Bulk-mediated surface transport in the presence of bias

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Surface transport, when the particle is allowed to leave the surface, travel in the bulk for some time, and then return to the surface, is referred to as bulk-mediated surface transport. Recently, we proposed a formalism that significantly simplifies analysis of bulk-mediated surface diffusion [A. M. Berezhkovskii, L. Dagdug, and S. M. Bezrukov, *J. Chem. Phys.* **143**, 084103 (2015)]. Here this formalism is extended to bulk-mediated surface transport in the presence of bias, i.e., when the particle has arbitrary drift velocities on the surface and in the bulk. A key advantage of our approach is that the transport problem reduces to that of a two-state problem of the particle transitions between the surface and the bulk. The latter can be solved with relative ease. The formalism is used to find the Laplace transforms of the first two moments of the particle displacement over the surface in time t at arbitrary values of the particle drift velocities and diffusivities on the surface and in the bulk. This allows us to analyze in detail the time dependence of the effective drift velocity of the particle on the surface, which can be highly nontrivial. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4991730>]

I. INTRODUCTION

Bulk-mediated surface transport is transport on the surface when the particle is allowed to unbind from the surface and travel in the bulk for some time. This is a ubiquitous phenomenon that arises in different contexts ranging from the search of a binding site for a protein on DNA to heterogeneous catalysis and many other physico-chemical processes playing an important role in biology and various technological applications.^{1–31} It was shown^{17–20} that bulk-mediated surface diffusion in infinite space has an interesting feature that attracted attention of many researchers, namely, the diffusion becomes anomalous at long times.

Our interest in this problem is motivated by recent studies on membrane-facilitated protein-protein interactions performed on biological beta-barrel channels reconstituted into planar lipid membranes.^{32–34} It was found that nanopores of these channels are able to capture small water-soluble proteins like alpha-synuclein and its derivatives, through a succession of events that crucially involve polypeptide binding to the membrane. In particular, it was shown³² that whenever the nanopore entrance protrudes out of the membrane surface by a distance exceeding the size of the bound molecule, the capture on-rate drops by orders of magnitude. This means that the capture is controlled by the polypeptide population on the membrane surface near the channel, and the capture rate is determined by a complex interplay between the polypeptide diffusion on the surface and in the bulk, as well as its reversible association with the membrane.

The conventional approach to the problem of bulk-mediated surface diffusion focuses on the particle propagator (Green's function), two components of which describe free diffusion of the particle on the surface and in the bulk. These components couple with each other. The coupling describes the exchange between the two components due to the particle unbinding from the surface and its rebinding to the surface from the bulk.

Recently we proposed an alternative approach to this problem³⁵ that focuses on the cumulative time spent by the particle on the surface. The approach exploits the fact that the free-particle propagators on the surface and in the bulk are Gaussian. As a consequence, the bulk-mediated particle propagation on the surface is determined by the cumulative times spent by the particle on the surface and in the bulk. These cumulative times are random variables which are not independent since their sum is equal to the total observation time. The quantity playing the key role in our approach is one of these times, namely, the cumulative time spent by the particle on the surface. The advantage of our approach is that the statistical properties of this cumulative time can be found by solving a relatively simple two-state problem of the particle transitions between the surface and the bulk.

One of the advantages of the formalism developed in Ref. 35 for the case of unbiased bulk-mediated surface diffusion is that it can be readily extended to the case where the particle is allowed to have arbitrary drift velocities in the bulk and on the surface. One can easily imagine that the particle has a drift velocity in the bulk, for example, due to the flow of the bulk liquid. As concerns the particle drift velocity on the surface, it is more difficult to imagine because it requires a special mechanism. We include the particle drift

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velocity on the surface into consideration to demonstrate the ability of the formalism to describe transport even under such conditions.

Although from the formalism point of view, the cases of biased and unbiased bulk-mediated surface transport are very similar (which is the advantage of the formalism), in some respect, these cases are different. Indeed, when the thickness of the bulk layer above the surface is finite, the unbiased transport is diffusive but the presence of drift destroys this transport property. This happens because the square of the leading term of the first moment of the particle displacement does not compensate the leading term of the second moment of the displacement. The situation is different in the absence of bias, where the first moment of the displacement is zero and the second moment at long times is proportional to time. Formally, the difference between biased and unbiased bulk-mediated surface transport is that the key quantity determining the transport in the absence of bias is the mean cumulative time spent by the particle on the surface, whereas analysis of transport in the presence of bias additionally requires the second moment of this random time.

