



Brownian dynamics of nanoparticles in contact with a confined biomembrane

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abstract

The system we consider is a fluid membrane confined to two parallel reflecting walls that are separated by a finite distance, L , assumed to be small in comparison to the bulk roughness. The attractive membrane is surrounded by small colloidal particles (nanoparticles). The purpose is the study of Brownian dynamics of these particles, under a change of a suitable parameter, such as temperature, T , or colloid-membrane interaction strength, w . The Brownian dynamics is investigated through the knowledge of the time particle density, which solves the Smoluchowski equation. Solving this equation around the mid-plane, where the essential of phenomenon occurs, we obtain the *exact form* of the local particle density, as a function of the perpendicular distance and time. In the derived expression, appears some time-scale, τ , which scales as $\tau \sim L^3/w$. This scale-time can be interpreted as the required time over which the colloidal suspension reaches their final equilibrium state. Also, τ can be regarded as the time-interval over which the particles are trapped in holes and valleys.

Key words: Biomembranes - Nanoparticles - Confinement - Brownian dynamics.

I. INTRODUCTION

The biomembranes play a crucial role in life. Indeed, they separate the cell from the surrounding environment, and act as a selective barrier for the import and export of materials. These biological materials are complex systems, but they possess a natural structural organization, where each component has a specific function [1 – 7]. Nowadays, the scientific community recognizes that the cell membranes essentially present as a phospholipid bilayer combined with a variety of proteins and cholesterol. For example, the function of the cholesterol molecules is to ensure the bilayer fluidity. A phospholipid is commonly defined as an amphiphile molecule that is composed of a hydrophilic polar head attached to two hydrophobic (fatty acyl) chains. We note that the phospholipids move freely on the membrane surface. On the other hand, the thickness of the bilayer is of the order of 5 nanometers. This two facts allow to consider this bilayer as a two-dimensional fluid membrane. Experiment shows that the fluid membranes, self-assembled from surfactant solutions, may have a variety of shapes and topologies [8]. These forms have been theoretically explained in terms of bending energy [9, 10].

Usually, the biomembranes are not immersed in liquids of infinite extent, but they are rather confined to geometrical boundaries. Typical examples are provided by white and red globules or liposomes, as drugs

transport agents [11 – 14], in blood vessels.

To obtain quantitative results, we consider the situation where the biomembrane is trapped in a liquid delimited by two parallel reflecting walls, which are a finite distance, L , apart. By finite distance, we mean that the separation L is much smaller than the bulk membrane mean-roughness, ξ_{\perp}^0 (film geometry). The latter can be regarded as the typical size of humps caused by the thermal fluctuations of the membrane. Of course, the scale ξ_{\perp}^0 depends on the nature of lipid molecules forming the bilayer. The condition $L < \xi_{\perp}^0$ then ensures the confinement of the biomembrane. Such a condition is similar to that usually encountered in confined polymers context [15].

In real situations, the biomembranes are not pure, but they are in the presence of various entities, like proteins, small and macro-ions, or more complex structures [16]. For example, the membrane suspensions used in detergency and cosmetics are usually in contact with numerous additives (macromolecules and colloids), in order to improve their efficiency and to control their viscoelastic properties [17]. A simple way to study this influence consists in regarding these entities as small spherical colloids. This assumption has a physical sense only when one is concerned with those phenomena occurring at scales greater than the characteristic size of neighboring entities (diameter of particles, gyration radius of macromolecules, etc.).

The organization of nanoparticles around a fluctuating fluid membrane, embedded in a liquid of infinite extent, is the subject of very recent theoretical works [18 – 20]. The question was addressed to statistical properties of the particles mediated by the membrane undulations. In particular, it was found that these undulations give rise to an aggregation of the beads in the vicinity of the fluid membrane. Such an aggregation is caused by the appearance of mutual attractive forces due to their contact with this membrane. Also, the attention has been paid to the investigation of the phase transition [18] that drives the colloids from a dispersed phase (gas) to a dense one (liquid).

In a very recent work [21], one has studied the Brownian dynamics of nanoparticles of very low density, which are in contact with an interacting fluid membrane. The colloids and membrane were assumed to be trapped in a liquid of infinite extent. More precisely, the problem to solve was how these particles are pushed by the external potential towards the interface. The Brownian dynamics was studied through the time evolution of the particle density, when some suitable parameter, such as temperature, pressure, or membrane environment, is changed from an initial value to a final one.

