Bulk-mediated diffusion on a planar surface: Full solution

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We consider the effective surface motion of a particle that intermittently unbinds from a planar surface and performs bulk excursions. Based on a random-walk approach, we derive the diffusion equations for surface and bulk diffusion including the surface-bulk coupling. From these exact dynamic equations, we analytically obtain the propagator of the effective surface motion. This approach allows us to deduce a superdiffusive, Cauchy-type behavior on the surface, together with exact cutoffs limiting the Cauchy form. Moreover, we study the long-time dynamics for the surface motion.

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I. INTRODUCTION

Interfaces and the interaction of particles with them play a crucial role on small scales in biology and technology. For instance, biopolymers such as proteins or enzymes diffusing in biological cells intermittently bind to cellular membranes, or individual bacteria forming a biofilm on a surface use bulk excursions to efficiently relocate. Similarly, the exchange between a liquid phase with a solid surface is an important phenomenon in the self-assembly of surface layer films and is a ubiquitous process in emulsions.

This bulk-mediated surface diffusion, schematically shown in Fig. 1, was previously analyzed in terms of scaling arguments, master equation, and simulations [1–5], and was unveiled in field cycling NMR experiments in porous glasses [6]. Moreover, the effects of bulk-surface interchange were reported on proton transport across biological membranes [7]. Recent studies have been concerned with the effects of bulk-surface exchange on narrow escape problems [8] and on reaction rates [9] in interfacial systems, and with surface diffusion of copper atoms in nanowire fabrication [10].

The remarkable finding of the bulk-mediated surface diffusion model is that the effective surface motion is characterized by a Cauchy propagator [1,2,4,5],

$$n_s(\mathbf{r},t) \simeq \frac{c^{1/2}t}{2\pi(r^2+ct^2)^{3/2}}, \tag{1}$$

where $\simeq$ denotes a scaling property ignoring multiplicative constants, and c is a dimensional factor. The associated stochastic transport is of a superdiffusive nature [1,2,4–6,11],

$$\langle \mathbf{r}^2(t)\rangle_s \simeq t^{3/2}. \tag{2}$$

Here we present an analytical approach to this process in terms of diffusion equations for the surface and the bulk densities, coupled through the adsorbing current. Our findings corroborate the previous scaling results for superdiffusion, however we also derive the cutoffs to this behavior: at sufficiently long distances, the Cauchy propagator changes to a Gaussian wing. Moreover, at longer times the effective surface diffusion becomes subdiffusive, due to the fact that the particle spends less and less time on the surface. Normalized to the time-dependent surface coverage, the effective surface diffusion changes from superdiffusion to normal diffusion.

II. DERIVATION OF THE MODEL EQUATIONS FROM A DISCRETE RANDOM-WALK PROCESS

We start with a derivation of the coupling between surface and bulk in a discrete random-walk process along the z coordinate perpendicular to the surface (Fig. 1). Let N_i with $i = 1,2,\ldots$ denote the number of particles at site i of this one-dimensional lattice with spacing a. The number of particles on the surface at lattice site $i = 0$ is termed $\mathcal{N}_0$. The exchange of particles is possible only via nearest-neighbor jumps. Each jump event between bulk sites $i = 1,2,\ldots$ is associated with the typical waiting time τ. For the exchange between the surface and site $i = 1$, we then have the following law:

$$\frac{d\mathcal{N}_0(t)}{dt} = \frac{1}{2\tau}N_1 - \frac{1}{\tau_{\rm des}}\mathcal{N}_0, \tag{3}$$

where $\tau_{\rm des}$ is the characteristic time for desorption from the surface. The probability of adsorption to the surface here is 1, i.e., a particle adds to the surface population automatically when moving from site 1 to site 0 (see Appendix A for the modification in the case of nonperfect adsorption). The exchange site at $i = 1$ between the surface at $i = 0$ and the next bulk site $i = 2$ is governed by the balance relation

$$\frac{dN_1(t)}{dt} = \frac{1}{\tau_{\rm des}}\mathcal{N}_0 - \frac{1}{\tau}N_1 + \frac{1}{2\tau}N_2. \tag{4}$$

The number of particles at site $i = 2$ is governed by the equation

$$\frac{dN_2(t)}{dt} = \frac{1}{2\tau}N_1 + \frac{1}{2\tau}N_3 - \frac{1}{\tau}N_2, \tag{5}$$

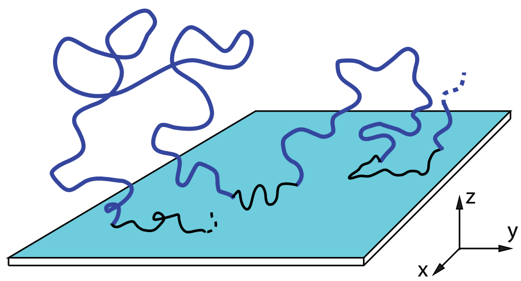

FIG. 1. (Color online) Schematic of the bulk-mediated surface diffusion: The thinner (black) lines show the motion along the planar surface with surface diffusivity D_s. Following dissociation from the surface, thicker (blue) lines depict excursions into the bulk volume, in which the diffusion constant is D_b. Eventually, the particle rebinds to the surface.

etc. Let us define the number of "bulk" particles at the surface site $i = 0$ through

$$N_0 \equiv \frac{2\tau}{\tau_{\rm des}}\mathcal{N}_0. \tag{6}$$

This trick allows us to formulate the exchange equation also for site $i = 1$ in a homogeneous form. Namely, from Eq. (3) we have

$$\frac{d\mathcal{N}_0(t)}{dt} = \frac{1}{2\tau}(N_1 - N_0). \tag{7}$$

Moreover, from Eqs. (5) we find

$$\frac{dN_i(t)}{dt} = \frac{1}{2\tau}(N_{i-1} - 2N_i + N_{i+1}) \tag{8}$$

for $i \geqslant 1$.

Let us now take the continuum limit. Toward that end, we make a transition $\mathcal{N}_0 \to n_s$ as the number of surface particles and $N_i \to a n_b$ for the bulk concentration of particles. The factor a may be viewed as the lattice constant measuring the distance between successive sites along the z axis. As the bulk density is a function of z while the surface particles are all assembled at $z = 0$, we need this length scale a to match dimensionalities between n_s and n_b which are $[n_s] = \text{cm}^{-2}$ and $[n_b] = \text{cm}^{-3}$. Expansion of the right-hand side of Eq. (7) yields the surface-bulk coupling,

$$\frac{\partial n_s(t)}{\partial t} = \frac{a}{2\tau} a \left.\frac{\partial n_b(z,t)}{\partial z}\right|_{z=0}. \tag{9}$$

Similarly from Eq. (8) we obtain the bulk diffusion equation

$$\frac{\partial n_b(z,t)}{\partial t} = \frac{1}{2\tau} a^2 \frac{\partial^2 n_b}{\partial z^2}. \tag{10}$$

Finally, the boundary condition

$$\left.\frac{a}{2\tau} n_b(z,t)\right|_{z=0} = \frac{1}{\tau_{\rm des}} n_s \tag{11}$$

stems from our definition (6). This completes the description of the particle exchange between surface and bulk, as well as the diffusion of bulk particles along the z axis.

We now turn back to the full three-dimensional problem and add to the above equations the (x,y) directions (see Fig. 1). As the motion in the perpendicular z direction is fully independent, we may simply adjust the Laplacian to three dimensions, ending up with the diffusion equation

$$\frac{\partial n_b(x,y,z,t)}{\partial t} = D_b\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{12}$$

with diffusivity D_b. For the surface diffusion along the x and y coordinates with $z = 0$, we end up with the two-dimensional diffusion equation with diffusivity D_s, plus the bulk-surface exchange term:

$$\frac{\partial n_s(x,y,t)}{\partial t} = D_s\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) n_s + D_b \left.\frac{\partial n_b}{\partial z}\right|_{z=0}. \tag{13}$$

These two equations are valid in the range $0 \leqslant z < \infty$ and $-\infty < x, y < \infty$, and are supplemented by the initial condition

$$n_s(x,y,t)|_{t=0} = n_0 \delta(x)\delta(y) \tag{14}$$

indicating that initially the particles are all concentrated on the surface at $x = y = 0$. Moreover, we observe the boundary condition for n_b,

$$n_b(x,y,z,t)|_{z=0} = \mu n_s(x,y,t), \tag{15}$$

and the bulk initial condition

$$n_b(x,y,z,t)|_{t=0} = 0. \tag{16}$$

In what follows, for simplicity of notation we use a unit initial concentration n_0.