The outline of this paper is as follows. The model of bulk-mediated surface transport is presented in Sec. II. In Sec. III, we discuss the particle propagator which is used in Sec. IV to find the first two moments of the bulk-mediated surface displacement of the particle. The effective particle drift velocity is considered in Sec. V. Section VI contains some concluding remarks.

II. MODEL

We study bulk-mediated transport in the flat geometry schematically shown in Fig. 1, assuming that the particle drift velocities and diffusivities on the surface (s) and in the bulk (b), respectively, are v_s , v_b , D_s , and D_b . It is assumed that both drift velocities are directed along the x -axis. Therefore, our attention is focused on the particle propagation in the x -direction. In the absence of the surface-bulk and bulk-surface transitions, the propagators on the surface and in the bulk for a particle that starts from $x = 0$ at time $t = 0$, denoted by $g_{s,b}(x, t)$, are given by

$$g_{s,b}(x, t) = \frac{1}{\sqrt{4\pi D_{s,b}t}} e^{-(x-v_{s,b}t)^2/(4D_{s,b}t)}. \quad (2.1)$$

These propagators also referred to as Green's functions are the probability densities of finding the particle at point x at time t .

FIG. 1. Schematic representation of the model geometry analyzed in the paper.

The first two moments of the displacement of such a particle in time t are

$$\langle x_{s,b}(t) \rangle = \int_{-\infty}^{\infty} x g_{s,b}(x, t) dx = v_{s,b}t \quad (2.2)$$

and

$$\begin{aligned} \langle x_{s,b}^2(t) \rangle &= \int_{-\infty}^{\infty} x^2 g_{s,b}(x, t) dx = \langle x_{s,b}(t) \rangle^2 + 2D_{s,b}t \\ &= v_{s,b}^2 t^2 + 2D_{s,b}t. \end{aligned} \quad (2.3)$$

It is assumed that the particle survival probability on the surface, $S_s(t)$, decays as a single exponential, $S_s(t) = e^{-kt}$, where k is the rate constant which is the inverse mean particle lifetime on the surface. The probability density, $\varphi_s(t)$, of this time is

$$\varphi_s(t) = -dS_s(t)/dt = ke^{-kt}. \quad (2.4)$$

In our further analysis, we use the Laplace transform of this probability density. [The Laplace transform of function $f(t)$, denoted by $\hat{f}(s)$, is defined as $\hat{f}(s) = \int_0^{\infty} e^{-st} f(t) dt$, where s is the Laplace parameter.] The Laplace transform of $\varphi_s(t)$ in Eq. (2.4) is

$$\hat{\varphi}_s(s) = \frac{k}{s+k}. \quad (2.5)$$

The particle rebinding to the surface from the bulk is determined by the surface trapping rate κ ($\kappa = 0$ and $\kappa = \infty$ correspond to perfectly reflecting and absorbing surfaces, respectively). It is taken that the particle motion in the bulk is constrained by a flat reflecting “lid” parallel to the surface, separated from the surface by distance L (see Fig. 1). In such a geometry, the probability density, $\varphi_b(t)$, of the particle lifetime in the bulk can be found by solving a one-dimensional diffusion problem in the direction normal to the surface. For the particle that starts from the surface, the Laplace transform of this probability density is³⁵

$$\hat{\varphi}_b(s) = \frac{\kappa}{\kappa + f(s)}, \quad f(s) = \sqrt{sD_b} \tanh\left(L\sqrt{s/D_b}\right). \quad (2.6)$$

At $L = \infty$, function $f(s)$ takes the form $f(s)|_{L=\infty} = \sqrt{sD_b}$. As a result, $\hat{\varphi}_b(s)$ in Eq. (2.6) reduces to

$$\hat{\varphi}_b(s)|_{L=\infty} = \frac{\kappa}{\kappa + \sqrt{sD_b}}. \quad (2.7)$$

Inverting this Laplace transform, one obtains

$$\varphi_b(t)|_{L=\infty} = \frac{\kappa}{\sqrt{\pi D_b t}} - \frac{\kappa^2}{D_b} e^{\kappa^2 t/D_b} \operatorname{erfc}\left(\kappa \sqrt{\frac{t}{D_b}}\right). \quad (2.8)$$

Using this or Eq. (2.7), one can check that the mean particle lifetime in the bulk diverges in the absence of the lid ($L = \infty$), which is the reason responsible for the anomalous bulk-mediated surface diffusion at long times under such conditions.^{17–20}

To summarize, our model contains seven parameters: the geometric parameter, L , the kinetic parameters, k and κ , and the transport parameters, v_s , v_b , D_s , and D_b . Our goal is to describe bulk-mediated particle propagation over the surface as a function of time. Special attention will be paid to the case of $L = \infty$ (infinite space), where bulk-mediated surface diffusion in the absence of bias becomes anomalous at long times.

