

Review

Modelling and Simulation of Surface Diffusion in Heterogeneous Porous Materials

Sean P. Rigby

Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK; sean.rigby@nottingham.ac.uk

Abstract: The surface diffusion flux is known to dominate mass transport within many amorphous porous materials, used as adsorbents, heterogeneous catalysts, and membranes, employed in many chemical processes. However, while the impact of surface coverage has been widely studied and reviewed, relatively little attention has been paid to the impact of surface geometric and energetic heterogeneity on the surface diffusion rate, which would inform intelligent materials selection. It was, thence, the aim of this work to survey studies of the impact of surface structure on surface diffusion. Since the so-called “maximally realistic” modelling approach is found to be infeasible, due to limitations on the degree of structural characterisation possible for complex disordered surfaces, and the level of detail and length scales it is possible to represent with current computing power, a range of alternative approaches have been adopted. It has been seen that the Galilean idealisation of atomistic models has rendered them sufficiently tractable in order to study the impact of certain surface features, such as traps or ruts, on surface diffusion. Theoretical justifications have been used to develop minimalist models of amorphous surfaces, and mass transport thereon, that do selectively include the key surface parameters, and have, therefore, been successfully empirically validated for a range of different surfaces and adsorbate types.

Keywords: surface diffusion; surface reconstruction; sphere packing; fractal; heterogeneity



Academic Editor: Gaetano Granozzi

Received: 2 April 2025

Revised: 4 May 2025

Accepted: 6 May 2025

Published: 7 May 2025

Citation: Rigby, S.P. Modelling and Simulation of Surface Diffusion in Heterogeneous Porous Materials.

Surfaces **2025**, *8*, 31. <https://doi.org/10.3390/surfaces8020031>

Copyright: © 2025 by the author.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the Creative Commons Attribution (CC BY) license

(<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In order to rationally design adsorption, catalytic, or separation processes using porous materials it is necessary to understand and predict the rates of mass transfer fluxes within the porous network. The specific surface areas of typical mesoporous adsorbent or catalyst pellets are generally of the order of hundreds of metres squared per gram, while microporous materials, such as zeolites and carbons, can be of the order of $\sim 1000 \text{ m}^2 \text{ g}^{-1}$. Given the large surface areas available for adsorption, in many adsorbent pellets, heterogeneous catalysts, and separation membranes the mass transport flux is dominated by surface diffusion. For example, it has been observed that, for ethane, propane, and butane adsorbed on a porous silica with a pore size of $\sim 2 \text{ nm}$, the contribution to the flux from surface diffusion was from 60 to 90%, while for a similarly pore-sized carbon it was 70–75% [1–3]. Simulations have also shown that the interaction between surface and (bulk) pore diffusion affects both diffusivities [4], since the interchange between motion on the surface and within the bulk of the pore core affects the pathway taken between any two points.

While the influence of surface coverage or occupancy on the surface diffusion flux has been much studied [5–7], the impact of the pore space and surface geometry on surface diffusion has received relatively little attention in the literature [8]. However, many of the materials, such as silica, alumina, and carbons, used in industrial processes where surface

diffusion is important are amorphous, and thus the interior pore networks are highly disordered. The surfaces of amorphous materials are also highly complex, and, thence, difficult to model. The atoms of surfaces are not located at random positions but tend to take up positions of minimum energy [9]. Further, these positions can relax following the first formation of the surface by a process like fracturing, the abrupt termination of particle growth, or cooling from melts, but also during the adsorption and diffusion of adsorbates. The most detailed models of surfaces are those that utilise potential energy functions to obtain radial structure functions and bond angle distributions for surface atoms. However, relatively few models are constructed with this high, “maximally realistic” level of detail because, first, it is hard to characterise real amorphous materials in sufficient detail, and, second, the computing power required to represent a substantial area of surface in such detail may be limiting. Hence, some level of simplification and/or idealisation is necessary. The process known as “Galilean idealisation” involves introducing omissions from, or distortions of, the original structure of the surface in order to achieve sufficient simplification such that the resulting model obtained is then mathematically or computationally tractable, both for aligning with characterisation data and using it to make predictions of physical processes occurring on the surface [10]. As mathematical and computational techniques have become more sophisticated over time, the level of simplification required in Galilean idealisation has diminished. However, it is typically not possible to know in advance which features of the real material to leave out and still keep a model predictive of the physical process of interest, and an empirical approach is, thus, needed. The underlying energetics and connectivity of a potential model surface can be tested indirectly via processes that involve the chemical interactions of the surface with specific molecules, such as predictions of the heat of adsorption, and the activation energy for surface diffusion. A different approach to Galilean idealisation is to actively only include in the model those features of the surface structure that are known to ‘make a difference to the occurrence or essential character of the phenomenon in question’ (which in this case is surface diffusion) [10]. This approach is known as minimalist modelling, and requires some sort of theoretical justification, prior experimentation, or trial and error testing, to determine these essential characteristics of the surface.

Heterogeneities in disordered porous materials can be of many different kinds, and each may have a characteristic length scale associated with it called the correlation length, such that above that size the structure is statistically homogeneous and the property concerned is constant [11]. For surface diffusion in such a heterogeneous system, at the very smallest length scales, where a molecule hops to a location in close vicinity to its initial location, it will obey the classical law that the mean square displacement scales with time as $\langle r^2 \rangle \propto t$. It will also obey this law for root-mean-square (rms) displacements much larger than the correlation length. However, at intermediate length scales, the surface diffusion may be anomalous, and rms displacement may scale with a power of time different to the classical law. The importance of key length scales within amorphous porous structures to surface diffusion will become apparent below.

The diffusion of molecules across disordered, heterogeneous surfaces is also a complex process, and several theories for the fundamental nature of the motion occurring have been presented. Theories of diffusion for molecules physisorbed onto surfaces generally fall into one of three classes, namely [12]: (1) mechanistic models in which the migrating molecule is described by the trajectory of a “hopping” molecule; (2) a two-dimensional Fick’s law with modifications, in which the surface flow is caused by a gradient in the surface concentration; and (3) hydrodynamic models in which the surface flow is treated as a two-dimensional fluid slipping along the walls of the pores.

Mechanistic models [13] involve modelling the movement of adsorbed molecules from site to site as a random walk. Small hopping movements of the molecules on the surface lead to their migration, and the hopping is assumed to be an activated process. The hops can take place in random directions but the presence of an overall gradient in concentration in the adsorbed phase in one direction will lead to a net flux in that direction. This type of model requires assumptions to be made concerning the nature of the hopping motion, such as whether it is to a nearest-neighbour site only or involves a longer ‘flight’. In addition, considerations concerning the impact of surface coverage on the blocking of available sites and the hopping motion must also be included. For example, the jump lengths are often assumed to decrease with increased surface coverage due to inter-molecular collisions becoming more common [14]. Approximate non-equilibrium statistical mechanical approaches have been used wherein the adsorbed phase is treated as a two-dimensional fluid [15,16]. However, MacElroy and Raghavan [17] suggested that this approach is probably most suitable for sub-monolayer coverages of macroporous materials at low temperature, but not for transport in micropores since the pore sizes and topologies in microporous materials mean that the two-dimensional fluid is not a good representation therein.

Increased computing power has permitted molecular dynamics simulations of the coupled migration and adsorption processes within models of porous media. In molecular dynamics, Newton’s Laws of Motion are explicitly solved for individual molecules. This permits the tracking of the pathways of individual molecules, as well as the whole collective. It will be seen that this possibility has provided great insights into the interaction between the nature of the pore structure and the surface diffusion processes therein.

The nature of the mathematical method for describing surface diffusion can determine the type of representation of a surface used for modelling. One way to improve the tractability of the model surface is to reduce the degree of randomness in the model as it reduces the number of parameter fields necessary to store. Further, the upper limit placed on the number of adsorbate molecules that can be handled by the available computing power also puts a limit on the size of the unit cell of the model that can be simulated, and thus the size of the region of surface that can be considered. This limitation can be partially overcome by averaging the results of simulations of adsorbate behaviour over many realisations of the solid model. The atomistic simulation of amorphous metal oxide, such as alumina, surfaces presents significant problems because (a) the charges of the individual aluminium and oxygen atoms depend upon their specific location and surrounding atoms, (b) there are variations in the local atomic structure between the interface and the bulk, and (c) there are difficulties in the atomistic representation at the buried interface [18].

The complexity of the structure of amorphous surfaces can be represented in a variety of ways and characterised by a similar variety of parameters or descriptors, which can then be correlated with surface diffusivity. It will be seen that surfaces can be defined by parameters such as porosities (voidage fractions), pore sizes (determining surface curvature and separation distances of pore walls), surface roughness factors, surface fractal dimensions, and energy distributions of barriers and traps. However, due to the difficulty in characterising amorphous materials in detail, an alternative, to structural characterisation and then the building of a matching model, is to attempt to simulate the formation process of the surface to create a resultant model to perform the surface transport simulations upon. The surface formation models also demonstrate a range of different levels of complexity in describing the physical processes involved, which, naturally, also determines the level of complexity of the description of the resultant surface. It is the aim of this work to survey the various ways in which descriptions of surface geometric and/or chemical heterogeneity have been incorporated into models of surface diffusion.

2. Random Packing and Surface Reconstruction Models

Surface and (bulk) pore diffusion can be considered to occur in parallel, and thus mathematical modelling schemes then omit any interaction between the two. In much past work, it has been tacitly assumed that the mean path length through a porous solid is the same for a bulk gas molecule in the pore void and for a surface diffusing molecule (as would be the case for straight, cylindrical pores). However, Horiguchi et al. [19] realised that an amorphous solid surface will possess irregularities of molecular dimensions and above that would not be perceived by a gas molecule diffusing in the Knudsen regime, and, thus, the path followed by a surface diffusing molecule will be potentially different and longer than for a bulk molecule. Hence, Horiguchi et al. [19] proposed that the pore tortuosity τ must be augmented by a surface roughness factor K to give a separate surface tortuosity:

$$\tau_s = K\tau. \quad (1)$$

They suggested that the pore roughness factor ought to be larger for, say, Vycor glass surfaces compared with, say, Graphon carbon, due to the chemical and energetic heterogeneity of the former compared to the relatively smooth and uniform surface of the latter [19]. However, this roughness factor was purely empirical and not very informative.

In the case of parallel bulk pore and surface diffusion, the impact of the statistical properties of the porous medium, namely the voidage fraction ϕ and average pore radius r_e , on the surface diffusion and pore diffusion can be incorporated into separate effective surface tortuosity τ_s and effective pore (void) tortuosity τ_p . Hence, in this context, the mass transport flux J per unit total area is given by the following [20]:

$$J = -\frac{2\phi}{r_e} \frac{D_s}{\tau_s} \frac{dc_s}{dx} - \frac{D\phi}{\tau_p} \frac{dc}{dx} \quad (2)$$

where the reference surface diffusivity D_s is that of a single molecule diffusing on a well-defined flat surface, and the bulk diffusivity D applies in the void of the pore. It is also further typically assumed that a local equilibrium is rapidly reached between the bulk fluid concentration c and the concentration of adsorbed phase on the surface c_s , which at low coverages would be characterised by a Henry's law relation. Ho and Strieder [20] defined the effective diffusivity as the ratio of the flux to the concentration gradient, and derived an expression for the effective diffusivity for a porous material with random, tortuous paths. In order to do this, they formulated the processes of void and surface diffusion locally for each infinitesimal void volume and pore wall element. The total flux, and effective diffusivity, was calculated for a model pore structure consisting of randomly placed, freely overlapping solid spheres. By employing variational principles, the calculations for the model were said to properly contain the tortuosity of the surface and void space pathways by including the perturbation in the flux due to the presence of the solid spheres. Hence, Ho and Strieder [20] obtained an algebraic expression for the surface tortuosity τ_s of a random packing of overlapping spheres:

$$\tau_s = 6(1 - 0.5\ln\phi)^2 / (9 - 2\ln\phi) \quad (3)$$

where it is a function of the voidage fraction ϕ . The necessity for only the single structural parameter ϕ to be specified in this expression probably reflects the relative simplicity of the structure of a random packing of well-defined spheres compared to a more complex model surface (as will be seen below).

The assumption of parallel in-pore and surface diffusion mentioned above has been questioned [21]. Wernert et al. [21] proposed an alternative approach considering the Brownian motion of molecules in the pore space. These authors also highlighted the issue

of whether the surface diffusion is considered to occur on a locally flat surface such that the overall tortuosity is shared with the pore diffusion as arising purely from the pore network interconnectivity, or whether the local surface curvature contribution is also considered. In the former case, this approximation may hold if a surface diffusion stage is short relative to the adjacent pore diffusion stages, as would likely arise with relatively little adsorption.

Based upon a suggestion by Havlin and Ben Avraham [22], that the geometrical part (the nature of the lattice) of the disorder of random materials is irrelevant to surface diffusion, and only energetic heterogeneity matters, Limoge and Bocquet [23] constructed a surface model consisting of a regular lattice where the energetic properties were distributed at random. The lattice both the sites and saddle points between sites were assigned characteristic energies. Hence, the model had two extreme types of potential disorder. The first is disorder in the site energy distribution, which corresponds to the so-called random-trapping model, and the second is the saddle disorder, which corresponds to the (activated) random hopping model. Further, Limoge and Bocquet [23] suggested that, in real amorphous materials, there may be some correlations between values of the energies of adjacent sites and saddle points. The simulation of surface diffusion on the model consisted of random walks of tagged particles performing thermally activated jumping between the lattice sites. The Einstein relation was used to determine the surface diffusivity. Based upon the analysis, using the continuous-time random walk (CTRW) approach, Limoge and Bocquet [23] found that the disorder in the site and saddle energies could compensate for each other. Complementary Monte Carlo simulations found that the presence of both types of disorder, in lattices with a range of coordination numbers from 4–12, could produce a compensation effect with the site disorder decreasing, through trapping, the infinite temperature limit of the surface diffusivity, and the saddle disorder increasing it. However, Limoge and Bocquet [23] suggested that, in real amorphous materials, there is probably some correlation between the disorder of the sites and saddles due to the particular structure of the material, and they cannot be taken as independent variables, and thereby capable of varying freely in such a way as to compensate for each other as in the model.

A surface model that takes into account the potential correlation between bond and site disorder is the Dual Site-Bond Model (DSBM) [24,25]. This consists of a two-dimensional lattice of given connectivity, such as a square lattice, composed of adsorption sites, that are local potential wells, joined by bonds, which are saddle points in energy between adjoining wells, as seen in Figure 1. Both the sites and the bonds have their own respective energy density functions. However, these two energy distribution functions for bonds and sites are not completely independent because the absolute energy of a site must be equal to, or higher than, all of its neighbouring bonds. This additional constraint is known as the Construction Principle [25]. Hence, the bond energy distribution curve must always lie to lower energy than the site distribution curve. If there is no overlap between the two distributions, such that all bonds are lower in absolute energy than all of the sites, then a completely random surface results. Progressively increasing the overlap of the energy distribution necessitates there is some weak spatial correlation between the distribution of bond and site energies, and more homogeneous patches develop. Surface diffusion in such a model can be simulated using Monte Carlo techniques. The surface diffusivity has been found to increase as the degree of overlap of the two energy distributions increases. When the impact of varying temperature on surface diffusivity was tested, and the diffusivities correlated via Arrhenius expressions, it was found that deviations from the Arrhenius law occurred at lower temperatures due to adsorbate molecules becoming trapped in deep sites, and grew with an increased overlap in the energy distributions due to the increased spatial correlation of these deep sites into extensive patches [24].

