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Article

# A Fractal-Based Correlation for Time-Dependent Surface Diffusivity in Porous Adsorbents

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**Abstract:** Fluid–solid adsorption processes are mostly governed by the adsorbate transport in the solid phase and surface diffusion is often the limiting step of the overall process in microporous materials such as zeolites. This work starts from a concise review of concepts and models for surface transport and variable surface diffusivity. It emerges that the phenomenon of hindered surface diffusion for monolayer adsorption, which is common in zeolites, and models able to fit a non-monotonic trend of surface diffusivity against adsorbate solid phase concentration, have received limited attention. This work contributes to the literature of hindered diffusion by formulating a time-dependent equation for surface diffusivity based on fractal dynamics concepts. The proposed equation takes into account the contributions of both fractal-like diffusion (a time-decreasing term) and hopping diffusion (a time-increasing term). The equation is discussed and numerically analyzed to testify its ability to reproduce the possible different patterns of surface diffusivity vs. time.

**Keywords:** surface diffusivity; adsorption; hindered diffusion; fractal-like dynamics; hopping; zeolites

## 1. Introduction

A typical fluid–solid adsorption process generally consists of three steps when referring to the adsorbate: (i) mass transfer by diffusion from the bulk of the fluid phase to the solid's external surface (film diffusion), (ii) mass transfer by diffusion into the solid phase (intraparticle diffusion), and (iii) adsorption (by physical and/or chemical mechanism) on the solid's internal surface. These steps are the same in adsorption and ion exchange processes, the difference being related to the stoichiometric nature of the latter [1]. Nevertheless, in practical applications both processes are modelled by using analogous equilibrium and kinetic equations. Adsorption in porous solids is typically controlled by the intraparticle diffusion step (ii), as film diffusion and adsorption are much faster processes [2]. Similar is the situation in ion exchange although the overall rate can be controlled by a slow chemical reaction, if such a reaction takes place [1]. The majority of adsorption models rely on empirical pseudo-first or -second order chemical reaction-like expressions, which ignore the diffusion steps always apparent in adsorption and ion exchange; thus, these models can fall short in representing the physical phenomena underlying the processes under scrutiny [3,4]. On the other hand, analytical solutions to diffusion-based models are possible under certain conditions such as those postulating linear or rectangular adsorption isotherm and infinite solution volume [5]. Analytical and/or approximate solutions are mostly based on the works of Crank [6], Boyd et al. [7], Paterson [8],

and Helfferich [9]. A comprehensive discussion on the mechanisms and models used in adsorption and ion exchange processes is provided by Inglezakis et al. [10,11].

The mass transport of an adsorbate in a porous solid occurs in macropores (>50 nm-diameter), mesopores (2–50 nm), and micropores (<2 nm). Adsorption is particularly relevant when referring to meso- and micro-pores, where surface (in both) and capillary (in mesopores) forces are present. In macro- and meso-pores at low adsorbate concentration, a monolayer coverage of the surface takes place and mass transport typically occurs by molecular/Knudsen and surface diffusion [12,13]. In the case of surface diffusion, the adsorbate transport occurs on the pores surface via “jumps” between adsorption sites and the process is energetically activated [14]. Surface diffusion is significantly affected by the adsorbed phase concentration which, in turn, can affect the apparent porosity and contribute positively or negatively to the adsorbate permeability as a function of the operating pressure, as discussed by Jia et al. [15]. When the adsorbate concentration increases, diffusion of multilayer-adsorbed molecules occurs. Monolayer adsorption is controlled by adsorbate–surface interactions, while multilayer adsorption by adsorbate–adsorbate interactions. A further increase of adsorbate concentration may result in capillary condensation. In micropores, the adsorbate diffusion accords to “configurational” or “intracrystalline” patterns and shares common characteristics with the surface diffusion [12]. Surface diffusion affects the adsorption rate and can be the limiting step of the process, as the diffusion coefficient may be orders of magnitude smaller than those typical of molecular/Knudsen diffusion.