III. PROPAGATOR

When a particle jumps between two states with different drift velocities and diffusivities, its propagator is determined by the cumulative times spent by the particle in each of the states. This is a consequence of the fact that the convolution of two Gaussian propagators is again a Gaussian propagator with the mean displacement and variance equal to the sums of the mean displacements and variances of the initial propagators. Let $G(x, t|\tau)$ be the propagator of a particle observed for time t on condition that the particle started from $x = 0$ at $t = 0$ and spent cumulative time τ on the surface and cumulative time $t - \tau$ in the bulk. This propagator is given by

$$G(x, t|\tau) = \int g_b(x - x', t - \tau) g_s(x', \tau) dx' \\ = \frac{1}{\sqrt{4\pi [D_s\tau + D_b(t - \tau)]}} e^{-[x - v_s\tau - v_b(t - \tau)]^2 / \{4[D_s\tau + D_b(t - \tau)]\}}. \quad (3.1)$$

Averaging this propagator over the random cumulative time τ on condition that the particle was bound to the surface at $t = 0$ and at time t , we obtain the propagator of interest, $G(x, t)$, that describes bulk-mediated surface transport. Denoting the corresponding probability density of the cumulative time τ by $\nu(\tau|t)$, we can write³⁵

$$G(x, t) = \int_0^t G(x, t|\tau) \nu(\tau|t) d\tau. \quad (3.2)$$

Note that the probability density $\nu(\tau|t)$ is normalized to the probability $P_s(t)$ of finding the particle bound to the surface at time t on condition that it was bound to the surface at $t = 0$. One can see this by integrating the propagator $G(x, t)$ over x from minus to plus infinity and using the fact that $\int_{-\infty}^{\infty} G(x, t|\tau) dx = 1$,

$$\int_{-\infty}^{\infty} G(x, t) dx = \int_0^t \nu(\tau|t) d\tau = P_s(t). \quad (3.3)$$

It is convenient to introduce the double Laplace transform of $\nu(\tau|t)$ defined as

$$\hat{\nu}(\sigma, s) = \int_0^{\infty} e^{-st} dt \int_0^t e^{-\sigma\tau} \nu(\tau|t) d\tau \\ = \int_0^{\infty} \int_0^{\infty} e^{-(st + \sigma\tau)} \nu(\tau|t) d\tau dt, \quad (3.4)$$

where s and σ are the Laplace parameters, and we have used the fact that $\nu(\tau|t)|_{\tau > t} = 0$. As shown in Ref. 35, $\hat{\nu}(\sigma, s)$ can be expressed in terms of the Laplace transforms of the probability densities $\varphi_s(t)$ and $\varphi_b(t)$,

$$\hat{\nu}(\sigma, s) = \frac{1 - \hat{\varphi}_s(s + \sigma)}{(s + \sigma)(1 - \hat{\varphi}_s(s + \sigma)\hat{\varphi}_b(s))}. \quad (3.5)$$

For $\hat{\varphi}_s(s)$ and $\hat{\varphi}_b(s)$ in Eqs. (2.5) and (2.6), the above expression reduces to

$$\hat{\nu}(\sigma, s) = \frac{1}{s + \sigma + k(1 - \hat{\varphi}_b(s))} = \frac{\kappa + f(s)}{(s + \sigma)\kappa + (s + \sigma + k)f(s)}. \quad (3.6)$$

As follows from Eq. (3.3), the Laplace transform of the probability $P_s(t)$ of finding the particle bound to the surface at

time t is

$$\hat{P}_s(s) = \hat{\nu}_s(\sigma = 0, s) = \frac{1}{s + k(1 - \hat{\varphi}_b(s))} = \frac{\kappa + f(s)}{s\kappa + (s + k)f(s)}. \quad (3.7)$$

This allows us to establish a simple relation between the double Laplace transform of the probability density $\nu(\tau|t)$ and the Laplace transform of the probability $P_s(t)$,

$$\hat{\nu}(\sigma, s) = \frac{\hat{P}_s(s)}{1 + \sigma\hat{P}_s(s)}. \quad (3.8)$$

