# How Stickiness Can Speed Up Diffusion in Confined Systems

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The paradigmatic model for heterogeneous media used in diffusion studies is built from reflecting obstacles and surfaces. It is well known that the crowding effect produced by these reflecting surfaces slows the dispersion of Brownian tracers. Here, using a general adsorption desorption model with surface diffusion, we show analytically that making surfaces or obstacles attractive can accelerate dispersion. In particular, we show that this enhancement of diffusion can exist even when the surface diffusion constant is smaller than that in the bulk. Even more remarkably, this enhancement effect occurs when the effective diffusion constant, when restricted to surfaces only, is lower than the effective diffusivity with purely reflecting boundaries. We give analytical formulas for this intriguing effect in periodic arrays of spheres as well as undulating microchannels. Our results are confirmed by numerical calculations and Monte Carlo simulations.

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Determining the transport properties of tracer particles in heterogeneous media at large timescales and length scales has applications in a range of physical problems including fluid mechanics, hydrology, chemical engineering, soft matter, and solid state physics [1–4]. The effective diffusivity is a crucial input for problems of mixing [5–7], sorting [8], chemical delivery [2,9], as well as chemical reactions [4,6]. Spatial variations of diffusion and advection can lead to drastic changes in the effective diffusion constant with respect to homogenous systems. Classic examples include Taylor dispersion, in hydrodynamic flows [10], and the decrease of dispersion due to the energy barriers created by time independent potentials [11]. In a number of systems, such as porous media [12], zeolites, and biological channels [13], the motion of tracer particles is hindered by hard (technically speaking reflecting) boundaries or obstacles. The effective trapping of the tracer in this case is of entropic origin but it again leads to a reduction of late time diffusivity [14–18]. The effect of the confining geometry on effective diffusivity has been widely studied [2,16,19–27], but the vast majority of existing theories focuses on perfectly *reflecting boundaries*.

However, the diffusion of a finite size tracer near a surface is actually much more complicated than that of simple Brownian motion at a reflecting wall. First, the tracer will typically be subject to nonspecific interactions with the surface, for example as the result of van der Waals long range attraction and electrostatic potentials, that can be attractive or repulsive, depending on geometry and charges [3,28]. Second, the components of the diffusion tensor in the vicinity of the wall are reduced due to the no-slip boundary condition on the ambient fluid [29]. A simple minimal model for these effects is that of a tracer particle that can transiently attach (or adsorb) to, diffuse on, and detach (desorb) from the surface, thus alternating between phases of bulk diffusion or surface diffusion (Fig. 1). This type of model was first proposed in the 1990s when it was realized that the effective lateral dispersion of molecules adsorbed at a fluid-solid interface is significantly modified by temporary excursions into the fluid [30]. The stochastic motion resulting from interplay of bulk and surface diffusion has recently been directly observed experimentally [31–35].

It is also known that surface mediated transport gives rise to nontrivial effects in the context of target search kinetics [36–39] and that in certain cases the search efficiency can be tuned via the parameters of the surface mediated diffusion model. A classic related example is the optimization of search on DNA by alternating phases of one-dimensional diffusion along the DNA, on which the target site is found, and three-dimensional bulk excursions [40–42]. It is less

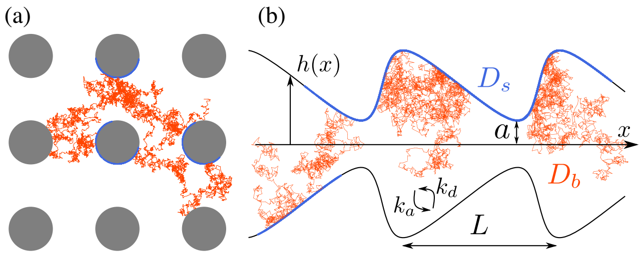

FIG. 1. Examples of trajectories of a tracer particle diffusing in the bulk (orange lines) or on the surface (thick blue lines) in a regular array of spherical obstacles (a) or in a microchannel (b).

clear if similar optimization effects appear for transport properties. In Ref. [43], the effect of adding a short range attraction to otherwise hard spheres was studied numerically. Remarkably, it was found that spending time trapped at the surface can lead to an increase in the late time diffusion of the tracer. The study of [43] neglects the fact that diffusion near the hard sphere is slowed down and one is naturally lead to ask the question as to whether the enhancement effect persists when this is taken into account. Moreover, for general geometries, there are no theories predicting this enhancement of dispersion: existing approaches deal with uniform channels (where the effect is absent) [44,45] or in fast exchange limit for nonplanar geometries [4,46,47], where no increase of dispersion due to sticky surfaces was found.