In this context, this work aims at proposing, discussing, and analyzing a time-dependent equation for the surface diffusivity, taking into account the phenomenon of hindered surface transport—described by fractal-like dynamics concepts—a topic limitedly explored in literature. To the best of our knowledge the available variable diffusivity equations are scarce, as discussed in the next section, while fractal-like dynamics is for the first time applied to a variable surface diffusivity equation.

## 2. Surface Transport and Variable Surface Diffusivity Models

The diffusion rate of an adsorbate into a solid is described by several coefficients. The adsorbate self-diffusivity  $D_{SS}(q)$  at a certain solid phase concentration ( $q$ ) measures the displacement of a tagged molecule (tracer) as it diffuses at equilibrium—a topic comprehensively discussed by Ruthven and Kärger [14,16] (please refer to the nomenclature section where symbols and their meaning are listed). For the macroscopic diffusion of an adsorbate, the surface transport diffusivity (or simply surface diffusivity)  $D_S(q)$  is used, which is defined as the proportionality constant relating the macroscopic flux ( $J$ ) to the macroscopic concentration gradient, which, recalling the Fick’s law expression, in radial ( $r$ ) coordinates is:

$$J = -D_S(q) \frac{dq}{dr} \quad (1)$$

The surface diffusivity is measured under non-equilibrium conditions in either steady-state or transient conditions [12]. The surface diffusivity can be also defined in terms of the chemical potential, which represents a more appropriate driving force than concentration [16]:

$$D_S(q) = D_{S0}(q) \left( \frac{\partial \ln f_{eq}}{\partial \ln q_{eq}} \right)_T \quad (2)$$

where  $f_{eq}$  is the fugacity of the bulk phase that is in equilibrium with the adsorbed phase when the latter has equilibrium concentration  $q_{eq}$  at constant temperature  $T$ , and  $D_{S0}(q)$  is the corrected diffusivity. The self-diffusivity, surface diffusivity, and corrected diffusivity are concentration dependent and, in general, not equal among each other [17]. They become equal in the limit of zero adsorbate solid phase concentration ( $q = 0$ ):

$$D_{SS}(0) = D_S(0) = D_{S0}(0) = D_{S0} \quad (3)$$

where  $D_{S0}$  will be referred to this paper as zero-loading surface diffusivity. Thus, the surface diffusivity can be also defined as:

$$D_S(q) = D_{S0}g(q) \quad (4)$$

where  $g(q)$  is a known non-dimensional correlation. For instance, a popular relationship is the Darken's approximation [18–20], where  $C_{eq}$  is the equilibrium concentration of the adsorbate in the fluid phase:

$$g(q) = \frac{\partial \ln C_{eq}}{\partial \ln q_{eq}} \quad (5)$$

By substituting Equation (5) into Equation (4), the surface diffusivity becomes equal to the zero-loading surface diffusivity multiplied by a thermodynamic correction factor, which is a function of the slope of the adsorption isotherm. For the Langmuir isotherm,  $g(q)$  is equal to  $(1 - q_{eq}/q_m)^{-1}$ , where  $q_m$  is the saturation (monolayer) capacity of the solid; for a linear isotherm, it is  $g(q) = 1$  and the surface diffusivity is constant.

