Heterogeneity of Surfaces and Materials, as Reflected in Multifractal Analysis

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Outline

A large variety of heterogeneous processes take place at solid interfaces. The heterogeneity of surfaces and materials plays a key role in most of those processes. Spatial variations in surface and material properties can result from complex geometries and chemical heterogeneities. To treat quantitatively the effects of complex geometries on specific processes, it is therefore important to characterize the geometrical and topological features associated with most porous solids. Many techniques have been developed for this purpose. Among them the simple gas adsorption technique gives the most information. From the standard nitrogen adsorption isotherms, values such as total pore volume, BET surface area and pore size distribution (PSD) can be obtained. However, more information about the complex structure of surfaces and materials could be obtained by adopting some new approaches or theories. Recent developments in percolation and fractal analysis of adsorption data will be reviewed in this article. The emphasis is placed on the practical application of these theories to obtain measures of the porous structure, and to interpret such results. The difficulties of applying the fractal concepts are also presented. In addition to percolation and fractal analysis, it has been recently realized that in many cases a more detailed characterization of disordered structures can be obtained by applying multifractal scaling analysis (MSA). Some discussion about its development and application to the geometrical characterization of the microstructure of heterogeneous materials is also given in this article. For chemical heterogeneities, the heterogeneous spatial distribution of components or elements in multicomponent materials as well as site residence or adsorption probabilities in catalysts and adsorbents can be described in terms of a fractal measure or multifractal distribution. This will also be reviewed in this article. On the other hand, the realization that many of these sophisticated geometrical structures are fractal-like has provided an appropriate approach to the study of chemical and physical processes taking place in such environments. The applicability of fractal and multifractal analysis to the characterization of heterogeneous processes, in particular, to illustrate the influence of the surface geometry on specific processes, will be given with a focus on heterogeneous catalysis reactions.

1. Introduction

It is well known that heterogeneity of surface and material plays an important role in chemical, physical, and biological processes. For instance, in heterogeneous catalysis, reaction performance depends strongly on the structure and geometry of the environment in which the catalytic process takes place, in particular, the surface defects like steps, holes, and terraces [1,2]. On the other hand, for the adsorption system the surface heterogeneity, which is mainly induced by the complexity of the crystallographical and geometrical structure of many solids and their complex chemical composition, also plays a key role in the adsorption on crystalline solids and noncrystalline, nonporous, and wide-porous solids. Due to its importance great efforts have been made to obtain a better understanding of heterogeneity effects on physical and chemical processes; nevertheless, the problem of how to quantify the heterogeneity is still difficult.

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For heterogeneous catalysis a traditional treatment for this problem is to select an 'ideal' reference shape, and to try to quantify how much the materials studied deviate from that ideal. Quite often, the result is a very cumbersome collection of the many parameters needed for the task [3]. For adsorption of gas on heterogeneous solids, reaching an analytical description of this process is very complex and the resultant equations obtained from proposed models are quite often mathematically unmanageable [4].

In practice most surfaces are both geometrically complex and chemically nonuniform. Real solids have complex microstructures and most materials are to some extent porous. As mentioned above, the macroscopic properties of solid materials are closely connected to their porous microstructure, which is usually characterized by quantities such as density, surface area, porosity, pore size, PSD, and pore geometry and topology. These common terms used to describe the microstructure of a porous material are in fact parameters related to certain macroscopic measurements. Many techniques have been applied to characterize a porous solid. They range from the simple pycnometry, gas adsorption, fluid penetration and calorimetric measurements, to the more recent radiation scattering, xenon NMR, size exclusion chromatography or ultrasonic methods [5]. However, the link between these macroscopic measurements and the microstructure is very complex. Some theories are always adopted to make the connection between a model pore structure and the real solid.

Among these techniques, gas adsorption and mercury penetration are the most popular for the characterization of porous solids. There are commercial equipments suitable for routine use in an industrial environment. Many of them come with standard software that directly prints out numbers for surface area, pore volume and the PSD with an unrealistic number of significant digits.

The data obtained by nitrogen adsorption and mercury porosimetry reflect the bulk behaviour of the pore network as a whole. To extract structural information from such data, a model of the porous network is required. The structure of porous materials is extremely complicated. A realistic description should include both the pore geometry (shape and size distribution) and the pore connectivity (the way different pores are connected). Nevertheless, very simple models are often used to analyze the nitrogen adsorption and mercury porosimetry data. The standard model is the simple ‘parallel tube bundles’ which assumes the pore behave as if they are independent of each other and individually connected to the surface. Most of the pore structure analysis calculations are still based on this simple model despite the fact that it does not predict the experimentally observed percolation threshold and hysteresis behaviors [6], which are best explained by the percolation theory, developed in 1957 by Broadbent and Hammersley [7].