We recall that the Brownian motion governs various time-dependent phenomena ranging from suspensions [22 – 27] to polymer solutions [28]. This motion can be investigated using two approaches, namely the Smoluchowski equation solved by the distribution function and Langevin equation. Although the two theoretical formulations are different, but they are physically equivalent. The Smoluchowski equation that is a generalization of the usual diffusion equation, has a clear relevance to thermodynamics of irreversible processes. The Langevin equation, however, has no direct relationship to thermodynamics, but it provides a successful tool for the description of wider classes of stochastic processes.

In this paper, the purpose is to extend the study to Brownian dynamics of colloidal particles in contact with an attractive fluid membrane, where the host liquid is delimited by two impenetrable walls. More precisely, the question is how this dynamics can be affected by confinement. As we shall see below, this confinement induces drastic changes of the statistical properties of beads.

To study the Brownian dynamics of a colloidal dispersion around a confined interacting fluid membrane, use is made of a theoretical approach based on the Smoluchowski equation. In fact, this equation describes the evolution of the particle density in time, and involves a known mean-force external potential experienced by the particles [19]. To simplify, the immersed particles are assumed to be point-like and of very low-density. The first assumption remains valid as long as we are concerned with strong membrane undulations, while the second means that the mutual interactions between particles can be ignored. Thus, the only remaining interaction is an external potential originating from the statistical fluctuations of this membrane. In the distance-range of interest, that is around the fluid membrane, we determine the *exact* form of the local particle density. The latter depends on the perpendicular distance z from the mid-plane located at $z = 0$, time t , and some characteristic time-scale $\tau \sim L^3/w$, where L is the separation between the confining walls and w is the colloid-membrane interaction strength. We emphasize that the time-scale τ can be regarded as the required time over which the beads are trapped in the new holes and valleys.

This paper is organized as follows. In Sec. II, we present the essential of field theory allowing the calculation of a basic quantity that is the mean-force potential due to the membrane undulations. Brownian dynamics study is the aim of Sec. III. Some concluding remarks are drawn in the last section.

II. THEORETICAL FORMULATION

Start with a fluctuating fluid membrane, free from particles, which is confined to two parallel *reflecting walls* 1 and 2. These are separated by a finite distance L that is assumed to be much smaller than the bulk membrane roughness, ξ_{\perp}^0 , when the system is unconfined (free membrane). The membrane is confined only when the condition $L < \xi_{\perp}^0$ is fulfilled.

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n the Monge representation, a point on the membrane can be described by the three-dimensional position vector $\mathbf{r} = (x, y, z = h(x, y))$, where $h(x, y) \in [-L/2, L/2]$ is the height-field. The latter then fluctuates around the mid-plane located at $z = 0$.

The Statistical Mechanics for the description of such a (tensionless) fluid membrane is based on the standard Canham-Helfrich Hamiltonian [9, 29]

$$\mathcal{H}_0 [h] = \frac{1}{2} \int dx dy \left[\kappa (\Delta h)^2 + \mu h^2 \right] , \quad (2.0)$$

with the elastic constant [30]

$$\mu = \frac{9 (k_B T)^2}{4 \kappa L^4} . \quad (2.0)$$

Here, κ is the bending rigidity constant that is directly proportional to the thermal energy $k_B T$. In fact, the term $\mu h^2/2$ describes a confinement potential that ensures the localization of the membrane around the mid-plane. Integral over the hole plane \mathbf{R}^2 of this term represents the loss entropy due to the confinement of the membrane. We recall that formula (2) of the elastic constant is compatible with the roughness expression, i.e.

$$\xi_{\perp}^2 = \langle h^2 \rangle - \langle h \rangle^2 = \frac{1}{8} \frac{k_B T}{\sqrt{\mu \kappa}} = \frac{L^2}{12} , \quad (2.0)$$

provided that one is in the confinement-regime where $L \ll \xi_{\perp}^0$. Such a quantity measures the fluctuations of the height-function (fluctuations amplitude) around the equilibrium plane located at $z = 0$. We recall that the result (3) was recently derived in Ref. [30].