The most common methods for the measurement of the surface diffusivity include (i) uptake rate measurements (transient) and (ii) the Wicke–Kallenbach permeability method (steady state and transient). These methods are called macroscopic to distinguish them from microscopic methods used to measure self-diffusivities [14]. Microscopic techniques include microimaging, (i.e., interference microscopy (IFM) and IR microscopy (IRM)) and pulsed field gradient NMR, as discussed in Kärger and Ruthven [21]. A comparison between them is provided, e.g., in [20,22]. In the Wicke–Kallenbach permeability method, the gas flux is measured through a porous plug under constant pressure or concentration gradient [12]. The surface diffusivity is calculated by using a simple equation involving permeability and equilibrium data [23–25]. In the uptake rate method, the surface diffusivity is calculated by use of adsorption models [14]. The simplest approach is to perform measurements over a pseudo-differential variation in the adsorbed phase concentration [16,26]. Under this condition, even if the diffusivity is variable, the assumption of constant diffusivity is acceptable [14]. This allows the use of simple analytical solutions assuming constant diffusivity in the diffusion model. However, the simplicity of the uptake rate measurements method is deceptive [27]. The problem is that there are several experimental factors that should be incorporated in the employed models, such as those related to other transport processes (film and/or pore diffusion) and heat transfer. In principle, such effects could be embodied into the model, as for example in [26], or the experiments could be designed so to exclude some effects, but such interventions may compromise the accuracy of the method [27]. Another approach is to perform experiments over a wide range of surface coverage values, and to use constant-diffusivity models where essentially the measured diffusivity is an apparent or average value [11]. The measured surface diffusivity can be correlated with the equilibrium surface coverage, as for example in [28]. However, because of the wide range of surface coverage values, the accuracy of this method is somewhat questionable [26]. Alternatively, the zero-loading surface diffusivity can be derived by applying variable diffusivity models [11,12].

Figure 1 shows the typical trends of surface diffusivity as a function of the adsorbate concentration in solid phase, adapted from Choi et al. [12]. In monolayer adsorption at increasing surface coverage the surface diffusivity generally increases, and it decreases in some systems with significant pore mass transfer restrictions, as discussed in literature [11,18,23,29,30]. In mesoporous-macroporous materials, when multilayer adsorption/capillary condensation occur, a non-monotonic trend can be observed, with surface diffusivity showing a maximum [30]. Moreover, in microporous materials (e.g., zeolites [31]) and for monolayer adsorption, “hindered” (intracrystalline) diffusion occurs: this is a phenomenon influenced by steric effects and in this sense it is different from surface diffusion [18], but similar approaches can be adopted for its modelling [12].

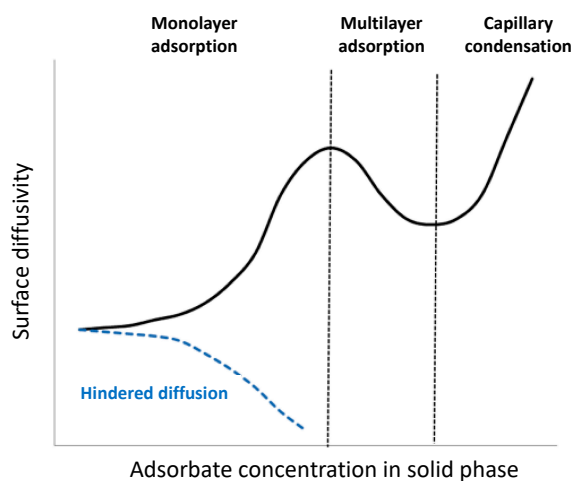
Monolayer adsorption correlations able to predict both increasing and decreasing (hindered) diffusion are discussed below, while comprehensive reviews on other correlations are provided elsewhere, e.g., in [12,18]. The theoretical equation of Chen and Yang [29] can be adopted for the

$g$ -function, that it is here expressed in terms of the surface coverage degree  $\theta = q/q_m$  and it can predict both increasing and decreasing trends for the surface diffusivity:

$$g(\theta) = \frac{D_S(\theta)}{D_{S0}} = \frac{1 - \theta + \frac{\lambda}{2} \theta(2 - \theta) + H[1 - \lambda](1 - \lambda) \frac{\lambda}{2} \theta^2}{(1 - \theta + \frac{\lambda}{2} \theta)^2} \quad (6)$$

where  $\lambda$  is the blockage parameter [11,29] and  $H[1 - \lambda]$  is the Heaviside step function (it is = 1 if  $\lambda < 1$ , otherwise it is = 0). At  $\lambda = 0$ , Equation (6) gives the Higashi–Ito–Oishi equation [32]:

$$g(\theta) = \frac{1}{1 - \theta} \quad (7)$$



**Figure 1.** Surface diffusivity as a function of adsorbate concentration in solid phase. Adapted version from Choi et al. [12].