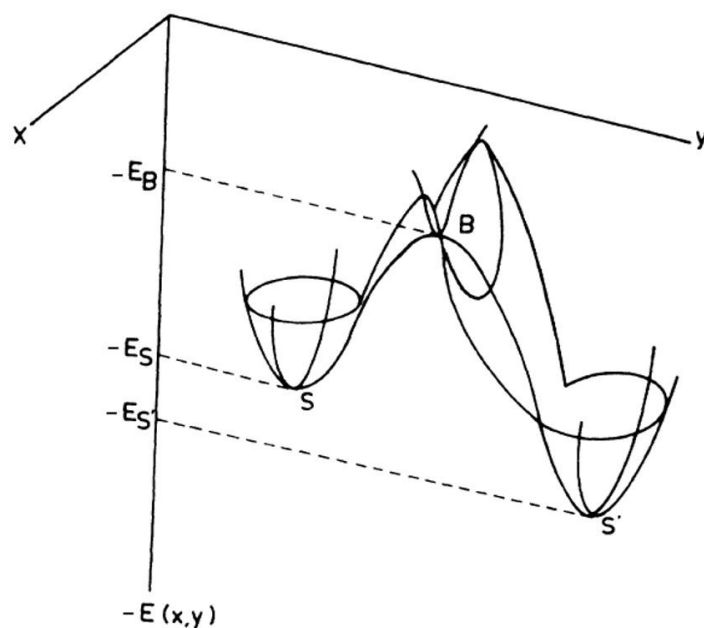


Figure 1. Three-dimensional adsorptive energy surface showing two nearest-neighbour adsorptive “sites”, S and S’, and their connecting “bond”, B. Reprinted with permission from Mayagoitia, V.; Rojas, F.; Riccardo, J.L.; Pereyra, V.D.; Zgrablich, G. Dual site-bond description of heterogeneous surfaces. *Phys. Rev. B* **1990**, *41*, 7150–7155. Copyright (1990) by the American Physical Society (College Park, MD, USA) [25].

Argyarakis et al. [26] compared the predictions, for the long time and high-temperature limit of the diffusivity for surface-hopping transport on random barrier models, with different distributions of barrier energies, made using critical path theory [27], the effective medium approximation (EMA), and Monte Carlo methods. At longer times, the diffusivity had an Arrhenius temperature dependence with a high temperature-limiting value. For symmetrical energy distributions on 2D square grids, it was found that, for both the critical path theory and the EMA, the limiting diffusion coefficient just depended upon the mean energy barrier, and not the spread in the distribution. This was because the percolation threshold for 2D square grids is 0.5 (i.e., corresponding then to the mean for a symmetrical distribution). However, for 3D grids, the limiting diffusivity did depend upon the spread of barrier energies. The theoretical results were confirmed using the numerical Monte Carlo methods.

MacElroy and Raghavan [28] suggested that the use of models of solids with smooth surfaces leads to uncertainties in the comparative analysis between theory and experiment. More realistic models can be constructed using molecular modelling. Stallons and Iglesia [9] proposed that it is necessary to use molecular modelling in order to be able to include the detailed topological connectivity between surface atoms, or between surface atoms and the bulk atoms immediately below, to better capture the heterogeneity of amorphous surfaces.

Electron microscopy and atomic force microscopy (AFM) studies (see Figure 2) show that silicas made by the sol–gel method, from colloidal suspensions, consist of packings of small spheres [29]. Random packings of spheres models come in a variety of types. The simplest consists of a random assembly of spheres where they are placed at random in space, either allowing overlapping (as mentioned above) or not. Overlapping sphere models can represent the results of processes such as sintering. Other types of assemblage include where the spheres do not overlap but are all constrained to be connected to (via touching) each other [17,28]. This system is generated from randomly placed spheres by an algorithm akin to diffusion-limited aggregation [17]. The size of the individual spheres used, and the overall density of spheres in the assemblage, are typically chosen

such that the porosity and specific surface area of the model matches that for real silicas. For example, MacElry and Raghavan [17] had silica spheres of diameter 2.75 nm. However, the silica spheres in a random, non-overlapping system often do not form a percolating network with a continuous surface for diffusion, but, instead, have many high-energy barriers to surface diffusion across empty gaps between spheres. Hence, the topology of the model makes a big difference to surface mobility. For example, Olivares and Aarão Reis [30] conducted simulations of tracer diffusion in a model porous medium consisting of a packing of spheres situated on a simple cubic lattice. Since the adjoining spheres in the model were considered to have a small contact area, these workers found that the extensive connectivity of the surface of their model solid enabled the tracers to migrate long distances across the surface. This contrasts with models described above where spheres were isolated or poorly connected.

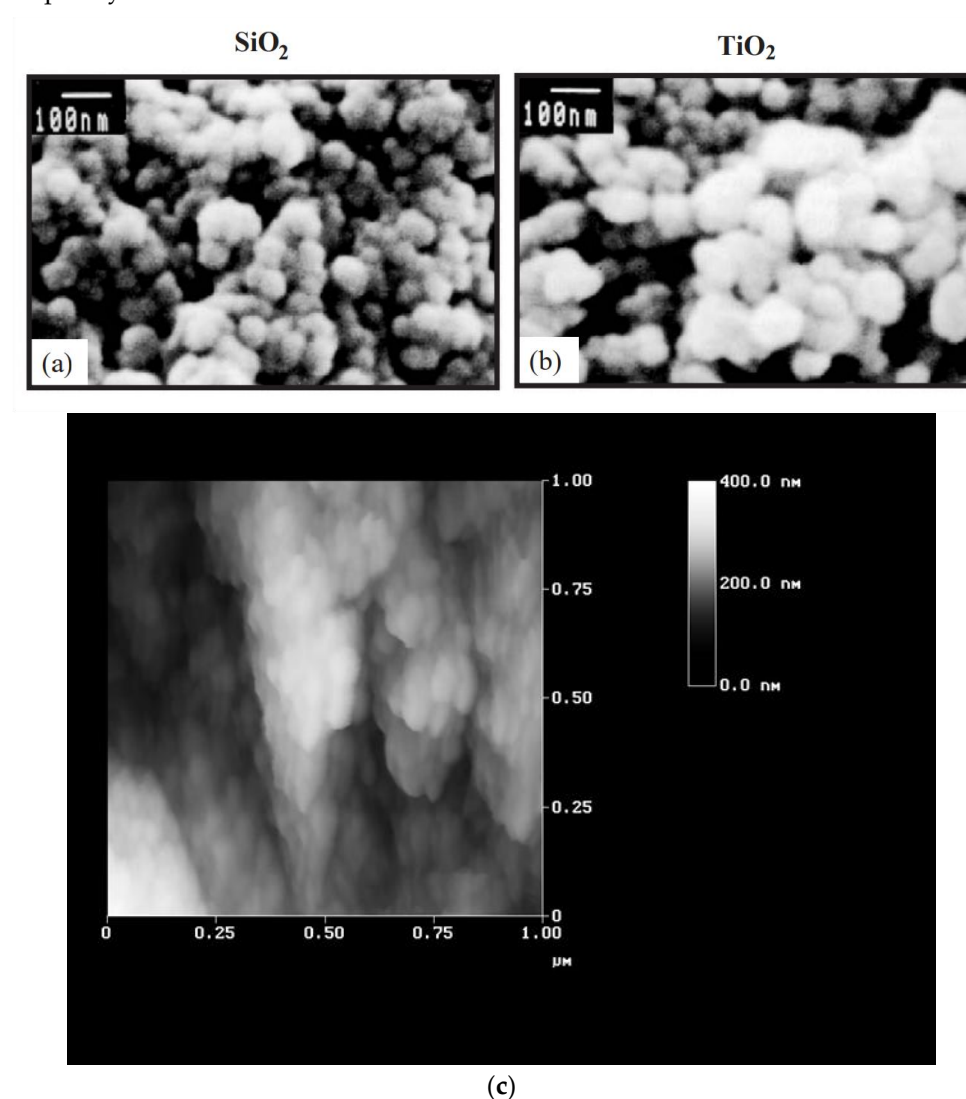


Figure 2. Scanning electron micrographs of commonly used catalyst supports: (a) SiO_2 and (b) TiO_2 . Reprinted with permission from Elsevier [29]. (c) Atomic force microscopy image of botryoidal aggregate of silica microspheres.

Zalc et al. [29,31] used Monte Carlo simulations to study the impact of pore-space structure on surface diffusion on a model consisting of a partially-overlapped random-loose sphere packing with a voidage fraction less than 0.5. In the case of no exchange with the bulk, they found large surface tortuosities at the void- and solid-percolation thresholds. In comparison, Wolf and Streider [32] derived formulae for how surface tortuosity τ_s

varied with voidage fraction ϕ for a model of two-dimensional random fibres consisting of overlapping parallel circular cylinders with different radii (aligned perpendicular to the average flux), such that:

$$\tau_s \approx \frac{2(1 - \ln\phi)^2}{(4 - \ln\phi)} \quad (4)$$

They assumed that pore and surface diffusion were independent and in parallel. These workers found that, relative to random beds of overlapping spheres, the surface flux was higher for the dilute fibre packings compared to the spheres.

However, experimental results suggest that the coupling of surface and bulk (pore) diffusion can significantly change the overall diffusion characteristics [33,34]. As a result, Mirbagheri and Hill [35] applied the model of Albaalbaki and Hill [36] that includes this coupling to study the effects of voidage fraction and pore size on surface diffusion within models consisting of arrays of solid spheres and spherical cavities. They found that, for solid sphere arrays, the permeability was controlled by surface diffusion for voidage fractions below the solid-percolation threshold, while for spherical cavities, permeability was limited by surface diffusion at voidage fractions between the void- and solid-percolation thresholds. For similar studies of potentially coupled surface and pore diffusion in models consisting of parallel pore and fibre models, Mirbagheri and Hill [37] found that surface diffusion was mainly controlled by specific surface area, especially in the parallel.

Molecular modelling of energetically and geometrically heterogeneous silica surfaces can be performed by a number of methods. MacElroy and Raghavan [28] created a molecular model of the bulk vitreous state by starting with crystalline β -cristobalite, and melting it at 10,000 K, and then quenching at a series of lower temperatures back down to 300 K using a Monte Carlo based methodology. A given sphere from a packing model was then cut from the bulk silica model. Any silicon atoms on the surface were discarded. The cutting-out also created numerous non-bridging oxygen atoms at the surface of the sphere which were then considered to form surface hydroxyl groups. However, any trisilanol groups formed were subsequently removed. The concentration of hydroxyl groups formed in this way was equivalent to 6.3 oxygens per nm², which is similar to that found experimentally for untreated silica [28]. The simulated silica surface contained both singlet hydroxyls and twin (doublet) non-bridging hydroxyl (known as geminal) groups. The motion of dilute (structureless) methane molecules across the surface of the silica spheres was modelled using a Monte Carlo method. The interactions between the methane and individual oxygen atoms in the silica framework were modelled using a Lennard-Jones (12-6) potential. Apart from considering the oxygen atoms of hydroxyl groups as having a slightly larger size, in the Lennard-Jones interactions, than bridging (between silicon) oxygen atoms, the hydrogen atoms of the hydroxyl groups were neglected. Microcanonical (NVE) ensemble molecular dynamics was used to calculate the trajectories of adsorbed molecules within the model. These can then be used to calculate the mean square displacements of the molecules, and, thence, diffusivity. However, MacElroy and Raghavan [17,28] did not explicitly differentiate between the surface and pore diffusion. When comparing molecular behaviour upon assemblies of spheres where the surface potential was smoothed versus spheres with inhomogeneous potential fields, MacElroy and Raghavan [28] found the latter led to more backscattering and localisation of adsorbed molecules. At low loadings, for simulations of three-component (one of which did not adsorb) mixtures on silica surfaces, MacElroy and Raghavan [28] found surface blocking behaviour by adsorbed molecules not unlike that postulated by surface hopping kinetic models. At higher coverages, the surface transport mechanism tended more toward a hydrodynamic regime, but small pore sizes limit the applicability of a continuum fluid model. MacElroy and Raghavan [28] found that, even with a molecular model surface, while it did not possess long-range order, it did

have some short-range order associated with the triangle of surface oxygen atoms in an exposed SiO_4 tetrahedron. Further, adsorbate molecules experienced a potential energy minimum at the centre of such triangles, and these minima tended to have similar spacings from each other. Hence, the molecular model exhibited a geometric feature similar to the lattices used in barrier-hopping models.

Models of amorphous surfaces can also be formed from the exposed face of a dense packing of hard spheres, known as the Bernal surface model [38]. The hard spheres are taken to represent the oxygen atoms in an oxide surface, such as titania, and are replaced by sites having Lennard-Jones interactions with adsorbate molecules [38]. Cations are not included as they have relatively weak interactions with adsorbates. The surface can be further roughened by the random deletion of surface ions, to form Corrugated Bernal Surfaces (CBSs). Surfaces of ~ 1520 atoms were constructed but periodic boundary conditions were also used to attempt to reduce the limitation caused by a small unit cell. The overall size of the simulated unit cell was $(57 \times 54) \text{ \AA}^2$. Riccardo and Steele [38] suggested that such surfaces, as seen in Figure 3, are similar to those seen in scanning tunnelling microscopy images. They also evaluated the surface fractal dimension D_s of the model surfaces by measuring the apparent monolayer (ML) capacity n_m for adsorbate molecules with different sizes σ_a . For fractal surfaces, the apparent monolayer capacity will scale with the adsorbate size according to the following [39]:

$$\ln(n_m) \propto \frac{D_s}{2} \ln(\sigma_a) \quad (5)$$

Since a monolayer is not strictly defined for this system, for the purposes of the simulation, an adsorbate molecule was considered to be in the monolayer if it directly touched a surface atom. It was found that the BS led to a surface fractal dimension of ~ 2.2 , and the progressive removal of surface atoms for the CBS led to surfaces with fractal dimensions up to ~ 2.5 , which are in the range found for many types of amorphous materials such as carbons, silica, and alumina [40].

