Diffusion coefficient of an inclusion in a liquid membrane supported by a solvent of arbitrary thickness

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The diffusion coefficient of an inclusion in a liquid membrane is investigated by taking into account the interaction between membranes and bulk solvents of arbitrary thickness. As a result, diffusion coefficients can be measured accurately and it is now possible to address the issue of the differences between Brownian motion of macromolecules embedded in membranes in various environments.

Vesicles with sizes of the order of 10 μm are frequently used in experiments while the typical distance of a supported membrane from the substrate is of the order of 20 Å [5,6]. Obviously, in both these general cases the coupling of a membrane with its environment is very different and hence it will influence the Brownian motion of inclusions. In this paper, we investigate the influence of solvent environments on diffusion of an inclusion embedded in a membrane. In the biological context, there are many examples of membranes coming in contact with a solvent of various depths such as in tissues.

Biological membranes can be regarded as two-dimensional (2D) viscous fluids. An important feature of membranes as a transport media is that they are not purely isolated [12–14]. Liquid membranes are coupled to surrounding solvents by interaction of polar head groups of lipid molecules with solvents; they form quasi-2D systems coupled to three-dimensional (3D) solvents. The coupling to the surrounding environments induces the momentum exchange between the membrane and the solvents. The influence of the momentum exchange on the Brownian dynamics has been theoretically investigated by introducing a phenomenological coupling constant or simplifying the solvents flow. These studies have also been extended to investigate the concentration fluctuations [18,19,22].

Despite the large number of studies, the Brownian motion of an object in liquid membranes has not yet been fully understood. In a hydrodynamic description, 2D flow in a bilayer membrane can be regarded as viscous and the interaction between liquid membranes and surrounding solvents can be taken into account by the stick boundary condition between them. Diffusion coefficients of macroscopic inclusions embedded in membranes were analytically investigated for a planar membrane surrounded by solvent layers of infinite [8–11] or very small thickness [12–17]. These studies revealed that the hydrodynamic flow in a membrane is screened by the solvent drag force and is characterized by a hydrodynamic screening length. When a planar membrane is surrounded by an infinite thickness of solvent, it is called the Saffman and Delbrück (SD) hydrodynamic screening length, ν−1, and is given by the ratio between the 2D membrane viscosity η and the 3D solvent viscosity η, ν−1 = η/η [8,9]. (As we shall see below, the dimension of the 2D membrane viscosity is that of 3D solvent viscosity times a length.) In the opposite limit of a thin solvent layer of the thickness h, the Evans and Sackmann (ES) hydrodynamic screening length given by \( \sqrt{h/\nu} \) is appropriate [14]. In both limits, the diffusion coefficients depend logarithmically on the size of the inclusions as long as the size is smaller than the hydrodynamic screening length. On the other hand, the diffusion coefficients depend on the size of the inclusions very differently when the size of the inclusions exceeds the hydrodynamic screening length. These studies naturally lead to the interest in the hydrodynamic screening length and its influence on the diffusion coefficients when the solvent layer has a finite thickness.

The solvent flow can be varied by changing the solvent thickness. The flow of solvents influences the membrane flow through the stick boundary condition imposed between the membrane and the solvents. As a result, the diffusion coefficients depend on the solvent thickness. The influence of the finite solvent thickness has been recently studied for diffusion of a disk [20], concentration fluctuations [21–23], correlated diffusion [24–27], and polymer diffusion in a membrane [28]. Diffusion coefficients of other types of inclusions on membranes [17,29–32] or on Langmuir monolayers [33] have also been theoretically calculated. However, the investigation on the influence of finite thickness of solvent was limited to numerical evaluation of the diffusion coefficients, where the dependence of the hydrodynamic screening length on the solvent thickness was not completely elucidated [20–28]. In this paper, the relation between the diffusion coefficients...
and the hydrodynamic screening lengths are thoroughly investigated for an arbitrary thickness of the solvent layers on the basis of the analytical expression on the hydrodynamic screening lengths.

The relation between the diffusion coefficients and the hydrodynamic screening lengths can be shown in a straightforward manner for a polymer embedded in a membrane by the Zimm model, where the equilibrium average of the hydrodynamic interactions is performed in two dimensions [17,28,31]. The multiple hydrodynamic screening lengths are then found for the finite solvent thickness. The diffusion coefficients are expressed by the weighted sum; each term in the sum is a product of the weight factor and the function of the dimensionless size of the polymer normalized by each hydrodynamic screening length. On the basis of the analytical expression, the condition that the diffusion coefficient is approximately represented solely by the ES hydrodynamic screening length can be discussed in detail. We show that the diffusion coefficient cannot be approximated by the ES hydrodynamic screening length when both $\nu^{-1} = \eta/\eta_s$ and the size of the macromolecule are smaller than the solvent thickness.

Essentially the same relation between the diffusion coefficients and the hydrodynamic screening lengths is obtained for diffusion of a circular liquid domain with the same viscosity as that of the host membrane. The diffusion coefficient of a circular liquid domain embedded in a membrane has been studied in relation to the recently proposed raft model [1,6,7,34–38]. It is believed that rafts undergo lateral Brownian motion within a bilayer membrane and act as platforms for protein association and signaling [35]. Previously, the diffusion coefficient of a circular liquid domain of arbitrary size was derived in the limit of infinite depth of solvent layer [7,16,39,40]. In this paper, the results are generalized for the arbitrary thickness of solvent layers. The diffusion coefficient is obtained as a simple integral that can be expressed again as the sum of the terms given by functions of the same hydrodynamic screening lengths multiplied by the same weight factors as those for the polymer diffusion coefficients.

In Sec. II, the membrane hydrodynamics is reviewed. The diffusion coefficient of a polymer embedded in a membrane is obtained in Sec. III. In Sec. IV, the relation between the hydrodynamic screening length and the solvent thickness is discussed. The diffusion coefficient of a liquid domain in a membrane is obtained in Sec. V. Finally, Sec. VI is devoted to conclusions.