In this Letter, we introduce a theory that quantitatively predicts the increase in late time dispersion (with respect to its value for reflecting boundaries) induced by making the boundaries attractive, even when the surface diffusivity is lower than the microscopic bulk diffusivity. As an example, we give analytical formulas characterizing dispersion in nondilute spherical sticky obstacles, which explain the simulation results of [43]. Results are then given for slowly undulating channels, in this case the increase of dispersion turns out to be stronger. For strongly undulating channels, we show that enhancement of dispersion no longer occurs. Our results identify in which situations dispersion is optimized by the interplay between diffusion in bulk and on the surface. The effect uncovered here can be viewed as an example of *catalysis* for diffusion where the introduction of the *surface state* via reaction with the surface induces an increase in the rate of dispersion.

*Model of surface mediated transport.*—We consider a tracer particle, of position $\mathbf{r}(t)$ at time $t$ in a $d$-dimensional space, a heterogeneous medium with obstacles, or confining boundaries. The particle can either diffuse in the *bulk* (“$b$”), with a bulk molecular diffusivity $D_b$, and local drift $\mathbf{u}_b(\mathbf{r})$, or diffuse along the *surface* (“$s$”) of the obstacles or confining surface, where it diffuses with diffusion coefficient $D_s$ (typically smaller than $D_b$). In our approach, we assume that the tracer particle is pointlike. This assumption can be made without loss of generality since the problem of a finite size tracer particle can be studied by modifying the obstacle geometry. In this way, the particle size influences the effective diffusivity. We will also neglect inertial effects, which are irrelevant for sufficiently small tracers in viscous fluids. We can also consider a local drift field $\mathbf{u}_s(\mathbf{r})$, within the surface. By $k_d$ we denote a detachment rate at which the tracer desorbs from the surface. When the transition between bulk and surface is viewed as a reaction, the binding kinetics is quantified by an imperfect reactivity parameter $k_a$ [48], which has the dimension of a velocity. In the context of Taylor dispersion it has been shown how the parameters $k_a$ and $k_d$ can be determined from a microscopic model [49].

The probability densities $p_b(\mathbf{r},t)$ and $p_s(\mathbf{r},t)$ to be at position $\mathbf{r}$ at time $t$ in the bulk and surface obey

$$\frac{\partial p_b}{\partial t} = \nabla \cdot [D_b \nabla p_b - \mathbf{u}_b(\mathbf{r}) p_b], \tag{1}$$

$$\frac{\partial p_s}{\partial t} = \nabla_s \cdot [D_s \nabla_s p_s - \mathbf{u}_s(\mathbf{r}) p_s] - k_d p_s + k_a p_b, \tag{2}$$

where $\nabla_s$ is the surface nabla operator. The boundary conditions, determined from probability conservation, are given by

$$\mathbf{n} \cdot [D_b \nabla p_b - \mathbf{u}_b(\mathbf{r}) p_b] = k_d p_s - k_a p_b, \tag{3}$$

where $\mathbf{n}$ is the surface normal vector, pointing away from the bulk. Finally, we assume that the geometry of the medium, as well as all fields $\mathbf{u}_b(\mathbf{r})$, $\mathbf{u}_s(\mathbf{r})$, are spatially periodic.