The surface dynamics of 260 adsorbed argon atoms were simulated using an isokinetic molecular dynamics (MD) algorithm where the kinetic energy of the adsorbed molecules was kept constant, equivalent to being isothermal. The surface itself was considered rigid. The intermolecular interactions between the adsorbate molecules were considered negligible, to approximate the dilute ($\sim$ zero coverage) limit. The surface diffusivity was calculated from the simulated trajectories of the adsorbed molecules using the Einstein relation. The trajectories of the argon atoms were also used to sample the distribution of maxima, minima, and barriers in the potential energy surface, and compare it to that of the Dual Site-Bond Model (DSBM) described above. Simulations were performed at several different temperatures and the surface diffusivities obtained correlated with the Arrhenius expression. The reduced activation energies for surface diffusion (from 3.5 to 6) thereby obtained for the BS, and the CBS after deleting 0.5 ML, were both similar to that (~ 3.15) assumed by Drain and Morrison [41] for barriers hindering the surface migration of Ar on powdered titania. Hence, this finding also suggested that relatively low levels of roughness, as for the BS and 0.5 ML CBS, did not affect the activation energy. However, the reduced activation energy (~ 5.3) was much higher for much rougher surfaces, like the 3 ML CBS. This corresponded to an increase in diffusion activation energy from ~ 4.7 to 7.1 kJ/mol for rougher surfaces. This finding is more in line with experimental results by other workers [42]. Further, deviations from pure Arrhenius behaviour were observed. Riccardo and Steele [38] suggested this result was similar to previous findings for activated diffusion on energetically heterogeneous lattices modelled as sets of adsorption sites separated by saddle points, as in the DSBM [43–45]. A common descriptor of surfaces is the energy

distribution of local minima in the surface potential. Bakaev and Steele [46] obtained this distribution for a BSM by sampling the adsorbate–solid interaction energy of argon atoms simulated in a full monolayer. However, in this method, atoms were forced onto sites that they would not necessarily occupy if isolated because the ML was found to be almost close-packed. Riccardo and Steele [38] went further and obtained additional descriptors of the surface. They obtained the frequency distribution of adsorption energies sampled along MD trajectories, and also the frequency distributions of the maxima, minima, and activation barriers of the argon–solid interaction encountered along the MD trajectories. It was found that the rougher surfaces had broader distributions, which were also shifted towards higher energies, than smoother surfaces. These higher energies with larger fractal dimension are in line with the theory by Rigby [47–49] described in Section 3.2. Further, Riccardo and Steele [38] found that the distributions of local maxima and minima overlapped, suggesting some local maxima along a given trajectory had a lower energy than some of the minima, but, clearly, could not arise in succession. Instead, there must have been a high degree of spatial correlation between the energies of successive extremes. This feature is similar to the scenario proposed by the DSBM, described above, and suggests that this model would be representative of the surfaces of amorphous materials.

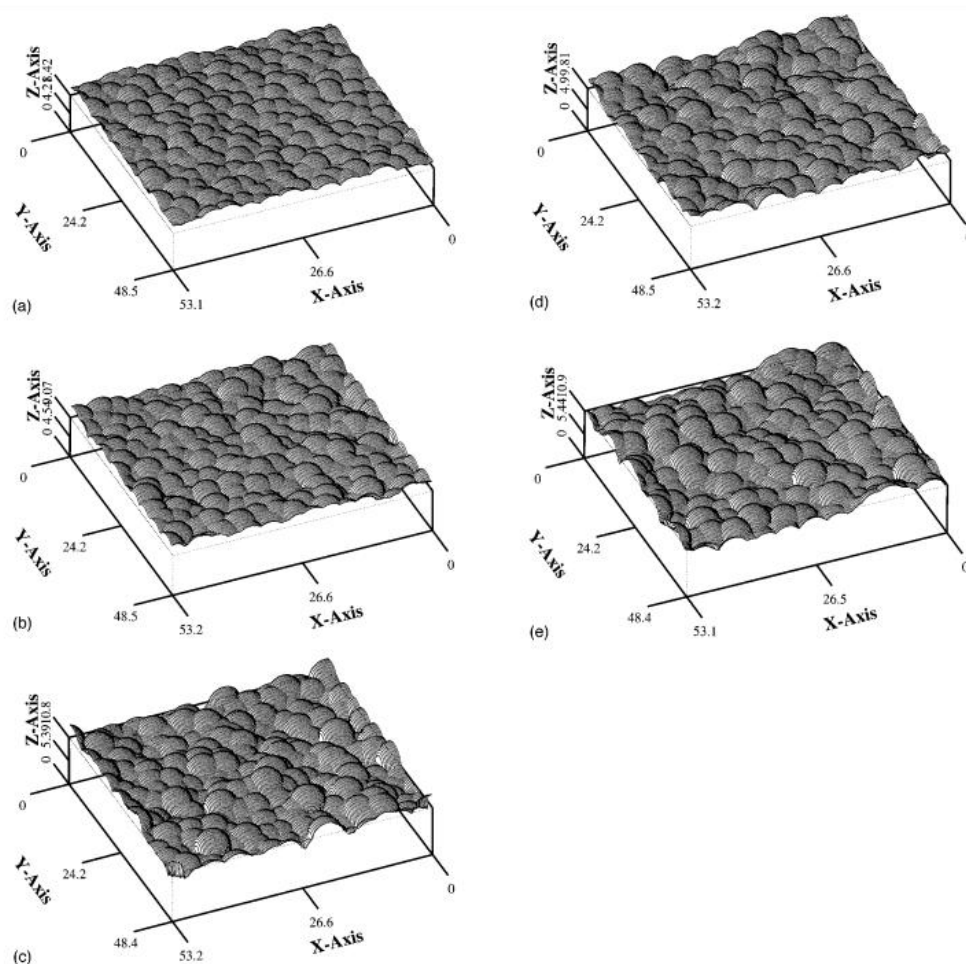


Figure 3. Graphical representations of amorphous surfaces of oxide ions in the Bernal Model of TiO_2 as seen by an Ar atom considered to be a hard sphere of radius $\sigma = 3.25 \text{ \AA}$. (a) Bernal Surface (BS); (b) Corrugated Bernal Surface (CBS) after deleting 0.25 ML (0.25 monolayers of oxides) from the BS sample; (c) CBS after deleting 0.5 ML (CBS ~ 0.5 ML); (d) CBS 1 ML; and (e) CBS 5 ML. The values of coordinates appearing in the figures are expressed in $\text{\AA}$. Reprinted from [38], with the permission of AIP Publishing.

Since, as mentioned above, it is not possible to know in advance the required level of idealisation for a model necessary to both achieve computational tractability and retain empirical adequacy, it is necessary to actively test models with different degrees of simplification. Stallons and Iglesia [9] compared the structural and transport properties of four models for the surface of amorphous silica: (1) an ordered surface created by cutting the structure of bulk α -cristobalite to the desired geometry and making dangling oxygen bonds into hydroxyl groups; (2) an unrelaxed surface obtained by cutting a bulk silica structure created via molecular dynamics; (3) a relaxed surface obtained using the same molecular dynamics simulation used to create a bulk structure; and (4) a surface created by fracturing a random sphere packing, generated by Monte Carlo methods, where the spheres represented oxygen atoms of the silica. The various surface hydroxyl concentrations ($\sim 6\text{--}8$ per nm^2) for the first three types of surface were at the high end of experimentally measured values, while the fourth type of model does not represent the silicon atoms needed for the calculation of surface hydroxyl concentration.

Predictions of the heat of adsorption for different adsorbates can be used to test the energetics of a surface model. However, potential energy functions that accurately describe the specific surface–adsorbate interactions are not typically available. Hence, it is necessary to use an interaction potential involving experimentally accessible parameters, such as atomic size and polarizability, and Henry’s law constants. Stallons and Iglesia [9] used a Lennard-Jones potential to describe interactions between adsorbates (dinitrogen, argon, and methane) and the two types of surface oxygen atom (hydroxyl and bridging oxygens). The interactions between adsorbates and silicon atoms were left out, since these were considered negligibly small relative to those of oxygen atoms. Potential energy surfaces, based upon a $0.2 \text{ \AA}$ pitch grid, were constructed for the four types of models and the adsorbate nitrogen, and those for the relaxed and unrelaxed surfaces are shown in Figure 4. From Figure 4, it can be seen that the relaxed silica surface had better defined peaks and valleys than the unrelaxed surface. The random surface had more localized and better-defined adsorption sites than the unrelaxed surface, but the potential energy surface was flatter than for the relaxed surface. The ordered surface had only one type of adsorption site with regular connectivity between these identical sites.

The distribution of adsorption energies, for each of the adsorbates dinitrogen, argon, and methane, were obtained from the potential energy surface by determining the energy values at the bottom of each potential energy well. It was found that, compared with experimentally obtained values, the number-weighted average heats of adsorption were within 0.2 kJ/mol for methane and 2 kJ/mol for dinitrogen and argon. The adsorption energy distributions for dinitrogen on the four types of model surfaces were obtained and are compared in Figure 5. While the ordered surface had just a single heat of adsorption of 14.3 kJ/mol , the heats of adsorption for the other three surfaces had a distribution with averages of 11.9 kJ/mol for the relaxed surface, 11.4 kJ/mol for the unrelaxed surface, and 12.8 kJ/mol for the random surface. The rougher relaxed surfaces had a broader distribution than the unrelaxed surface, which is similar to the findings of Riccardo and Steele [38].

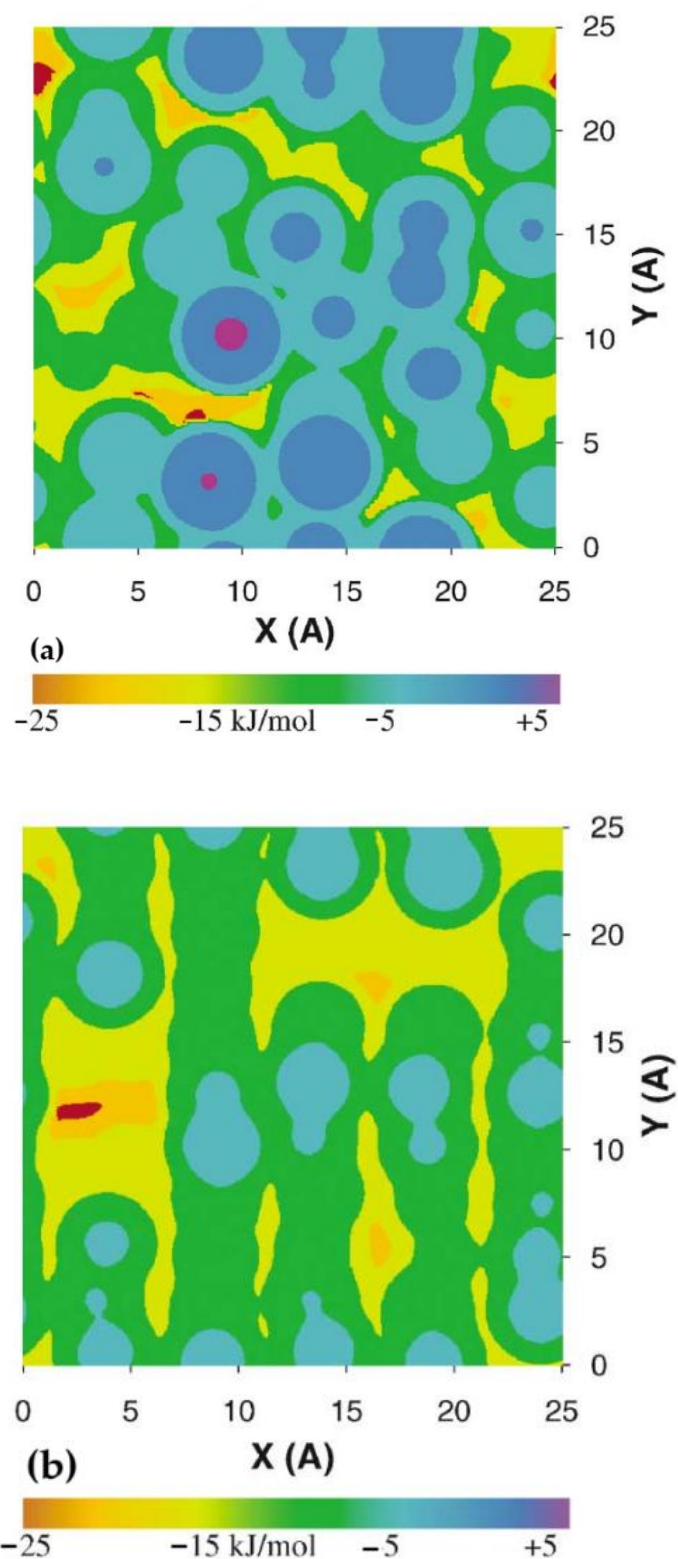


Figure 4. Potential energy contour plots for dinitrogen on (a) a relaxed simulated silica surface and (b) an unrelaxed simulated silica surface. Reprinted with permission from Ref. [9], 2001, Elsevier.

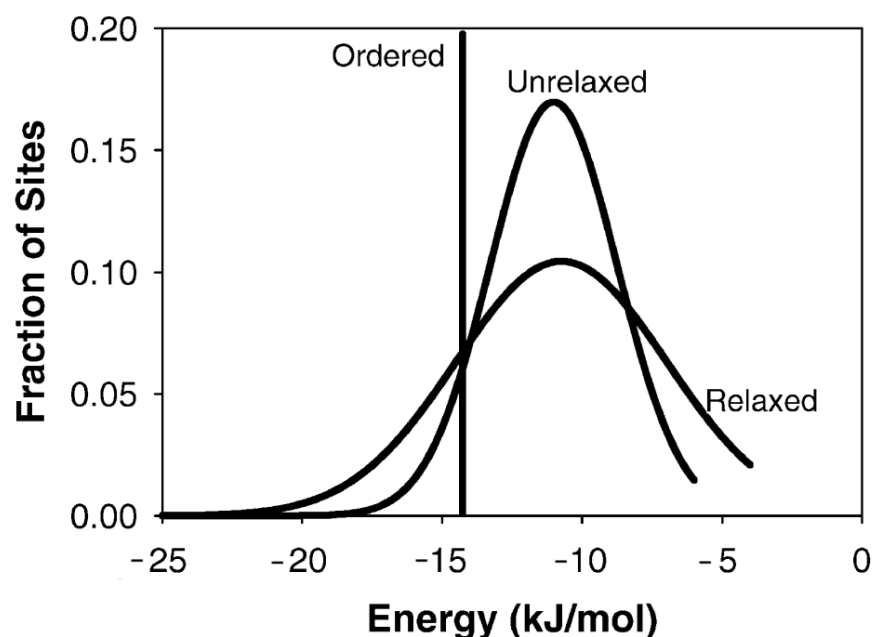


Figure 5. Adsorption energy distributions for dinitrogen on various types of simulated silica surfaces. Reprinted with permission from Ref. [9], 2001, Elsevier.

The surface diffusion of adsorbates, interacting weakly via a Lennard-Jones potential, was simulated, using molecular dynamics methods, in order to provide information on the connectivity of adsorption sites [9]. The surface was considered to be rigid, even though in reality the surface would be vibrating due to random thermal motion. Stallon and Iglesia [9] suggested this simplification was reasonable for weakly interacting adsorbates like dinitrogen. Further, they suggested that the surface diffusivity estimates for static surfaces are within ~5–10% of those where the top layers of the surface are allowed to relax during the migration of adsorbed species. While the potential and kinetic energy of migrating adsorbates was allowed to fluctuate, the temperature was kept constant. The surface diffusivity was estimated using the Einstein relation of the velocity auto-correlation function, and correlated for different temperatures using the Arrhenius expression. Overall, the simulated activation energies were similar in value to those found by experiment by Barrer et al. [50]. The trajectories of adsorbate molecules typically followed the lowest energy path across the surface. The surface diffusivity was lowest on the relaxed surface, and highest on the unrelaxed surface, which had a similar average heat of adsorption but a narrower range. The surface diffusivity was also higher on the random and ordered surfaces than on the relaxed surface. This is because the latter had some stronger binding sites (it had the largest diffusion activation energy of 7.8 kJ/mol) than the former two (activation energies ~7 kJ/mol), even though the overall average was lower. However, Stallon and Iglesia [9] acknowledged that the individual activation energies obtained were too close together, and, thus, insufficiently discriminatory to assess the relative empirical adequacy of the different model surfaces against the limited experimental data available. They also suggested that the connectivity of binding sites on a given surface was critical since they found that the relaxed surface also had a higher density of unconnected sites when compared with the random and ordered surfaces. In contrast, the unrelaxed surface had extended “channels” between energy sites, as can be seen in Figure 4, which provided routes for enhanced diffusion. Overall, Stallon and Iglesia [9] suggested that the relaxed surface model was probably the best representation of a real amorphous silica surface, but acknowledged that the possible level of discrimination between models provided by the experimental tests available was low.