II. HYDRODYNAMIC FLOW IN A MEMBRANE AND SOLVENT

As shown in Fig. 1, we consider the situation where the liquid membrane is supported by a bulk solvent on the solid substrate. The situation where the membrane is also supported by a solvent from above will be considered in Sec. VI. We denote the 2D flow in the membrane by $v(r)$ where $r = (x, y)$ represents a position within the plane of the membrane. The membrane is regarded to be incompressible,

$$ \nabla \cdot v(r) = 0. $$

FIG. 1. Schematic picture showing a planar liquid membrane with 2D viscosity $\eta$ located at $z = 0$. It is supported on a solvent with 3D viscosity $\eta_s$. A substrate is located at $z = -h$ bounding the solvent.

Here $\nabla$ is a differential operator in the 2D Euclidean space. The viscous flow in the membrane can be expressed by the Stokes equation in two dimensions,

$$ \eta \nabla^2 v(r) - \nabla p(r) + f_s(r) = 0, $$

where $\eta$ is the 2D membrane viscosity, $p(r)$ the in-plane pressure, and $f_s(r)$ the in-plane force exerted on the membrane from the solvent. The last quantity can be obtained when the solvent fluid velocities are determined. The stress tensor of the liquid membrane is given by

$$ \sigma_{\alpha\beta}(r) = -p(r) \delta_{\alpha\beta} + \eta_{s} [\partial_{\alpha} v_{\beta}(r) + \partial_{\beta} v_{\alpha}(r)], $$

where $\delta_{\alpha\beta}$ is the Kronecker delta, and $\alpha, \beta$ are $x, y$. Then Eq. (2) can be represented in terms of the stress tensor as

$$ \text{div} \sigma + f_s(r) = 0, $$

where $(\text{div} \sigma)_\alpha = \sum_{\beta} \partial \sigma_{\alpha\beta}/\partial x_\beta$.

As shown in Fig. 1, the membrane is located in the plane at $z = 0$. The solvent velocities $v^{(3)}(r, z)$, satisfy the incompressibility condition

$$ \nabla \cdot v^{(3)}(r, z) = 0, $$

where $\nabla$ represents a differential operator in the 3D Euclidean space. We denote the 3D viscosity of the solvent as $\eta_s$, and the solvent flow also obeys the 3D Stokes equation

$$ \eta_s \nabla^2 v^{(3)}(r, z) - \nabla p^{(3)}(r, z) = 0, $$

where $p^{(3)}(r, z)$ represents the pressure of the solvent. The solvent is supported on the substrate, which is located at $z = -h$. The no-slip boundary condition is imposed at $z = -h$ as well as between the membrane flow and the solvent flow. Through this boundary condition, the surrounding solvent exerts a drag force on the liquid membrane.

The drag force in Eq. (2) can be expressed as $f_s = -(I - \hat{e}_z \cdot \hat{e}_z) \cdot \sigma^{(3)}(r, 0) \cdot \hat{e}_z$, where $\hat{e}_z$ is the unit vector along the $z$ axis. The tensorial component of $I$ is given by $\delta_{ij}$, and $I - \hat{e}_z \cdot \hat{e}_z$ denotes the projection to the in-plane space. The stress tensor of solvent is given by

$$ \sigma^{(3)}_{ij}(r, z) = -p^{(3)}(r, z) \delta_{ij} + \eta_s \left[ \tilde{\delta}_{ij} v^{(3)}_{ij}(r, z) + \tilde{\delta}_{ij} v^{(3)}_{ij}(r, z) \right], $$

where $i, j$ denote $x, y, z$. 

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DIFFUSION COEFFICIENT OF AN INCLUSION IN A …

Using the stick boundary conditions at \( z = 0 \) and \( z = -h \), we solve the hydrodynamic equations from Eq. (5) to Eq. (6) to obtain \( \mathbf{f}_f \). In the Fourier space, \( \mathbf{f}_f \) is calculated to be [22,33,41]

\[
\mathbf{f}_f[k] = -\eta k \coth(kh) v[k],
\]

where \( k = (k_x, k_y) \) and \( k = |k| \). The real space velocity field of the membrane flow \( v(\mathbf{r}) \) can be expressed as

\[
v(\mathbf{r}) = \int \frac{d^2k}{(2\pi)^2} v[k] \exp(i\mathbf{k} \cdot \mathbf{r}).
\]

The Fourier space mobility tensor \( G[\mathbf{k}] \) associated with the velocity field is given by [22,33,41]

\[
G_{\alpha\beta}[k] = \frac{1}{\eta (k^2 + \nu k \coth(kh))} \left( \delta_{\alpha\beta} - \frac{k_{\alpha} k_{\beta}}{k^2} \right).
\]

In order to calculate diffusion coefficients, the mobility tensor in Fourier space should be transformed into real space. Previously, the inverse Fourier transform of the mobility tensor was analytically performed in the limits of infinite or zero thicknesses of a solvent layer. In the next section, the inverse Fourier transformation of the mobility tensor is analytically performed for an arbitrary thickness of a solvent.

### III. DIFFUSION COEFFICIENT OF A TWO-DIMENSIONAL POLYMER CHAIN

As an illustrative example for the influence of finite thickness of solvent on the diffusion coefficient of a macromolecule embedded in a 2D planar membrane, we consider the diffusion of a polymer chain confined in the membrane [17,28,31]. Previously, the influence of the solvent on diffusion coefficients is analytically investigated in the limits of very thin or infinite thicknesses of solvent layers. In these works, the hydrodynamic screening length is a key quantity in characterizing the screening of the flow of membrane by the presence of solvent layers. The influence of finite thickness of solvent was investigated by numerically evaluating the inverse Fourier transform of the mobility tensor, where the hydrodynamic screening length was not even defined. In this section, the hydrodynamic screening lengths are obtained from an analytical equation for arbitrary thickness of solvent layer.