The correlation by Marbán et al. [33] is empirical and covers both increasing and decreasing trends for the surface diffusivity:

$$g(\theta) = \frac{D_S(\theta)}{D_{S0}} = \frac{D_{S0} + (D_{S,m} - D_{S0})\theta^m}{D_{S0}} \quad (8)$$

where  $D_{S,m}$  is the surface diffusivity at maximum loading ( $\theta = 1$ ) and  $m$  is an exponent. This equation gives  $\theta$ -increasing surface diffusivity values for  $D_{S,m} > D_{S0}$ , constant surface diffusivity for  $D_{S,m} = D_{S0}$ , and decreasing surface diffusivity when  $D_{S,m} < D_{S0}$ .

To the best of our knowledge, at least in the area of adsorption kinetics modelling, the only equations dealing with both increasing and decreasing trends of variable surface diffusivity are those of Chen and Yang [29] and Marbán et al. [33]. Thus, the phenomenon of hindered surface diffusion, mainly occurring in microporous adsorbents such as zeolites, is worthy of investigation, in particular when expressions for the surface diffusivity with a well-defined theoretical basis are sought. In the following, a contribution in this sense is given by formulating a time-dependent correlation for the surface diffusivity based on fractal dynamics concepts.

### 3. Results and Discussion

#### 3.1. Formulation of a Time-Dependent Correlation for Surface Diffusivity

The literature analysis of surface diffusion phenomena shows that several concurrent factors determine the increasing, decreasing, or non-monotonic trends of the surface diffusivity as a function

of the adsorbent surface coverage degree. In particular, the enhancement of surface diffusion with loading is imputed to the progressive occupation of active sites characterized by lower binding energies (increasing mobility of the adsorbate), whereas pore blocking by adsorbate species hinders surface transport [18,23,29]. Moreover, it has been demonstrated, by means of Monte Carlo simulations applied to describe diffusion in a lattice (a common model adopted to represent porous materials such as zeolites), that intermolecular interactions can modify the free energy barrier associated with molecular jumps, and consequently the hopping rate [34,35]. More specifically, attractive and repulsive forces retard and accelerate diffusion with increased loading, respectively, when compared to systems with non-interacting atoms.

From the previous arguments it is clear that the geometric and energetic features of the porous diffusion medium, coupled with the properties of the diffusing species (molecular size, shape, and chemical nature), affect the evolution of the diffusion process considerably. For example, the diffusion coefficient taking into account the tortuosity of a porous medium can be 1 or 2 orders of magnitude smaller than the one measured in the bulk fluid phase [36]. Hence, in the surface diffusivity equation we propose herein all factors contributing in enhancing and impeding this transport phenomenon are embedded in two distinct terms, each of them exhibiting a time-dependence to explicitly address “temporal memory” effects on the transport process. This approach is inspired by equations previously developed in the literature, in the framework of both anomalous transport and fractal-like kinetics:

- In the case of anomalous transport (such as single-file diffusion in zeolites), for which the mean square displacement of the diffusing entity exhibits a nonlinear growth with time, the time variation of the diffusion coefficient can be expressed via a power-law scaling equation, and the diffusivity decreases or increases with time for sub-diffusion and super-diffusion, respectively, as discussed in the works by Kärger and colleagues [37,38], Metzler and Klafter [39], de Gauw et al. [40], Lutz et al. [41], Wu and Berland [42];
- Kopelman [43] applied fractal-like kinetics to describe the dynamics of diffusion-limited heterogeneous processes, for which the time-decrease of rate coefficients derives from the non-re-randomization of the reactants position in the diffusion space due to dimensional or topological constraints. Fractal-like kinetic models have been successfully applied to interpret kinetic data for gas–solid reactive systems and fluid–solid adsorption processes, as in Haerifar and Azizian [44] and in the works by Balsamo and Montagnaro [45–48].