In what follows, we use the moments of the cumulative time τ , denoted by $\langle \tau^m(t) \rangle$ and defined as

$$\langle \tau^m(t) \rangle = \int_0^t \tau^m \nu(\tau|t) d\tau, \quad m = 1, 2, \dots \quad (3.9)$$

The Laplace transforms of the moments are

$$\langle \hat{\tau}^m(s) \rangle = \int_0^{\infty} e^{-st} \langle \tau^m(t) \rangle dt, \quad m = 1, 2, \dots \quad (3.10)$$

There is a simple relation between these Laplace transforms and the Laplace transform of the probability $P_s(t)$ of finding the particle bound to the surface at time t . To establish this relation we note that, as follows from Eq. (3.4), the double Laplace transform of the probability density $\nu(\tau|t)$ can be written in terms of the Laplace transforms of the moments $\langle \tau^m(t) \rangle$ as

$$\hat{\nu}(\sigma, s) = \sum_{m=0}^{\infty} \frac{(-\sigma)^m}{m!} \langle \hat{\tau}^m(s) \rangle. \quad (3.11)$$

Then we have

$$\langle \hat{\tau}^m(s) \rangle = (-1)^m \left. \frac{d^m \hat{\nu}(\sigma, s)}{d\sigma^m} \right|_{\sigma=0} = m! (\hat{P}_s(s))^{m+1}, \quad (3.12)$$

where we have used $\hat{\nu}(\sigma, s)$ in Eq. (3.8). In particular, the Laplace transforms of the first two moments are

$$\langle \hat{\tau}(s) \rangle = \hat{P}_s^2(s), \quad \langle \hat{\tau}^2(s) \rangle = 2\hat{P}_s^3(s). \quad (3.13)$$

These relations are used in Sec. IV when analyzing the first two moments of the bulk-mediated surface displacement of the particle.

IV. MOMENTS OF DISPLACEMENT

The moments of the bulk-mediated surface displacement of the particle in time t , denoted by $\langle x^m(t) \rangle$, are given by

$$\langle x^m(t) \rangle = \int_{-\infty}^{\infty} x^m G(x, t) dx, \quad m = 1, 2, \dots \quad (4.1)$$

Substituting here the propagator $G(x, t)$ in Eq. (3.2), we can write these moments as

$$\langle x^m(t) \rangle = \int_0^t \langle x^m(\tau|t) \rangle \nu(\tau|t) d\tau, \quad m = 1, 2, \dots, \quad (4.2)$$

where $\langle x^m(\tau|t) \rangle$ is the m th moment of the displacement on condition that the cumulative time spent by the particle on the surface is τ ,

$$\langle x^m(\tau|t) \rangle = \int_{-\infty}^{\infty} x^m G(x, \tau|t) dx. \quad (4.3)$$

We find the first two moments of the conditional displacement by using the propagator $G(x, t|\tau)$ in Eq. (3.1). The result is

$$\langle x(t|\tau) \rangle = v_s \tau + v_b (t - \tau) = v_b t + (v_s - v_b) \tau \quad (4.4)$$

and

$$\begin{aligned} \langle x^2(t|\tau) \rangle &= [v_s \tau + v_b (t - \tau)]^2 + 2 [D_s \tau + D_b (t - \tau)] \\ &= v_b^2 t^2 + 2v_b (v_s - v_b) t \tau + (v_s - v_b)^2 \tau^2 \\ &\quad + 2 [D_b t + (D_s - D_b) \tau]. \end{aligned} \quad (4.5)$$

Substituting these moments into Eq. (4.2) and performing the averaging over τ , we obtain

$$\langle x(t) \rangle = v_b t P_s(t) + (v_s - v_b) \langle \tau(t) \rangle \quad (4.6)$$

and

$$\begin{aligned} \langle x^2(t) \rangle &= v_b^2 t^2 P_s(t) + 2v_b (v_s - v_b) t \langle \tau(t) \rangle + (v_s - v_b)^2 \langle \tau^2(t) \rangle \\ &\quad + 2 [D_b t P_s(t) + (D_s - D_b) \langle \tau(t) \rangle]. \end{aligned} \quad (4.7)$$

To find the long-time behavior of these moments, we need to know the asymptotic behavior of the probability $P_s(t)$ and the first two moments of the cumulative time τ as $t \rightarrow \infty$.