The conformation of a 2D polymer chain embedded in a 2D membrane is represented by \( N \) beads with position vectors, \( \{\mathbf{R}_n\} = (\mathbf{R}_1, \ldots, \mathbf{R}_N) \), under the potential energy

\[
U = \frac{k_B T}{b^2} \sum_{n=2}^N (\mathbf{R}_n - \mathbf{R}_{n-1})^2.
\]

where \( b \) is the Kuhn length [42]. The mobility tensor associated with the beads is given by the inverse Fourier transform of Eq. (10) as

\[
G_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) = \int \frac{d^2k}{(2\pi)^2} G_{\alpha\beta}[k] \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)].
\]

Within the pre-averaging approximation [42], the polymer diffusion coefficient is expressed as

\[
D_{\text{poly}} = k_B T \int_0^N \frac{dn}{N} \int_0^N \frac{dm}{N} g(n-m),
\]

where \( g(n-m) \) is the isotropic component of mobility tensor \( G_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m) \) [28]. By using Eq. (12), two analytical expressions for the diffusion coefficients have been derived from Eq. (13) in the limits of very thin or infinite thickness of solvent layers [17,28]. Here, we investigate the diffusion coefficient by keeping the finite depth of the solvent layer without taking the limits. By expanding \( 1/(k + \nu \coth(kh)) \) in partial fractions, we note the general relation [43]

\[
\int_0^\infty \frac{k f(k)}{k + \nu \coth(kh)} = \sum_{j=1}^{\infty} \frac{C_j}{k^2 + \kappa_j^2},
\]

where \( f(k) \) is an arbitrary function, \( \kappa_j \) and \( C_j \) will be later given by Eqs. (16) and (17), respectively. By introducing Eq. (14) into Eqs. (12) and (13), we obtain,

\[
g(n-m) = -\sum_{j=1}^{\infty} \frac{C_j}{8\pi \eta} \exp \left[ \frac{1}{4} b^2 \kappa_j^2 |n-m| \right]
\times \text{Ei} \left( -\frac{1}{4} b^2 \kappa_j^2 |n-m| \right),
\]

where \( \text{Ei}(\cdot) \) is the exponential integral [44].

In the real space, the mobility tensor is expressed in terms of an infinite number of characteristic lengths, \( \kappa_j^{-1} \), where \( \kappa_j \) is determined by the following characteristic equation

\[
\cot(\kappa_j h) = \frac{\kappa_j}{\nu}.
\]

All the roots of the equation are given by \( \kappa_j = \pm \kappa_j \) with \( j = 1, 2, \ldots \). The characteristic lengths relative to \( h, 1/(\kappa_j h) \), depend on \( \nu h \) given by the viscosity ratio \( \nu = \eta_s/\eta \), and represent the screening of hydrodynamic flow in a 2D membrane due to the presence of the solvent. The contribution of each screening length is weighted by the factor

\[
C_j = \frac{2\nu}{h\kappa_j^2 + h\nu^2 + \nu}.
\]

Using Eq. (15), the diffusion coefficient is obtained as

\[
D_{\text{poly}} = \sum_{j=1}^{\infty} \frac{C_j}{4\pi \eta} \frac{k_B T}{\epsilon_j} \left[ (1 + \epsilon_j^2)(2 \ln \epsilon_j + \gamma) \right.
\]

\[
\left. -\epsilon_j^2 \exp(\epsilon_j^2) \text{Ei}(\epsilon_j^2) \right],
\]

where \( \gamma = 0.5772 \ldots \) is Euler’s constant. In the above, we have defined the dimensionless polymer size as \( \epsilon_j \equiv \sqrt{N} b \kappa_j / 2 = R_s \kappa_j \), and \( R_s = \sqrt{N} b / 2 \) is the radius of gyration for the 2D Gaussian polymer chain.

The limiting expression for \( \epsilon_j \ll 1 \) is

\[
D_{\text{poly}} \approx C_1 \frac{k_B T}{4\pi \eta} \left( -\ln \epsilon_1 - \frac{\gamma}{2} + \frac{3}{4} \right).
\]

As will be discussed in the next section, the above expression is close to the exact result under the additional condition of \( \nu h < 1 \), which is needed to replace the sum in Eq. (18) with the term related to \( \epsilon_1 \). When \( \epsilon_1 \gg 1 \), Eq. (18) reduces to

\[
D_{\text{poly}} \approx C_1 \frac{k_B T}{4\pi \eta} \frac{1}{\epsilon_1^2}(2 \ln \epsilon_1 + \gamma - 1).
\]

This expression holds regardless of the value of \( h \) as long as it is finite. The sum in Eq. (18) can be represented by the single
dominant term as long as $\epsilon_1 \gg 1$. However, the additional condition of $\nu h < 1$ is required when $\epsilon_1 \ll 1$, about which we shall discuss in the next section.

**IV. HYDRODYNAMIC SCREENING LENGTH VERSUS SOLVENT THICKNESS**

If the approximated diffusion coefficient obtained by taking into account only the smallest positive value of $\kappa_j$ (denoted by $\kappa_j$) reproduces the exact results, then $\kappa_j^{-1}$ can be regarded as the effective hydrodynamic screening length.

First, we consider the value of $\kappa_1$, which is the inverse of the effective hydrodynamic screening length as long as the higher-order ($j \geq 2$) terms can be ignored. We first note the series expansion,

$$x \cot x = 1 + 2 + \infty\sum_{n=1}^{\infty} \frac{x^2}{x^2 + \pi^2}.$$  \hspace{1cm} (21)

Since the lowest-order term can be estimated as $1 + 2x^2/(x^2 - \pi^2) \approx x^2/(\nu h)$, the approximate expression for $\kappa_1$ turns out to be

$$\kappa_1 \approx \left( \frac{2\nu h + \pi^2 \sqrt{3\nu h + 2\nu h \pi^2 + \pi^2}}{2h^2} \right)^{1/2}. \hspace{1cm} (22)$$

In the limit of $\nu h / \pi^2 < 1$, $\kappa_1$ can be further approximated as

$$\kappa_1 \approx \kappa \left( 1 - \frac{\nu h}{\pi^2} \right), \hspace{1cm} (23)$$

where $\kappa = \sqrt{\nu / h}$ is the inverse of the ES hydrodynamic screening length defined in the limit of $h \to 0$. In Fig. 2, the smallest positive values for the inverse of the characteristic lengths are presented against the solvent layer thickness, $h$. By increasing the solvent layer thickness $h$, the inverse of the hydrodynamic screening length rapidly decreases as shown in Fig. 2.