Molecular dynamics has also been used to construct relaxed, flat alumina surfaces, of simulated size 30 nm^2 , and simulate xenon surface diffusion upon them [51]. Bläckberg et al. [51] also created a ridged alumina surface by introducing valleys by removing atoms on the surface and then performing an energy minimisation. The potential energy distribution of each type of surface was mapped by creating a 3D mesh of non-interacting xenon atoms with a spacing of 0.5 Å , and then calculating the potential energy of the system for every xenon atom. Examples of the minimum potential energy are shown in Figure 6. From Figure 6, it can be seen that, for the ridged valleys, the potential energy minima are located in the valleys, where adsorbed molecules also tend to localise, and it was found to have a wider distribution of minimum energy values than the flat surface. The surface diffusivity was calculated from the xenon trajectories using the Einstein relation. It was found that the surface diffusivity for the flat surface was 2.3 times higher than for the ridged surface. Surface diffusion on the ridged surface was dominated by movement along the valleys, with little movement perpendicular to them. Hence, the difference in diffusivity with the flat surface may be the result of the restriction in the dimensionality of the molecular migrations.

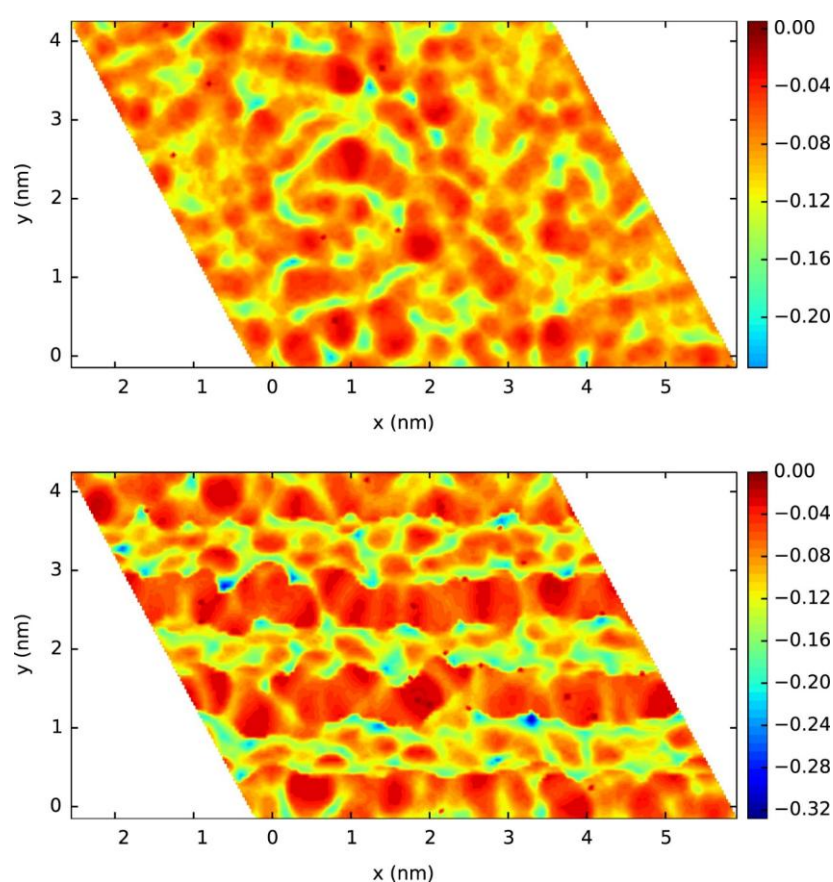


Figure 6. Minimum potential energy of the xenon-alumina system in eV as a function of Xe xy position, compared to the total system energy when no Xe is present. The top panel corresponds to the flat surface, and the bottom panel to the ridged surface. Reprinted from [51] with permission from Elsevier.

Sonwane and Li [18] used the approach of Streit and Mintmire [52] to construct atomistic models of hollow nanospheres and nanotubes. They also constructed models of porous media consisting of a packing of spheres. The porosity of the model was varied using densification (allowing overlapping of the spheres) or coarsening (the random removal of spheres from a dense packing) algorithms. These authors used a Monte Carlo model to

study surface diffusion on the sphere packing model and obtained the diffusivity from the Einstein relation. Sonwane and Li [18] defined the tortuosity of the surface phase in the porous solid as follows:

$$\tau_s = \frac{\phi}{E_s} \quad (6)$$

where ϕ is the voidage fraction and where E_s is as follows:

$$E_s = \frac{\langle r^2 \rangle|_{pack}}{\langle r^2 \rangle|_{ref}} \quad (7)$$

E_s is the normalised surface diffusion coefficient, $\langle r^2 \rangle$ is the mean square displacement, the subscript “*pack*” is the packing, and “*ref*” is the reference material, which was a cylinder. It was found that, for a densified packing of unimodal sized spheres, the variation in surface tortuosity with voidage fraction had a “U” shape, with the relatively horizontal portion corresponding to voidages of ~0.2–0.35. This behaviour was considered due to the fact that, at one extreme, as the degree of overlap, and hence contact area, between individual spheres decreased, then the chance of a tracer molecule finding a path between adjacent spheres reduced. At the other extreme, highly densified spheres created many relatively inaccessible ‘dead-end’ pore features that were hard for tracers to escape. In contrast, the surface diffusivity for the coarsened spherical packing decreased with increasing voidage fraction up to values of ~0.3, and thereafter was fairly constant up to high porosities. This was said to be because the coarsened packings retained many aggregates with good connectivity. For low porosities, the surface tortuosity was lower than the pore tortuosity, but at porosities higher than ~0.28 the reverse was the case. For models of bimodal solids constructed of packings of spheres that were themselves porous, it was found that the surface tortuosity increased with increased macroporosity around the spheres, due to less contact between them.

Aldo Ledesma-Durán et al. [53] identified the requirement for an adequate definition of the surface diffusion coefficient that can be experimentally measured for surface diffusion within chemical reactors, where the individual molecular trajectories are not of interest but simply quantities reflecting the average flow rate. They initially computed a position-dependent diffusivity, namely the Fick-Jacobs coefficient, which contains information about the variations in the surface and the internal geometry of the boundary. Subsequently, they obtained an effective diffusivity given in terms of the parameters typically utilised in the description of pores, such as their concavity, tortuosity, and degree of constriction. This second diffusivity permitted the use of a 1D diffusion equation along an effective longitudinal coordinate, whose solution closely approximates the numerically calculated surface diffusion on model surfaces with constrictions that restricted molecular trajectories.

Song et al. [54] constructed 3D pore structure models of coal using a noise algorithm that altered the random distribution of holes in a lattice by adjusting the scale, intensity, and type of noise such that the resulting model matched the pore size and pore growth ratio from experimental characterization results. The model pore structure was then smoothed, by operations such as the removal of disconnected voids. Numerical simulations of the kinetic uptake of oxygen were then performed on these models. This type of model naturally incorporated the impacts of the convoluted surface of the void space on surface diffusion.

In contrast, some authors have considered surface diffusion in more slit-shaped pores. For example, Zhao et al. [55] conducted molecular dynamics simulations of methane diffusion in graphene slit-shaped pores, while Zhou et al. [56] conducted molecular dynamics simulations of the diffusion of mixtures of carbon dioxide and methane within atomistic

models of slit-shaped kaolinite pores in shales. Both sets of authors found that the influence of surface diffusion diminished as the pore size increased.

The issue with just considering single slit-shaped pores is that, even in disordered materials with such pores, the void space actually consists of an interconnected network of such pores with different sizes, and the surface diffusion molecular motion occurs continuously between the various pores [57]. Hence, a full representation of this interconnectivity is required, so Di Pino et al. [57] conducted molecular dynamics simulations of the diffusion of oxygen, carbon dioxide, and methane in models of carbon slit-shaped micropores, both smooth-walled and rough-walled carbon nano-tubes (CNTs), and amorphous, microporous carbon structures. The rough-walled CNTs were created by randomly adding atoms to the surface of smooth-walled CNTs. The amorphous materials were created with a linear quenched molecular dynamics method. It was found that surface diffusion was the dominant migration mechanism in all cases except for the amorphous model. Further, while for smooth-walled structures the self-diffusivity decreased with increased pore size, for rough-walled structures the opposite trend with pore size held. This effect was attributed to the enhanced adsorption of molecules in the ruts present on rough surfaces. However, for the amorphous structural model, these roughness features were so prevalent that they added so much additional tortuosity to surface-bound molecular migration that gas phase transfer was the dominant mechanism. These diverse findings for variously roughened models showed that it is not currently possible to know in advance what level of this type of additional complexification is necessary for a minimalist idealization model to be predictive.

Shan et al. [58] compared the surface diffusion of methane in smooth, organic pores with that in rough, inorganic (calcite) pores in shale using molecular dynamics. They found that the roughness made a difference to the relative importance of surface diffusion to the overall mass transfer. It was found that surface diffusion in inorganic pores could be ignored when the characteristic length of the flow domain exceeded 8 nm, while enhanced surface diffusion could only be ignored in organic pores when this length exceeded 30 nm. Hou et al. [59] conducted a similar study of surface diffusion in shale organic and inorganic pores using the lattice Boltzmann technique. They found that gas transport was dominated by the surface diffusion in the organic pores when their width was less than 5 nm owing to the greater gas adsorption effect therein.

Yu et al. [60] constructed models of amorphous organic nanopores in shales using realistic kerogen molecules. They then conducted molecular dynamics simulations of gas transport through these pore models. They found that the gas-transport velocity of methane in the amorphous organic nanopores dropped substantially (40, 70, and 90%) even with only very tiny roughness factors (0.3, 0.6, and 1.2%) when compared with the corresponding ideally smooth nanochannels.

Molecular dynamics has permitted the following of individual trajectories of surface diffusing molecules within hierarchical porous carbon (HPC) structures [61]. These models were constructed by first creating carbon nanotubes of pore diameters of 5, 3, and 1.9 nm using computer modelling software. The two larger-sized nanotubes formed mesopores, while the 1.9 nm CNTs formed micropores. The CNTs were connected up by symmetrically excavating eight circular holes of diameter 1.9 nm in the walls of mesopores (with a certain size) of length 6 nm, followed by the docking of eight micropores of length 3 nm with these holes. The liquid phase diffusion of nalidixic acid, as a solution in water, was simulated using molecular dynamics. By following the individual trajectories of molecules it was found that the majority of solute molecules first adsorbed on the surface of mesopores (of whichever size) and then migrated to the micropores by surface diffusion, rather than by entering the latter directly. This process allowed a more efficient penetration of the

micropores (by solute) that would otherwise be blocked by the very stable configurations of solvent molecules that typically exist therein [61]. These findings suggested the advantage of HPC structures, coupled with surface diffusion, for enhancing the adsorption of solutes.

Zheng et al. [62] conducted simulations of flow including surface diffusion through self-affine fractures using lattice Boltzmann techniques. They used the simulations to confirm that, for self-affine fractures, the scaling relation for the surface tortuosity τ_s is of the following form:

$$\tau_s(\langle\delta\rangle) = \left(\frac{\langle\delta\rangle}{l_c}\right)^{H-1} \quad (8)$$

where $\langle\delta\rangle$ is the mean aperture size, l_c is characteristic length of the self-affine surface, and H is the scaling law exponent.

3. Kinetic Models Incorporating Surface Parameters

3.1. Zeolites and Other Microporous Materials

Diffusion in zeolites and other microporous materials, such as the clays in shale, has many similarities with surface diffusion since all of the adsorbed phase in very small pores is in contact with the surface. For example, Ho and Wang [63] found that, for molecular dynamics simulations of diffusion in a nanopore, as shown in Figure 7, with a size of 8 Å, there was no free gas present and, thence, the diffusion was pure surface diffusion. Hence, many of the features of diffusion in zeolites are similar to surface diffusion. While not extensively done, the model for pyrophyllite could be potentially validated by comparing model predictions of key descriptors, such as adsorption isotherms and transport coefficients, with experimental values.

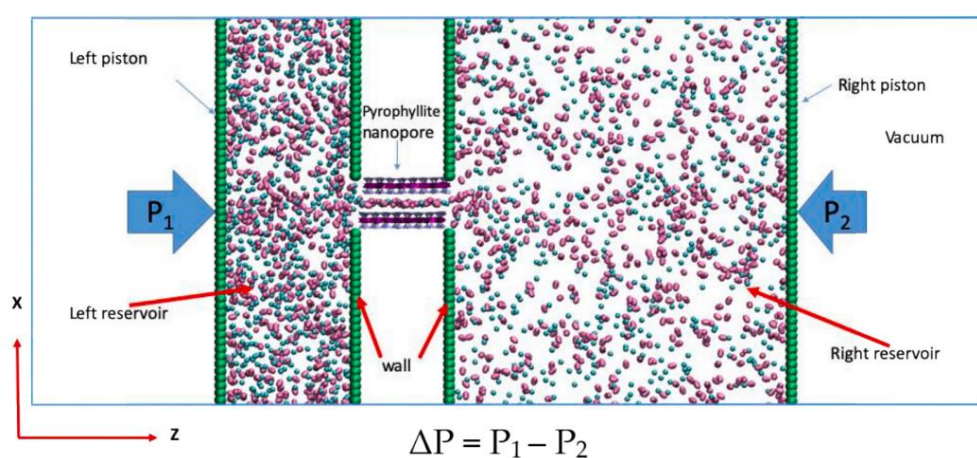


Figure 7. Simulation system for gas transport through a pyrophyllite nanopore. Methane (cyan) and ethane (pink) were simulated using TRAPPE force field. Carbon atoms (green) composing the pistons and walls were simulated using Lennard-Jones potential with $\sigma = 3.4$ Å and $\epsilon = 0.055688$ kcal/mol and not allowed to interact with pyrophyllite atoms. The pyrophyllite slab length and width are ~ 55 Å (in z direction) and 31.06 Å (in y direction), respectively. When applying periodic boundary conditions in all directions, the pyrophyllite slab becomes infinite in the y direction and finite in the x and z directions. Depending on the gas composition (pure or mixtures) and the pore size considered, the simulation box size and the number of gas molecules simulated vary. For example, when the pore size is 18 Å more gas molecules would be simulated, compared to the 8 Å. In the figure, the simulation box size is $400 \times 31.06 \times 2000$ Å³. Short-range interactions were calculated using a cut-off distance of 10 Å. Long-range electrostatic interactions were computed using the PPPM (particle–particle–particle–mesh) solver. All simulations were performed using LAMMPS with 1.0 fs timestep and temperature $T = 300$ K using the Nose-Hoover thermostat. Reproduced from [63] with permission from Elsevier.