*Effective transport properties.*—The late time transport properties in a given spatial direction (say, the $x$ direction) are quantified by an effective drift $v_e$ and effective diffusivity $D_e$ in this direction:

$$v_e = \frac{\overline{x(t) - x(0)}}{t}, \qquad D_e = \lim_{t\to\infty} \frac{\overline{[x(t) - x(0) - v_e t]^2}}{2t}, \tag{4}$$

where the overline denotes the average over stochastic trajectories. The average drift is straightforward to calculate [see Supplemental Material (SM) [50] ]

$$v_e = \int_V d\mathbf{r} (\nabla x) \cdot \mathbf{j}_b + \int_S dS (\nabla_s x) \cdot \mathbf{j}_s, \tag{5}$$

$$\mathbf{j}_b = (\mathbf{u}_b - D_b \nabla) P_b^{st}, \qquad \mathbf{j}_s = (\mathbf{u}_s - D_s \nabla_s) P_s^{st}, \tag{6}$$

where the integrals are evaluated over the volume $V$ and the surface $S$ of the walls in one period. The functions $P_b^{st}(\mathbf{r})$ and $P_s^{st}(\mathbf{r})$ are the stationary probability densities of the position modulo the period and are time-independent solutions of Eqs. (1) and (2) with periodic conditions.

To compute $D_e$ in the absence of any advection, we use the fluctuation dissipation theorem that relates it to the effective drift when a small force $F$ acts on the tracer particle:

$$D_e(F=0) = k_B T \times \left[\frac{d}{dF} v_e(F)\right]_{F=0}, \tag{7}$$

where $k_B T$ is the thermal energy. Here, a force $F$ in the $x$ direction corresponds to the following drift fields:

$$\mathbf{u}_b(\mathbf{r}) = \beta D_b F (\nabla x), \qquad \mathbf{u}_s(\mathbf{r}) = \beta D_s F (\nabla_s x), \tag{8}$$

with $\beta = 1/k_B T$. At zero force, we denote the stationary probability densities by $P_b^{st,0}$, $P_s^{st,0}$, both are uniform and are given by

$$P_b^{st,0}(\mathbf{r}) = \frac{1}{V + S\delta}, \qquad P_s^{st,0}(\mathbf{r}) = \delta P_b^{st,0}, \tag{9}$$

where $\delta = k_a/k_d$ is an adsorption length (that can be much larger than the range of interactions with the surface). The length $\delta$ quantifies how "sticky" the surface is, with surfaces becoming nonreflecting in our problem when $\delta$ is comparable to $V/S$, in which case the fraction of time spent on the surface become significant. We now introduce two auxiliary fields $f_b$ and $f_s$ which quantify the deviation of the stationary probability density from the uniform distribution at low forces:

$$P_b^{st} \simeq P_b^{st,0} + \beta F f_b(\mathbf{r}), \qquad P_s^{st} \simeq P_s^{st,0} + \beta F f_s(\mathbf{r}). \tag{10}$$

Inserting this ansatz into Eqs. (5) and (7), we see that $D_e(F = 0)$ (denoted simply by $D_e$) is given by

$$\begin{aligned} D_e = D_b \int_V d\mathbf{r}(\nabla x) \cdot \nabla[P_b^{st,0}x - f_b] \\ + D_s \int_S dS(\nabla_s x) \cdot \nabla_s[P_s^{st,0}x - f_s]. \end{aligned} \tag{11}$$

The equations for $f_b, f_s$ are obtained by inserting the ansatz (10) into the transport equations (1), (2), (3) and expanding to linear order in $F$, which yields

$$\nabla^2 f_b = 0, \qquad D_s \nabla_s^2[f_s - P_s^{st,0}x] = k_d f_s - k_a f_b, \tag{12}$$

$$D_b \mathbf{n} \cdot \nabla f_b = k_d f_s - k_a f_b + D_b P_b^{st,0}(\nabla x) \cdot \mathbf{n}. \tag{13}$$

The above equations, together with periodic boundary conditions, define $f_b$ and $f_s$ up to an unimportant additive constant. This kind of formula linking micro- and macrotransport properties can also be found in macrotransport theory [4], homogenization methods or Kubo formulas [55,56]. In the case of surface mediated transport, the above equations are general and in the limit of fast exchange between bulk and surface ($k_d, k_a \to \infty$ keeping $k_a/k_d$ constant) reproduce the results given in [4,46,47]. Note that surface curvature effects arise in Eq. (12) via the term $\nabla_s^2 x$ which does not vanish (as it would in the bulk). The above partial differential equations can be numerically solved by standard finite element routines. However we will also derive analytical results in certain limits.