On the basis of the above discussion, the time-decreasing term of surface diffusivity  $D_S^{fr}(t)$  (“fr” stands for fractal) due to hindered surface transport is expressed by means of a fractal-like equation:

$$D_S^{fr}(t) = D_{S0}^{fr}(t + t_1)^{-h} \quad 0 \leq h \leq 1 \quad (9)$$

where  $t$  is the time,  $t_1$  is a particular value of time having modulus = 1, and  $h$  is the fractal exponent. In particular,  $h$  is related to the spectral dimension of the diffusion medium, with the spectral dimension being a function of both the anomalous diffusion exponent and the fractal dimension. The spectral dimension regulates the probability for a diffusing species to come back to its original position after a certain time [43,49];  $h$  has an upper limit value of 1, corresponding to spectral dimension tending to zero. In Equation (9),  $D_{S0}^{fr}$  is a coefficient whose meaning can be analyzed when re-writing the equation at the process initiation (i.e.,  $t = 0$ ):

$$D_S^{fr}(t = 0) = D_{S0}^{fr} t_1^{-h} = D_{S0} \quad (10)$$

as  $D_S^{fr}(t)$  must equal the zero-loading surface diffusivity  $D_{S0}$  when  $t = 0$ ; therefore, it is:

$$D_{S0}^{fr} = \frac{D_{S0}}{t_1^{-h}} \quad (11)$$

On the other hand, the time-increasing term of surface diffusivity  $D_S^{hop}(t)$  (“hop” stands for hopping to recall the Higashi–Ito–Oishi model [32] predicting an increasing diffusivity with loading due to surface hops) is expressed as:

$$D_S^{hop}(t) = D_{S0}^{hop}(t + t_1)^\alpha \quad \alpha \geq 0 \quad (12)$$

with  $\alpha$  being the hopping exponent. Similarly,  $D_{S0}^{hop}$  is a coefficient whose meaning can be analyzed when re-writing Equation (12) at  $t = 0$ :

$$D_S^{hop}(t = 0) = D_{S0}^{hop} t_1^\alpha = D_{S0} \quad (13)$$

as also  $D_S^{hop}(t)$  must equal  $D_{S0}$  when  $t = 0$ ; therefore, it is:

$$D_{S0}^{hop} = \frac{D_{S0}}{t_1^\alpha} \quad (14)$$

We assume that the fractal and hopping contributions to surface diffusivity act as mechanisms in series, and therefore we here propose the following equation (called MBI equation as acronym of the authors’ surnames) by also taking into account Equations (11) and (14):

$$\frac{1}{D_S(t)} = \frac{\beta}{D_S^{fr}(t)} + \frac{(1-\beta)}{D_S^{hop}(t)} = \frac{\beta}{D_{S0}^{fr}(t+t_1)^{-h}} + \frac{(1-\beta)}{D_{S0}^{hop}(t+t_1)^\alpha} = \frac{\beta}{D_{S0} \frac{(t+t_1)^{-h}}{t_1^{-h}}} + \frac{(1-\beta)}{D_{S0} \frac{(t+t_1)^\alpha}{t_1^\alpha}} = \frac{1}{D_{S0}} \left[ \frac{\beta}{\frac{(t+t_1)^{-h}}{t_1^{-h}}} + \frac{(1-\beta)}{\frac{(t+t_1)^\alpha}{t_1^\alpha}} \right] \quad (15)$$

where  $\beta$  is the fractional contribution of the fractal diffusion resistance to the overall resistance, while  $1 - \beta$  the one related to the hopping surface diffusivity. For ease of reading, remembering that  $t_1 = 1$ , the MBI Equation (15) can be also informally re-written as:

$$\frac{1}{D_S(t)} = \frac{1}{D_{S0}} \left[ \frac{\beta}{(t+1)^{-h}} + \frac{(1-\beta)}{(t+1)^\alpha} \right] \quad (16)$$

Noteworthy, a similar combination of diffusion resistances is found in the work of Kapoor and Yang [50], where the authors applied the effective medium approximation to derive one-dimensional surface diffusion in energetically heterogeneous adsorbents and considered the surface as constituted by energy patches with discrete energy distribution.