Non-ideal structure defects in the external surface region of zeolite crystals often create diffusion barriers that dominate mass transfer resistance [64,65]. Hedlund et al. [64] found that the activation energy for surface diffusion at the pore mouth was higher than that within the pores, which they attributed to the different geometries at each respective location. The potential defects of a chemical nature often include isolated silanol groups, which can greatly hinder surface diffusion. Gao et al. [65] simulated the diffusion of propylene in contact with a model H-SAPO-34 framework with explicit terminal groups at the surface using the force field molecular dynamics (FFMD) approach. These workers found that isolated silanol groups exposed at the edge of crystallites significantly retarded the permeation of guest molecules through the boundary. Further, the presence of isolated silanol groups at the external surface was the origin of different molecular diffusion paths between uptake and desorption.

Do and co-workers [66–68] developed a kinetic model for surface diffusion on energetically heterogeneous surfaces of microporous adsorbents, where the surface was patchwise heterogeneous such that adsorption sites of a given energy were locally grouped into spatially extended patches. The heterogeneity in the surface (energy) was attributed to differences in local pore size. It was also assumed that the activation energy for surface diffusion was proportional to the heat of adsorption, and that adsorbate–adsorbent interactions were much stronger than adsorbate–adsorbate interactions such that the latter could be neglected. A free-fitting parameter in the model was the pre-exponential factor for the Arrhenius expression for the surface diffusivity (corresponding to the limiting value at high temperature or zero activation (interaction) energy). The value obtained for this parameter, from experimental data, such as kinetic uptake curves for hydrocarbons on carbon adsorbents, was found to depend upon the choice of the isotherm equation to account for the local adsorption equilibrium [66].

Alexander and Gladden [69] developed a kinetic model for describing diffusion in zeolites and used it to interpret deuteron NMR studies of the motion of fully-deuterated (d_6) benzene in zeolites. The peak-width at the half-maximum height of deuteron spectral lines for benzene adsorbed in a zeolite can be used to determine the correlation time for translational motion. The temperature at which such spectra are obtained can be varied, and, thereby, the variation in the translational motion correlation time with temperature derived. Where more than one such independent motion, with individual correlation times τ_1 and τ_2 , are arising simultaneously then they will give rise to a combined correlation time τ which is given by the following:

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}. \quad (9)$$

Each of the translational motions represented by the correlation time is considered to be a thermally activated process, such that the temperature dependence is given by the Arrhenius expression:

$$\tau = \tau_0 \exp(E/RT) \quad (10)$$

where E is the activation energy. One such activated process is considered to involve the desorption from a given adsorption site, followed by adsorption at another site within the same zeolite cavity, or passage through a window between such cavities by overcoming an additional activation energy barrier. If there are n sites within a single zeolite cavity, and jumps between them are what lead to the narrowing of the NMR line-width but these are

not guaranteed, then the rate of jumps v will depend upon the number of available sites such that the following applies:

$$\tau = \frac{1}{v} = \frac{\tau_0}{n-1} \exp(E/RT). \quad (11)$$

To allow for jumps between cavities, it was considered that there were a number w of a second kind of site located in the windows between cavities, which might be thought of as the number of different orientations that a molecule might adopt while making the passage through the window. The inter-cavity jump was considered to require an additional activation energy D such that the probability of making such a jump, p_w , was proportional to $w \exp(-D/RT)$. The potential to make the inter-cavity jump increased the probability of a successful jump leading to line narrowing. If the coordination number of neighbouring cavities (i.e., the number of windows per cavity) is n , and if an explicit form for the probability p_w is inserted, then the following expression is obtained:

$$\frac{1}{\tau} = \frac{n \exp(-E/RT)}{\tau_0(1 + w \exp(-\Delta/RT))} \left[\frac{n-1}{n} + cw \exp(-\Delta/RT) \right]. \quad (12)$$

The particular mathematical form of Equation (12) gives rise to three regimes, as shown in Figure 8, in the low, intermediate, and high ranges of temperature, such that, at a low temperature, the correlation time is given by the following:

$$\tau = \tau_0 \frac{\exp\left(\frac{E}{RT}\right)}{n} \quad (13)$$

while, at a high temperature, it is given by the following:

$$\tau = \tau_0 \frac{\exp\left(\frac{E}{RT}\right)}{cn} \quad (14)$$

and at intermediate temperatures, it is given by the following:

$$\tau = \tau_0 \frac{\exp\left(\frac{E+\Delta}{RT}\right)}{cwn}. \quad (15)$$

The predictions of the model were compared with experimental data for zeolite HY, and also dealuminated HY, loaded with 0.8 molecules per supercage [69–71], and the data for the former are shown in Figure 9. From Figure 9, it can be seen that the overall form of the data is the same as that predicted in Figure 8. For zeolite HY, the activation energies in the lower and upper ranges were 9 kJ/mol and 13 kJ/mol, respectively. The observed difference in activation energies in these limiting ranges suggests that the associated activated jump processes are not the same, even though the motion is supposed to be within a cavity for both. Alexander and Gladden [69] proposed that the lower activation energy is associated with a faster jump, from one kind of intra-cavity site, that predominates at lower temperatures, while the slower jump, from a different type of cavity site with higher activation energy, occurs at higher temperatures. The gradient of the line fitted to the intermediate temperature range suggested that the total activation energy associated with an inter-cavity jump was ~23 kJ/mol, thereby suggesting that the jump through the inter-cavity windows required an additional ~10–14 kJ/mol. Further, the offset between the high and low temperature regimes, shown schematically in Figure 8 and experimentally in Figure 9, corresponded to a measured coordination number of ~4, which is consistent with the known structure of zeolite HY. The decrease in the transition temperature, between

the intermediate to lower temperature regimes, that occurred with the dealumination of the zeolite, was considered to arise from a preferential loss of the lower activation energy cavity site due to the dealumination [69–71].

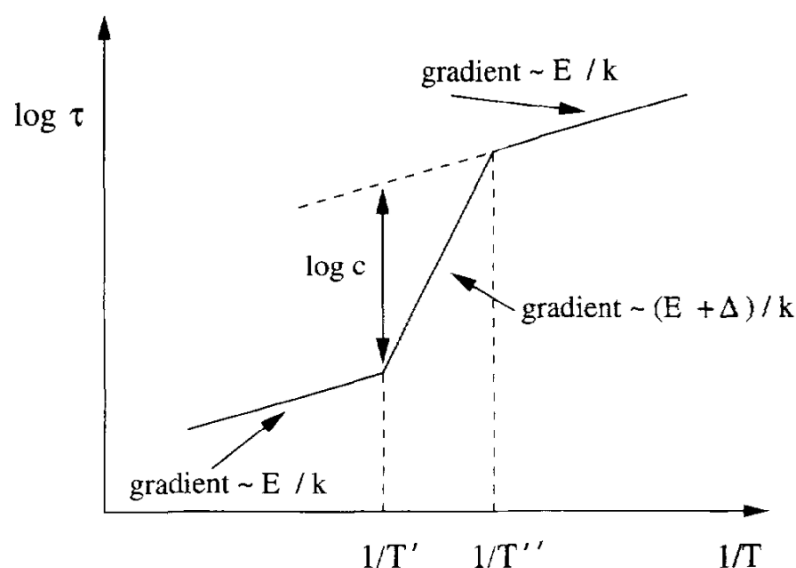


Figure 8. The behaviour of the motional correlation time as a function of inverse temperature as predicted by the model described in the text is shown. The three temperature regimes are separated by the characteristic temperatures T' and T'' . The model predicts that the gradients of the experimental data in each of the three regimes will approximate the values indicated in the figure. In particular, activation to molecular desorption events and energy barriers to intercage jump processes can be estimated. An estimate of the coordination of the pore network as seen by the sorbed species under study is also obtained. Reproduced from [69] with permission from Elsevier.

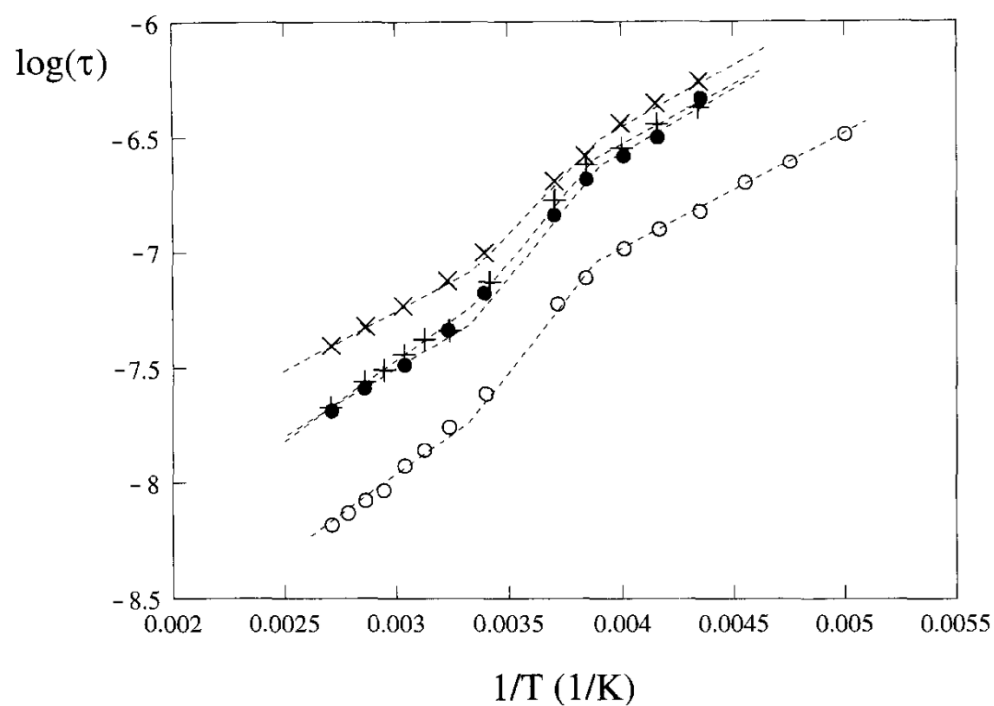


Figure 9. Motional correlation time, τ (s), as a function of reciprocal temperature (K^{-1}) for benzene- d_6 , adsorbed in fresh HY ($\circ$) and HY coked during exposure to the ethanol dehydration reaction for 1 h (+), 3.5 h ($\bullet$), and 15 h ($\times$) on stream. Reproduced from [71] with permission from Elsevier.

The dependence of the above-described kinetic model on structural characteristics of the zeolite structure, such as the coordination number between cavities, means it can be used to probe the structural evolution of a zeolite pore network. For example, it was used to examine, via the deuterium NMR of an adsorbed probe benzene, the pore structural changes that occurred as a result of coke deposition arising from side reactions during the use of the zeolite HY as a catalyst for ethanol dehydration [71]. It was found that an increasing time on stream led to the loss of the aforementioned within-cavity site with the lower activation energy. It was also found that, following 15 h on stream, the coordination of the network declined from 4 to 3.4.

A similar model was used to analyse the deuterium NMR spectra for ethane and ethene adsorbed in zeolite NaA [70]. The correlation times obtained from the spectra were used as input to a Monte Carlo Lattice Dynamics (MCLD) simulation of diffusion of these molecules in the zeolite. The lattice used for the simulations was that derived from molecular dynamics simulations by van Tassel et al. [72], and is shown in Figure 10. In this model of molecular motion, the effect of molecular interactions was included by assigning a different jump rate ν to a site depending upon the number of nearest neighbours such that the following applies [70]:

$$\frac{1}{\tau_i} = \frac{1}{\tau_{i0}} \exp\left(\frac{-E_m}{RT}\right) \exp\left(\frac{-N_a E_{aa}}{RT}\right) \quad (16)$$

where N_a is the number of nearest neighbours, and E_{aa} is the interaction energy between them. In the simulations it was found that this interaction reduced the ethene activation energy to desorption by 1 kJ per molecule adsorbed per cavity. The inter-molecular interactions led to an increase in diffusivity with loading (the average number of molecules per zeolite cage).

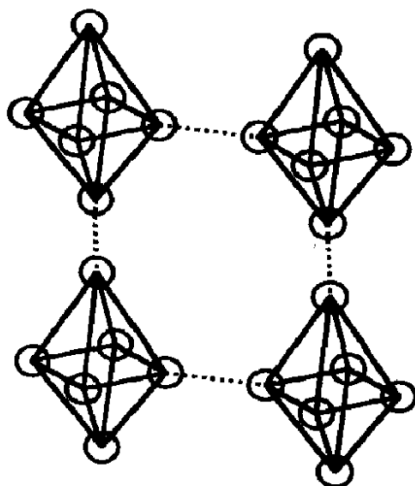


Figure 10. A lattice of adsorption sites (circles) composed of connected octahedral sublattices. Solid lines represent possible hops within each sublattice (site hops) and dotted lines represent possible hops between neighbouring sublattices (window hops). Reprinted from [72] with permission from Elsevier.

Sometimes a distinction is still made between bulk (pore) and surface diffusion in microporous materials. Predictions of multi-component diffusion including surface diffusion can be made using the Dusty Gas model for bulk transport coupled in parallel with surface diffusion [73]. However, this approach is not appropriate for smaller pores, as in zeolites, due to an increasing steric effect from adsorbed molecules. Caravella et al. [73] used another approach based upon the Maxwell–Stefan approach. These authors highlighted that,

in smaller pores, the effective porosity, effective pore size, and tortuosity for bulk mass transport become affected by the steric effects from the adsorbed molecules undergoing surface diffusion, as shown schematically in Figure 11. In contrast, the tortuosity for surface diffusion is considered unaltered.

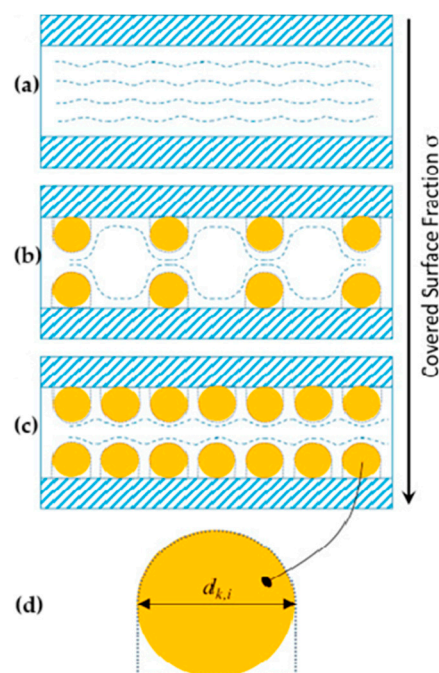


Figure 11. Scheme of the different geometrical volumes available for Knudsen diffusion at different coverage degrees: (a) No coverage, (b) medium coverage, (c) total coverage, and (d) representation of the effective volume occupied by the molecules. (a) and (c) are characterized by more linear, short paths and, thus, lower tortuosity. Reprinted from [73] with permission from Elsevier.