The surface and bulk diffusivities can be expressed in terms of the lattice constant a and the typical waiting times between jumps in the bulk, τ, and on the surface, τ_s, through

$$D_b \equiv \frac{a^2}{6\tau} \tag{17}$$

and

$$D_s \equiv \frac{a^2}{4\tau_s}, \tag{18}$$

respectively. In the continuum limit, both a and τ (or τ_s) tend to zero such that the diffusion constants remain finite. In many physical systems, bulk diffusion is considerably faster, such that $D_s \ll D_b$. Above, we also introduced the coupling parameter

$$\mu \equiv \frac{a}{D_b \tau_{\rm des}} \tag{19}$$

of physical dimension $[\mu] = 1/\text{cm}$. Small values of μ at fixed a and D_b correspond to slow bulk-surface exchange.

For consistency, we derive the overall number of particles. To this end, we define the number of particles on the surface, $N_s(t)$, and in the bulk, $N_b(t)$, through the relations

$$N_s(t) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, n_s(x,y,t) \tag{20}$$

and

$$N_b(t) = \int_0^{\infty} dz \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, n_s(x,y,t). \tag{21}$$

From integration of Eq. (13), we find

$$\frac{dN_s(t)}{dt} = D_b \frac{\partial}{\partial z} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, n_b(x,y,z,t)\Big|_{z=0}. \tag{22}$$

Similarly, Eq. (12) yields

$$\frac{dN_b(t)}{dt} = D_b \int_0^\infty dz \frac{\partial^2}{\partial z^2} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, n_b(x,y,z,t) = -D_b \frac{\partial}{\partial z} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, n_b(x,y,z,t)\Big|_{z=0}. \quad (23)$$

A combination of Eqs. (22) and (23) produces

$$\frac{d}{dt}[N_s(t) + N_b(t)] = 0. \quad (24)$$

Thus the overall number of particles is conserved, as it should be.

III. SOLUTION OF THE COUPLED DIFFUSION PROBLEM

To solve the set of coupled equations (13) and (12) for the specified initial and boundary value problem, we start by defining the two-dimensional Green's function

$$G_s(x,x',y,y',t) \equiv G_s(x-x',y-y',t) = \frac{1}{\sqrt{4\pi D_s t}} \exp\left(-\frac{(x-x')^2+(y-y')^2}{4D_s t}\right). \quad (25)$$

Then, the solution of Eq. (13) becomes

$$n_s(x,y,t) = \int dx' \int dy' G_s(x,x',y,y',t) n_s(x',y',t=0) + \int_0^t dt' \int dx' \int dy' G_s(x,x',y,y',t-t') \times \left(D_b \frac{\partial n_b(x',y',z,t')}{\partial z}\right)_{z=0}. \quad (26)$$

With initial condition (14), we thus find

$$n_s(k_x,k_y,s) = G_s(k_x,k_y,s) + G_s(k_x,k_y,s)\mathscr{L}\left\{\mathscr{F}\left\{D_b\left(\frac{\partial n_b(x,y,z,t)}{\partial z}\right)_{z=0}; x\to k_x; y\to k_y\right\}; t\to s\right\}, \quad (27)$$

where

$$G_s(k_x,k_y,s) = \frac{1}{s + D_b\left[k_x^2 + k_y^2\right]} \quad (28)$$

is the Fourier-Laplace transform of the surface Green's function G_s. Here and in the following, we denote the Laplace and Fourier transform of a function by explicit dependence on the image variables, that is,

$$f(s) = \mathscr{L}\{f(t); t\to s\} = \int_0^\infty f(t)e^{-st}dt$$

$$\text{and} \quad g(k) = \mathscr{F}\{g(x); x\to k\} = \int_{-\infty}^{\infty} g(x)e^{ikx}dx. \quad (29)$$

The bulk particle density according to Eq. (12) is given by the formal expression [12]

$$n_b(x,y,z,t) = \frac{z}{(4\pi D_b)^{3/2}} \int_0^t dt' \int dx' \int dy' \frac{\mu n_s(x',y',t')}{(t-t')^{5/2}} \times \exp\left(-\frac{(x-x')^2+(y-y')^2+z^2}{4D_b(t-t')}\right). \quad (30)$$

From this expression one can indeed show that, despite the factor z, the coupling equation (15) is fulfilled; see Appendix B. Now, Eq. (27) requires the derivative of expression (30) with respect to z, evaluated at $z = 0$. To find that expression, we first differentiate

$$\frac{\partial n_b}{\partial z} = \frac{\mu}{(4\pi D_b)^{3/2}} \int_0^t dt' \int dx' \int dy' \frac{n_s(x',y',t')}{(t-t')^{5/2}} \times \exp\left(-\frac{(x-x')^2+(y-y')^2+z^2}{4D_b(t-t')}\right) \times \left[1 - \frac{z^2}{2D_b(t-t')}\right] \quad (31)$$

and then calculate its Fourier-Laplace transform

$$\mathscr{L}\left\{\mathscr{F}\left\{D_b\left(\frac{\partial n_b}{\partial z}\right)_{z=0}\right\}\right\} = \frac{\mu D_b}{\sqrt{4\pi D_b}} n_s(k_x,k_y,s)\mathscr{L}\left\{\frac{\exp\left(-D_b\left[k_x^2+k_y^2\right]t\right)}{t^{3/2}}\right\}_{z=0}, \quad (32)$$

due to the convolution nature of expression (31). The Laplace transform is evaluated by help of the shift theorem, yielding

$$\mathscr{L}\left\{\frac{\exp\left(-D_b[k_x^2+k_y^2]t\right)}{t^{3/2}}\right\} = \mathscr{L}\left\{\frac{1}{t^{3/2}}\right\}_{s\to s+D_b[k_x^2+k_y^2]} = -\sqrt{4\pi\left(s + D_b[k_x^2+k_y^2]\right)}. \quad (33)$$

We thus finally obtain

$$\mathscr{L}\left\{\mathscr{F}\left\{D_b\left(\frac{\partial n_b}{\partial z}\right)_{z=0}\right\}\right\} = -\mu D_b^{1/2}\sqrt{s + D_b\left(k_x^2+k_y^2\right)}\, n_s(k_x,k_y,s). \quad (34)$$

Insertion of this equation into expression (27) delivers the solution for the surface density in Fourier-Laplace space,

$$n_s(k_x,k_y,s) = \frac{G_s(k_x,k_y,s)}{1 + \mu D_b^{1/2} G_s(k_x,k_y,s)\sqrt{s + D_b\left[k_x^2+k_y^2\right]}}, \quad (35)$$

where the Fourier-Laplace transform of the Green's function G_s was defined in Eq. (28). After some transformations, we arrive at the exact closed-form expression,

$$n_s(k_x,k_y,s) = \frac{1}{s + D_s\left[k_x^2+k_y^2\right] + \chi\sqrt{s + D_b\left[k_x^2+k_y^2\right]}}, \tag{36}$$

with the rescaled coupling parameter

$$\chi \equiv \mu D_b^{1/2} = \frac{a}{D_b^{1/2}\tau_{\rm des}} \tag{37}$$

of dimension $[\chi] = 1/{\rm s}^{1/2}$. Relation (36) is the main result of this work, and we now consider the consequences to the surface motion effected by the bulk mediation.

