migration patterns of marine mammals. While the planar diffusion has been studied extensively both analytically and numerically, there have been fewer analytical studies of diffusion on spherical surfaces.

In this work, using Pickering emulsions as template, we establish the diffusion laws of particles, confined on the surface of a sphere, undergoing Brownian motion.

This paper is organized as follows. In Sec. 1, we present the useful theoretical backgrounds. Results and discussion are the aim of Sec. 2. Finally, some concluding remarks are drawn in the last section.
2. Theory
In this section, we compute the Green’s function that is solution of the spherical diffusion equation enabling us the derivation of the diffusion laws.

When modeling the diffusion phenomena in an infinite medium, one often solves the diffusion equation for the probability density, \( u(x, t) \), which is subject to given initial condition: \( u(x, t = 0) = f(x) \).

A one dimensional linear diffusion equation with constant coefficient is defined as
\[
\Delta u(x, t) = \frac{1}{D} \frac{\partial}{\partial t} u(x, t),
\]
where the parameter \( D \) is called the diffusion coefficient. The spherical diffusion equation is given by
\[
\Delta_{S^2} u(\theta, \varphi, t) = \frac{1}{D} \frac{\partial}{\partial t} u(\theta, \varphi, t).
\]

Here, \( \Delta_{S^2} \) accounts for the spherical Laplace operator defined as
\[
\Delta_{S^2} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{(\sin \theta)^2} \frac{\partial^2}{\partial \varphi^2}.
\]

In obtaining the solutions to the Laplace’s equation in spherical coordinates, it is traditional to introduce the spherical harmonics, \( Y^m_l(\theta, \varphi) \),
\[
Y^m_l(\theta, \varphi) = N_{lm} P^m_l (\cos \theta) e^{im \varphi},
\]
with the normalization factor
\[
N_{lm} = \frac{\sqrt{(2l+1)(l-m)!}}{4\pi (l+m)!},
\]
and the associated Legendre functions
\[
P^m_l(x) = \frac{(-1)^m (1-x)^{m/2}}{2^m m!} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l.
\]

For solving the diffusion equation, we use the standard separation of variables,
\[
u_{lm}(\theta, \varphi, t) = Y^m_l(\theta, \varphi) T(t).
\]

Inserting this decomposition into the diffusion equation and using the fact that the spherical harmonics are eigen-functions of the spherical Laplace operator yields
\[
u_{lm}(\theta, \varphi, t) = Y^m_l(\theta, \varphi) e^{-l(l+1)kt}.
\]

In order to obtain the Green’s function, we will impose the following initial condition
\[
u_{lm}(\theta, \varphi, 0) = \delta_{S^2}(\theta, \varphi),
\]
where the symbol \( \delta_{S^2}(\theta, \varphi) \) is the spherical Dirac function defined by [9]
\[ \delta s^2 = \sum_{l \in \mathbb{N}} \frac{2l+1}{4\pi} p_l(\cos \theta). \quad (10) \]

Thus, we obtain for the Green’s function the final result

\[ G(\theta, \varphi, t) = \sum_{l \in \mathbb{N}} \sqrt{\frac{2l+1}{4\pi}} u_l(\theta, \varphi, t), \quad (11) \]

with

\[ u_l(\theta, \varphi, t) = Y_l^0(\theta, \varphi)e^{-l(l+1)kt}. \quad (12) \]

3. Results and discussion

The statistical properties of a Brownian particle moving on the liquid-liquid interface, are well described by the Green’s function (propagator), \( G(\theta, \varphi, t) \), which represents the probability density of finding a particle at point \( r \) at time \( t \), together with the initial condition: \( G(r, r', 0) = \delta(r - r') \). Once the propagator is known, all the statistical properties can be evaluated. For instance, the mean-square displacement (MSD) is obtained from

\[ \langle r^2 \rangle = R^2 \sum_{l=0}^{\infty} (2l+1)e^{-(l+1)\tau t} \int_0^\pi d\theta \sin \theta (1 - \cos \theta) p_l(\cos \theta), \quad (13) \]

where \( \tau = R^2/D \) is the relaxation time, with the particle radius \( R \).

From the well-known results of integrals [10], we find

\[ \langle r^2 \rangle = 2R^2 \left( 1 - e^{-2t/\tau} \right). \quad (14) \]

Let us comment the above obtained result. Firstly, as expected, MSD saturates to \( \langle r^2 \rangle = 2R^2 \), in the long-time limit that is for \( t \gg \tau \). Secondly, in the short-time limit \( t \ll \tau \), however, we find that MSD does not depend on the radius of the sphere and we recover, in this limit, the celebrated Einstein’s diffusion law on the two-dimensional Euclidean space. This result can be explained by the fact that in short-time limit the particle has not enough time to feel the influence of curvature of the sphere.

4. Conclusion

In this paper, we have discussed the diffusion of the confined particles on the spherical surface of liquid-droplets in Pickering emulsions, using the Green’s function techniques. In particular, we have found that, for short-times, when they move, these particles do not feel the influence of the geometrical shape.

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