3.2. Amorphous Materials

The explicit dependence on the number of available adsorption sites of the correlation times in the kinetic model of Alexander and Gladden [69] has been tested by applying it to a model system like a zeolite which possesses a known pore network structure. For example, it has been seen that the cavity coordination number extracted, via the kinetic model, from deuterium NMR data for deuterated benzene adsorbed within zeolite HY was found to match that known from the crystal structure of the zeolite [69]. The inverse relationship between the correlation time and the number of available adsorption sites within a zeolite cavity has been generalised, for more disordered materials, to that within the characteristic jump range of the molecule on an (apparently) amorphous surface [47]. If an apparently amorphous rough surface is, in actuality, fractal, and, therefore, possesses the type of order, known as self-similarity, characterised by a surface fractal dimension d , then the particular surface area A perceived by a probe molecule within a Euclidean (planar) zone of area A_g (proportional to the square of the jump range), will be given by the following [39]:

$$A = A_g \sigma^{(2-d)/2} \quad (17)$$

where σ is the cross-sectional area of the probe molecule (e.g., 0.16 nm^2 for nitrogen or 0.4 nm^2 for benzene). It was then assumed that, as suggested by the zeolite kinetic model [69], the correlation time for the surface diffusion of a given probe molecule is inversely proportional to the area perceived by that molecule within the characteristic jump range at a given temperature. Hence, the Arrhenius pre-exponential factors for correlation times for the same molecular probe on two different surfaces (denoted one and two and

indicated by the relevant subscripts) with differing degrees of roughness characterised by different fractal dimensions will be related as in the following [47]:

$$\log(\tau_{01}) - \log(\tau_{02}) = \left[\frac{d_1 - d_2}{2} \right] \log(\sigma). \quad (18)$$

In some amorphous materials, the two different surfaces with different fractal scaling (as indicated by different fractal dimensions) may be still within the same material but over different length scales. For example, the pore structure within sol-gel silica materials has some similarities with that of zeolites in that it consists of cavities joined via windows. In sol-gel silicas, cavities are formed by the gaps left between the individual silica sol microspheres in the packing forming the bulk silica material. These cavities are, themselves, connected together via windows framed by adjoining silica microspheres. This type of structure thus has two types of surface over different length scales. The first is the outer surface of individual silica microspheres, and the surface roughness is over length scales smaller than the size of one microsphere. The second is the envelope surface of the convoluted, interconnected void volume formed between the spheres of the packing, and the roughness arises over length scales of the size of one microsphere and above. Given that these two surfaces are formed by different physical processes, they may have different degrees of roughness, as indicated by different surface fractal dimensions, say d and D_R [74]. The cross-over between the two fractal scaling regimes will correspond to a certain length scale R , likely to be closely related to the overall size of a single microsphere. When the hopping motion of surface-diffusing molecules arises at lower temperatures, the jumps will be of short range, and, thus, just confined to the surface of one microsphere. However, as the temperature rises, the jump range may increase (see below), and surface-diffusing molecules may begin to probe the larger length scales associated with passage between different microspheres. In this case, the Arrhenius pre-exponential factors for the correlation times for motions over length scales above and below (denoted by subscripts 1 and 2) the transitional length scale R would be related by the following:

$$\log(\tau_{01}) - \log(\tau_{02}) = [d - D_R] \log(R). \quad (19)$$

Given that the longer-range hops may involve leaving the surface of one silica microsphere, and/or passage through a window, to land on an adjoining microsphere, then, by analogy with inter-cavity jumps in zeolites, this may require an additional activation energy too [47].

The Arrhenius parameters for the correlation times for the surface diffusion of fully-deuterated benzene were obtained, using deutron NMR, for a range of different silica surfaces. It was found that the pre-exponential factors for pairs of the correlation times were related to each other via their surface fractal dimensions, determined by nitrogen adsorption, and Equation (18) [47]. At higher temperatures, it was found that the Arrhenius plot of the correlation time for one sol-gel silica had a kink similar to that observed in the analogous data for zeolites mentioned above. It was found that the pre-exponential factors for the correlation times for motions occurring above and below the transition temperature could be related by Equation (19) using the surface fractal dimension for the silica microspheres from nitrogen adsorption and that for the larger-scale void space envelope surface determined from the mercury porosimetry pore size distribution. The size of the characteristic length scale for the cross-over between fractal scaling regimes, R , was found to be ~10–11 nm which corresponded to both the modal pore size from mercury porosimetry, and the silica microsphere size as determined by small angle X-ray scattering (SAXS). This might be expected as the size of voids in a packing of spheres is roughly

similar to that of the size of the constituent solid particles. The transition temperature was also found to be that where the molecular jump length (defined below), determined from gas uptake studies, became the same size as the constituent silica particles [40].

Expressions of the mathematical form of Equation (18) can also be derived explicitly by the application of the transition state theory (TST) proposed by Eyring to surface diffusion on a homotattic patch model of a heterogeneous multi-fractal surface [48,49]. According to classical TST, the rate of a process is given by the following:

$$k_r = \frac{1}{\tau} = K \frac{kT}{h} \exp(\Delta S'/R) \exp(-\Delta H'/RT) \quad (20)$$

where τ is the correlation time for the motion, k is Boltzmann's constant, h is Planck's constant, K is the transmission coefficient, $\Delta S'$ is the entropy difference between the initial and transition state, and $\Delta H'$ is the enthalpy difference between the initial and transition state.

The surface of structurally (and, thence, energetically) heterogeneous materials is described by a multi-fractal version of the homotattic patch model. In the model, the surface is considered to consist of spatially extended patches within which the surface heterogeneity is described by a single-surface fractal dimension, and the adsorption sites are all considered equal, but that fractal dimension may differ between neighbouring patches. However, the key feature of the model for surface diffusion is that, at the microscopic scale, the rate-controlling step for surface diffusion is considered to be when molecules have become adsorbed on particular patches of the surface. The patchwork of regions of different fractal dimensions on the surface constitute a two-dimensional network of varying resistances to diffusion. The critical path theory suggests that for diffusion in a network, the observed rate is determined by a critical small fraction of resistances, since any resistances lower than this do not impact the flux much, and the diffusive flux tends to avoid passing through regions of higher resistance [27]. On a partially occupied surface, the already filled patches correspond to those with sites with the highest heats of adsorption, and so molecules adsorbed there will experience high resistance for surface diffusion. The currently empty patches typically correspond to sites with a low heat of adsorption, and thus present low resistance to surface diffusion. The critical fraction of sites corresponds to the patches that have just filled at the current coverage, as these straddle the gap between the sites with higher and lower heats of adsorption. The identity of this critical fraction will change as the surface coverage builds. Hence, at any given coverage the critical fraction of molecules controlling the observed rate of surface diffusion will be those on the spatially-extended patches just filled at the current coverage.

For a surface-hopping motion, the initial state of the rate-controlling step corresponds to the surface of the relevant patch being fully covered with at least a statistical monolayer of adsorbed molecules. If an instantaneous 'snapshot' were then to be taken of the surface, then nearly all molecules would be in the close vicinity of adsorption sites, and very few molecules would be in interstitial positions. For a completely homogeneous surface, this situation corresponds to an overall monolayer coverage, or, for a patchwise heterogeneous surface, it could be there is overall only sub-monolayer adsorption but where local coverage approaches a monolayer on occupied extended patches. The transition process for surface diffusion corresponds to when a molecule desorbs from its initial adsorption site directly upon the substrate, and hops to another site, located within its ultimate jump range, but in the second adsorbed layer directly above the first. Surface diffusion is, thence, considered to be happening under so-called "dilute" conditions, i.e., there is only relatively low concentrations of transitional molecules and resultant "holes".

In the initial and transitional states, the corresponding entropy of the adsorbed phase can be considered to comprise the sum of two contributions. The first contribution comes from the thermal entropy S^{th} , originating from vibrations of the molecules in the neighbourhood of the adsorption site, and the second contribution comes from the configurational entropy S^{config} , originating from the number of ways of arranging the molecules among the adsorption sites. The configurational entropy depends upon the number (Ω) of distinct arrangements of M adsorbed molecules across N adsorption sites according to the Boltzmann equation, as follows:

$$S^{config} = R \ln \Omega. \quad (21)$$

Typically, the initial state would comprise M molecules within the first adsorbed layer arranged amongst N adsorption sites on the substrate, with a further μ molecules situated within the second adsorbed layer located above the first. The generalised transition state would then comprise $M - 1$ molecules within the first layer and $\mu + 1$ molecules in the second layer. Hence, the change in configurational entropy between these two states would be given by the following:

$$\Delta S^{config} = R \ln \left[\frac{(M - \mu)(M - \mu - 1)}{(\mu + 1)(N - M + 1)} \right]. \quad (22)$$

For a particular molecule undertaking a molecular hop specifically in the dilute case, then it would be very likely to have initially had all nearest-neighbour adsorption sites occupied by other molecules. Further, in the dilute case M would be similar to N , and μ would be small (tending to zero). Hence, for large N , the limiting value of the term inside the square bracket in Equation (22) would be $\sim N^2$. In the initial state, there would only be one possible arrangement of the molecules, and, thence, then $\Omega = 1$, and $S^{config} = 0$. For the transition state, it was assumed there would be N adsorption sites within the jump range of the molecule, and that N is large. When there is a single hole in the first adsorbed layer, there would be N ways of arranging that one empty site, and the accompanying $N - 1$ full sites, amongst N adsorption sites. If N is a large number, for the single molecule located in the second adsorbed layer, then there would also be roughly $\sim N$ ways of arranging it amongst the roughly $\sim N$ possible sites. Hence the number of distinct arrangements for the transition-state is $\sim N^2$ for large N . Hence, from Equation (22), the change in entropy between the initial and transition state is given by the following:

$$\Delta S' = \Delta S^{th} + \Delta S^{config} = \Delta S^{th} + R \ln N^2. \quad (23)$$

For a fractal surface with scaling dimension d , then the number of adsorption sites N for a molecule with a characteristic size r , within a molecular jump range R_∞ , is given by the following:

$$N = \left(\frac{R_\infty}{r} \right)^d. \quad (24)$$

Hence, combining Equations (20), (23), and (24), for surface diffusion at monolayer coverage on a fractal surface, the correlation time is given by the following:

$$\begin{aligned} \tau &= \frac{h}{kT} \exp(-\Delta S^{th}/R) \left(\frac{R_\infty}{r} \right)^{-2d} \exp(\Delta H'/RT) \\ &= B \left(\frac{R_\infty}{r} \right)^{-2d} \exp(\Delta H'/RT) \end{aligned} \quad (25)$$

where the group denoted as B is only weakly dependent on temperature relative to the exponential term, and, thence, is usually considered to be a constant.

Therefore, the pre-exponential factor for the correlation time, τ_0 , can also be written as follows:

$$\frac{\tau_0}{\tau_{0r}} = \left(\frac{R_\infty}{r} \right)^{2(d_r-d)} \quad (26)$$

where the subscript r refers to the relevant quantity for a suitable reference material. It is noted that Equation (26) is similar to the equation above (Equation (18)), derived in earlier work [47,75], based upon the empirical findings from studies of molecular hopping motion in zeolites [69,71], except for the location of the factor of two in the exponent, and the explicit constant R_∞ .

It is noted that, if the fractal dimension is measured by gas adsorption using an adsorbate that has a strong specific interaction with particular patches of a chemically heterogeneous surface (e.g., nitrogen on partially dehydroxylated silica), then there can be a systematic error in the absolute value of the fractal dimension thereby obtained consisting of a fixed offset δ from the true value that depends upon the areal extent of the surface patch [47]. The fractal dimension, as measured, then apparently has a value $d + \delta$. However, since Equation (26) above only involves the difference between two surface fractal dimensions, and if the offset δ is indeed fixed for each surface, then Equation (26) would still be correct.

From Equation (26), the fractal dimension of the surface of interest is given by the following:

$$d = \left[\frac{\ln \tau_{0r}}{2 \ln \left(\frac{R_\infty}{r} \right)} + d_r \right] - \frac{\ln \tau_0}{2 \ln \left(\frac{R_\infty}{r} \right)} = b + a \ln \tau_0 \quad (27)$$

where a and b consist entirely of constants. It is noted that Equation (27) has the same overall mathematical form, but with slightly different constants, to the corresponding expression derived elsewhere [75].

By analogy with Equation (16) for zeolites, it was suggested that the heat of adsorption E_0 of a molecule in the initial state mentioned above would be given by the following:

$$E_0 = E_{s0} + n_1 \varepsilon_1 + n_2 \varepsilon_2 + n_3 \varepsilon_3 + \dots \rightarrow E_{s0} + n_1 \varepsilon_1 \quad (28)$$

where E_{s0} is the interaction between that molecule and the substrate surface immediately below it, n_i is the number of neighbouring molecules occupying each subsequent annular ring i moving outwards from the central molecule, and ε_1 is the particular energy of interaction between a single molecule in layer i and the central molecule. It was presumed that it was the limiting case such that $\varepsilon_1 \gg \varepsilon_i$ (where $i > 1$). In general, for a given site, the particular number of nearest neighbouring adsorption sites surrounding it depends on the connectivity, and hence roughness, of the surface. Therefore, the heat of adsorption E_0 on a fractal surface of dimension d , is given by the following [75]:

$$E_0 = E_{s0} - \varepsilon_1 + \pi \varepsilon_1 \left(\frac{R}{r} \right)^d \quad (29)$$

where R is the distance from the centre of one adsorbed molecule to the outer periphery of a neighbouring molecule, and hence $R/r = 1.5$, since all more distant interactions are considered negligible. As shown in the Supplementary Materials, equations of the form of Equations (27), (S1)–(S6) can be combined to give the following:

$$\ln \tau_0 = \frac{\Delta H'}{agvs} - \frac{(f + g + gvsb)}{agvs} = m \Delta H' + c \quad (30)$$

which is of the particular mathematical form associated with the compensation effect [76].

The overall surface diffusion process was then modelled, at the molecular scale [77], as a pseudo-two-dimensional random walk, in which the steps consist of hops between adsorption sites. The surface diffusivity was then given by the following:

$$D_S = D_0 \exp(-E_D/RT) = \frac{\lambda^2}{4\tau} = \frac{\lambda_0^2 \exp(-2E_\lambda/RT)}{4\tau_0 \exp(\Delta H'/RT)} \quad (31)$$

where λ is the characteristic jump length of the distribution of molecular hops at temperature T (with constant Arrhenius parameters λ_0 and E_λ), and D_0 and E_D are the pre-exponential factor and activation energy, respectively, for the surface diffusivity. In that case, it would be expected that the Arrhenius parameter for the surface diffusivity would also exhibit the compensation effect with the same gradient m as for that for just the correlation time, since inserting Equation (31) into Equation (30) gives the straight line with the following equation:

$$\ln D_0 = mE_D - 2mE_\lambda - c + \ln(k\lambda_0^2). \quad (32)$$

This is indeed what has been found by comparing the surface diffusivity data for benzene adsorbed on Aerosil, for adsorbed amounts equivalent to 0.75 to 1.375 times that needed for a statistical monolayer, to that for just the correlation time for benzene adsorbed at monolayer coverage on a variety of surfaces, obtained using deuterium NMR, as shown in Figure 12 [40,42]. The slope of the compensation plot for the correlation time, m , was 0.54 ± 0.04 , while that for the surface diffusivity was 0.53 ± 0.01 , which are identical within the fitting error. It is noted that, from the BET model for the adsorption of benzene on the carbon in question, the actual fractional surface coverages for adsorbed amounts of 0.75 to 1.375 times that needed for a statistical monolayer would be, in fact, in the corresponding range 0.63 to 0.83. Further, in Figure 12a, even at lower adsorbed amounts, the individual data points for the Arrhenius parameters for the surface diffusivity follow, within their individual errors, the line of the compensation plot for the correlation time for surface coverages down to ~ 0.25 , and only thereafter diverge. However, for these lower surface coverages, if the temperature range used in the Arrhenius fit is constrained to the lower values of 18.4–39.6 °C, rather than the full range up to 51.8 °C obtained by Haul and Boddenberg [78], then a better fit of the surface diffusivity data points to the compensation effect line for the correlation time could then be obtained. Hence, it was suggested that this was because, at higher temperatures, the typical jump length λ began to exceed the overall size of the individual surface patches occupied at lower coverages (which might be a bit smaller than those occupied at higher coverages), and the fractal dimension was no longer constant within the jump range, as is needed to obtain the gradient in Equation (30) [40]. It was noted that the Arrhenius parameters obtained for the typical jump length λ meant that the jump length was ~ 20 nm at the higher temperatures, and the original mean size of the constituent silica particles that Haul and Boddenberg compressed to porous plugs for their experiments was 16 nm [78]. Hence, the patches in the homotactic patch model may well correspond to the individual feed particles within the porous plugs, for which random variation in the processing conditions experienced during their fabrication may have led to slightly different degrees of surface roughness.