Now, consider an assembly of N colloidal particles moving around a fluctuating fluid membrane. To simplify calculations, the particles are assumed to be point-like. In fact, this assumption makes sense only if the particle size is much smaller than the membrane roughness $\xi_{\perp} = L/2\sqrt{3}$. Typically, the considered particles have diameter of a few tens of nanometers, while the roughness is of the order of 1 micrometer. In addition, we suppose that there is no direct colloid-colloid interaction. This assumption is valid only when the colloidal dispersion is of very low-density. We recall that, in this paper, we are concerned with the influence of the membrane undulations on the particles movement. Of course, the primitive mutual interactions between nanoparticles should be taken into account when one is interested in their phase transition (colloidal aggregation) near an attractive fluid interface [19].

The total Hamiltonian describing physics of colloids and membrane reads [19]

$$\mathcal{H} [h] = \mathcal{H}_0 [h] + \mathcal{H}_{cm} [h] , \quad (2.0)$$

where $\mathcal{H}_0 [h]$ is the bare Hamiltonian defined in Eq. (1). In the above definition, \mathcal{H}_{cm} accounts for the colloid-interface interaction, which is generally a complicated function of particles positions and configurations of the interface. For the sake of simplify, we suppose that the interaction \mathcal{H}_{cm} is of contact type, and depends only on the relative perpendicular distances between particles and surface. Then, the proposed form is

$$\frac{\mathcal{H}_{cm} [h]}{k_B T} = -\frac{w}{2} \sum_{i=1}^N \delta [z_i - h(\boldsymbol{\rho}_i)] . \quad (2.0)$$

Here, δ is the one-dimensional Dirac function. The discrete sum is performed over all particles positions, $\mathbf{r}_i = (\boldsymbol{\rho}_i, z_i)$, $1 \leq i \leq N$. In the above definition, $w > 0$ represents the surface coupling constant that

measures the colloid-membrane interaction strength. In fact, w plays the role of an *extrapolation length* as usually encountered in Surface Critical Phenomena [31 – 33]. We note that the interaction magnitude w may be influenced by a change of temperature or membrane environment. In this model, we suppose that the attractive interface is penetrable and the colloids can accommodate on its both sides.

As shown in Ref. [19], the membrane undulations give rise to one, two and more bodies interactions between beads. The *exact* calculations of these effective interactions were achieved taking advantage of the so-called *cumulant method* traditionally used in Statistical Field Theory [34, 35]. In this work, we focus our attention on those colloidal suspensions of very low-density (ideal gases), only. In these conditions, the mutual interactions between particles can be neglected. Therefore, the only remaining interaction is the attractive one-body interaction, $U(z)$, which describes the direct potential between colloids and interface. Its expression was found to be [19]

$$U(z) = U_0 \exp \left\{ -\frac{6z^2}{L^2} \right\}, \quad (2.0)$$

with the *negative* amplitude

$$U_0 = -\sqrt{\frac{3}{2\pi}} \frac{w}{L} k_B T. \quad (2.0)$$

The quantity $|U_0|$ is the potential depth. Originally [19], the above relations explicitly incorporate the roughness ξ_\perp that we replaced by its expression : $\xi_\perp = L/2\sqrt{3}$.

Let us discuss the above expression of the external potential felt by the nanoparticles.

Firstly, in addition to the perpendicular distance z , the interaction potential naturally depends on the separation L between the reflecting walls, and the surface coupling constant w .

Secondly, this one-body potential exhibits a minimum at the mid-plane $z = 0$. In addition, it is symmetric around this point.

Thirdly, remark that the potential depth $|U_0|$ depends on three kinds of parameters, which are the absolute temperature T , the surface coupling constant w , and the film thickness L . For instance, if T and w are fixed, the potential depth is inversely proportional to separation L . This means that the external potential experienced by beads has a significant magnitude only for those membranes confined to very narrow geometries. If T and L are now fixed to some values, the potential depth linearly increases with increasing surface coupling constant w .

Fourthly, we emphasize that $|U_0|$ must be small in comparison with the thermal energy $k_B T$. This implies that the coupling constant w is bounded from above, i.e. $w < w^* = \sqrt{2\pi/3} \times L \simeq 1.4472 \times L$.