Consequently, percolation analysis has been given considerable attention in recent years. It deals with the transmission of a 'fluid' to a site within a 'medium' against randomly distributed barriers. The height of the barrier determines the probability of moving the fluid from one site to an adjacent one. To apply this theory to nitrogen adsorption and mercury porosimetry data, one must map the adsorption and mercury penetration processes onto a percolation process. Through the percolation analysis, other important structural information on materials such as the connection of pores may be obtained. This is discussed in Section 3.2.1.

Another useful tool to describe the complex structure of most porous solids is the fractal geometry. Adsorption data serve as a convenient tool to determine the fractal dimension of a porous solid [5]. One may also perform pore structure analysis with fractal geometry from which a single scaling exponent characterizes the structure of the materials. In Section 3.2.2, we introduce some concepts about the determination of surface fractal dimension from adsorption data. On the other hand, it was recently found that the geometry of the objects observed in fractal growth phenomena and the pore space distribution in solids may exhibit multifractal properties, i.e., an infinite number of exponents is needed to account for the complicated structure. Some discussion about the application of MSA to the characterization of the microstructure of materials is given in Section 3.2.3.

Owing to the realization that many of these sophisticated geometrical structures are fractal-like, the fractal theory has provided an appropriate approach to the study of chemical and physical processes taking place in such environments. Following the development of the fractal concept, some fractal approaches have been applied to surface science involving adsorption [8–16] and reaction processes. For the former, the main applications include thermodynamics of gas adsorption on fractal surfaces [8], multilayer adsorption phenomena [9–13], and adsorption isotherms on fractal surfaces [14–16]. For the latter, the approaches are mainly concerned with heterogeneous catalysis [17,18]. On applying the fractal approach to those heterogeneous physical and chemical processes, some interesting phenomena were found which seem to require not one but an infinite number of exponents for their description. Such multifractal phenomena reflect the heterogeneity of surface and materials.
and have recently become an extremely active area of investigation.

The main contribution of fractal and multifractal analysis to those heterogeneous phenomena is to provide a more appropriate and convenient method for the quantitative treatment of the effects caused by the complex structure and morphologies on the chemical and physical processes in those environments. For catalysis, beyond extracting a few useful parameters from plentiful data, the fractal approach also allows the development of predictive theories for transport and reaction rates. The main task of using fractal geometries to provide concepts for designing optimal catalytic structures to achieve their best performance has only just begun. Therefore, the remainder of this review (Section 4) is devoted to the fractal and multifractal analysis of heterogeneous phenomena on surfaces and materials with a focus on heterogeneous catalysis. It is certain that this analysis will disclose more information about the high sensitivity of heterogeneous processes to the structure of materials. As more scientists become aware of these techniques, and more data are collected, we may eventually have a consistent understanding of the effects of heterogeneity on heterogeneous processes. In what follows, we first introduce some basic concepts about these new theories.

2. Basic concepts of percolation theory, fractal geometry, and MSA

2.1. Percolation theory

‘Percolation’ means spreading or penetration from one side of the system to another. It represents the simplest model of a disordered system. Percolation processes were formally introduced in the mathematical literature by Broadbent and Hammersley in 1957 [7] when studying the spreading of a hypothetical fluid through a random medium. They also introduced the relevant geometrical and probabilistic ideas. However, the first practical application of percolation theory goes back to Flory [19] and Stockmayer [20] about 50 years ago, when studying the gelation process. They developed a theory of gelation which today is called the percolation theory on a Bethe lattice (or Cayley tree). A Bethe lattice or network is a branching structure with no closed loops.

The present understanding of percolation is the result of a series of significant scientific and engineering developments. The developments of phase transition theory in past years, in particular the series expansion method by Domb [21] and the renormalization group theory by Wilson, Fisher and Kadanoff [22], stimulated a tremendous amount of research activity on the geometric percolation transition. The fractal dimension introduced by Mandelbrot [23] is another powerful new tool, which together with the development of large-scale computers offers a different approach to the intrinsic properties of a percolation system.

Parallel to the developments in fundamental theory, an enormous number of applications have been found for the new approach. Problems from such diverse fields as the porous structure of amorphous materials [24,25], fluid transport in porous media [26], fragmentation of solids [27], kinetics of the gelation process [28], and epidemics and forest fires [29,30] have benefited from percolation research. More recently, percolation theory has been applied to describe the phenomena observed during the preparation of microporous glass membrane, and to interpret the structure dependencies of porosity, surface area, and tortuosity factor [31].