Next we consider the condition for which the diffusion coefficient can be characterized by a single hydrodynamic screening length as a good approximation for the exact expression including multiple hydrodynamic screening lengths associated with higher-order $\kappa_j$. Judging from Eq. (16) and Fig. 3(a), $\kappa_j$ takes discrete values that are almost equally separated. When $\kappa_1 R_g$ is well separated from $\kappa_2 R_g$ and the diffusion coefficient is given by the weighted sum of monotonically decreasing functions of $\kappa_j R_g$ multiplied by the rapidly decreasing weights, the sum can be well represented by the term associated with $\kappa_1 R_g$ alone. Below, we show that $\kappa_1 R_g$ is well separated from $\kappa_2 R_g$ when $R_g > h$ and the weights rapidly decay when $h < 1/\nu$.

Since we have $\kappa_j \approx \kappa_1 + \pi (j - 1)/h$, the hydrodynamic screening lengths are separated by the factor $1/h$. Hence $\kappa_3 R_g$ is well separated from $\kappa_2 R_g$ when $R_g/h > 1$. It is convenient to define the cutoff size $R_g^* = h$ over which the expression with $\kappa_1 R_g$ could be very different from that with $\kappa_2 R_g$.

In Fig. 3(b), the weight factors $C_j$ are shown against $\kappa_j/\nu$. The weight factors $C_j$ in Eq. (17) decrease with

![FIG. 2. (Color online) The smallest positive values for the inverse of the characteristic lengths against the solvent thickness. Both quantities are normalized by $\nu = \eta_s/\eta$. The red thick line represents the smallest positive root of the characteristic equation, Eq. (16), calculated numerically. The long dashed line represents $\kappa_j/\nu = 1/\sqrt{\nu h}$. The short dashed line represents the result of Eq. (23). The thin solid line represents the result of Eq. (22).](image)

![FIG. 3. (Color online) (a) The pictorial solution of the characteristic equation, Eq. (16); cot$(x)$ against $x$ and $x/(\nu h)$ against $x$ for $\nu h = 1$. The cross points of lines are $x_j = \kappa_j h$. The smallest positive value is $x_1, \kappa_1$ is obtained by $\kappa_1 = x_1/\nu h$ (b) $C_j$ against $\kappa_j/\nu$. $C_j$ represents the weight associated with each hydrodynamic screening length, Eq. (17). Blue squares, red circles, and dots represent $\nu h = 0.1, \nu h = 1.0$, and $\nu h = 10.0$, respectively.](image)
increasing $\kappa_j$. The ratio of $C_2/C_1$ is an important factor in estimating whether the term related to $\kappa_1$ is dominant over other terms. Fig. 3(b) shows that the difference between $C_1$ and $C_2$ increases by decreasing the thickness of solvent layer. Specifically, we have $\kappa_j \approx \kappa_1 + \pi (j - 1)/h$ and $C_2/C_1 \approx \kappa_j^2/\kappa_1^2 \approx \nu h / \pi^2$. Hence the diffusion coefficient can be approximated by the expression involving $\kappa_1$ alone when $\nu h / \pi^2 < 1$. When the condition $\nu h < 1$ is satisfied, $C_2/C_1 < 1$ and the diffusion coefficients can be approximated by those obtained by Evans and Sackmann, where $C_1 \sim 1/(1 + \nu h/2) \sim 1$. It is then convenient to define the critical thickness of solvent $h^* = 1/\nu$. If the solvent depth exceeds $h^*$, the weight of $C_2$ is not much different from that of $C_1$. It should be noticed, however, that the precise estimation of the contribution from the higher modes requires the whole expression besides the weights.

The expression of the diffusion coefficient depends on the kind of inclusions. As a representative example, we consider the diffusion coefficient of a polymer to study conditions to use a single effective hydrodynamic screening length given by $1/\kappa_1$. In Fig. 4, we show the polymer diffusion coefficients against the size of the polymer $R_g$ to study whether the polymer diffusion coefficients can be approximated by an expression without summation. When $\nu h \ll 1$, the polymer diffusion coefficients can be approximated by taking into account only $\kappa_1$ as shown in Fig. 4. It is consistent with the fact that the weight $C_2$ is smaller than $C_1$ when $\nu h \leq 1$ since $C_2/C_1 \sim \nu h / \pi^2$. The situation corresponds to that considered by Evans and Sackmann.

When $\nu h > 1$, $C_1$ is close to $C_2$ and the functional form of the diffusion coefficient should be carefully examined. When $\nu h > 1$ and $R_g > h$ holds, $\kappa_1 R_g > 1$ is satisfied. Then the diffusion coefficient is well approximated by Eq. (20) showing $1/(\kappa_1 R_g)^2$ dependence. Notice that $1/(\kappa_1 R_g)^2$ decays relatively fast by increasing $j$. When $\nu h > 1$ and the size of the polymer $R_g$ exceeds the solvent thickness $h$, the diffusion coefficient is approximated by the expression given in terms of $\kappa_1 R_g$ alone.