Finally, as it should be, in the absence of the colloid-membrane interaction ($w = 0$), the one-body potential vanishes.

The (reduced) external potential experienced by the nanoparticles, $U(z)/k_B T$, is depicted in Fig. 1, upon the renormalized perpendicular distance z/L , for two values of the surface coupling constant w : $w_1 = 0.5 \times L$ and $w_2 = 0.9 \times L$. As it should be, the curve drawn with parameter w_2 is below that associated with $w_1 < w_2$.

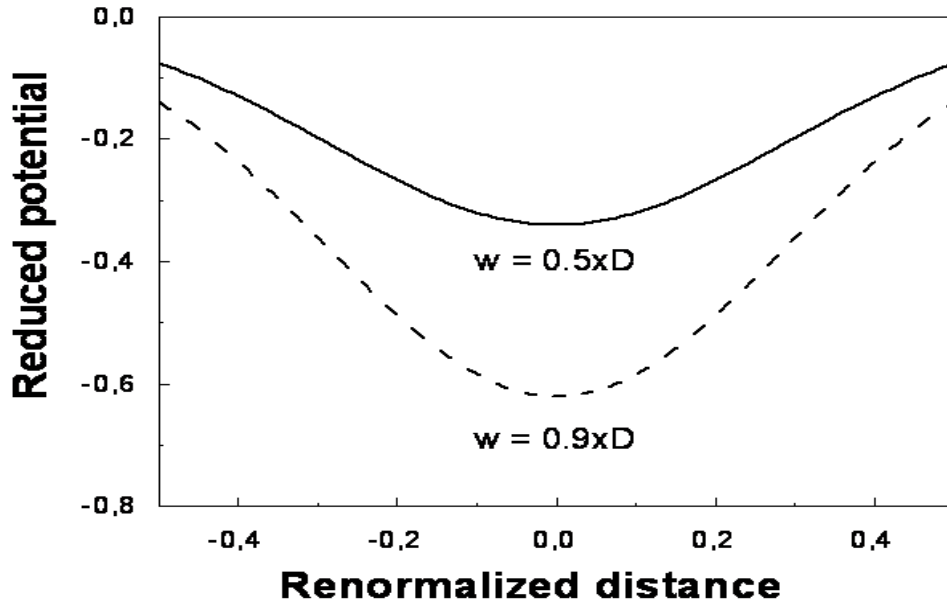


FIG. 1. Reduced mean-force potential versus the renormalized perpendicular distance z/L , for two values of the surface coupling constant w : $w_1 = 0.5 \times L$ and $w_2 = 0.9 \times L$.

The above expression of the one-body potential is the principal ingredient for the Brownian dynamics study of very low-density particles, which are located near a soft membrane. But, in order to facilitate calculations and get exact results, the above expression for the external potential must be simplified. Since the essential of phenomenon occurs in the interval $|z| < \xi_{\perp} = L/2\sqrt{3}$, such a potential reduces to [21]

$$U(z) \simeq U_0 + W(z) , \quad z < L_{\perp} , \quad (2.0)$$

with the harmonic potential

$$W(z) = \frac{1}{2}kz^2, \quad (2.0)$$

where the elastic constant k is as follows

$$k = -\frac{U_0}{\xi_{\perp}^2} = 12\sqrt{\frac{3}{2\pi}} \frac{w}{L^3} k_B T > 0 . \quad (2.0)$$

The above equality shows that the elastic constant k scales with separation L as : $k \sim L^{-3}$. We note that the potential depth $|U_0|$ has as effect to renormalize the density amplitude [21].

III. TIME EVOLUTION OF THE PARTICLE DENSITY

Consider, now, an assembly of colloidal particles moving around a fluctuating fluid membrane. Under a sudden change of a suitable parameter, such as temperature, pressure or membrane environment, the

system is out equilibrium. We assume that the system is subject to Brownian dynamics by changing the colloid-membrane interaction strength w , but the temperature and film thickness remain fixed. This change may be caused by affecting the membrane environment. The problem can be studied through the local particle density, $n(z, t)$. The latter represents the number of colloids per unit volume, at distance z and at time t . More precisely, we are interested in how this density evolves in time before the colloidal suspension reaches its final equilibrium state. For simplicity, we will neglect mutual interactions between nanoparticles. This hypothesis makes sense at least for small particle densities. Hence, the only interaction experienced by the beads is an external potential caused by the membrane undulations. Within the harmonic approximation, this potential is defined in Eqs. (9) and (10).