*Dispersion in regular arrays of spheres.*—One the most studied models of a crowded environment is that of a regular array of spherical obstacles. Here, we consider the cases of a square lattice (in 2D, $d = 2$) or a cubic lattice (in 3D, $d = 3$), see Fig. 1(a). We denote by $L$ the distance between the centers of nearest neighboring spheres, $R$ their radius, and $\varphi$ their volume fraction. An exact analytical expression for the dispersion for any $\varphi$ is difficult to obtain even without the surface interactions. However, in the limit of small $R/L$ (equivalently, the small $\varphi$ limit), we can look for solutions in terms of matched asymptotic expansions, with an inner solution for $f_b(\mathbf{r})$ that varies at the scale $|\mathbf{r}| \sim R$, and an outer solution varying at the scale $L$. The auxiliary fields in the limit $R \to 0$ are written as

$$f_b(\mathbf{r}) = \begin{cases} \sum_{n\geq 0} R^{n+1} f_b^{(n)}(r/R, \omega) & (r \ll L, \text{inner}) \\ \sum_{n\geq 0} R^{d+n} F_b^{(n)}(r, \omega) & (r \gg R, \text{outer}) \end{cases}, \tag{14}$$

where $r$ is the distance to the center of the nearest obstacle and $\omega$ denote angular variables. The solutions at successive orders are found by inserting Eq. (14) into our formalism and imposing that both outer and inner solutions are equal in the regime $R \ll r \ll L$ (where they are both valid). To order $\varphi^4$ (see SM [50]), we find

$$\begin{aligned} D_e &= \frac{D_b}{1 + (d\xi - 1)\varphi} \frac{1 - \alpha\varphi}{1 + \alpha\varphi/(d-1)} + o(\varphi^4), \\ \alpha &= \frac{D_b + D_s\xi(\gamma - 1)(d-1)}{D_b + D_s\xi[\gamma(d-1) + 1]}, \qquad \gamma = \frac{D_b}{k_a R}, \qquad \xi = \frac{\delta}{R}. \end{aligned} \tag{15}$$

The above formula is exact up to the order $\varphi^4$ in the small $\varphi$ limit, when $\xi$ and $\gamma$ are kept constant. It is valid for a large range of values of $\varphi$, as shown in Fig. 2 where it is compared to numerical solution of the full transport equations (12) and (13). The theory also agrees with the Monte Carlo simulations of Ref. [43]. This expression (15) is a generalization of similar Maxwell type formulas obtained for reflecting obstacles, see, e.g., Refs. [57–60]. We can define a critical surface diffusivity $D_s^*$ as the

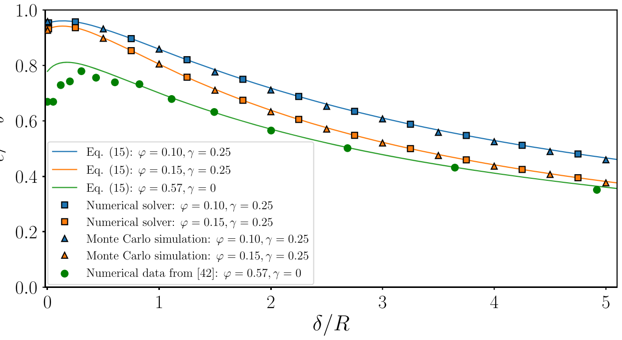

FIG. 2. Long-time dispersion for a periodic array of spherical obstacles ($d = 3$) with $D_s = D_b$. Lines: theoretical prediction, Eq. (15). Squares: data obtained by numerical integration of Eqs. (12) and (13). Triangles: results of stochastic simulations of the stochastic process $\mathbf{r}(t)$ associated to the Fokker-Planck equations (1) and (2). Circles: Monte Carlo simulation data taken from [43], where the tracer particles are submitted to an exponentially decaying potential. The parameter $\delta$ was adjusted so that the stationary probability densities (9) in our description are the same as in the case of this potential (see SM for details [50]).