When $\nu h > 1$ and $R_g < h$, on the other hand, a significant deviation is seen for the diffusion coefficients if the higher-order terms are ignored, as can be seen from Fig. 4. This deviation originates from the fact that the weak logarithmic dependence on $\kappa_1 R_g$ and $\kappa_3 R_g$ is not well separated from $\kappa_1 R_g$ if $R_g/h < 1$. Also notice that $C_1$ is close to the other values of $C_j$ if $\nu h > 1$. In such a situation, multiple hydrodynamic screening lengths should be taken into account.

To summarize, we have four length scales: the critical thickness of the solvent $h^* = 1/\nu$, the cutoff size of the polymer $R_g^* = h$, the SD hydrodynamic screening length $\nu^{-1}$, and the ES hydrodynamic screening length $\kappa_1^{-1}$ [see Eq. (22)]. Although $h^*$ is identical to the SD hydrodynamic screening length $\nu^{-1}$, their physical meanings are different as explained below.

The diffusion coefficient can be approximately expressed by using either $\nu^{-1}$ or $\kappa_1^{-1}$. For the thin solvent layer, $h < 1/\nu$, the weights rapidly decrease with increasing $j$ and the diffusion coefficient is given by $\kappa_1^{-1}$ regardless of the macromolecule size. This is the limiting case considered by Evans and Sackmann. For thick solvent layers exceeding the critical thickness $h^* = 1/\nu$, the diffusion coefficient can be approximated by the expression including only the single hydrodynamic screening length $\kappa_1^{-1}$, when the size of the macromolecule is larger than $R_g^* = h$. In this case, we have $(\kappa_2 - \kappa_1)R_g^* \sim R_g^*/h > 1$ and $\kappa_1 R_g$ is well separated from $\kappa_3 R_g$. When the solvent thickness exceeds $h^* = 1/\nu$ and the size of macromolecules is smaller than $R_g^* = h$, on the other hand, the diffusion coefficient shows weak logarithmic dependence on $\kappa_1 R_g$ and multiple hydrodynamic screening lengths should be taken into account. The diffusion coefficient is expressed by the hydrodynamic screening length $\nu^{-1}$ in the limit of $h \to \infty$.

V. DIFFUSION COEFFICIENT OF A CIRCULAR DOMAIN

In this section, we consider the diffusion coefficient of a circular liquid domain in a membrane (see Fig. 5). Although
the characteristic equation, Eq. (16) associated with the solvent and the membrane flow should not be altered by changing the inclusion from polymers to liquid domains, the condition that the diffusion coefficient can be approximated by truncating the infinite sum to a single expression depends on the size dependence of the diffusion coefficients. The size dependence can differ between polymers and liquid domains. For simplicity, we consider the case when the viscosity of the circular liquid domain is the same as that of the host membrane denoted by $\eta$. Previously, simple expressions for the diffusion coefficients were obtained for either infinite or very thin limits of the solvent layers [16,39]. Here we generalize the results to arbitrary thickness of solvent layers.

We consider the situation for which the center of the circular object moves with the velocity $\mathbf{U}$, and its edge is assumed to keep a circular shape without any deformation. The velocity field inside and outside the circular domain satisfy [45]

$$\eta \nabla^2 \mathbf{v}(r) - \nabla p(r) + \mathbf{f}(r) + F^{(I)}(r) \frac{\delta(r - R)}{2\pi R} = 0, \quad (24)$$

and the incompressibility condition given by Eq. (1) for all $r$. Here $\mathbf{f}$, was defined before in Eq. (8), and $F^{(I)}$ is the force exerted at the periphery of the circular membrane in the direction normal to the circular boundary [39]. If we take the origin of the coordinates at the center of the circular domain and choose the $x$ coordinate in the direction of $\mathbf{U}$, $F^{(I)}$ should vary according to the velocity $\mathbf{U}$ at the periphery of the circle. From the symmetry with respect to $\mathbf{U}$, $F^{(I)}$ can be expressed as [39]

$$F^{(I)}(r) = \mathbf{F}^{(\infty)} \cdot \mathbf{n}, \quad (25)$$

where $\mathbf{n} = \mathbf{r}/r$ is the outward normal unit vector at the surface of the circle of radius $R$, and $\theta$ is the angle between $\mathbf{U}$ and $\mathbf{r}$.

Our task is to calculate the total force exerted on the circular domain in the steady state

$$\mathbf{F} = \int_{r = R} d\sigma \cdot \mathbf{n} + \int_{r < R} d\mathbf{f}, \quad (26)$$

where $\sigma$ is the stress tensor of the liquid membrane given by Eq. (3) and $d\sigma$ denotes the line integration. The first term represents the force exerted from the membrane flow field, and the second term represents the direct friction force exerted from the solvent surrounding the membrane to the circular domain.

By using Gauss’s theorem, we find

$$\mathbf{F} = \int_{r = R} d\sigma \cdot \mathbf{n} + \int_{r < R} d\mathbf{f},$$

$$= \int_{r < R} dr \delta \sigma \cdot \mathbf{n} + \int_{r < R} dr d\mathbf{f},$$

$$= -\int_{r < R} dr F^{(I)}(r) \frac{\delta(r - R)}{2\pi R},$$

$$= -\frac{\mathbf{F}^{(\infty)}}{2} \hat{\mathbf{e}}_x \int_0^{2\pi} d\theta \frac{\cos \theta}{2\pi} = -\frac{\mathbf{F}^{(\infty)}}{2} \hat{\mathbf{e}}_x, \quad (27)$$

where Eq. (4) and Eq. (24) are used to obtain the third equality, and $\hat{\mathbf{e}}_x$ denotes the unit vector along the $\alpha$ direction. Equation (27) shows that it is sufficient to calculate $\mathbf{F}^{(\infty)}$ to obtain the total force exerted on the circular object from the membrane flow field and the solvent.