To determine the time evolution of the local particle density, use will be made of the Smoluchowski equation [27, 28], which is a linear partial differential equation, of first order and second order, with respect to time and perpendicular distance, respectively.

Before writing and solving this equation, we shall need some backgrounds. We first recall the expression of the equilibrium particle density

$$n_{eq}(z) = A \exp \left\{ -\frac{U(z)}{k_B T} \right\}, \tag{3.0}$$

where A is a normalization constant and $U(z)$ is the one-body potential due to the membrane undulations. If this potential is approximated by its harmonic form, the above definition becomes

$$n_{eq}(z) = n_0 \exp \left\{ -\frac{W(z)}{k_B T} \right\}, \tag{3.0}$$

where n_0 is now the value of the particle density at the mid-plane $z = 0$.

When the colloidal dispersion is out of equilibrium, in addition to distance, the density depends on time. This means that the nanoparticles execute Brownian dynamic but in the presence of the harmonic potential $W(z)$. In order to compute this local density, we first recall that the Brownian diffusion is correctly described by the Fick's law. The latter stipulates that the flux of matter, $j(z, t)$, is directly proportional to the spatial gradient of density, that is

$$j = -D \frac{\partial n}{\partial z} - \frac{1}{\zeta} \frac{\partial W}{\partial z}, \tag{3.0}$$

with

$$D = \frac{k_B T}{\zeta} \tag{3.0}$$

the diffusion constant and ζ the friction coefficient, of which the inverse $1/\zeta$ is the mobility. If we design by a the particle radius and by η_s the solvent viscosity, the friction coefficient ζ can be calculated from hydrodynamics [36] : $\zeta = 6\pi\eta_s a$. Equality (14) states that the diffusion constant characterizing the thermal motion is related to the quantity ζ , which expresses the response to an external field. Such an equality is a consequence of the well-known dissipation-fluctuation theorem [27, 28].

On the other hand, relation (13) must be combined with the local conservation law of matter

$$\frac{\partial n}{\partial t} + \frac{\partial j}{\partial z} = 0. \tag{3.0}$$

Combining Eqs. (13) and (15) yields the Smoluchowski equation

$$\frac{\partial n}{\partial t} = \frac{1}{\zeta} \frac{\partial}{\partial z} \left(k_B T \frac{\partial n}{\partial z} + n \frac{\partial W}{\partial z} \right) \tag{3.0}$$

solved by the local particle density $n(z, t)$. At equilibrium, that is $\partial n/\partial t = 0$, the above equation reduces to : $k_B T \partial n/\partial z + n \partial W/\partial z = 0$, whose solution is $n_{eq}(z) = n_0 \exp \{ -W(z)/k_B T \}$, which is nothing else but the density defined in Eq. (12).

Replacing the harmonic potential $W(z)$ by its explicit form (9) gives

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2} + \frac{k}{\zeta} z \frac{\partial n}{\partial z} + \frac{k}{\zeta} n. \tag{3.0}$$

This new Smoluchowski equation must be supplemented by two boundary conditions, which are

$$n(z, t = 0) = n_i(z) , \quad n(z, t = \infty) = n_f(z) . \tag{3.0}$$

If the temperature T and separation L are fixed, the initial and final equilibrium particle densities, $n_i(z)$ and $n_f(z)$, are completely determined by the initial and final surface coupling constants w_i and w_f , respectively. Therefore, the dynamic is caused by a change of the membrane environment. Taking advantage of those mathematical techniques used in Ref. [21], we show that the solution to the Smoluchowski equation (17) is given by

$$n(z, t) = n_f(z) + \left[2\pi D\tau_f (1 - e^{-2t/\tau_f}) \right]^{-1/2} \int_{-\infty}^{\infty} dy \exp \left\{ -\frac{(ze^{t/\tau_f} - y)^2}{2D\tau_f (e^{2t/\tau_f} - 1)} \right\} [n_i(y) - n_f(y)] , \tag{3.0}$$