Asymptotic time dependences of these functions can be found by inverting the small- s limiting behavior of their Laplace transforms, which are given by

$$\hat{P}_s(s)|_{s \rightarrow 0} = \begin{cases} P_s^{eq}/s + \Delta P_L/k, & L < \infty \\ \sqrt{\theta_\infty/s}, & L = \infty \end{cases}, \quad (4.8)$$

$$\langle \hat{\tau}(s) \rangle|_{s \rightarrow 0} = \hat{P}_s^2(s)|_{s \rightarrow 0} = \begin{cases} (P_s^{eq}/s)^2 + \theta_L/s, & L < \infty \\ \theta_\infty/s, & L = \infty \end{cases}, \quad (4.9)$$

and

$$\begin{aligned} \langle \hat{\tau}^2(s) \rangle|_{s \rightarrow 0} &= 2\hat{P}_s^3(s)|_{s \rightarrow 0} \\ &= \begin{cases} 2(P_s^{eq}/s)^3 + 3\theta_L P_s^{eq}/s^2, & L < \infty \\ 2(\theta_\infty/s)^{3/2}, & L = \infty \end{cases}. \end{aligned} \quad (4.10)$$

In the above equations, the following notations are introduced: the equilibrium probability P_s^{eq} of finding the particle bound to the surface,

$$P_s^{eq} = \frac{\kappa}{\kappa + kL}, \quad (4.11)$$

the probability ΔP_L defined as

$$\Delta P_L = (P_b^{eq})^2 \left(1 + \frac{\kappa L}{3D_b}\right), \quad P_b^{eq} = \frac{kL}{\kappa + kL}, \quad (4.12)$$

where $P_b^{eq} = 1 - P_s^{eq}$ is the equilibrium probability of finding the particle in the bulk, and times θ_L and θ_∞ given by

$$\theta_L = (2/k) \Delta P_L P_s^{eq}, \quad \theta_\infty = \kappa^2 / (k^2 D_b). \quad (4.13)$$

Inverting the Laplace transforms in Eqs. (4.8)–(4.10), we obtain

$$P_s(t)|_{t \rightarrow \infty} = \begin{cases} P_s^{eq}, & L < \infty \\ \sqrt{\theta_\infty/(\pi t)}, & L = \infty \end{cases}, \quad (4.14)$$

$$\langle \tau(t) \rangle|_{t \rightarrow \infty} = \begin{cases} (P_s^{eq})^2 t + \theta_L, & L < \infty \\ \theta_\infty, & L = \infty \end{cases}, \quad (4.15)$$

and

$$\langle \tau^2(t) \rangle|_{t \rightarrow \infty} = \begin{cases} (P_s^{eq})^3 t^2 + 3\theta_L P_s^{eq} t, & L < \infty \\ 4\sqrt{\theta_\infty^3 t}/\pi, & L = \infty \end{cases}. \quad (4.16)$$

The asymptotic behaviors in Eqs. (4.14)–(4.16) allow us to find the long-time behavior of the first two moments of the bulk-mediated surface displacement of the particle given in Eqs. (4.6) and (4.7),

$$\langle x(t) \rangle|_{t \rightarrow \infty} = \begin{cases} v_{eff}^{conv} t P_s^{eq} + \Delta x_L, & L < \infty \\ v_b \sqrt{\theta_\infty t/\pi} + \Delta x_\infty, & L = \infty \end{cases} \quad (4.17)$$

and

$$\langle x^2(t) \rangle|_{t \rightarrow \infty} = \begin{cases} (v_{eff}^{conv} t)^2 P_s^{eq} + \{ \Delta x_L [2v_{eff}^{conv} + (v_s - v_b) P_s^{eq}] + 2D_{eff}^{conv} P_s^{eq} \} t, & L < \infty \\ v_b^2 \sqrt{\theta_\infty t^3/\pi} + 2\Delta x_\infty v_b t + 4\Delta x_\infty^2 \sqrt{t/(\pi \theta_\infty)} + 2D_b \sqrt{\theta_\infty t/\pi}, & L = \infty \end{cases}. \quad (4.18)$$