Since the pre-exponential factor (high temperature limiting value) and activation energy are obtained from the same fit, it is often suggested that the compensation, (also known as the enthalpy–entropy effect) is just an artefact of the correlation to be expected due to obtaining the two parameters from the same fit [76]. However, an expression of the form of Equation (29), relating an enthalpy to the surface roughness, will also be expected to hold for the heat of adsorption as well as the activation energy for surface diffusion. This means a similar linear relation should hold between the heat of adsorption and the

logarithm of the pre-exponential factor for surface diffusivity, as also holds for the activation energy. Further, the heat of adsorption can be measured entirely independently of the activation energy for surface diffusion, so there would be no potential intrinsic correlation due to being from the same fit. The heats of adsorption for sulphur dioxide on a range of surfaces has been found to follow the form predicted by Equation (29). In addition, the expected linear relation between the heat of adsorption and the logarithm of the pre-exponential factor for surface diffusivity has been found for benzene on silica [40], sulphur dioxide on various surfaces [42], and carbon dioxide on shales [79]. The homotactic patch model is naturally applicable to rock samples, like shale, as they are typically constituted of a random patchwork of different mineral grains with different surfaces (and, thence, different degrees of surface roughness), such as kerogen (carbon), clays (e.g., illite), quartz, and feldspar. Hence, the above homotactic patch model of surface diffusion is readily applicable to rocks [79].

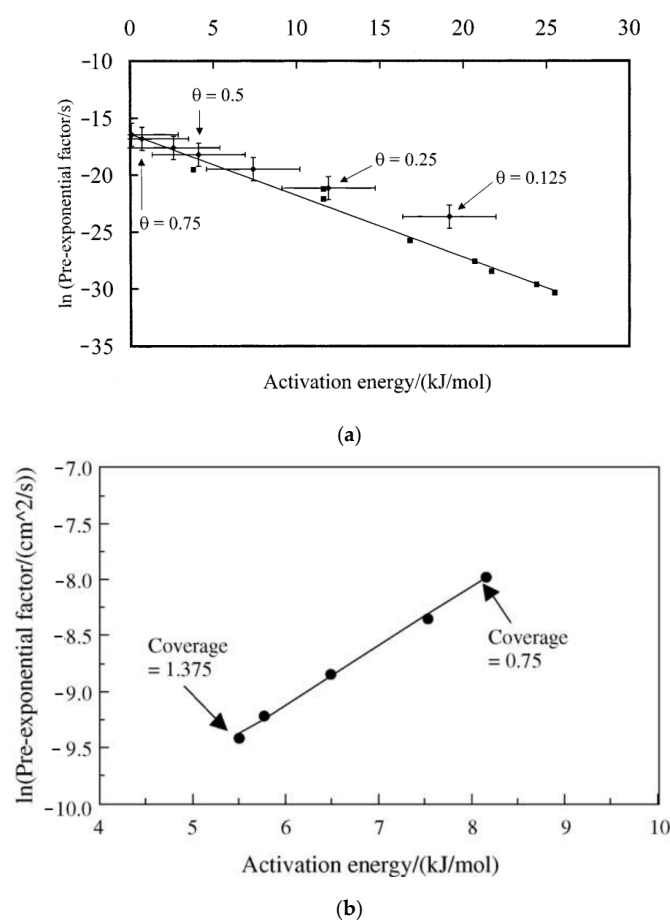


Figure 12. (a) A so-called “compensation effect plot” of the natural logarithm of the pre-exponential factor against the activation energy for the correlation times (◆) calculated, using the method described in the text, from the data for benzene diffusion on Aerosil at different values of surface coverage θ obtained by Haul and Boddenberg [78]. The arrows indicate the values of fractional surface coverage for selected data points. Also shown is a plot of the natural logarithm of the pre-exponential factor against the activation energy for the correlation times (■), determined [75] directly using deuterium NMR, for benzene diffusion, at a monolayer coverage, on various different surfaces with differing degrees of surface roughness. The straight line shown is a fit of the deuterium NMR data to Equation (30). Reprinted with permission from [40]. Copyright 2003, American Chemical Society. (b) Compensation effect plot of the Arrhenius parameters for the surface diffusivities of benzene on Aerosil obtained by Haul and Boddenberg [78] for coverages in the range 0.75–1.375 times that of a statistical monolayer. The straight line shown is a fit to Equation (30) with parameters $m = 0.53 \pm 0.01$ and $c = -12.3 \pm 0.2$. Reprinted from [42] with permission from Elsevier.

3.3. Liquid Phase Surface Diffusion

Miyabe and Guichon [80] have proposed a kinetic model, for surface diffusion in liquid-phase adsorption during reversed-phase liquid chromatography, known as the restricted diffusion model, and based upon absolute rate theory [81]. In this model, the surface and pore diffusion are considered to occur in parallel, and the mechanism of surface diffusion is similar to that for molecular pore diffusion, and consists of two processes. First, for a molecule to gain the activation energy for surface diffusion, a hole must be made in the solvent above the surface for the surface-diffusing molecule to occupy, requiring energy E_h^s , and then, second, the interaction between the adsorbate and adsorbent must be broken in a jumping step requiring energy E_b^s . Hence, the total activation energy for surface diffusion E_s is given by the following:

$$E_s = E_h^s + E_b^s. \quad (33)$$

Since the E_h^s requires motion of the solvent molecules amongst themselves, then it is considered related to the activation energy for the solvent viscosity E_v , since viscosity also involves motion of solvent molecules past each other, and almost equal to the activation energy for molecular pore diffusion. However, the hole formation for the pore (and surface) diffusing molecule may require more energy than the activation energy for solvent viscosity because the surface-diffusing molecule may be larger than the solvent molecules. The E_b^s is considered to be proportional to the heat of adsorption Q_{st} of the surface-diffusing molecule on the adsorbate, with a constant of proportionality of β .

Miyabe and Guichon [80] have interpreted experimental data, where the surface-diffusing molecules were selected from the homologous series of either *n*-alkylbenzenes or *p*-alkylphenols, the adsorbents were silicas carpeted in alkyl ligands, and the solvent was a methanol–water mixture. In these experiments, a compensation effect was observed for the Arrhenius parameters for the surface diffusivity, and a linear correlation between the activation energy for the surface diffusivity and the heat of adsorption of the adsorbate, which is similar to what has been reported for surface-diffusing molecules in a gas phase system mentioned in Section 3.2. The differences in the intercepts for corresponding plots of E_s against Q_{st} for different surface ligands were attributed to different structural situations for the solvent in the vicinity of the hydrophobic adsorbent surface, and, thence, different activation energies for hole formation. Miyabe and Guichon [80] also reported a linear correlation on a log–log plot of the surface diffusivity and the adsorption equilibrium constant for alkylbenzene adsorbates irrespective of the surface adsorbent ligand. They attributed this finding to an underlying linear relationship between the relevant free energies, and thus a similar mechanism for the surface diffusion and adsorption processes.

4. Conclusions

It has been seen that the differences in the pathways followed by surface-diffusing molecules, compared to molecules diffusing in the pore core, necessitates the definition of a specific surface tortuosity, different to the pore diffusivity. The additional deviations in the paths followed by surface-diffusing species arises from the particular patterns of surface geometric and energetic heterogeneities encountered on the surface. Hence, explicit representations of these heterogeneities are needed.

The ideal model for predicting the impact of surface geometrical and energetic heterogeneity of amorphous surfaces on surface-diffusion rates would be the “maximally realistic” atomistic representation of the surface and molecular dynamics simulations of the surface diffusion upon that surface. However, it is difficult, if not impossible, to obtain, experimentally, the level of detailed characterisation information required to produce such

a complete representation of a heterogeneous, amorphous surface. Even if it were possible to fully characterise a real surface, then the overall size of the surface that it would be feasible to represent would be limited by current computing power. Hence, some sort of Galilean idealisation of the surface is necessary to make the model tractable, and one such strategy seen above is severely restricting the range of length scales represented in the model. However, the correlation length of the types of disorder seen in amorphous materials may easily exceed the feasible upper length scale.

A strategy to avoid the problems with obtaining a complete atomistic-level characterisation of a highly complex amorphous surface and reproducing that in the model, is to, instead, attempt to simulate the physical processes involved in the formation of the surface in the first place and, thereby, obtain an accurate representation of the surface to be modelled. A hybrid approach where some characterisation data, particularly electron microscopy images, can be used to limit the necessary scope of the formation simulation and inform the nature of the surface reconstruction can also be used.

It has also been seen that theoretical justification can be used to select de facto the key statistical features of a surface, such as its porosity or fractal dimension, required to develop a minimalist model of the surface structure that captures all of the features that affect the surface transport parameters of interest. These theoretical justifications can also extend to the model of surface motion selected. For example, it was found that theorising the surface as patchwise multi-fractal in nature, but with a constant scaling regime within the jump range, led to explicit predictions of the observed compensation effect, and the relation between the heat of adsorption and the Arrhenius parameters for surface diffusion via an activated hopping motion.

5. Future Perspectives

As alluded to in the Introduction, and is now evident from the survey above, the key hurdles, to achieving a maximally realistic representation of surface diffusion on heterogeneous surfaces, are the limitations in obtaining a sufficiently detailed structural and chemical characterization of the surface, and on available computing power to simulate the surface formation and/or structure, and mass transport thereon. However, as computing power is always growing, more and more complex systems will become amenable to “brute force” simulation. In particular, atomistic surface reconstruction algorithms, that simulate the surface formation from first principles, offer a potential way around the limitations on the level of detail that it is possible to extract via characterization methods if the sophistication of the latter does not keep up with the capabilities of computing to store and manipulate the findings.

In addition, the above survey has shown that diffusion on many apparently complex, heterogeneous surfaces is, in fact, controlled by particular aspects of that surface, that can often be adequately described by a characteristic set of descriptors. Hence, an alternative strategy to the brute force approach, for future work, is to develop new representational paradigms (as was done with fractals), and identify further key parameters, for different types of surfaces.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/surfaces8020031/s1>, Equations (S1)–(S6).

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analysed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The author declares no conflict of interest.

References

- Schneider, P.; Smith, J.M. Chromatographic study of surface diffusion. *AIChE J.* **1968**, *14*, 886–895. [\[CrossRef\]](#)
- Costa, E.; Calleja, G.; Domingo, F. Adsorption of gaseous hydrocarbons on activated carbon: Characteristic kinetic curve. *AIChE J.* **1985**, *31*, 982–991. [\[CrossRef\]](#)
- Kapoor, A.; Yang, R.T. Surface diffusion on energetically heterogeneous surfaces- an effective medium approximation approach. *Chem. Eng. Sci.* **1990**, *45*, 3261–3270. [\[CrossRef\]](#)
- Hori, T.; Kamino, T.; Yoshimoto, Y.; Takagi, S.; Kinefuchi, I. Mutual influence of molecular diffusion in gas and surface phases. *Phys. Rev. E* **2018**, *97*, 013101. [\[CrossRef\]](#)
- Bukowski, B.C.; Keil, F.J.; Ravikovitch, P.I.; Sastre, G.; Snurr, R.; Coppens, M.-O. Connecting theory and simulation with experiment for the study of diffusion in nanoporous solids. *Adsorption* **2021**, *27*, 683–760. [\[CrossRef\]](#)
- Choi, J.-G.; Do, D.D.; Do, H.D. Surface diffusion of adsorbed molecules in porous media: Monolayer, multilayer and capillary condensation regimes. *Ind. Eng. Chem. Res.* **2001**, *40*, 4005–4031. [\[CrossRef\]](#)
- Chen, Y.D.; Yang, R.T. Concentration dependence of surface diffusion and zeolitic diffusion. *AIChE J.* **1991**, *37*, 1579–1582. [\[CrossRef\]](#)
- Do, D. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press: London, UK, 1998.
- Stallons, J.M.; Iglesia, E. Simulations of the structure and properties of amorphous silica surfaces. *Chem. Eng. Sci.* **2001**, *56*, 4205–4216. [\[CrossRef\]](#)
- Weisberg, M. *Simulation and Similarity: Using Models to Understand the World*; Oxford University Press: Oxford, UK, 2013.
- Nsumovets, A.G.; Zhang, Z. Fidgety particles on surfaces: How do they jump, walk, group, and settle in virgin areas. *Surf. Sci.* **2002**, *500*, 414–436. [\[CrossRef\]](#)
- Medved, I.; Černý, R. Surface diffusion in porous media: A critical review. *Microporous Mesoporous Solids* **2011**, *142*, 405–422. [\[CrossRef\]](#)
- Kapoor, A.; Yang, R.T.; Wong, C. Surface diffusion. *Catal. Rev. Sci. Eng.* **1989**, *31*, 129–214. [\[CrossRef\]](#)
- Arena, M.V.; Deckert, A.A.; George, S.M. Coverage-dependent surface diffusion expected from a multiple-site hopping model. *Surf. Sci.* **1991**, *241*, 369–377. [\[CrossRef\]](#)
- Sitarski, M.; Popielawski, J. On the kinetic theory of diffusion, self-diffusion and thermal diffusion in adsorbed gases. *Mol. Phys.* **1970**, *19*, 741–743. [\[CrossRef\]](#)
- Lee, C.S.; O’Connell, J.P. Statistical mechanics of partially-mobile adsorption of gases on homogeneous solid surfaces. *J. Colloid Interface Sci.* **1972**, *41*, 415–429. [\[CrossRef\]](#)
- MacElroy, J.M.D.; Raghavan, K. Transport of an adsorbing vapour in a model silica system. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 1971–1987. [\[CrossRef\]](#)
- Sonwane, C.G.; Li, Q. Structure and transport properties of nanostructured materials. *J. Phys. Chem. B* **2005**, *109*, 5691–5699. [\[CrossRef\]](#)
- Horiguchi, Y.; Hudgins, R.R.; Silveston, P.L. Effect of surface heterogeneity on surface diffusion in microporous solids. *Can. J. Chem. Eng.* **1971**, *49*, 76–87. [\[CrossRef\]](#)
- Ho, F.-G.; Strieder, W. A variational calculation of the effective surface diffusion coefficient and tortuosity. *Chem. Engng Sci.* **1981**, *36*, 253–258. [\[CrossRef\]](#)
- Wernert, V.; Nguyen, K.L.; Levitz, P.; Coasne, B.; Denoyel, R. Impact of surface diffusion on transport through porous materials. *J. Chromatogr. A* **2022**, *1665*, 462823. [\[CrossRef\]](#)
- Havlin, S.; Ben-Avraham, D. Diffusion in disordered media. *Adv. Phys.* **1987**, *36*, 695–798. [\[CrossRef\]](#)
- Limoge, Y.; Bocquet, J.L. Temperature behaviour of tracer diffusion in amorphous materials: A random walk approach. *Phys. Rev. Lett.* **1990**, *65*, 60–62. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bulnes, F.M.; Pereyra, V.; Riccardo, J.L.; Zgrablich, G. Effects of the heterogeneous energetic topography on the collective motion of adsorbed particles. *J. Chem. Phys.* **1999**, *111*, 5181–5190. [\[CrossRef\]](#)
- Mayagoitia, V.; Rojas, F.; Riccardo, J.L.; Pereyra, V.D.; Zgrablich, G. Dual site-bond description of heterogeneous surfaces. *Phys. Rev. B* **1990**, *41*, 7150–7155. [\[CrossRef\]](#)
- Argyris, P.; Milchev, A.; Pereyra, V.; Kehr, K.W. Dependence of the diffusion coefficient on the energy distribution of random barriers. *Phys. Rev. E* **1995**, *52*, 3623–3631. [\[CrossRef\]](#)
- Ambegaokar, V.; Halperin, B.I.; Langer, J.S. Hopping conductivity in disordered systems. *Phys. Rev. B* **1971**, *4*, 2615–2620. [\[CrossRef\]](#)
- MacElroy, J.M.D.; Raghavan, K. Adsorption and diffusion of a Lennard-Jones vapor in microporous silica. *J. Chem. Phys.* **1990**, *93*, 2068–2079. [\[CrossRef\]](#)
- Zalc, J.M.; Reyes, S.C.; Iglesia, E. Monte-Carlo simulations of surface and gas phase diffusion in complex porous structures. *Chem. Eng. Sci.* **2003**, *58*, 4605–4617. [\[CrossRef\]](#)