where the initial and final equilibrium particle densities are given by

$$n_i(z) = n_0^i \exp \left\{ -\frac{k_i z^2}{2k_B T} \right\} = n_0^i \exp \left\{ -\frac{z^2}{2D\tau_i} \right\} , \tag{3.0}$$

$$n_f(z) = n_0^f \exp \left\{ -\frac{k_f z^2}{2k_B T} \right\} = n_0^f \exp \left\{ -\frac{z^2}{2D\tau_f} \right\} , \tag{3.0}$$

with the time-scales τ_i and τ_f

$$\tau_i = \frac{\zeta}{k_i} = \frac{1}{12} \sqrt{\frac{2\pi}{3}} \frac{D^{-1}}{w_i} L^3 , \quad \tau_f = \frac{\zeta}{k_f} = \frac{1}{12} \sqrt{\frac{2\pi}{3}} \frac{D^{-1}}{w_f} L^3 , \tag{3.0}$$

where w_i and $w_f > w_i$ are the initial and final surface coupling constants. This means that the colloid-membrane interaction is suddenly increased from w_i to w_f . The above relations suggest that the times τ_i and τ_f depend on the colloid-membrane interaction and film thickness. In particular, the time-scale τ_f may be interpreted as the time beyond which the colloidal system reaches its final equilibrium state. Then, a weak colloid-membrane interaction necessitates a great time before the colloidal system tends to its final state. In fact, τ_f has another physical meaning, and can be regarded as the required time over which the particles are trapped in new holes and valleys.

Now, after integration over the y variable, in Eq. (19), we obtain a *closer form* for the time particle density

$$n(z, t) = n_0^i \left[1 + \eta (e^{-2t/\tau_f} - 1) \right]^{-1/2} \exp \left\{ -\frac{1}{1 + \eta (e^{-2t/\tau_f} - 1)} \frac{z^2}{2D\tau_i} \right\} , \tag{3.0}$$

with the reduced time-shift

$$\eta = \frac{\tau_i - \tau_f}{\tau_i} = \frac{w_f - w_i}{w_f} > 0 . \tag{3.0}$$

The quantity η then represents the relative shift of the colloid-membrane interaction strengths w_i and w_f . The density amplitude, in Eq. (23), was obtained using the matter conservation law

$$\int_{-\infty}^{+\infty} n_i(z) dz = \int_{-\infty}^{+\infty} n_f(z) dz \equiv \Gamma . \tag{3.0}$$

Here, Γ represents the *adsorbance*, which is defined as the total number of colloids (per unit area) located near membrane. Combining Eqs. (20), (21) and (25) yields the relationship

$$\sqrt{2\pi D\tau_f} n_0^f = \sqrt{2\pi D\tau_i} n_0^i = \Gamma . \tag{3.0}$$

Let us comment the density expression (23).

First, we note that, it is easy to see that the solution (23) satisfies the two boundary conditions (18).

The initial and final equilibrium states are defined in Eqs. (20) and (21).

Second, when it is reduced by n_0^i , the time particle density depends on three dimensionless factors, namely the renormalized distance $z/\sqrt{2D\tau_i}$, the time-ratio t/τ_f and the time-shift $\eta = (\tau_i - \tau_f)/\tau_i$. Therefore, all microscopic details (colloid-membrane interaction) are entirely contained in τ_i and τ_f .

Finally, we emphasize that the time particle density curve exhibits a maximum at $z = 0$, and it is symmetric around this point, whatever be the values of t/τ_f and η .

We depict, in Fig. 2, the reduced time particle density $n(z, t)/n_0^i$ versus the renormalized distance $z/\sqrt{2D\tau_i}$, choosing three values of the time-ratio t/τ_f : 0, 0.5, and ∞ . The former corresponds to the initial state and the second to the final one. These curves are drawn with parameter $\eta = 0.5$. This value means that the final surface coupling constant w_f is *two times* more important than the initial one w_i , that is $w_f = 2w_i$.