In the MBI Equation (15), if  $h = \alpha = 0$ , a time-invariant surface diffusivity is obtained, i.e.,  $D_S(t) = D_{S0}$  (the zero-loading surface diffusivity). Moreover, Equation (15) allows to predict a maximum for the  $D_S(t)/D_{S0}$  ratio, by equating to zero its first derivative with respect to  $t$ . The obtained value of time  $t^*$  for which the surface diffusivity exhibits a maximum is:

$$t^* = t_1 \left\{ \left[ \frac{\alpha(1-\beta)}{\beta h} \right]^{\frac{1}{\alpha+h}} - 1 \right\} \quad (17)$$

and the corresponding value of maximum surface diffusivity ratio reads:

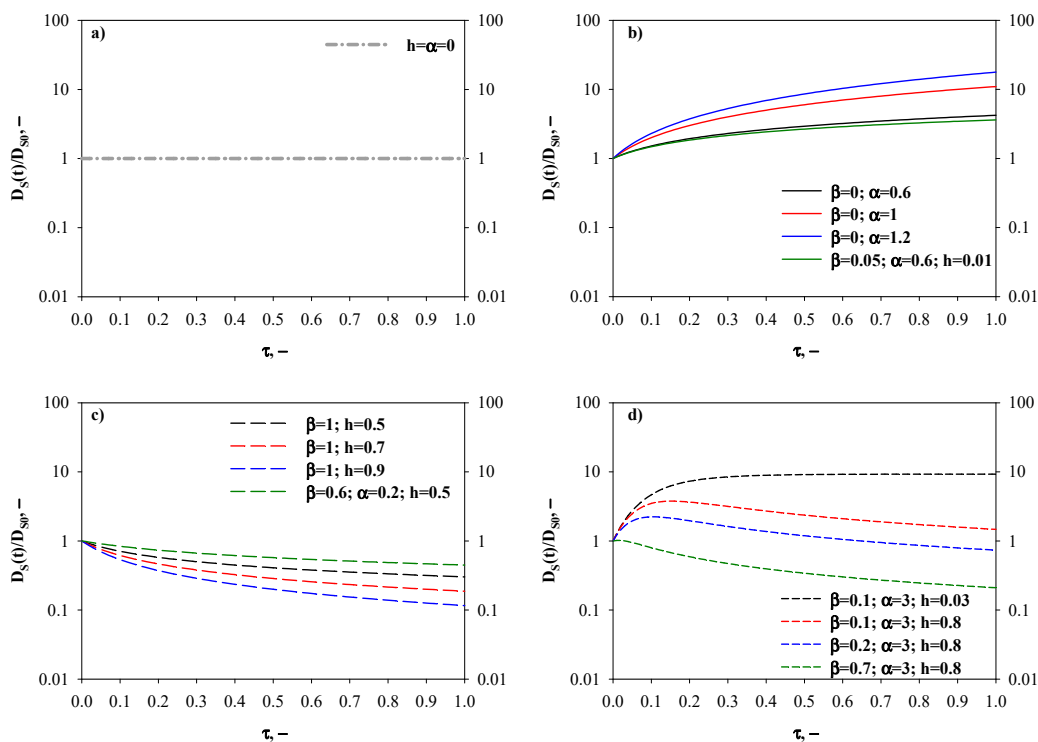
$$\frac{D_S(t)}{D_{S0}} \Big|_{max} = \frac{\left[ \frac{\alpha(1-\beta)}{\beta h} \right]^{\frac{\alpha}{\alpha+h}}}{(1-\beta) \left( \frac{\alpha}{h} + 1 \right)} \quad (18)$$

### 3.2. Analysis of the Time-Dependent Equation for Surface Diffusivity

In this section, the time-dependent  $D_S(t)/D_{S0}$  trends predicted by the elaborated MBI Equation (15) are critically discussed, with a main focus on the effect of the different parameters on the time evolution of the surface diffusivity ratio. Data are now conveniently expressed as a function of the dimensionless time  $\tau = t/t_{eq}$ , where  $t_{eq}$  is the equilibrium time. The results are summarized in Figure 2a–d.