Here we have introduced the following notations: Δx_L and Δx_∞ are constant terms in the long-time behavior of the mean displacement in the presence and absence of the lid, respectively, given by

$$\Delta x_L = (v_s - v_b) \theta_L, \quad \Delta x_\infty = (v_s - v_b) \theta_\infty, \quad (4.19)$$

and v_{eff}^{conv} and D_{eff}^{conv} are conventional (*conv*) expressions for the effective (*eff*) drift velocity and diffusivity,

$$v_{eff}^{conv} = v_s P_s^{eq} + v_b P_b^{eq}, \quad (4.20)$$

$$D_{eff}^{conv} = D_s P_s^{eq} + D_b P_b^{eq}. \quad (4.21)$$

At $L = \infty$, the equilibrium probabilities of finding the particle on the surface and in the bulk take the forms $P_s^{eq}|_{L=\infty} = 0$ and $P_b^{eq}|_{L=\infty} = 1$ since the fraction of time spent by the particle on the surface vanishes as $t \rightarrow \infty$. As a consequence, the effective drift velocity and diffusivity, Eqs. (4.20) and (4.21), reduce to $v_{eff}^{conv}|_{L=\infty} = v_b$ and $D_{eff}^{conv}|_{L=\infty} = D_b$, as must be expected, since the particle spends most of the time in the bulk.

Expressions in Eqs. (4.14)–(4.18) clearly demonstrate the difference in the long time behavior of the corresponding quan-

ties in the presence and absence of the lid. Nevertheless, the moments in Eqs. (4.17) and (4.18) can be written in the form that shows some resemblance between the cases of $L < \infty$ and $L = \infty$. Using Eq. (4.14) that gives the asymptotic form of the probability of finding the particle on the surface, Eqs. (4.17)

and (4.18) can be written as

$$\langle x(t) \rangle|_{t \rightarrow \infty} = \begin{cases} v_{eff}^{conv} t P_s^{eq} + \Delta x_L, & L < \infty \\ v_b t P_s(t)|_{t \rightarrow \infty} + \Delta x_\infty, & L = \infty \end{cases} \quad (4.22)$$

and

$$\langle x^2(t) \rangle|_{t \rightarrow \infty} = \begin{cases} (v_{eff}^{conv} t)^2 P_s^{eq} + \{ \Delta x_L [2v_{eff}^{conv} + (v_s - v_b) P_s^{eq}] + 2D_{eff}^{conv} P_s^{eq} \} t, & L < \infty \\ (v_b t)^2 P(t)|_{t \rightarrow \infty} + 2\Delta x_\infty v_b t + 2(2\Delta x_\infty^2 + D_b \theta_\infty^2) \sqrt{t/(\pi \theta_\infty)}, & L = \infty \end{cases}. \quad (4.23)$$

The above expressions show that the leading terms of the both moments are the products of the conventional expressions for these moments and the probability of finding the particle bound to the surface at long times, as might be expected based on common sense arguments.

As can be seen from Eqs. (4.17) and (4.18), the square of the leading term of $\langle x(t) \rangle|_{t \rightarrow \infty}$ does not compensate the leading term of $\langle x^2(t) \rangle|_{t \rightarrow \infty}$. Therefore, there is no effective diffusivity in the presence of bias. Nevertheless, the effective drift velocity is a well-defined quantity which is discussed in Sec. V.

V. EFFECTIVE DRIFT VELOCITY

We define the effective drift velocity, $v_{eff}(t)$, of bulk-mediated surface transport as the ratio of the mean displacement, $\langle x(t) \rangle$, to time t ,

$$v_{eff}(t) = \langle x(t) \rangle / t. \quad (5.1)$$

This is a conditional drift velocity, calculated using only those realizations of the particle trajectory, which are bound to the surface at time t . Substituting here $\langle x(t) \rangle$ in Eq. (4.6), we arrive at

$$v_{eff}(t) = v_b P_s(t) + (v_s - v_b) \langle \tau(t) \rangle / t. \quad (5.2)$$

As follows from Eqs. (4.17) and (4.22), $v_{eff}(t)$ at long times is given by

$$\begin{aligned} v_{eff}(t)|_{t \rightarrow \infty} &= v_{eff}^{conv} P_s(t)|_{t \rightarrow \infty} \\ &= \begin{cases} v_{eff}^{conv} P_s^{eq} = (v_s \kappa + v_b \kappa L) \kappa / (\kappa + \kappa L)^2, & L < \infty \\ v_b P_s(t)|_{t \rightarrow \infty} = v_b \sqrt{\theta_\infty / (\pi t)}, & L = \infty \end{cases}. \end{aligned} \quad (5.3)$$

As $t \rightarrow \infty$, the mean cumulative time spent by the particle on the surface in the absence of the lid tends to a finite value, θ_∞ , given by Eq. (4.13). As a consequence, the second term in Eq. (5.2) can be neglected, and $v_{eff}(t)$ is the product of the bulk velocity and the probability of finding the particle on the surface at time t , which vanishes at long times, Eq. (4.14). In the absence of bias, this leads to anomalous diffusion.