IV. EFFECTIVE SURFACE BEHAVIOR

We first determine the number of particles on the surface,

$$N_s(t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} n_s(x,y,t)dx\,dy, \tag{38}$$

whose Laplace transform is

$$N_s(s) = n(k_x,k_y,s)\Big|_{k_x=k_y=0} = \frac{1}{s+\chi s^{1/2}}. \tag{39}$$

Inverse Laplace transformation then yields the exact expression

$$N_s(t) = e^{\chi^2 t}\mathrm{erfc}(\chi t^{1/2}), \tag{40}$$

where we use the complementary error function

$$\mathrm{erfc}(z) = \frac{2}{\sqrt{\pi}}\int_z^{\infty} e^{-\xi^2}d\xi = 1 - \mathrm{erf}(z). \tag{41}$$

At short times $t \ll \chi^{-2}$, this leads to the initial decay

$$N_s(t) \sim 1 - \frac{2\chi}{\sqrt{\pi}}t^{1/2} \tag{42}$$

of the number of surface particles, eventually turning into the long time behavior

$$N_s(t) \sim \frac{1}{\chi\sqrt{\pi t}}. \tag{43}$$

The asymptotic $1/\sqrt{\pi t}$ decay stems from the returning dynamics to the origin $z = 0$ of a Brownian motion along the z coordinate, i.e., it is proportional to the normalization factor of a one-dimensional Brownian motion. The additional prefactor χ rescales time with respect to the efficiency of the surface-bulk exchange.

We now turn to the surface dynamics, as quantified by the effective mean squared displacement along the surface. In the Laplace domain,

$$\begin{aligned}\langle \mathbf{r}^2(s)\rangle_s &= -\nabla^2_{k_x,k_y} n(k_x,k_y,s)\Big|_{k_x=k_y=0}\\ &= -\left[\frac{\partial^2}{\partial k^2} + \frac{1}{k}\frac{\partial}{\partial k}\right] n(k_x,k_y,s)\Big|_{k_x=k_y=0}\\ &= \frac{4D_s}{s(\sqrt{s}+\chi)^2} + \frac{2\chi D_b}{s^{3/2}(s^{1/2}+\chi)^2},\end{aligned} \tag{44}$$

where $k = |\mathbf{k}| = \sqrt{k_x^2+k_y^2}$. From this expression, we obtain the limiting behaviors at short and long times. Thus, we observe that the short time limit $t \ll 1/\chi^2$ in the Laplace domain corresponds to $s \gg \chi^2$, such that

$$\langle \mathbf{r}^2(s)\rangle_s \sim \frac{4D_s}{s^2} + \frac{2\chi D_b}{s^{5/2}}. \tag{45}$$

This translates into the asymptotic time evolution

$$\langle \mathbf{r}^2(t)\rangle_s \sim 4D_s t\left(1 + \frac{2}{3\sqrt{\pi}}\frac{D_b}{D_s}[t\chi^2]^{1/2}\right). \tag{46}$$

As long as the ratio D_b/D_s is sufficiently large, there is a superdiffusive component $\langle \mathbf{r}^2(t)\rangle_s \sim t^{3/2}$ winning over the normal surface diffusion proportional to D_s. This is exactly the famed bulk-mediated superdiffusion originally obtained from scaling arguments by Bychuk and O'Shaugnessy [1,2]. Note that this diffusional enhancement is accompanied by an almost constant number of surface particles; cf. Eq. (42).

Conversely, at long times $t \gg 1/\chi^2$ (or $s \ll \chi^2$ in Laplace domain) we find

$$\langle \mathbf{r}^2(s)\rangle_s \sim \frac{4D_s}{\chi^2 s} + \frac{2D_b}{\chi s^{3/2}}, \tag{47}$$

corresponding to the temporal behavior

$$\langle \mathbf{r}^2(t)\rangle_s \sim \frac{4D_s}{\chi^2}\left(1 + \frac{1}{\sqrt{\pi}}\frac{D_b}{D_s}[t\chi^2]^{1/2}\right). \tag{48}$$

Somewhat surprisingly, at sufficiently long times the bulk contribution to the effective mean squared displacement dominates over the surface contribution for arbitrary ratio D_b/D_s, giving rise to *subdiffusive* behavior. This subdiffusion occurs due to the ongoing loss of surface particles into the bulk; see Eq. (43).

Instead of considering the surface mean squared displacement $\langle \mathbf{r}^2(t)\rangle_s$, we introduce the normalized effective surface mean squared displacement

$$\langle \mathbf{r}^2(t)\rangle_s^{\rm norm} \equiv \frac{1}{N_s(t)}\langle \mathbf{r}^2(t)\rangle_s. \tag{49}$$

This quantity can be interpreted as the surface mean squared displacement covered by an individual particle that effectively stays on the surface and does not fully escape to the bulk. At long times, this quantity has the limiting form

$$\langle \mathbf{r}^2(t)\rangle_s^{\rm norm} \sim 4D_b t. \tag{50}$$

The long time diffusion corrected for the number of escaping particles displays normal diffusion, albeit with the *bulk diffusivity*.

In the following, we neglect contributions from the surface diffusion proportional to D_s in order not to overburden the presentation. The interesting behavior is due to the bulk mediation with weight D_b. We quantify the motion in terms of fractional order moments before embarking for the surface propagator.

A. Fractional order moments

We now study the behavior of the qth-order moments $(0 < q < 2)$,

$$\langle |\mathbf{r}|^q(t)\rangle_s = \int |\mathbf{r}|^q n_s(\mathbf{r},t) d^2\mathbf{r}. \tag{51}$$

The expression for the moments in the Laplace space is derived in Appendix C, with the result

$$\langle r^q(s)\rangle_s = 2\pi K(q) \frac{\chi D_b^{q/2}}{s^{(1+q)/2}(s-\chi^2)}\{I_1(q) - I_2(q)\}, \tag{52}$$

where $K(q)$ is defined by Eq. (C3), and two integrals I_i are

$$I_1(q) = \int_0^\infty \frac{y^{1-q}}{1+\sqrt{1+y^2}} dy \tag{53}$$

and

$$I_2(q) = \int_0^\infty \frac{y^{1-q}}{\sqrt{s}/\chi + \sqrt{1+y^2}} dy. \tag{54}$$

Now we analyze the temporal behavior of the qth-order moment at short and long times.

1. *Long time behavior*

At long times $t \gg 1/\chi^2$ (or $s/\chi^2 \ll 1$), we see that

$$I_1(q) - I_2(q) \sim \int_0^\infty \left(\frac{1}{1+\sqrt{1+y^2}} - \frac{1}{\sqrt{1+y^2}}\right)\frac{dy}{y^{q-1}} < 0 \tag{55}$$

and

$$\langle r^q(s)\rangle_s \simeq \frac{1}{s^{(1+q)/2}}, \tag{56}$$

corresponding to the time evolution

$$\langle r^q(t)\rangle_s \simeq t^{(q-1)/2}. \tag{57}$$

Taking normalization by the number of surface particles into account, we find

$$\langle r^q(s)\rangle_s^{\text{norm}} = \frac{\langle r^q(s)\rangle_s}{N_s(t)} \simeq t^{q/2}. \tag{58}$$

That is, at long times the surface diffusion exhibits normal scaling behavior.