value of $D_s$ above which a weak attraction increases $D_e$ (so $[\partial D_e/\partial\delta]_{\delta=0} = 0$ at $D_s = D_s^*$). Using Eq. (15), we find

$$D_s^* = D_b\left(1 - \frac{1-\varphi}{d}\right). \tag{16}$$

Interestingly, $D_s^*$ depends only on $\varphi$ and is independent of the adsorption and desorption rates. At this level of perturbation theory we also see that $D_s^* < D_b$. Consequently, if the surface and bulk diffusivities are equal ($D_s = D_b$), making the surfaces weakly attractive *generically increases* dispersion. This effect holds even when $D_s < D_b$ (as long as $D_s > D_s^*$). Hence, spending time on a surface, even with reduced diffusion, can actually lead to faster dispersion than in the case of purely reflecting obstacles. A similar formula to Eq. (15) was found in Ref. [61] in the fast exchange limit ($\gamma = 0$), however this formula does not predict an increase of dispersion for weakly attractive spheres, and it disagrees with our theory and with numerical simulations (see SM [50]). Finally, the increase in $D_e$ is rather marginal in this geometry, as can be seen in Fig. 2.

*Dispersion in slowly undulating channels.*—We now analyze the case of a surface-mediated diffusion process in a symmetric channel of half-width $h(x)$ (if $d = 2$) or in an axisymmetric channel of radius $h(x)$ (if $d = 3$), see Fig. 1(b). Such geometries are often viewed as a paradigm for transport in confined media [14,17]. We consider the limit of slowly varying undulations ($L \to \infty$), where the problem can be solved using a perturbation expansion:

$$f_b = \sum_{n\geq 0} \frac{1}{L^n} f_b^{(n)}\left(\frac{x}{L}, \mathbf{r}_\perp\right), \qquad f_s = \sum_{n\geq 0} \frac{1}{L^n} f_s^{(n)}\left(\frac{x}{L}\right), \tag{17}$$

where $\mathbf{r}_\perp$ is the position perpendicular to the direction $x$. Inserting the above ansatz into our formalism and writing all equations order by order, we obtain (see SM [50])

$$D_e \underset{L\to\infty}{=} \frac{1}{\langle h^{d-2}[h + (d-1)\delta]\rangle \langle \frac{h^{2-d}}{D_b h + (d-1) D_s \delta}\rangle}, \tag{18}$$

where $\langle\cdot\rangle = (1/L)\int_0^L \cdot dx$ denotes the spatial average over one period $L$. Note that $D_e$ is not given by a simple steady state average between effective bulk diffusion and surface diffusion as it is the case for a flat channel [44]. For reflecting walls ($\delta = 0$), we recover the well known result obtained with the Fick-Jacobs approximation, $D_e(\delta{=}0) = D_b[\langle h^{d-1}\rangle\langle h^{-(d-1)}\rangle]^{-1}$ [16,24]. Once again, defining $D_s^*$ as the value of $D_s$ for which $[\partial D_e/\partial\delta]_{\delta=0} = 0$, we find

$$D_s^* = D_b \frac{\langle h^{d-2}\rangle\langle h^{1-d}\rangle}{\langle h^{d-1}\rangle\langle h^{-d}\rangle}. \tag{19}$$