The velocity field can be formally expressed as

$$\mathbf{v}_\sigma(r) = \int dr' G_{\alpha\beta}(r - r')e^{(II)}(r') \frac{\delta(r' - R)}{2\pi R}. \quad (28)$$

In real space, the mobility tensor is expressed by the Fourier transform of Eq. (10) as

$$G_{\alpha\beta}(\mathbf{r}) = \int \frac{d^2k}{(2\pi)^2} G_{\alpha\beta}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (29)$$

Equation (28) can be rewritten as

$$\mathbf{v}_\sigma(r) = \int \frac{d^2k}{(2\pi)^2} \int dr' \exp(i\mathbf{k} \cdot \mathbf{r}) G_{\alpha\beta}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{r}') \times F^{(II)}(\mathbf{r}) \frac{\delta(r' - R)}{2\pi R}. \quad (30)$$

Let $\varphi$ denote the angle between $\mathbf{r}'$ and $\mathbf{U}$. Then we obtain

$$\int dr' \exp(-i\mathbf{k} \cdot \mathbf{r}') F^{(II)}(\mathbf{r}') \frac{\delta(r' - R)}{2\pi R},$$

$$= \int_0^{2\pi} \frac{d\varphi}{2\pi} \exp[-i(k_x \cos \varphi + k_y \sin \varphi)R]\mathbf{F}^{(\infty)} \cos \varphi \frac{r'_\beta}{r'}, \quad (31)$$

where $r'/r$ is the unit orientational vector. Equation (30) can be rewritten by using Eq. (31) and the relation

$$\left(\delta_{\alpha\beta} - \frac{k_x k_\beta}{k^2}\right) \frac{r'_\alpha}{r'} = \frac{k_\alpha}{k^2}(k_x \cos \varphi + k_y \sin \varphi). \quad (32)$$

The integration with respect to $\varphi$ can be performed (see Appendix for the useful relations to perform this integration), and the result becomes

$$\mathbf{v}(r) = \int \frac{d^2k}{(2\pi)^2} \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{\eta[k^2 + \nu k \coth(kh)]} \left[ \frac{k_x^2}{k^2} J_1(kR) \hat{\mathbf{e}}_x + \left( \frac{k_y}{k^2} J_2(kR) - \frac{k_x}{k^2} k^2 J_1(kR) \right) \hat{\mathbf{e}}_y \right] \mathbf{F}^{(\infty)}. \quad (33)$$

Finally, we note $\mathbf{k} = (k \cos \phi, k \sin \phi)$ and $\mathbf{r} = (r \cos \theta, r \sin \theta)$ as well as the relation

$$\int_0^{2\pi} \frac{d\varphi}{2\pi} \int_0^\infty dk \frac{1}{2\pi} \int_0^\infty dk' \frac{1}{2\pi} \exp[-ikr \cos \theta \cos \phi + \sin \theta \sin \phi], \quad (34)$$

Then the integration with respect to $\phi$ can be performed to obtain

$$\mathbf{v}(r) = \hat{\mathbf{e}}_x \int_0^\infty dk \frac{J_1(kR) J_1(kr)}{2\pi \eta k R [k^2 + \nu k \coth(kh)]} \mathbf{F}^{(\infty)}. \quad (35)$$

By identifying the velocity at the periphery of the domain to be $\mathbf{U}$ and using Eq. (27), we obtain

$$\mathbf{U} = -\mathbf{F} \int_0^\infty dk \frac{J_1(kR)^2}{\pi \eta k R [k^2 + \nu k \coth(kh)]}. \quad (36)$$

The friction coefficient is given by $\zeta = -\mathbf{F}/\mathbf{U}$. Following the Einstein relation $D = k_B T/\zeta$, we obtain the diffusion coefficient of a domain as

$$D_{\text{dom}} = k_B T \int_0^\infty dk \frac{J_1(kR)^2}{\pi \eta k R [k^2 + \nu k \coth(kh)]}. \quad (37)$$
This is the generalization of the result obtained by De Koker to the case of finite solvent depth [39].

A. Limit of infinite thickness of the solvent layer

In this limit, the diffusion coefficient of the circular object was first calculated for the solid circular disk by Saffman and Delbrück [8,9]. For a circular liquid domain that has the same viscosity as the outside of the domain, the diffusion coefficient was obtained by De Koker [39]. The similar expression was obtained for the domain shape relaxation times [46].

By taking the limit of $kh \gg 1$ in Eq. (10), the mobility tensor can be written as [22,24]

$$G_{a\beta}[k] = \frac{1}{\eta (k^2 + \nu k)} \left( \delta_{a\beta} - \frac{k_a k_\beta}{k^2} \right). \quad (38)$$

If the above mobility tensor is used in Eq. (37), it reduces to that derived by De Koker [39]. In this case, the integration can be performed by using MATHEMATICA with the use of Meijer G functions [47]

$$D_{\text{dom}} = \frac{k_B T}{2\pi \eta (\nu R)^2} \left\{ -\frac{2}{(\nu R)^2} - 1 \right. + \frac{1}{\nu R} \left[ (\nu R)^2 \left\{ \begin{array}{c} 1/2, 3/2 \nu R, \nonumber \\ 1/2, 3/2, -1 \end{array} \right. \right] \right\}. \quad (39)$$

This expression is useful to take the limits with respect to $\nu R$.

In the case of $\nu R \ll 1$, the above expression reduces to

$$D_{\text{dom}} \approx \frac{k_B T}{4\pi \eta} \left[ \ln \left( \frac{2}{\nu R} \right) - \gamma + \frac{1}{4} \right]. \quad (40)$$

The difference from the result by Saffman and Delbrück is the additional factor $1/4$ in the right-hand side of Eq. (40) [8,9]. This means that the diffusion coefficient of a circular domain is slightly larger than that of the disk, since the flow induced inside the domain reduces the friction between the membrane flow and the domain periphery compared to that between the membrane flow and the solid edge. In the opposite limit of $\nu R \gg 1$, the diffusion coefficient is obtained as

$$D_{\text{dom}} \approx \frac{4k_B T}{\pi^2 \eta R}, \quad (41)$$

which is inversely proportional to the domain radius, $R$. The obtained diffusion coefficient is again slightly larger than that of the disk in the same limit [10,11]

$$D_{\text{disk}} \approx \frac{k_B T}{8\eta R}. \quad (42)$$

The fact that $D_{\text{dom}}$ is inversely proportional to $R$ is consistent with the result of the 2D polymer chain in the membrane [28].