To demonstrate this we note that the long-time behavior of the effective drift velocity is determined by the long-time behavior of the mean displacement. The latter, according to Eqs. (4.17) and (4.22), is given by

$$\langle x(t) \rangle|_{t \rightarrow \infty} = v_b \sqrt{\theta_\infty t / \pi} = v_b t P_s(t)|_{t \rightarrow \infty}, \quad L = \infty. \quad (5.4)$$

This should be compared with the long-time behavior of the second moment of the unbiased ($v_s = v_b = 0$) displacement in the absence of the lid. Using Eqs. (4.18) and (4.22), we obtain

$$\langle x^2(t) \rangle|_{t \rightarrow \infty} = 2D_b \sqrt{\theta_\infty t / \pi} = 2D_b t P(t)|_{t \rightarrow \infty}, \quad L = \infty. \quad (5.5)$$

FIG. 2. The time dependences of the effective drift velocity $v_{eff}(t)$ scaled by the particle drift velocity in the bulk, v_b , with $v_s = 0$, for several values of L , $L = 0.5, 1, 5, 10$, and ∞ , and $k = \kappa = 1$. Different panels show the dependences in different ranges of time. The black dashed lines in panels (b) and (c) represent the long-time asymptotic values of the corresponding $v_{eff}(t)$ at finite L . When $L = \infty$, $v_{eff}(t)$ vanishes as $t \rightarrow \infty$; its long-time asymptotic behavior is given by Eq. (5.3), $v_{eff}(t)|_{t \rightarrow \infty} = v_b \sqrt{\theta_\infty / (\pi t)}$.

One can see that at long times, both $\langle x(t) \rangle$ in the presence of bias, Eq. (5.4), and $\langle x^2(t) \rangle$ in the absence of bias, Eq. (5.5), grow with time as $\sqrt{t}$. The latter describes anomalous diffusion with the exponent 1/2. In both cases, this happens because in the absence of the lid, the probability, $P_s(t)$, of finding the particle bound to the surface at time t vanishes at long times as $1/\sqrt{t}$.

The time dependence of the effective drift velocity at different values of the parameters is illustrated in Figs. 2 and 3. When the particle has no drift velocity on the surface, $v_s = 0$, Eq. (5.2) reduces to

$$v_{eff}(t) = v_b [P_s(t) + \langle \tau(t) \rangle / t]. \quad (5.6)$$

The time dependences of the effective drift velocity in this case are presented in Fig. 2 which shows $v_{eff}(t)$ scaled by the bulk drift velocity, v_b , at several values of L , $L = 0.5, 1, 5, 10$, and ∞ , for $k = \kappa = 1$. All time dependences go from zero at $t = 0$ (since $v_s = 0$) to their long-time asymptotic values which can be found using Eq. (5.3). The dependences are monotonic at $L = 0.5, 1, 5$ and nonmonotonic at $L = 10$ and $L = \infty$. Different panels

show the dependences in different ranges of time. All five time dependences are distinguishable only in panel (b). In the range of time shown in panel (a), $0 \leq t \leq 2$, the time dependences at $L = 10$ and $L = \infty$ are indistinguishable from that at $L = 5$. In panel (c), the time dependence at $L = 1$ is omitted due to its similarity with that at $L = 0.5$. The black dashed lines in panels (b) and (c) show the long-time asymptotic values of the drift velocities at finite L , given by Eq. (5.3).

The time dependences of the effective drift velocity at finite particle drift velocity on the surface, $v_s \neq 0$, are presented in Fig. 3 which shows $v_{eff}(t)$ scaled by v_s , with $v_b = \pm 5v_s$, at the same values of L as in Fig. 2 for $k = \kappa = 1$. Here all dependences go to their long-time asymptotic values starting from unity. As in Fig. 2, the dependences at $L = 10$ and $L = \infty$ are indistinguishable from that at $L = 5$ in panel (a). In contrast to Fig. 2, there are indistinguishable dependences in panel (b): these are the dependences at $L = 10$ and $L = \infty$. The black dashed lines in panels (b) and (c) show the long-time asymptotic values of the drift velocities at finite L , given by Eq. (5.3). At $v_b/v_s = -5$, these asymptotic values at $L = 0.5$ and $L = 5$ are identical and equal to $2/3$, as can be seen in panel (c).