A simple example of percolation phenomena is the electrical conductivity of a composite material made of metal and insulator. If the metallic domains constitute only a small fraction of the system volume, the composite system will be an insulator. However, if the metallic domains comprise a sufficiently large fraction of the system, electricity may be able to flow from one domain to another and the composite system becomes a conductor. When we introduce the volume fraction \( \phi \) of the metallic material as a system variable, an abrupt transition between insulator and conductor will be observed at some critical value of \( \phi \). This transition is associated with the sudden emergence of a connected path for the metallic material. Thus, percolation theory describes how the connectivity of a system affects its macroscopic properties.

To describe the change from insulator to conductor, or other similar process, one may consider a square lattice of linear dimension \( L \), where each bond is occupied randomly with probability \( p_b \) or is empty with probability \( 1 - p_b \). This is called a bond percolation model. The occupancy of bonds may stand for any physical properties, such as open to flow, diffusion and reaction, or connected for conduction. When the network size is large, the probability assignment is equivalent to the random removal of a \( 1 - p_b \) fraction of the bonds.

Two sites are called connected if there exists at least one path between them consisting solely of occupied bonds. A group of connected sites bounded by vacant bonds is called a cluster. If \( p_b \) is small, the size of any connected cluster is likely to be small (see Fig 1a). If \( p_b \)
are occupied with probability $q$, we speak of a site–bond percolation model. Two occupied nearest neighbor sites belong to the same cluster if they are connected by an occupied bond. Such a site–bond model has been applied in the study of sol–gel transformation. Another type of model is the correlated percolation process, where the occupancy probability of a bond or site depends on its environment. The most natural model, perhaps, is a continuum percolation, where the positions of the components in a random binary mixture are not restricted to the discrete sites of a regular lattice. For instance, we can place disks of unit radius at random in a box. Two disks are in the same cluster if they touch or overlap each other. We can again ask what is the minimum density of disks necessary for a connected path to exist.

The percolation threshold $p_c$ plays an essential role in percolation processes. However, several other quantities, including mean cluster-size distribution, mean cluster size, percolation probability, and the correlation length, are also important to the understanding of the percolation process. Among these, the percolation probability $P_\infty(p)$ plays a key role in percolation description of capillary phenomena. It corresponds, for example, to the desorption branch of the nitrogen sorption isotherm and the extrusion curve of mercury porosimetry (see Fig 2). The probability is defined as an occupied site belonging to the

![Fig 2 Behavior of percolation probability as a function of bond occupation probability for finite and infinite systems (the finite size curve is an average over an ensemble of small systems). It should be noted that the curve in finite size is similar to the nitrogen desorption isotherm which is an average over all the particles in the sample.](image-url)
spanning cluster:

\[ P_\infty = \frac{\text{number of sites in the spanning cluster}}{\text{total number of occupied sites}}. \]

For an infinite lattice, \( P_\infty(p) = 0 \) for \( p < p_c \) and is an increasing function of \( p \) for \( p > p_c \). In the language of critical phenomena, \( P_\infty \) is known as the order parameter of the system.

In the above discussion, we only give a brief introduction to percolation theory. However, to understand the information one may obtain from the sorption hysteresis with percolation analysis, some background of percolation theory is needed. The interested reader is advised to consult the references [32] for further reading.

2.2. Fractal geometry

Random processes and disorder structures which are self-similar on certain length and time scales are very common in nature. Owing to the wide occurrence of self-similarity in nature, the scientific interest in this phenomenon is very broad. Some of the basic properties of objects with anomalous dimension were noticed and investigated at the beginning of this century mainly by Hausdorff [33] and Besicovitch [34]. The major achievement in recent years that has increased our understanding of structural disorder and its formation by random processes is the fractal geometry pointed out by Mandelbrot [23]. The knowledge of second order phase transition theory in recent years, in particular the renormalization group theory based on the scale invariance of thermodynamical systems at their critical point, stimulated a tremendous amount of research activity on scaling in growth processes because growing fractals are also scale-invariant objects. A wide range of complex structures occurring in many physical, technological, and biological processes have been shown to be related and described by objects with noninteger (fractal) dimensionality. The key to this progress is the recognition that many objects produced by random processes possess self-similar random structures. (However, unlike the situation in critical phenomena, it is still not certain that a full theory can classify the growing structures into universality classes with a few characteristics.) Recently, it has become evident that multifractal scaling, which is the generalization of simple scaling, represents an important characteristic of many growth phenomena. It is a general belief that fractal growth and chaos are closely related, but the two fields have not been lumped into a unified picture yet. Interest in the properties of fractal growth phenomena has grown considerably in the last few years. Some reviews [35], books [36], and conference proceedings [37] on various aspects of fractal growth and related topics have been published.