B. The limit of thin solvent layer

The diffusion in supported membranes in the $\nu h \ll 1$ limit was originally considered by Evans and Sackmann for the solid disk immersed in the membrane [14]. The diffusion coefficient of a circular viscous domain embedded in the membrane was recently studied by the present authors [16]. In this case, Eq. (10) takes the following form

$$G_{a\beta}[k] = \frac{1}{\eta (k^2 + \nu k)} \left( \delta_{a\beta} - \frac{k_a k_\beta}{k^2} \right), \quad (43)$$

where $\kappa \equiv (\nu/h)^{1/2}$. The above mobility tensor was previously used by the present authors [15–19].

We replace $\nu k \coth(\nu h) \simeq \kappa^2$ for $h \to 0$ in the integrand of Eq. (37). A rigorous condition of small $h$ needs some care since $\kappa = (\nu/h)^{1/2}$ diverges in the limit of $h \to 0$ when $\nu$ is finite. In the previous section, we have discussed the condition in detail and shown that the results are valid under the condition given by $\nu h < 1$. With this replacement, we obtain

$$D_{\text{dom}} \approx \frac{k_B T}{\pi \eta (\kappa R)^2} \left[ \frac{1}{2} - I_1(\kappa R)K_1(\kappa R) \right], \quad (44)$$

which coincides with our previous result [16]. However, it should be noted that the mobility coefficient was obtained by taking into account the hydrodynamic forces from the membrane alone in Ref. [16]. In order to compare the present result with our previous result, the direct friction between the solvent and the domain, $\pi \eta (\kappa R)^2$, should be added to the previous result. This leads to adding $k_B T/\pi \eta (\kappa R)^2$ to the diffusion coefficient. For comparison, we also write the result by Evans and Sackmann [14]

$$D_{\text{ES}} = \frac{k_B T}{\pi \eta (\kappa R)^2} \left[ 2 + \frac{4k_B T}{\pi \eta} \right]^{-1} \left[ \left( \frac{2}{\nu R} \right) - \gamma + \frac{1}{4} \right], \quad (45)$$

where the direct friction between the solvent and the domain is added. As pointed out before, Eq. (44) is slightly larger than Eq. (45) [16]. This is because the fluid flow in the domain reduces the friction between the domain and the host membrane at the edge.

In the limit of $\kappa R \ll 1$, the previous result is reproduced [16]

$$D_{\text{dom}} \approx \frac{k_B T}{4\pi \eta (\kappa R)^2} \left[ \ln \left( \frac{2}{\nu R} \right) - \gamma + \frac{1}{4} \right]. \quad (46)$$

In the opposite limit of $\kappa R \gg 1$, the diffusion coefficient is obtained as

$$D_{\text{dom}} \approx \frac{k_B T}{2\pi \eta (\kappa R)^2}. \quad (47)$$

In this limit, $D_{\text{dom}}$ decays as $1/R^2$ as pointed out before [16].

C. Finite thickness of solvent layer

In the case of finite $h$, the integration of Eq. (37) can be transformed into the summations as employed before

$$D_{\text{dom}} = \sum_{j=1}^{\infty} C_j \frac{k_B T}{\pi \eta (\kappa_j R)^2} \left[ \frac{1}{2} - I_1(\kappa_j R)K_1(\kappa_j R) \right], \quad (48)$$

where $C_j$ is the weight factor given by Eq. (17) and $\kappa_j$ is determined by Eq. (16).

When $\nu h < 1$, $C_j$ decreases rapidly as $j$ increases as already shown in the previous section. In this case, Eq. (48) can be approximated by the lowest order expression,

$$D_{\text{dom}} \approx C_1 \frac{k_B T}{\pi \eta (\kappa_1 R)^2} \left[ \frac{1}{2} - I_1(\kappa_1 R)K_1(\kappa_1 R) \right], \quad (49)$$

where $\kappa_1$ is the smallest positive value of $\kappa_j$. For $\kappa_1 R \ll 1$, Eq. (49) reduces to

$$D_{\text{dom}} \approx C_1 \frac{k_B T}{4\pi \eta} \left[ \ln \left( \frac{2}{\kappa_1 R} \right) - \gamma + \frac{1}{4} \right], \quad (50)$$
whereas for $\kappa_1 R \gg 1$, it reduces to

$$D_{\text{dom}} \approx C_1 \frac{k_B T}{2 \pi \eta (\kappa_1 R)^2}.$$  \hspace{1cm} (51)

When $\nu h > 1$, Eq. (49) approximates the exact expression, Eq. (48), only when the expression multiplied to $C_1$ rapidly decreases with increasing $j$ as we have already stated in the previous section. Since the hydrodynamic screening lengths and the weights factors are common, the difference between the polymer and the circular liquid domain originates from the nondimensional size dependence. However, the size dependence is very similar between the polymer and the circular domain (i.e., weak logarithmic dependence for relatively small sizes and the algebraic dependence at large sizes). As a consequence, essentially the same results as those shown in Fig. 4 are obtained for the two cases. The condition that the diffusion coefficient can be approximated by the expression with a single hydrodynamic screening length is essentially the same for the polymer and the circular liquid domain. When $\nu h > 1$, Eq. (51) is a good approximate expression of Eq. (48) but Eq. (50) is not.