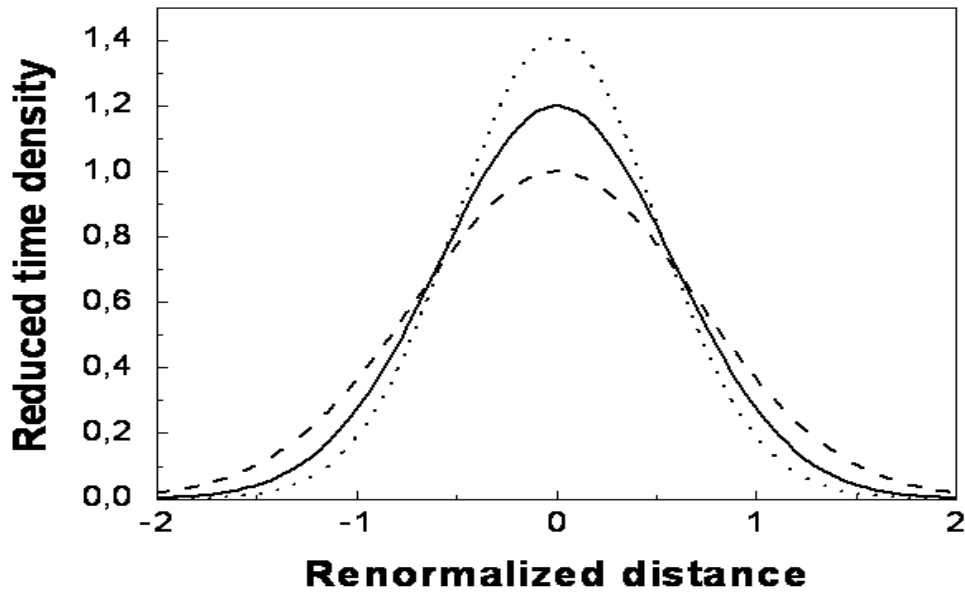


FIG. 2. Reduced local particle density, $n(z, t)/n_0^i$, versus the renormalized distance $z/\sqrt{2D\tau_i}$, with three values of the time-ratio t/τ_f : 0 (dashed line), 0.5 (solid line), ∞ (line in dots). These curves are drawn choosing the value $\eta = 0.5$ ($w_f = 2w_i$).

IV. CONCLUSIONS

This work is dedicated to the Brownian dynamics study of small colloidal particles in contact with an attractive penetrable fluid membrane. The host liquid was assumed to be delimited by two parallel reflecting walls, which are a finite distance apart. The membrane surrounded by beads is confined only if the film thickness is much smaller than the bulk membrane mean-roughness.

Physics was discussed in terms of three relevant parameters, which are the absolute temperature, T , the separation between walls, L , and colloid-membrane interaction strength, w . In our study, we have fixed the temperature and film thickness to some values, and varied the surface coupling constant. This can be experimentally achieved modifying the membrane environment.

For the present study, we have started from three hypotheses : (1) the particles are point-like, (2) they are of very low-density (in order to forget their mutual interactions), and (3) strongly interact with the membrane.

To achieve the investigation of the Brownian dynamics, use was made of a theoretical formalism based on the Smoluchowski equation. The latter is solved by the time particle density we were interested in. We have *exactly* computed this physical quantity, around the mid-plane of the film, where the essential of phenomenon occurs. Within this distance-domain, the mean-force external potential was approximated

by an harmonic one. This means that we were in the presence of Brownian particles moving in an harmonic potential, that is, in addition to the usual diffusion, these experience small oscillations with a frequency ν scaling as $\nu \sim \sqrt{w/L^3}$. Hence, the harmonic approximation used for the mean-force potential is largely justified for those fluid interfaces of small enough colloid-membrane interaction strength.

As we have shown, the time particle density depends on a time-scale, τ , scaling as $\tau \sim L^3/w$. We have interpreted this scale-time as the required time over which the nanoparticles reach their final equilibrium state. Also, τ can be regarded as the time-interval where the particles are trapped in holes and valleys of size slightly smaller than the film thickness L .

We note that, when the separation L is much greater than the bulk roughness ξ_{\perp}^0 , in addition to the above evoked parameters, the physical phenomenon depends on the specific membrane characteristic (via the bending rigidity constant κ). In this case, the Brownian dynamics can be caused by a change of the parameter κ . This situation has *less* physical interest, since, in this case, finite size effects contribute to the leading behavior only by exponentially small corrections.

As last word, we emphasize that the results derived in this paper may be extended to bilayer surfactants, although the two systems are not of the same structure and composition.

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