1. Time-invariant diffusivity ratio—Figure 2a. The simplest case, for which  $D_S(t) = D_{S0}$ , occurs when both the fractal and hopping exponents are zero (i.e.,  $h = \alpha = 0$ ). This indicates a memoryless transport process, that is to say the adsorbate surface diffusion is not affected by alterations of the porous diffusion environment taking place along the adsorption process.
2. Monotonically increasing diffusivity ratio—Figure 2b. In this scenario, the surface transport of the diffusing species is continuously enhanced as new adsorbate molecules/ions are captured by the adsorbent. First of all, this pattern can be established when there is no contribution of the fractal diffusion resistance to the overall one, i.e.,  $\beta = 0$  and therefore the surface diffusivity is equal to its time-increasing hopping term only ( $D_S(t) = D_S^{hop}(t)$ ). The time-increase of the diffusivity ratio is more marked at greater values of the hopping exponent  $\alpha$ , and the differences in  $D_S(t)/D_{S0}$  values become augmented as the adsorption time proceeds. For instance, at  $\tau = 0.5$  the surface diffusivity ratio is 2.93 and 8.58 for  $\alpha = 0.6$  and 1.2, respectively. Under equilibrium conditions,  $D_S(t)/D_{S0}$  is 4.21 and 17.77 for  $\alpha = 0.6$  and 1.2, respectively. Furthermore, a time-increasing surface diffusivity ratio can be also obtained for a non-zero value of  $\beta$ . In this case, the constraint  $\left[\frac{\alpha(1-\beta)}{\beta h}\right]^{\frac{1}{\alpha+h}} \geq t_{eq}+1$  (i.e.,  $t^* \geq t_{eq}$ ) needs to be satisfied, because otherwise the maximum for the surface diffusivity ratio would fall in the existence domain for  $\tau$ .
3. Monotonically decreasing diffusivity ratio—Figure 2c. This is the case of a hindered diffusion process, for which the surface diffusivity decreases with time, and it is common for diffusion in zeolites. A monotonically decreasing  $D_S(t)/D_{S0}$  pattern can be predicted by setting  $\beta = 1$ , therefore the surface diffusivity is equal to its time-decreasing fractal term only ( $D_S(t) = D_S^{fr}(t)$ ). In this context, the fractal exponent  $h$  regulates the time-decay of the surface diffusivity. For  $h = 0.5$ , a slight decrease of the surface diffusivity with time can be observed:  $D_S(t)/D_{S0}$  is 0.41 and 0.30 for  $\tau = 0.5$  and 1, respectively. An increase of  $h$  produces a more relevant reduction of the surface diffusivity. In fact, for  $h = 0.9$  the surface diffusivity diminishes by about one order of magnitude when comparing the initial value with respect to the one retrieved at  $\tau = 1$ . In addition, a time-decreasing trend for surface diffusivity can be also derived for a non-negligible contribution of the hopping transport resistance when the condition  $\left[\frac{\alpha(1-\beta)}{\beta h}\right]^{\frac{1}{\alpha+h}} \leq 1$  is fulfilled (i.e.,  $t^* \leq 0$ ).
4. Diffusivity ratio exhibiting a maximum—Figure 2d. In this scenario, factors determining an increase of surface diffusivity prevail for short adsorption times, whereas hindered transport rules thereafter. From a mathematical standpoint, the constraint  $1 < \left[\frac{\alpha(1-\beta)}{\beta h}\right]^{\frac{1}{\alpha+h}} < t_{eq}+1$  needs to be satisfied to obtain a maximum value for  $D_S(t)$ . The effects of  $\beta$ ,  $\alpha$  and  $h$  on the time evolution of the surface diffusivity are shown in Figure 2d. In particular, when fixing  $\alpha$  and  $h$ , an increase of the fractional contribution of the fractal diffusion resistance (i.e., greater values of  $\beta$ ) determines a shift of the maximum towards shorter adsorption times and an associated reduction of the maximum value of the surface diffusivity (i.e., the diffusion process is negatively affected by increases in  $\beta$ ). As an example, when  $\alpha = 3$  and  $h = 0.8$ ,  $\tau^*$  equals to 0.15 (maximum diffusivity ratio = 3.76) and 0.10 (maximum diffusivity ratio = 2.23) for  $\beta = 0.1$  and 0.2, respectively. Very interestingly, sufficiently high values of  $\beta$  also allow to predict surface diffusivity values smaller than  $D_{S0}$ . Finally, it is worth observing that when the  $\alpha/h$  ratio is very high (example in the figure:  $\alpha = 3$  and  $h = 0.03$ ), the surface diffusivity decreases very weakly with time after having reached its maximum value.