2. *Short time behavior*

The more interesting case is the short time behavior corresponding to the limit $t \ll 1/\chi^2$ (or $s/\chi^2 \gg 1$). Here we consider three separate cases:

(i) The case $1 < q < 2$: Since both integrals I_1 and I_2 converge, we may simply neglect $I_2(q)$. Then

$$\langle r^q(s)\rangle_s \simeq s^{-(3+q)/2}, \tag{59}$$

such that after Laplace inversion we find

$$\langle r^q(t)\rangle_s \simeq t^{(q+1)/2}. \tag{60}$$

(ii) The case $0 < q < 1$: Now we should take into account both integrals,

$$I_1(q) - I_2(q) \sim \frac{\sqrt{s}}{\chi}\int_0^\infty \frac{y^{1-q}dy}{(1+\sqrt{1+y^2})(\sqrt{s}/\chi + \sqrt{1+y^2})}. \tag{61}$$

To estimate the main contribution from this difference, we split it into three parts, namely

$$I_1(q) - I_2(q) \sim \frac{\sqrt{s}}{\chi}\left\{\int_0^1 \cdots dy + \int_1^{\sqrt{s}/\chi} \cdots dy + \int_{\sqrt{s}/\chi}^\infty \cdots dy\right\}, \tag{62}$$

and we evaluate each contribution separately. We find

$$\int_0^1 \cdots dy \simeq \frac{\chi}{\sqrt{s}} \tag{63a}$$

and then

$$\int_1^{\sqrt{s}/\chi} \cdots dy \sim \int_1^{\sqrt{s}/\chi} \frac{1}{y\sqrt{s}/\chi}\frac{dy}{y^{q-1}} \sim \left(\frac{\chi}{\sqrt{s}}\right)^q > \frac{\chi}{s}. \tag{63b}$$

Finally,

$$\int_{\sqrt{s}/\chi}^\infty \frac{dy}{y^{1+q}} \simeq \left(\frac{\chi}{\sqrt{s}}\right)^q. \tag{63c}$$

Thus the main contributions come from Eqs. (63b) and (63c), and

$$I_1(q) - I_2(q) \simeq s^{(1-q)/2}. \tag{64}$$

With this estimate, the Laplace transform of the qth-order moment, Eq. (52), has the leading order behavior

$$\langle r^q(s)\rangle_s \simeq \frac{s^{(1-q)/2}}{s^{(3+q)/2}} \simeq \frac{1}{s^{1+q}}. \tag{65}$$

This corresponds to

$$\langle r^q(t)\rangle_s \simeq t^q \tag{66}$$

in the time domain.

(iii) The case $q = 1$: This special case requires some care. We start with the substitution $y = \tan\phi$ in Eqs. (53) and (54). Then the integrals I_i become

$$I_1(1) = \int_0^{\pi/2} \frac{d\phi}{\cos\phi(1+\cos\phi)} \tag{67}$$

and

$$I_2(1) = \int_0^{\pi/2} \frac{d\phi}{\cos\phi(1+\sqrt{s}\cos\phi/\chi)}. \tag{68}$$

We can now rewrite Eq. (52) in the form

$$\langle r(s)\rangle_s = 2\pi K(1)\frac{\chi D_b^{1/2}}{s(s-\chi^2)} \times \left(\frac{\sqrt{s}}{\chi}\int_0^{\pi/2} \frac{d\phi}{1+\sqrt{s}\cos\phi/\chi} - 1\right), \tag{69}$$

where we used [13]

$$\int_0^{\pi/2} \frac{d\phi}{1+\cos\phi} = 1. \tag{70}$$

For $s/\chi^2 < 1$, the integral in the parentheses of Eq. (69) becomes [13]

$$\int_0^{\pi/2} \frac{d\phi}{1+\sqrt{s}\cos\phi/\chi} = \frac{2}{\sqrt{1-s/\chi^2}} \arctan\sqrt{\frac{1-\sqrt{s}/\chi}{1+\sqrt{s}/\chi}}. \tag{71}$$

Thus, for Eq. (69) we find

$$\langle r(s)\rangle_s = 2\pi K(1)\frac{\chi D_b^{1/2}}{s(s-\chi^2)} \times \left(\frac{2\sqrt{s}}{\chi}\frac{1}{\sqrt{1-s/\chi^2}}\arctan\sqrt{\frac{1-\sqrt{s}/\chi}{1+\sqrt{s}/\chi}} - 1\right), \tag{72}$$

so that we find the $s \to 0$ behavior

$$\langle r(s)\rangle_s \sim \frac{D_b^{1/2}}{\chi s}. \tag{73}$$

After Laplace inversion,

$$\langle r(t)\rangle_s \sim \frac{D_b^{1/2}}{\chi} \quad \text{and} \quad \langle r(t)\rangle_s^{\text{norm}} \sim (D_b t)^{1/2} \tag{74}$$

at long times, $t \gg 1/\chi^2$, consistent with Eq. (58). Conversely, for $s/\chi^2 > 1$ we employ [13]

$$\int_0^{\pi/2} \frac{d\phi}{1+\sqrt{s}\cos\phi/\chi} = \frac{1}{\sqrt{s/\chi^2-1}} \ln\frac{\sqrt{s/\chi^2-1}+\sqrt{s}/\chi-1}{\sqrt{s/\chi^2-1}+1-\sqrt{s}/\chi}. \tag{75}$$

Thus we find

$$\langle r(s)\rangle_s = 2\pi K(1)\frac{\chi D_b^{1/2}}{s(s-\chi^2)}\left[\frac{\sqrt{s}/\chi}{\sqrt{s/\chi^2-1}}\ln\left(\frac{2\sqrt{s}}{\chi}\right) - 1\right]. \tag{76}$$

We thus obtain the limiting form at large s,

$$\langle r(s)\rangle_s \sim \frac{\chi D_b^{1/2}}{s^2}\ln\left(\frac{2\sqrt{s}}{\chi}\right). \tag{77}$$

Back-transformed, this results in

$$\langle r(t)\rangle_s \approx \langle r^q(s)\rangle_s^{\text{norm}} \sim t\ln t \tag{78}$$

at short times $t \ll 1/\chi^2$.

Summarizing our results for qth-order moments, at short times $t \ll 1/\chi^2$ the effective surface diffusion exhibits anomalous scaling: the qth-order moment of the radius scales like t^q for $0 < q < 1$ and $t^{(q+1)/2}$ for $1 < q < 2$, while the first moment includes a logarithmic contribution, $t\ln t$, consistent with the earlier results in Ref. [2]. At long times $t \gg 1/\chi^2$ the qth-order moments scale normally with time, proportional to $t^{q/2}$.

V. SURFACE PROPAGATOR

We now turn to the behavior of the surface propagator. If we neglect surface diffusion (i.e., $D_s = 0$), the surface propagator from Eq. (36) becomes

$$n_s(\mathbf{k},s) = \frac{1}{s+\chi\sqrt{s+D_b k^2}}. \tag{79}$$

An inverse Laplace transformation is performed in Appendix D. In compact form,

$$n_s(\mathbf{k},t) = \frac{1}{\alpha+\beta}\{\alpha e^{\alpha\chi^2 t}\text{erfc}(\alpha\chi\sqrt{t}) + \beta e^{-\beta\chi^2 t}\text{erfc}(-\beta\chi\sqrt{t})\}, \tag{80}$$

with

$$\alpha = \sqrt{\kappa^2+\frac{1}{4}}+\frac{1}{2}, \quad \beta = \sqrt{\kappa^2+\frac{1}{4}}-\frac{1}{2}, \tag{81}$$

and $\kappa^2 = D_b k^2/\chi^2$. We now calculate the surface propagator $n_s(\mathbf{r},t)$ in the limits of short and long times.

A. Short time behavior

At short times $t \ll \chi^{-2}$ we distinguish between the central part of the propagator and its wings. Starting with the central part, we thus focus on distances $r \ll (D_b t)^{1/2}$. Due to $\kappa^2 = D_b k^2/\chi^2$, this means that we consider $\kappa\chi\sqrt{t} \gg 1$, and therefore $\kappa^2 \gg 1$. Consequently, we find $\alpha \approx \beta \approx \kappa$, $\alpha\chi\sqrt{t} \approx \beta\chi\sqrt{t} \approx \kappa\chi\sqrt{t} \gg 1$, and thus

$$\text{erfc}(\alpha\chi\sqrt{t}) \sim \frac{\exp(-\alpha^2\chi^2 t)}{\sqrt{\pi}\alpha\chi\sqrt{t}}. \tag{82}$$

Then, the first term in the curly brackets of Eq. (80) is (note that $\alpha^2 - \alpha = \kappa^2$)

$$\alpha e^{\alpha\chi^2 t}\text{erfc}(\alpha\chi\sqrt{t}) \approx \frac{1}{\sqrt{\pi\chi^2 t}} e^{-\kappa^2\chi^2 t}. \tag{83}$$