FIG. 3. The time dependences of the effective drift velocity $v_{eff}(t)$ scaled by the particle drift velocity on the surface, v_s , with $v_b/v_s = \pm 5$, for several values of L , $L = 0.5, 1, 5, 10$, and ∞ , and $k = \kappa = 1$. Different panels show the dependences in different ranges of time. The black dashed lines in panels (b) and (c) represent the long-time asymptotic values of the corresponding $v_{eff}(t)$ at finite L . When $L = \infty$, $v_{eff}(t)$ vanishes as $t \rightarrow \infty$; its long-time asymptotic behavior is given by Eq. (5.3), $v_{eff}(t)|_{t \rightarrow \infty} = v_b \sqrt{\theta_\infty / (\pi t)}$.

To summarize, the dependences presented in Figs. 2 and 3 show both monotonic and nonmonotonic behaviors, depending on the values of the parameters. The origin of such complex behavior lies in the fact that the curves in Figs. 2 and 3 show the conditional effective drift velocities, i.e., the effective drift velocities over the surface on condition that the particle is on the surface at time t . Therefore, it is not surprising that these dependencies are much more complex than their unconditional counterparts, $v_{eff}^{conv}(t)$, which are the time-dependent version of v_{eff}^{conv} in Eq. (4.20),

$$v_{eff}^{conv}(t) = v_s P_s(t) + v_b P_b(t) = v_s + (v_b - v_s) P_b(t). \quad (5.7)$$

In contrast to $v_{eff}(t)$ in Eq. (5.2), $v_{eff}^{conv}(t)$ gives the particle effective drift velocity independent of whether the particle is on the surface or in the bulk at time t . As follows from Eq. (5.7), $v_{eff}^{conv}(t)$ is always a monotonic function of time: Since $P_b(t)$ monotonically increases with time from zero to P_b^{eq} , $v_{eff}^{conv}(t)$ increases (decreases) with time when $v_b > v_s$ ($v_s > v_b$). One can see the origin of the nonmonotonic behavior of the conditional effective drift velocity from a “naïve” formula,

$$v_{eff}^{naive}(t) = v_{eff}^{conv}(t) P_s(t), \quad (5.8)$$

which correctly predicts $v_{eff}(t)$ at asymptotically short and long times. The nonmonotonic behavior of $v_{eff}^{naive}(t)$ arises because of the competition of the monotonic decrease of $P_s(t)$ and monotonic increase of $v_{eff}^{conv}(t)$ when $v_b > v_s$.

VI. CONCLUDING REMARKS

This paper extends the formalism developed for unbiased bulk-mediated surface diffusion in Ref. 35 to the case where the particle has arbitrary drift velocities on the surface and in the bulk. This is done in Secs. III and IV. In Sec. V, we discuss the time dependence of the effective drift velocity of a particle performing bulk-mediated surface motion, given by the theory, which can be highly nontrivial, as illustrated in Figs. 2 and 3.

Our analysis exploits the fact that the first two moments of the bulk-mediated particle displacement over the surface in time t , Eqs. (4.6) and (4.7), are determined by the first two moments of the cumulative time τ spent by the particle on the surface, $\langle \tau(t) \rangle$ and $\langle \tau^2(t) \rangle$, and the probability, $P_s(t)$, of finding the particle on the surface at time t . It is important that the Laplace transforms of the moments $\langle \tau^m(t) \rangle$ are related to the Laplace transform of the probability $P_s(t)$ by a simple relationship given in Eq. (3.12). Therefore, the problem of finding the Laplace transforms of the moments of the bulk-mediated surface displacement reduces to that of finding the Laplace transform of the probability $P_s(t)$. The latter Laplace transform is obtained by solving a two-state problem of the bulk-surface transitions of the particle, which can be done with relative ease.

Bulk-mediated surface transport is a special case of transport in multilayer structures. The idea to analyze transport in such systems focusing on the cumulative times spent by the particle in different layers, to our knowledge, was first suggested in Ref. 36. Recently, we applied this idea to study biased and unbiased diffusion in three-dimensional comb-like structures.^{37,38} We believe that this is a useful general approach that can be applied to other problems.

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