**Figure 2.** Different patterns of the surface diffusivity ratio as a function of the dimensionless time, predicted by the developed time-dependent MBI Equation (15): (a) time-invariant function; (b) monotonically increasing function; (c) monotonically decreasing function; (d) function exhibiting a maximum.

#### 4. Conclusions

In the present study, the concepts of fractal theory of process dynamics were applied to describe hindered surface (or intracrystalline) transport of an adsorbate species in porous materials upon adsorption from a fluid phase. The latter process refers to an energetically activated diffusion which can significantly affect the adsorption rate, in particular when pores blocking by adsorbates or strong adsorbate–adsorbate interactions come into play. The equation formulated to describe the temporal variation of the surface diffusivity accounts for two mechanisms acting in series: a fractal-like (time-decreasing) and hopping (time-increasing) surface transport. The time-dependence of each mechanism follows a power law with a specific scaling exponent. The mathematical and numerical analysis of the proposed expression witnesses its potentiality to depict monotonic or non-monotonic trends of surface diffusivity as a function of the adsorption time. It is noted that theoretical equations are available in literature to interpret surface diffusivity patterns exhibiting a maximum are rare, in particular when monolayer adsorption is dealt with.

Future numerical investigations will be aimed at using the developed fractal-like correlation in combination with a diffusion-based model in order to assess its ability to fit adsorption capacity experimental data vs. time for different fluid–solid adsorption systems, in comparison with commonly adopted models including constant diffusion coefficients. Fitting will help to derive proper correlations among fractal and hopping exponents, chemico-physical and textural properties of the adsorption systems (including e.g., the tortuosity of the porous medium and the properties of the bulk fluid), and operating conditions of the process, which in turn can provide deeper insights into mechanistic aspects of the diffusion process.

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## Nomenclature

$C$	concentration of adsorbate in fluid phase	(M/L <sup>3</sup> )
$D_S$	adsorbate surface diffusivity	(L <sup>2</sup> /t)
$D_{S0}$	zero-loading adsorbate surface diffusivity	(L <sup>2</sup> /t)
$D_{S0}^{fr}$	coefficient introduced in Equation (9)	(L <sup>2</sup> /t <sup>(1-h)</sup> )
$D_{S0}^{hop}$	coefficient introduced in Equation (12)	(L <sup>2</sup> /t <sup>(1+α)</sup> )
$D_{SS}$	adsorbate self-diffusivity	(L <sup>2</sup> /t)
$f$	fugacity	(-)
$g$	function defined in Equation (4)	(-)
$H$	Heaviside function	(-)
$h$	fractal exponent	(-)
$J$	mass flux (with respect to density)	(L/t)
$m$	exponent in Equation (8)	(-)
$q$	concentration of adsorbate in solid phase	(M/M)
$r$	radial coordinate of the adsorbent particle	(L)
$T$	temperature	(T)
$t$	time	(t)
$t_1$	unitary value of time ( $t_1 = 1$ )	(t)
Greek letters:		
$\alpha$	hopping exponent	(-)
$\beta$	fractional contribution defined in MBI Equation (15)	(-)
$\theta$	surface coverage degree	(-)
$\lambda$	blockage parameter	(-)
$\tau$	dimensionless time	(-)
Superscripts:		
*	point of maximum	
$fr$	fractal	
$hop$	hopping	
Subscripts:		
$eq$	equilibrium value	
$m$	saturation (monolayer) conditions	
$max$	maximum value	
L	length	
M	quantity	
T	temperature	
t	time	

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