The error function in the second term of Eq. (80) is approximately 2. Thus, the second term in the curly brackets of Eq. (80) prevails, and we obtain

$$n_s(\mathbf{k},t) \sim \exp(-\kappa\chi^2 t). \tag{84}$$

The Fourier inversion is accomplished with the help of the integral [13]

$$\int_0^\infty x e^{-px} J_0(cx)dx = \frac{p}{(p^2+c^2)^{3/2}}, \tag{85}$$

and we obtain

$$n_s(\mathbf{r},t) \sim \int e^{-i\mathbf{k}\cdot\mathbf{r}} n_s(\mathbf{k},t)\frac{d\mathbf{k}}{4\pi^2} \sim \int_0^\infty e^{-\chi\sqrt{D_b}kt} J_0(kr)\frac{kdk}{2\pi} \tag{86}$$

such that

$$n_s(\mathbf{r},t) \sim \frac{\chi D_b^{1/2} t}{2\pi(r^2+\chi^2 D_b t^2)^{3/2}}. \tag{87}$$

This is exactly the two-dimensional Cauchy distribution obtained by Bychuk and O'Shaugnessy from scaling arguments [1]. We see that indeed radius and time are coupled linearly in superdiffusive fashion, $r \sim t$. However, as we will see, this Cauchy form holds only for the central part of the surface propagator. It assumes steeper wings such that at all times any moment of the propagator exists. We are quantifying these wings below.

The number of particles populating this cental Cauchy domain of the propagator, i.e., within a circle of radius $(D_b t)^{1/2}$, is

$$\int^{(D_b t)^{1/2}} n_s(\mathbf{r},t)d\mathbf{r} \sim 1 - \chi\sqrt{t}, \tag{88}$$

i.e., at sufficiently short times a major portion of the particles are contained in the Cauchy domain. Indeed, these particles show the superdiffusive mean squared displacement

$$\langle \mathbf{r}^2\rangle_s = \int^{(D_b t)^{1/2}} \mathbf{r}^2 n_s(\mathbf{r},t)d\mathbf{r} \approx \chi D_b t^{3/2}, \tag{89}$$

consistent with result (46) for $D_s = 0$, the prefactor differing by approximately a factor $3/2$.

The outer part of the propagator at short times is found for $r \gg (D_b t)^{1/2}$. This region can be divided into two subregions, namely $\kappa^2 \gg 1$ corresponding to $D_b t \ll r^2 \ll D_b/\chi^2$, and $\kappa^2 \ll 1$ corresponding to $r^2 \gg D_b/\chi^2$. However, it is easy to check that in both of these subregions we have $\alpha\chi\sqrt{t} \ll 1$ and $\beta\chi\sqrt{t} \ll 1$, due to the combination of the conditions of short times ($\chi\sqrt{t} \ll 1$) and large radii ($\kappa\chi\sqrt{t} \ll 1$). Thus both error functions in Eq. (80) are expanded at small values of their arguments,

$$\mathrm{erfc}(\pm z) \sim 1 \mp \frac{2}{\sqrt{\pi}}z \pm \frac{2}{3\sqrt{\pi}}z^3 + \cdots, \tag{90}$$

with $z = \alpha\chi\sqrt{t} < 1$ and $z = \beta\chi\sqrt{t} < 1$, respectively. Our result is

$$n_s(\mathbf{k},t) \sim 1 - \frac{2}{\sqrt{\pi}}\chi\sqrt{t} - \frac{2}{3\sqrt{\pi}}k^2 D_b \chi t^{3/2} \tag{91}$$

plus terms of order k^4 and higher. We conclude that at the wings the central Cauchy distribution is truncated by Gaussian tails whose dispersion grows like $t^{3/2}$.

B. Long time behavior

This is the limit $t \gg 1/\chi^2$. As this implies $\alpha\chi\sqrt{t} \gg 1$, we may expand the error function as

$$\mathrm{erfc}(\alpha\chi\sqrt{t}) \sim \frac{\exp(-\alpha^2\chi^2 t)}{\sqrt{\pi}\alpha\chi\sqrt{t}}. \tag{92}$$

We consider the shape of the propagator in the main part excluding the region near the origin, i.e., we have

$$r^2 \gg D_b\sqrt{t}/\chi \gg D_b/\chi^2. \tag{93}$$

In this domain, we may use $\kappa \ll 1$, $\alpha \approx 1$, and $\kappa^2\chi\sqrt{t} \ll 1$. Since $\beta = \sqrt{\kappa^2 + 1/4} - 1/2 \approx \kappa^2$, we have $\beta\chi\sqrt{t} \ll 1$, and thus the second error function becomes

$$\mathrm{erfc}(-\beta\chi\sqrt{t}) \approx 1. \tag{94}$$

The surface propagator thus assumes the shape (recall that $\alpha^2 - \alpha = \kappa^2$)

$$\begin{aligned} n_s(\mathbf{k},t) &\sim \frac{1}{\alpha}\left(\alpha e^{\alpha\chi^2 t}\frac{\exp(-\alpha^2\chi^2 t)}{\sqrt{\pi}\alpha\chi\sqrt{t}} + \kappa^2\exp(-\beta\chi^2 t)\right) \\ &\sim \frac{\exp(-\kappa^2\chi^2 t)}{\sqrt{\pi}\chi\sqrt{t}} + \kappa^2 e^{-\kappa^2\chi^2 t} \sim \frac{\exp(-\kappa^2\chi^2 t)}{\sqrt{\pi}\chi\sqrt{t}}. \end{aligned} \tag{95}$$

Equivalently, this means that

$$n_s(\mathbf{k},t) \sim \frac{\exp(-k^2 D_b t)}{\sqrt{\pi}\chi\sqrt{t}}. \tag{96}$$

Inverse Fourier transform produces the propagator at long times,

$$\begin{aligned} n_s(\mathbf{r},t) &\sim \int e^{-i\mathbf{k}\cdot\mathbf{r}} n_s(\mathbf{k},t)\frac{d\mathbf{k}}{4\pi^2} \\ &\sim \frac{1}{\chi\sqrt{\pi t}}\int_0^\infty J_0(kr)e^{-k^2 D_b t}\frac{kdk}{2\pi}. \end{aligned} \tag{97}$$

From this, we obtain the Gaussian form

$$n_s(\mathbf{r},t) \sim \frac{1}{\chi\sqrt{\pi t}}\frac{\exp(-r^2/[4D_b t])}{4\pi D_b t}. \tag{98}$$

The number of particles contained in this part of the long-time propagator follows from

$$\int_{r^2 \geqslant D_b\sqrt{t}/\chi} n_s(\mathbf{r},t)d\mathbf{r} \sim \frac{1}{\chi\sqrt{\pi t}}. \tag{99}$$

Comparison to Eq. (43) shows that these are virtually all particles still on the surface. Thus the Gaussian (98) indeed dominates the behavior at long times. This statement is also corroborated from calculation of the surface mean squared displacement from Eq. (98) in the domain $r^2 \geqslant D_b\sqrt{t}/\chi$:

$$\begin{aligned} \langle \mathbf{r}^2\rangle_s &\sim \int_{r^2 \geqslant D_b\sqrt{t}/\chi} r^2 n_s(\mathbf{r},t)d\mathbf{r} \\ &\sim \frac{4D_b t}{\chi\sqrt{\pi t}}\left[1 + o\left(\frac{1}{t\chi^2}\right)\right]. \end{aligned} \tag{100}$$

Again, up to a small correction, this term coincides with our exact result for the long time behavior, Eq. (48).