30. Olivares, C.; Aarão Reis, F.D.A. Interplay of adsorption and surface mobility in tracer diffusion in porous media. *Phys. Rev. E* **2019**, *100*, 022120. [[CrossRef](#)]
31. Zalc, J.M.; Reyes, S.C.; Iglesia, E. The effects of diffusion mechanism and void structure on transport rates and tortuosity factors in complex porous solids. *Chem. Eng. Sci.* **2004**, *59*, 2947–2960. [[CrossRef](#)]
32. Wolf, J.R.; Streider, W. Surface and void tortuosities for a random fiber bed: Overlapping, parallel cylinders of several radii. *J. Membr. Sci.* **1990**, *49*, 103–115. [[CrossRef](#)]
33. Bell, W.K.; Brown, L.F. Interactions between a mobile adsorbed phase and diffusing gases in porous media—an experimental study. *J. Chem. Phys.* **1973**, *59*, 3566–3575. [[CrossRef](#)]
34. Bell, W.K.; Brown, L.F. Kinetic theory approach to simultaneous gas and surface diffusion in capillaries. *J. Chem. Phys.* **1974**, *61*, 609–618. [[CrossRef](#)]
35. Mirbagheri, M.; Hill, R.J. Diffusion in sphere and spherical-cavity arrays with interacting gas and surface phases. *Chem. Eng. Sci.* **2017**, *160*, 419–427. [[CrossRef](#)]
36. Albaalbaki, B.; Hill, R.J. On molecular diffusion in nanostructured porous media: Interfacial exchange kinetics and surface diffusion. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **2012**, *468*, 3100. [[CrossRef](#)]
37. Mirbagheri, M.; Hill, R.J. Diffusion in randomly overlapping parallel pore and fiber networks: How pore geometry and surface mobility impact membrane selectivity. *Ind. Eng. Chem. Res.* **2017**, *56*, 4517–4526. [[CrossRef](#)]
38. Riccardo, J.L.; Steele, W.A. Molecular dynamics study of tracer diffusion of argon adsorbed on amorphous surfaces. *J. Chem. Phys.* **1996**, *105*, 9674–9685. [[CrossRef](#)]
39. Avnir, D. *The Fractal Approach to Heterogeneous Chemistry: Surfaces, Colloids, Polymers*; John Wiley & Sons Ltd.: Chichester, UK, 1989.
40. Rigby, S.P. A model for the surface diffusion of molecules on a heterogeneous surface. *Langmuir* **2003**, *19*, 364–376. [[CrossRef](#)]
41. Drain, L.E.; Morrison, J.A. Thermodynamic properties of argon adsorbed on rutile. *Trans. Faraday Soc.* **1952**, *48*, 840–847. [[CrossRef](#)]
42. Rigby, S.P. Predicting surface diffusivities of molecules from equilibrium adsorption isotherms. *Colloids Surf. A* **2005**, *262*, 139–149. [[CrossRef](#)]
43. Sapag, K.; Bulnes, F.; Riccardo, J.L.; Pereyra, V.; Zgrablich, G. Tracer diffusion on correlated heterogeneous surfaces. *Langmuir* **1993**, *9*, 2670. [[CrossRef](#)]
44. Sapag, K.; Pereyra, V.; Riccardo, J.L.; Zgrablich, G. Temperature behavior of tracer diffusion on heterogeneous surfaces. *Surf. Sci.* **1993**, *295*, 433–444. [[CrossRef](#)]
45. Bulnes, F.; Sapag, K.; Riccardo, J.L.; Pereyra, V.; Zgrablich, G. Simulation of tracer diffusion on heterogeneous energy surfaces. *J. Phys. Condens. Matter* **1993**, *5*, A223. [[CrossRef](#)]
46. Bakaev, V.A.; Steele, W.A. Grand canonical ensemble computer simulation of adsorption of argon on a heterogeneous surface. *Langmuir* **1992**, *8*, 148–154. [[CrossRef](#)]
47. Rigby, S.P. NMR and modelling studies of structural heterogeneity over several lengthscales in amorphous catalyst pellets. *Catal. Today* **1999**, *53*, 207–223. [[CrossRef](#)]
48. Rigby, S.P. Chapter 4—A Unified Model for the Effects of Surface Heterogeneity on Gas Absorption and Surface Diffusion on Silica Surfaces. In *Colloid and Surface Research Trends*; Fong, P., Ed.; Nova Scientific Publishers: Hauppauge, NY, USA, 2007; pp. 147–167.
49. Rigby, S.P. Chapter 13: NMR and Complementary Approaches to Establishing Structure–Transport Relationships in Disordered Porous Solids. In *Diffusion NMR of Confined Systems: Fluid Transport in Porous Solids and Heterogeneous Materials*; Valiullin, R., Ed.; Royal Society of Chemistry: London, UK, 2019; pp. 435–463.
50. Barrer, R.M.; Gabor, F.R.S.; Gabor, T. A comparative structural study of cracking catalyst, porous glass, and carbon plugs by surface and volume flows of gases. *Proc. Roy. Soc. Lon. A* **1959**, *251*, 353–368.
51. Bläckberg, L.; Metsanurk, E.; Tamm, A.; Aabloo, A.; Klintonberg, M. Molecular dynamics study of xenon on amorphous Al₂O₃ surface. *Nucl. Instrum. Methods Phys. Res. A* **2014**, *759*, 10–15. [[CrossRef](#)]
52. Streitz, F.H.; Mintmire, J.W. Electrostatic potentials for metal-oxide surfaces and interfaces. *Phys. Rev. B* **1994**, *50*, 11996. [[CrossRef](#)]
53. Ledesma-Durán, A.; León-Velasco, D.A.; Chacón-Acosta, G.; Juárez-Valencia, L.H. Surface diffusion in narrow channels on curved domains. *Phys. Rev. E* **2023**, *107*, 034801. [[CrossRef](#)]
54. Song, Z.; Dong, Z.; Lu, Z.; Ren, K.; Xie, P.; Wang, J. Construction of a noise Algorithm–Based three-dimensional porous adsorption model of coal and study of coal-oxygen physisorption kinetics. *Microporous Mesoporous Mater.* **2025**, *390*, 113580. [[CrossRef](#)]
55. Zhao, X.; Sang, Q.; Yao, J. Determination of the type of nanoconfined gas transport and quantification of their velocity contributions from molecular perspectives. *Sci. Rep.* **2025**, *15*, 10145. [[CrossRef](#)]
56. Zhou, W.; Zhu, J.; Wang, H.; Kong, D. Transport diffusion behaviours and mechanisms of CO₂/CH₄ in shale nanopores: Insights from molecular dynamics simulations. *Energy Fuels* **2022**, *36*, 11903–11912. [[CrossRef](#)]
57. Di Pino, S.M.; Churio, O.; de la Llave, E.; Sánchez, V.M. Amorphousness matters: Its role on nonpolar gas diffusion at the nanoscale. *Microporous Mesoporous Mater.* **2025**, *388*, 113540. [[CrossRef](#)]

58. Shan, B.; Wang, R.; Guo, Z.; Wang, P. Contribution quantification of nanoscale gas transport in shale based on strongly inhomogeneous kinetic model. *Energy* **2021**, *228*, 120545. [[CrossRef](#)]
59. Hou, P.; Gao, F.; He, J.; Liu, J.; Xue, Y.; Zhang, Z. Shale gas transport mechanisms in inorganic and organic pores based on lattice Boltzmann simulation. *Energy Rep.* **2020**, *6*, 2641–2650. [[CrossRef](#)]
60. Yu, H.; Xu, H.; Fan, J.; Wang, F.; Wu, H. Roughness Factor-Dependent Transport Characteristic of Shale Gas through Amorphous Kerogen Nanopores. *J. Phys. Chem. C* **2020**, *124*, 12752–12765. [[CrossRef](#)]
61. Xu, H.; Xu, L.; Wang, Z.; Wei, F.; Zhang, M. Diffusion-adsorption synergistic mechanism in the adsorption of hierarchical porous carbon for antibiotics removal from water. *Colloids Surf. A* **2025**, *711*, 136327. [[CrossRef](#)]
62. Zheng, J.; Liu, X.; Jin, Y.; Dong, J.; Wang, Q. Effects of surface geometry on advection-diffusion process in rough fractures. *Chem. Eng. J.* **2021**, *414*, 128745. [[CrossRef](#)]
63. Ho, T.H.; Wang, Y. Pore size effect on selective gas transport in shale nanopores. *J. Nat. Gas Sci. Eng.* **2020**, *83*, 103543. [[CrossRef](#)]
64. Hedlund, J.; Nobandegani, M.S.; Yu, L. The origin of the surface barrier in nanoporous materials. *J. Membr. Sci.* **2022**, *641*, 119893. [[CrossRef](#)]
65. Gao, M.; Li, H.; Tian, Y.; Yu, J.; Ye, M.; Liu, Z. Surface Diffusion Barriers and Catalytic Activity Driven by Terminal Groups at Zeolite Catalysts. *ACS Catal.* **2023**, *13*, 11598–11609. [[CrossRef](#)]
66. Do, D.D.; Hu, X. An energy-distributed model for adsorption kinetics in large heterogeneous microporous particles. *Chem. Eng. Sci.* **1993**, *48*, 2119–2127. [[CrossRef](#)]
67. Do, D.D.; Wang, K. Dual diffusion and finite mass exchange model for adsorption kinetics in activated carbon. *AIChE J.* **1998**, *44*, 68–77. [[CrossRef](#)]
68. Wang, K.; Do, D.D. Sorption equilibria and kinetics of hydrocarbons onto activated carbon samples having different micropore size distributions. *Adsorption* **1999**, *5*, 25–37. [[CrossRef](#)]
69. Alexander, P.; Gladden, L.F. A kinetic description of sorbate motion in zeolites using ²H n.m.r. *Zeolites* **1997**, *18*, 38–43. [[CrossRef](#)]
70. Gladden, L.F.; Sousa-Gonçalves, J.A.; Alexander, P. Adsorption and transport of ethane and ethene in zeolite NaA: ²H NMR and Monte-Carlo Lattice Dynamics Studies. *J. Phys. Chem.* **1997**, *101*, 10121–10127. [[CrossRef](#)]
71. Cheah, K.Y.; Alexander, P.; Gladden, L.F. Investigation of coking phenomena in zeolite HY using deuterium NMR. *Appl. Catal. A* **1997**, *148*, 387–403. [[CrossRef](#)]
72. Van Tassel, P.R.; Somers, S.A.; Davis, H.T.; McCormick, A.V. Lattice model and simulation of dynamics of adsorbate motion in zeolites. *Chem. Eng. Sci.* **1994**, *49*, 2979–2989. [[CrossRef](#)]
73. Caravella, A.; Zito, P.F.; Brunetti, A.; Drioli, E.; Barbieri, G. A novel modelling approach to surface and Knudsen multicomponent diffusion through NaY zeolite membranes. *Micropor. Mesopor. Mater.* **2016**, *235*, 87–99. [[CrossRef](#)]
74. Rolle-Kampczyk, U.; Kärger, J.; Caro, J.; Noack, M.; Klobes, P.; Röhl-Köhn, B. PFG NMR Self-Diffusion Study of n-Paraffins Adsorbed on Silica Gel. *J. Colloid Interface Sci.* **1993**, *159*, 366–371. [[CrossRef](#)]
75. Rigby, S.P. Fractal Theory for the Compensation Effect Observed in a Surface Diffusion Process Studied Using Deuteron NMR. *Langmuir* **2002**, *18*, 1613–1618. [[CrossRef](#)]
76. Bond, G.C. Source of the activation energy in heterogeneously catalysed reactions. *Catal. Today* **1993**, *17*, 399–410. [[CrossRef](#)]
77. Gilliland, E.R.; Baddour, R.F.; Perkinson, G.P.; Sladek, K.J. Diffusion on Surfaces. I. Effect of Concentration on the Diffusivity of Physically Adsorbed Gases. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 95–99. [[CrossRef](#)]
78. Haul, R.; Boddenberg, B. *The Porous Structure of Catalysts and Transport Processes in Heterogeneous Catalysts*; Boreskov, G.K., Ed.; Akademiai Kiado: Budapest, Hungary, 1972; pp. 309–321.
79. Spanakos, D.; Rigby, S.P. Predicting Surface Diffusivities of Gas Molecules in Shale. *Energy Fuels* **2020**, *34*, 12417–12428. [[CrossRef](#)]
80. Miyabe, K.; Guiochon, G. Restricted diffusion model for surface diffusion in reversed-phase liquid chromatography. *Anal. Chem.* **2000**, *72*, 1475–1489. [[CrossRef](#)] [[PubMed](#)]
81. Glasstone, S.; Laidler, K.J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, NY, USA, 1984.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.