Before closing the section, we compare in Fig. 6 the generalized solution of De Koker given by Eq. (37) with the results in the two limits; the original solution of De Koker obtained in the limit of $h \to \infty$ and the results of Eq. (44) obtained in the limit of $h \to 0$. The results of Eq. (37) with $\nu h = 0.1$ overlap with the results of Eq. (44). The diffusion coefficient of Eq. (44) is slightly larger than that of the solid disk, Eq. (45). By increasing $\nu h$ the results shift toward the original solution of De Koker. In the asymptotic limit, the diffusion coefficient scales with $1/R^2$ in the generalized solution of De Koker, while the diffusion coefficient scales with $1/R$ in the the original solution of De Koker. In the opposite limit of $R \to 0$, all the results of Eq. (37) as well as the original solution of De Koker show the logarithmic dependence on $R$ as represented by Eq. (40).

VI. CONCLUSIONS

The diffusion coefficient of an inclusion in a membrane is strongly influenced by the presence of solvents due to the stick boundary condition between the membrane and the solvent. The thickness of the solvent layer is a key parameter controlling the diffusion of an inclusion in a membrane. In this work, the diffusion coefficient of a polymer confined in a membrane is obtained for an arbitrary thickness of solvents. We also study the influence of a finite thickness of solvent on the diffusion coefficient of a circular liquid domain with the same viscosity as that of the host membrane. Previously, the diffusion coefficient of a circular liquid domain was expressed by a single integral in the limit of infinite solvent thickness [39]. In this work, the integral expression is generalized to the case of finite solvent depth. The various analytical expressions are obtained from the integral expression.

In general, the diffusion coefficient of inclusions decreases as the solvent thickness decreases. The solvent induces drag against the membrane flow, and as a result diffusion is suppressed. The drag increases as the distance between the membrane and the substrate decreases. More precisely, the influence of the solvent on the membrane flow is characterized by the hydrodynamic screening lengths. Multiple hydrodynamic screening lengths can be obtained from the characteristic equation, Eq. (16), when the solvent thickness is nonzero. The largest hydrodynamic screening length characterizes the length scale of momentum dissipation from the membrane to the solvent. The membrane flow dissipates the momentum to the solvent through the stick boundary condition. For finite solvent depth, the largest hydrodynamic screening length is approximately given by $\sqrt{h/\nu}$. The diffusion coefficients are expressed by the weighted sum of the functions of the nondimensional size of the inclusion normalized by the hydrodynamic screening lengths. The weights are given by Eq. (17).

By examining both the weights and the nondimensional size dependence, we find that the diffusion coefficient can be approximated by the expression given by the largest hydrodynamic screening length alone except when both $\nu^{-1}$ and the size of the inclusion are smaller than the solvent thickness. (The results are summarized in Table I.) When the solvent thickness is larger than $\nu^{-1}$, $h > \nu^{-1}$, the weights decrease slowly with increasing $j$. Hence $\nu^{-1}$ can be viewed as the critical solvent depth below which there is a dominant mode given by the largest hydrodynamic screening length. If the size of the inclusion is smaller than the solvent thickness, $\kappa_1 R$ is close to $\kappa_2 R$ since we have $\kappa_2 R - \kappa_1 R \sim R/h$. Besides, if the diffusion coefficient depends weakly on $\kappa_j R$, the diffusion coefficient expressed by $\kappa_j R$ alone cannot represent the exact summed result. In particular, the sum of logarithmic functions of screening lengths weighted by the similar factors cannot be represented by one of the terms. The situation is met when
For simplicity, we have considered the situation where the membrane is floated on a solvent layer. In general, both sides of a membrane are surrounded by solvents. We consider the case that the solvent layer on the membrane is covered by a substrate and is not a freestanding film. We denote the 3D viscosity of solvent and the thickness in the upper domain as $\eta^+$ and $h^+$, respectively, and those in the lower domain as $\eta^-$ and $h^-$, respectively.

Equations (10) and (37) are valid if we replace $k + v \coth(kh)$ with $k + v^+ \coth(kh^+) + v^- \coth(kh^-)$, where $v^+ = \eta^+ / \eta$ and $v^- = \eta^- / \eta$ [23]. Correspondingly, the characteristic equation becomes

$$v^+ \cot(k_j h^+) + v^- \cot(k_j h^-) = \kappa_j.$$  \hfill (52)

The influence of solvents on both sides of the membrane can be investigated by studying the roots of Eq. (52). By using $\cot x \approx 1/x$, we obtain

$$\kappa_1 = \sqrt{\frac{v^+}{h^+} + \frac{v^-}{h^-}},$$  \hfill (53)

when $k_1 h^+ < 1$ and $k_1 h^- < 1$.

In the simple situation where the membrane is sandwiched by the same depth of solvent layers $h = h^+ = h^-$, both the characteristic equation, Eq. (16) and the weights given by Eq. (17) still hold by using the renewed definition of $v = v^+ + v^-$. The diffusion coefficients in this particular case can be obtained from those presented in this paper by substituting $v = v^+ + v^-$. Our study on the influence of the finite solvent thickness indicates that the diffusion coefficient can be approximately expressed in terms of $\kappa_1$ except when both the SD screening length and the size of the inclusion are smaller than both $h^+$ and $h^-$.  

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APPENDIX: USEFUL RELATIONS

We have used the relations,
\[
\int_0^{2\pi} \frac{d\varphi}{2\pi} \exp[-i(k_x \cos \varphi + k_y \sin \varphi)a] = J_0(ka)
\]  
(A1)

and
\[
\int_0^{2\pi} \frac{d\varphi}{2\pi} \exp[-i(k_x \cos \varphi + k_y \sin \varphi)a] \cos^2 \varphi = -\frac{1}{a^2} \frac{\partial^2}{\partial k_x^2} J_0(ka) - \frac{k_y^2}{k_x^2} J_2(ka),
\]
(A2)

\[
\int_0^{2\pi} \frac{d\varphi}{2\pi} \exp[-i(k_x \cos \varphi + k_y \sin \varphi)a] \cos \varphi \sin \varphi = -\frac{1}{a^2} \frac{\partial^2}{\partial k_x \partial k_y} J_0(ka) - \frac{k_y}{k_x} J_2(ka).
\]
(A3)