VI. CONCLUSIONS

Complementing our earlier studies of bulk-mediated surface diffusion on a cylinder [14], we presented an analytical treatment of the bulk-mediated surface diffusion problem on a flat surface in terms of diffusion equations for the surface and the bulk densities, coupled through the adsorbing current. Our analysis is based on the exact representation of the surface propagator in Fourier-Laplace space from which systematic expansions are obtained. The main results are summarized in Table I. The typical time scale is determined by the bulk diffusivity D_b, desorption time τ_{des}, and typical length scale a, and is given by $1/\chi^2 = D_b\tau_{\mathrm{des}}^2/a^2$. Respectively, there is a different behavior of the relevant physical quantities at times shorter and longer than the typical time scale. Namely, for the number of surface particles we find an initial stagnation, followed at longer times by a decrease proportional to $1/\sqrt{t}$. The mean squared displacement $\langle \mathbf{r}^2\rangle_s$ turns from the initial superdiffusive behavior proportional to $t^{3/2}$ to a subdiffusive form $\langle \mathbf{r}^2\rangle_s \simeq t^{1/2}$. The latter corresponds to normal diffusion, albeit with the bulk diffusivity, if normalized to the decay of the surface particles. Our analysis is complemented with the derivation of fractional order moments for the surface propagation, which exhibit anomalous scaling obtained earlier from scaling arguments. Finally, while our analysis corroborates previous scaling results of superdiffusion and the Cauchy form

TABLE I. Properties of bulk-mediated surface diffusion at short and long times.

Characteristics of effective surface diffusion	Short times $t \ll \chi^{-2}$	Long times $t \gg \chi^{-2}$
Number of particles on the surface, $N_s(t)$	$\sim 1 - \frac{2\chi}{\sqrt{\pi}} t^{1/2}$, Eq. (42)	$\sim \frac{1}{\chi\sqrt{\pi t}}$, Eq. (43)
MSD, $\langle \mathbf{r}^2(t)\rangle_s$	$\sim 4D_s t(1 + \frac{2}{3\sqrt{\pi}} \frac{D_b}{D_s}[t\chi^2]^{1/2})$, Eq. (46)	$\sim \frac{4D_s}{\chi^2}(1 + \frac{1}{\sqrt{\pi}} \frac{D_b}{D_s}[t\chi^2]^{1/2})$, Eq. (48)
Normalized MSD, $\langle \mathbf{r}^2(t)\rangle_s^{\text{norm}} \equiv \frac{1}{N_s(t)}\langle \mathbf{r}^2(t)\rangle_s$	$\sim \langle \mathbf{r}^2(t)\rangle_s$	$\sim 4D_b t$, Eq. (50)
Fractional order moments, $\langle |\mathbf{r}|^q(t)\rangle_s$	$\simeq t^q$, $0 < q < 1$, Eq. (66)	
	$\simeq t \ln t$, $q = 1$, Eq. (78)	$\simeq t^{(q-1)/2}$, Eq. (57)
	$\simeq t^{(q+1)/2}$, $1 < q < 2$, Eq. (60)	
Normalized fractional order moments, $\langle |\mathbf{r}|^q(t)\rangle_s^{\text{norm}} \equiv \frac{\langle |\mathbf{r}|^q(t)\rangle_s}{N_s(t)}$	$\sim \langle |\mathbf{r}|^q(t)\rangle_s$	$\simeq t^{q/2}$, Eq. (58)
Surface propagator, $n_s(\mathbf{r},t)$	$\sim \frac{\chi D_b^{1/2} t}{2\pi(r^2+\chi^2 D_b t^2)^{3/2}}$, $r < (D_b t)^{1/2}$, Eq. (87)	$\sim \frac{1}{\chi\sqrt{\pi t}} \frac{\exp(-r^2/[4D_b t])}{4\pi D_b t}$, $r^2 > D_b\sqrt{t}/\chi$, Eq. (98)

of the surface propagator, we find corrections to this behavior sufficiently far away from the origin, and at long times. Thus, the Cauchy domain is rectified by a Gaussian decay of the extremities of the propagator which we derive explicitly. As a consequence, finite spatial moments of any order remain finite. At long times, a Gaussian regime takes over, assembling virtually all particles.

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APPENDIX A: ALTERNATIVE DERIVATION OF THE SURFACE DENSITY

In this appendix, we derive the Lévy flight behavior recovered in the main part of the text based on a complementary approach developed in Refs. [15–17] that allows for nonperfect adsorption. We start with the coupled diffusion equation along the surface [equivalent to Eq. (13)] as

$$\frac{\partial n_s}{\partial t} = D_s\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) n_s - \frac{1}{\tau_{\text{des}}} n_s + \frac{1}{\tau_{\text{des}}}\int dx' \times \int dy' \int_0^t dt'\, W_{\text{bulk}}(x-x',y-y',t-t') n_s(x',y',t'), \tag{A1}$$

where the last term represents rebinding events of particles that previously desorbed from the surface. The kernel $W_{\text{bulk}}(x,y,t)$ in the convolution is the probability density to attach at (x,y) at time t after desorption from the origin at time zero. Together, the last two terms of Eq. (A1) represent jumps along the surface mediated by the bulk. Note that we have implicitly assumed that all particles start at the surface at $t = 0$. Otherwise an additional term would be needed to represent particles binding time to the surface for the first time.

To obtain W_{bulk}, we need to solve the bulk diffusion equation, Eq. (12), with a single particle released from the boundary at the origin at time zero. This can be achieved by choosing a boundary condition corresponding to the current of particles into the surface as

$$D_b \left.\frac{\partial n_b}{\partial z}\right|_{z=0} = \frac{1}{\mu\tau_{\text{des}}} n_b|_{z=0} - j_{\text{des}}, \tag{A2}$$

where $j_{\text{des}} = \delta(x)\delta(y)\delta(t)$ represents the initial desorption of the particle from the surface. Supplementing this by boundary conditions of vanishing density at infinity, $n_b \to 0$ as $|x|, |y|, z \to \infty$, and the initial condition of finding no particles in the bulk, $n_b(x,y,z,t=0) = 0$, we can obtain W_{bulk} from the solution in terms of the flux into the boundary after the initial release: $W_{\text{bulk}}(x,y,t) = n_b(x,y,z=0,t)/(\mu\tau_{\text{des}})$.

We remark here that Eq. (A2) with $j_{\text{des}} = n_s/\tau_{\text{des}}$ replaces the boundary condition (15) in the case of bulk coupling with nonperfect adsorption to the surface: If a probability ϵ for adsorption to the surface is introduced in Eq. (3) by multiplying the first term on the right-hand side by ϵ and correspondingly in Eq. (4) by multiplying the middle term by $(1+\epsilon)/2$, then we obtain Eq. (A2) with the modification that now $\mu \equiv a/(\epsilon D_b \tau_{\text{des}})$ instead of the definition (19).

Returning to $j_{\text{des}} = \delta(x)\delta(y)\delta(t)$, we solve Eq. (12) by Fourier transform along x and y ($x \to k_x$ and $y \to k_y$) and Laplace transform in time ($t \to s$). Together with the initial condition and the boundary conditions at infinity, it is easily found that

$$n_b(k_x,k_y,z,s) = e^{-z\sqrt{k^2+s/D_b}} n_b(k_x,k_y,z=0,s), \tag{A3}$$

where $k^2 = k_x^2 + k_y^2$. Insertion of Eq. (A3) into Eq. (A2) leads to a bulk density at the boundary which is

$$n_b(k_x,k_y,z=0,s) = \frac{1}{(\mu\tau_{\text{des}})^{-1} + D_b\sqrt{k^2+s/D_b}}. \tag{A4}$$

Multiplication by the rate constant $1/(\mu\tau_{\text{des}})$ then leads to

$$W_{\text{bulk}}(k_x,k_y,s) = \frac{1}{1 + \mu\tau_{\text{des}} D_b\sqrt{k^2+s/D_b}}. \tag{A5}$$

We are now ready to obtain the surface density n_s in Fourier-Laplace space. From Eq. (A1) with the initial condition

$n_s(x,y,t=0) = n_0\delta(x)\delta(y)$, we obtain

$$n_s(k_x,k_y,s) = \frac{n_0}{s + D_sk^2 + \tau_{\text{des}}^{-1}[1 - W_{\text{bulk}}(k_x,k_y,s)]}, \quad \text{(A6)}$$

in which Eq. (A5) can be directly inserted. To obtain the expression in Eq. (36) of the main text, one takes the limit of the desorption rate constant τ_{des}^{-1} and the adsorption rate constant $1/(\mu\tau_{\text{des}})$ going to infinity while keeping their ratio μ fixed, which leads to

$$\tau_{\text{des}}^{-1}[1 - W_{\text{bulk}}(k_x,k_y,s)] \to \mu D_b\sqrt{k^2 + s/D_b}. \quad \text{(A7)}$$

Together with $\chi = \mu\sqrt{D_b}$ and $n_0 = 1$, this makes Eq. (A6) equivalent to Eq. (36).