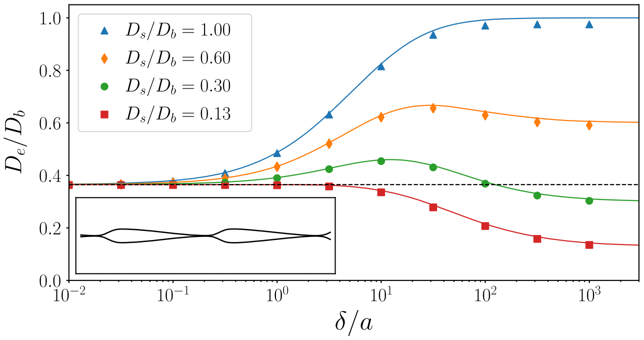

FIG. 3. Longtime diffusion coefficient for a two-dimensional channel of height profile $h/a = 16 + 15\arctan[\cos u/(\sin u + 3/2)]/\arctan(2/\sqrt{5})$ with $u = 2\pi x/L$. Symbols: results of the numerical integration of Eqs. (12) and (13) for $k_a a/D_b = 10$ and $L/a = 500$; for this value the channel shape is shown in the inset. Lines: predictions of Eq. (18) in the limit of slowly varying width.

It can be shown that $D_s^*$ is smaller than $D_b$ for any choice of profile $h$. Figure 3 illustrates the increase of dispersion when surfaces are made weakly attractive for one example of a two-dimensional channel. Interestingly, the increase of dispersion can be as high as 250% (upper curve), this change could be made arbitrarily high for sharper channel undulations. The enhancement effect can thus be significantly larger than that observed for sticky spheres as studied above and in Ref. [43].

It is clear that the enhancement of diffusion is related to the fact that diffusing along the surface avoids bottlenecks (or entropic barriers) in the channel. However, the effect of the surface interaction is more subtle than just this basic effect. As seen in Fig. 3 from the curve with solid circles, a finite interaction with the surface can enhance diffusion with respect to both the case $\delta = 0$ (pure reflection) and $\delta \to \infty$ (diffusion restricted to the surface), even when the surface diffusion is 30% of that of bulk diffusion. Actually, it can be shown that when $D_e(0) = D_e(\infty)$, then the inequality $D_s > D_s^*$ always holds (see SM [50]). Hence, for any channel geometry, there is a regime for which the effective diffusivity is larger than the effective diffusivity for completely reflecting ($\delta = 0$) or completely sticky ($\delta \to \infty$) boundaries. The subtlety of the effect is also highlighted by the earlier results on spherical obstacles, where the enhancement effect actually shows up at first order in the volume fraction, thus in absence of significant bottlenecks.

*Dispersion in highly undulating channels.*—Finally, we investigate rapidly varying channels ($L \ll a$, with $a$ the minimal channel height), for which we obtain (see SM [50])

$$D_e \underset{L\ll a}{=} \frac{V_c}{V + S\delta} D_b, \tag{20}$$

where $V_c$ is the volume of a central region (a cylinder of radius $a$, so $V_c = 2aL$ in 2D and $V_c = \pi a^2 L$ in 3D).

This formula can be deduced from a simple ergodic argument. In the central region, the tracer particle can freely diffuse, but in the peripheral regions made of very thin dead ends, the tracer particle does not contribute to dispersion along the channel axis (at leading order). Hence, the late time diffusivity is the product of $D_b$ with the fraction of time spent in the central region, leading to Eq. (20). In this geometric limit, we see that surface interactions only *decrease* dispersion.

*Conclusion.*—It is well established that first passage kinetics to a target can be optimized by an appropriate combination of Sojourn of diffusion in spaces of different dimensions [36,37,41], as exemplified by the search of a gene sequence on DNA [40–42]. However, this optimization is not linked to an acceleration of diffusivity. Here, we have theoretically demonstrated a similar optimization effect holds for transport features: dispersion in crowded media can be enhanced if the obstacles or surfaces exhibit a short ranged attraction for the tracer. This enhancement phenomenon was first noted in Ref. [43] for hard spheres. Using a surface mediated diffusion model, we have developed a general transport theory to analyze the effect of short range attractive interactions on dispersion. This theory explains the results of Ref. [43] and we have provided analytical results for dilute systems (which work rather well even for large volume fractions). We have also analyzed dispersion in symmetric channels where the particle can adsorb and detach from the walls. For slowly undulating channels, we have shown that an even stronger diffusion enhancement can occur and have given exact results. In both geometries, we find that even when the surface diffusion constant $D_s$ is smaller than that in the bulk $D_b$ (as must be the case physically) this enhancement can still occur and we have determined the critical values of $D_s$ above which this happens.

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