As a byproduct of the approach of this appendix, we remark that we can now obtain the distribution of bulk-mediated jump lengths. These are given by $\lambda(r = \sqrt{x^2 + y^2}) = 2\pi r W_{\text{bulk}}(x,y,s=0)$. From Eq. (A5), we find [performing the angular part of the inverse Fourier transform similarly to Eq. (87)]

$$\lambda(r) = 2\pi r \int_0^\infty \frac{kdk}{2\pi}\frac{J_0(kr)}{1 + \mu\tau_{\text{des}}D_bk} = \frac{1}{\mu\tau_{\text{des}}D_b} - \frac{\pi r}{2(\mu\tau_{\text{des}}D_b)^2}\left[\mathbf{H}_0\left(\frac{r}{\mu\tau_{\text{des}}D_b}\right) - Y_0\left(\frac{r}{\mu\tau_{\text{des}}D_b}\right)\right], \quad \text{(A8)}$$

where $\mathbf{H}_\nu$ are the Struve functions and Y_ν are the Bessel functions of the second kind. If we expand $\lambda(r)$ asymptotically at large r, we obtain a power law,

$$\lambda(r) \sim \frac{\mu\tau_{\text{des}}D_b}{r^2}. \quad \text{(A9)}$$

Thus we see that the Cauchy propagator (87), arising for $D_s = 0$ in the short time regime where almost all particles are still bound on the surface, is connected with a Lévy flight behavior based on a power law jump length distribution.

APPENDIX B: DERIVATION OF THE COUPLING EQUATION (15)

We start by rewriting Eq. (30) in the form

$$n_b(x,y,z,t) = \frac{\mu z}{(4\pi D_b)^{3/2}}\int_0^t d\tau \int dx' \int dy' \frac{n_s(x',y',t-\tau)}{\tau^{5/2}} \times \exp\left(-\frac{(x-x')^2 + (y-y')^2 + z^2}{4D_b\tau}\right). \quad \text{(B1)}$$

We know that the Gaussian is a limiting representation of the δ function:

$$\lim_{\tau\to 0}\frac{1}{\sqrt{4\pi D_b\tau}}\exp\left(-\frac{(x-x')^2}{4D_b\tau}\right) = \delta(x-x'). \quad \text{(B2)}$$

Let us now introduce the new variable $\tau' = \tau/z^2$, such that relation (B1) turns into

$$n_b(x,y,z,t) = \frac{\mu z}{(4\pi D_b)^{3/2}}\int_0^{t/z^2} z^2 d\tau' \int dx' \int dy' \frac{n_s(x',y',t-\tau'z^2)}{z^5(\tau')^{5/2}} \times \exp\left(-\frac{(x-x')^2}{4D_b\tau'z^2} - \frac{(y-y')^2}{4D_b\tau'z^2} - \frac{z^2}{4D_b\tau'z^2}\right). \quad \text{(B3)}$$

Rearranging terms,

$$n_b(x,y,z,t) = \int_0^{t/z^2} d\tau' \int dx' \int dy' \frac{\mu n_s(x',y',t-\tau'z^2)}{(\tau')^{3/2}} \times \frac{\exp\left(-\frac{(x-x')^2}{4D_b\tau'z^2}\right)}{\sqrt{4\pi D_b\tau'z^2}}\frac{\exp\left(-\frac{(y-y')^2}{4D_b\tau'z^2}\right)}{\sqrt{4\pi D_b\tau'z^2}}\frac{\exp\left(-\frac{1}{4D_b\tau'}\right)}{\sqrt{4\pi D_b}}. \quad \text{(B4)}$$

We are now in the position to take the limit $z \to 0$, producing (we omit the prime in τ')

$$\lim_{z\to 0} n_b(x,y,z,t) = \int_0^\infty d\tau \int dx' \int dy' \frac{\mu n_s(x',y',t)}{\tau^{3/2}} \times \delta(x-x')\delta(y-y')\frac{\exp\left(-\frac{1}{4D_b\tau}\right)}{\sqrt{4\pi D_b}}, \quad \text{(B5)}$$

which directly reduces to the expression

$$\lim_{z\to 0} n_b(x,y,z,t) = \mu n_s(x,y,t)\frac{1}{\sqrt{4\pi D_b}}\int_0^\infty d\tau \frac{\exp\left(-\frac{1}{4D_b\tau}\right)}{\tau^{3/2}}. \quad \text{(B6)}$$

Finally, with the substitution $\zeta = \tau^{-1/2}$ with the Jacobian $d\zeta = -1/(2\tau^{3/2})$, the remaining integral represents the normalization of a Gaussian,

$$\lim_{z\to 0} n_b(x,y,z,t) = \mu n_s(x,y,t)\frac{2}{\sqrt{4\pi D_b}}\int_0^\infty d\zeta \exp\left(-\frac{\zeta^2}{4D_b}\right) = \mu n_s(x,y,t), \quad \text{(B7)}$$

and the equivalence with the coupling equation (15) is established.

APPENDIX C: FRACTIONAL ORDER MOMENTS IN LAPLACE SPACE

We utilize the following integral on the plane:

$$\int [1 - \cos(\mathbf{k}\cdot\mathbf{r})]\frac{dk}{|\mathbf{k}|^{2+q}} = 2\pi\int_0^\infty [1 - J_0(kr)]\frac{dk}{k^{1+q}} = 2\pi r^q \int_0^\infty [1 - J_0(z)]\frac{dz}{z^{1+q}}, \quad \text{(C1)}$$

where we used polar coordinates $r = |\mathbf{r}|$ and $k = |\mathbf{k}|$ corresponding to the two-dimensional vectors $\mathbf{r} = x\mathbf{e}_x + y\mathbf{e}_y$ and $\mathbf{k} = k_x\mathbf{e}_x + k_y\mathbf{e}_y$. Thus we identify

$$r^q = K(q)\int [1 - \cos(\mathbf{k}\cdot\mathbf{r})]\frac{d\mathbf{k}}{k^{2+q}} \quad \text{(C2)}$$

with the definition

$$K(q) = \left(2\pi\int_0^\infty [1 - J_0(z)]\frac{dz}{z^{1+q}}\right)^{-1} = \frac{2^q}{\pi^2}\sin\left(\frac{\pi q}{2}\right)\left[\Gamma\left(1 + \frac{q}{2}\right)\right]^2. \quad \text{(C3)}$$

With this trick, we can rephrase the qth-order moment (51) as follows:

$$\begin{aligned}\langle r^q(t)\rangle_s &= K(q)\iint [1-\cos(\mathbf{k}\cdot\mathbf{r})]\,n_s(\mathbf{r},t)\frac{d\mathbf{k}}{k^{2+q}}d\mathbf{r}\\ &= K(q)\int\left[\int n_s(\mathbf{r},t)d\mathbf{r}-\int\cos(\mathbf{k}\cdot\mathbf{r})\,n_s(\mathbf{r},t)d\mathbf{r}\right]\frac{d\mathbf{k}}{k^{2+q}}.\end{aligned}\tag{C4}$$

The integral over $d^2\mathbf{r}$ of the surface density is merely the number of surface particles, such that

$$\langle r^q(t)\rangle_s = K(q)\int\frac{d^2\mathbf{k}}{k^{2+q}}[N_s(t)-\mathrm{Re}\{n_s(\mathbf{k},t)\}],\tag{C5}$$

where we replaced the Fourier cosine transform of $n_s(\mathbf{r},t)$ by the real part of the exponential Fourier transform.

With the Fourier-Laplace transform (36) of the surface propagator with D_s set to zero, for the Laplace transform of the qth-order moment we obtain

$$\begin{aligned}\langle r^q(s)\rangle_s &= K(q)\int[n_s(\mathbf{k}=0,s)-n_s(\mathbf{k},s)]\frac{d\mathbf{k}}{k^{2+q}} = 2\pi K(q)\left[\frac{1}{s+\chi\sqrt{s}}-\frac{1}{s+\chi\sqrt{s+D_bk^2}}\right]\frac{dk}{k^{1+q}}\\ &= 2\pi K(q)\frac{\chi}{s+\chi\sqrt{s}}\int_0^\infty\frac{\sqrt{s+D_bk^2}-\sqrt{s}}{s+\chi\sqrt{s+D_bk^2}}\frac{dk}{k^{1+q}}\\ &= 2\pi K(q)\frac{\chi D_b}{s+\chi\sqrt{s}}\int_0^\infty\frac{1}{(\sqrt{s}+\sqrt{s+D_bk^2})(s+\chi\sqrt{s+D_bk^2})}\frac{dk}{k^{q-1}}\\ &= 2\pi K(q)\frac{\chi^2}{s+\chi\sqrt{s}}\left(\frac{D_b}{s}\right)^{q/2}\int_0^\infty\frac{1}{(\chi+\chi\sqrt{1+y^2})(\sqrt{s}+\chi\sqrt{1+y^2})}\frac{dy}{y^{q-1}}\\ &= 2\pi K(q)\frac{\chi D_b^{q/2}}{s^{(1+q)/2}(s-\chi^2)}\{I_1(q)-I_2(q)\},\end{aligned}\tag{C6}$$

where we introduced the substitution $y=\sqrt{D_b/s}k$. The two integrals I_i are defined by

$$I_1(q)=\int_0^\infty\frac{y^{1-q}}{1+\sqrt{1+y^2}}dy\tag{C7}$$

and

$$I_2(q)=\int_0^\infty\frac{y^{1-q}}{\sqrt{s}/\chi+\sqrt{1+y^2}}dy.\tag{C8}$$

APPENDIX D: SURFACE PROPAGATOR IN FOURIER SPACE

We perform an inverse Laplace transformation of Eq. (79) along the Bromwich path:

$$\begin{aligned}n_s(\mathbf{k},t) &= \int_{\mathrm{Br}}\frac{\exp(st)}{s+\chi\sqrt{s+D_bk^2}}\frac{ds}{2\pi i} = \int_{\mathrm{Br}}\frac{\exp(s\chi^2t)}{s+\sqrt{s+\kappa^2}}\frac{ds}{2\pi i} = e^{-\kappa^2\chi^2t}\int_{\mathrm{Br}}\frac{\exp(s\chi^2t)}{s+\sqrt{s}-\kappa^2}\frac{ds}{2\pi i}\\ &= e^{-\kappa^2\chi^2t}\int_{\mathrm{Br}}\frac{\exp(s\chi^2t)}{\left(\sqrt{s}+\frac12+\sqrt{\kappa^2+\frac14}\right)\left(\sqrt{s}+\frac12-\sqrt{\kappa^2+\frac14}\right)}\frac{ds}{2\pi i}\\ &= \frac{\exp(-\kappa^2\chi^2t)}{2\sqrt{\kappa^2+1/4}}\left(\int_{\mathrm{Br}}\frac{\exp(s\chi^2t)}{\sqrt{s}+\frac12-\sqrt{\kappa^2+\frac14}}\frac{ds}{2\pi i}-\int_{\mathrm{Br}}\frac{\exp(s\chi^2t)}{\sqrt{s}+\frac12+\sqrt{\kappa^2+\frac14}}\frac{ds}{2\pi i}\right)\\ &= \frac{\exp(-\kappa^2\chi^2t)}{2\sqrt{\kappa^2+1/4}}\left(\mathscr{L}^{-1}\left\{\frac{1}{\sqrt{s}-b};s\to t'\right\}_{b=\sqrt{\kappa^2+1/4}-1/2,t'=t\chi^2}-\mathscr{L}^{-1}\left\{\frac{1}{\sqrt{s}+a};s\to t'\right\}_{a=1/2+\sqrt{\kappa^2+1/4},t'=t\chi^2}\right),\end{aligned}\tag{D1}$$

where we introduced the substitutions $s'=s/\chi^2$ and $\kappa^2=D_bk^2/\chi^2$. With [18]

$$\mathscr{L}^{-1}\left\{\frac{1}{\sqrt{s}+a};s\to t\right\}=\frac{1}{\sqrt{\pi t}}-ae^{a^2t}\mathrm{erfc}(a\sqrt{t}),\tag{D2}$$

we finally arrive at the Fourier transform of the surface propagator,

$$n_s(\mathbf{k},t) = \frac{1}{2\sqrt{\kappa^2+1/4}}\left\{\left[\frac{1}{2}+\sqrt{\kappa^2+\frac{1}{4}}\right]\exp\left(\left[\frac{1}{2}+\sqrt{\kappa^2+\frac{1}{4}}\right]t\chi^2\right)\mathrm{erfc}\left(\left[\frac{1}{2}+\sqrt{\kappa^2+\frac{1}{4}}\right]\chi\sqrt{t}\right)\right.$$
$$\left.+\left(\sqrt{\kappa^2+\frac{1}{4}}-\frac{1}{2}\right)\exp\left(\left[\frac{1}{2}-\sqrt{\kappa^2+\frac{1}{4}}\right]t\chi^2\right)\mathrm{erfc}\left(\left[\frac{1}{2}-\sqrt{\kappa^2+\frac{1}{4}}\right]\chi\sqrt{t}\right)\right\}. \tag{D3}$$

[1] O. V. Bychuk and B. O'Shaughnessy, Phys. Rev. Lett. **74**, 1795 (1995).
[2] O. V. Bychuk and B. O'Shaugnessy, J. Chem. Phys. **101**, 772 (1994).
[3] O. V. Bychuk and B. O'Shaugnessy, Langmuir **10**, 3260 (1994).
[4] R. Valiullin, R. Kimmich, and N. Fatkullin, Phys. Rev. E **56**, 4371 (1997).
[5] J. A. Revelli, C. E. Budde, D. Prato, and H. S. Wio, New J. Phys. **7**, 16 (2005).
[6] S. Stapf, R. Kimmich, and R.-O. Seitter, Phys. Rev. Lett. **75**, 2855 (1995).
[7] Y. Georgievskii, E. S. Medvedev, and A. A. Stuchebrukhov, J. Chem. Phys. **116**, 1692 (2002).
[8] G. Oshanin, M. Tamm, and O. Vasilyev, J. Chem. Phys. **132**, 235101 (2010).
[9] O. Bénichou, D. Grebenkov, P. Levitz, C. Loverdo, and R. Voituriez, Phys. Rev. Lett. **105**, 150606 (2010); J. Stat. Phys. **142**, 657 (2011).
[10] M. E. Toimil-Molares, L. Röntzsch, W. Sigle, K.-H. Heinig, C. Trautmann, and R. Neumann, Adv. Funct. Mater. **22**, 695 (2012).
[11] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000); J. Phys. A **37**, R161 (2004).
[12] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Clarendon, Oxford, UK, 1959), Chap. 2; A. N. Tikhonov and A. A. Samarskii, *Equations of Mathematical Physics* (Pergamon, Oxford, UK, 1963), Chap. 3.
[13] A. B. Prudnikov, Yu. A. Brychkov, and O. I. Marichev, *Integrals and Series. Elementary Functions* (Gordon and Breach, New York, 1986).
[14] A. V. Chechkin, I. M. Zaid, M. A. Lomholt, I. M. Sokolov, and R. Metzler, Phys. Rev. E **79**, 040105(R) (2009); J. Chem. Phys. **134**, 204116 (2011).
[15] M. A. Lomholt, I. M. Zaid, and R. Metzler, Phys. Rev. Lett. **98**, 200603 (2007).
[16] I. M. Zaid, M. A. Lomholt, and R. Metzler, Biophys. J. **97**, 710 (2009).
[17] M. A. Lomholt, B. van den Broek, S.-M. J. Kalisch, G. J. L. Wuite, and R. Metzler, Proc. Natl. Acad. Sci. (USA) **106**, 8204 (2009).
[18] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1972).