Parallel to the developments in fractal growth phenomena, fractal geometry has been also applied to other fields [38]. Among those, much attention has been paid to its application to materials science problems. It is found that fractal geometry has a new possibility as an analytical tool which is suitable for the description of complex structures, such as a geometric irregularity at the surface and the porous structure of solids (see Fig 3). The degree of surface irregularity may be characterized by the fractal dimension, which takes values between two and three. The noninteger fractal dimension is not only pertinent as an operative measure of the surface irregularity, but also useful for studying the porous structure of solids and the

![](https://example.com/fractal_images.png)

**Fig 3** Three classes of fractal surfaces [39]. (a) Surface fractal: a dense object with a fractal surface. (b) Mass fractal: both the object itself and its surface are fractal. (c) Pore fractal: a dense object in which there exists a distribution of holes or pores with a fractal structure
adsorbate–adsorbent interactions. It follows from the present studies that the fractal dimension will be accepted as a standard parameter for characterizing the surface roughness. On the other hand, it has been realized recently that in many cases a more detailed characterization of complex geometries of materials could be achieved with the help of multifractal analysis. Since the intrinsic property of fractal geometry is closely concerned with the heterogeneous effect, it is natural to apply it to heterogeneous phenomena occurring on surfaces and materials, ranging from reaction kinetics, adsorption, and diffusion to other transport phenomena. Various effects of heterogeneous geometry on these processes have been analyzed with fractal geometry. A detailed discussion is given in Section 4.1. In some cases, it is found that certain measures defined on fractal substrates, e.g., reaction probability distribution (RPD) in fractal catalysts, should be interpreted in terms of an infinite hierarchy of exponents, i.e., multifractal scaling is needed to account for the complicated structure of such measures. The MSA has become a useful tool in the study of processes in environments of complex geometry. Some of its basic concepts are given in the next section. In what follows, we first briefly introduce some basic properties of fractal objects. For in-depth reviews of the physical meaning and consequences of fractal dimensions one may refer to the useful monographs mentioned earlier.

As mentioned above, one of the main fields in which fractal geometry is widely applied is the physics of far-from-equilibrium growth phenomena, which are common in many areas of science and technology. Some examples are viscous fingering which is observed when a less viscous fluid is injected into a more viscous one, dendritic solidification in an undercooled medium, and electrodeposition of ions onto an electrode as well as the aggregation phenomena of similar particles in which the process may take place particle by particle or aggregate by aggregate. It is noteworthy that the motion or growth of the interfaces of these processes may be characterized by the spatial distribution of a quantity which satisfies the Laplace

Fig 4 A relatively small fractal cluster consisting of 4000 particles generated on a square lattice according to the algorithm for diffusion-limited aggregation (DLA) model, as first suggested by Witten and Sander [40]. The fractal dimension \( D \) of the DLA cluster is \( 1.72 \pm 0.02 \). The model is an example of how random motion can give rise to beautiful self-similar clusters and has strongly influenced our understanding of the formation of disorder structures by random processes. It has become an important paradigm for far-from-equilibrium pattern formation and provides a basis for understanding a broad range of natural and laboratory phenomena including electrodeposition, crystal growth, viscous fingering and bacterial colonies. A very recent review of progress in the simulation and quantitative characterization of DLA clusters is [41].

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equation with moving boundary condition. They may generate growing patterns possessing a rather special kind of geometrical complexity with an open branching structure (see Fig 4). Such a cluster displays some common features of fractal objects. One of them is that it is self-similar (scale invariant) in a statistical sense (i.e. objects look the same on many different scales of observation). Another typical property of fractals is that they obey the following simple scaling relation:

\[
\text{number of features} \propto (\text{resolution of measurement})^D
\]

(1)

where \(D\) is the fractal dimension of the object. One example is the volume \(V(L)\) of the region bounded by the interface scales with the increasing linear size \(L\) of the fractal object. It is noteworthy that for fractals observed in physical phenomena the above scaling holds only for length scales between a lower and an upper cutoff. A lower cutoff length is provided by a microscopic distance such as a lattice spacing or the linear size of one particle in the aggregate. On the other hand, an upper cutoff length is usually provided by the finite system linear size. The presence of these cutoffs complicates the estimation of the fractal dimension.

The fractal dimension value of the object is closely related with the property of nontrivial self-similarity. This can be seen from the fact that the object occupies a negligible volume in the \(d\) dimensional embedding space since \(D < d\). For growing fractals \(V(L)/L^d \rightarrow 0\) as \(L \rightarrow \infty\) implies that the structure must possess large empty regions (holes) with diameter comparable to its actual linear size \(L\). The presence of holes on every length scale is the origin of nontrivial scale invariance.

The DLA cluster shown in Fig 4 is an example of a random or statistical fractal since the scaling relation is satisfied only “on the average”, i.e., the scaling relation is averaged over many clusters and different origins in the cluster. Another type of fractal is called nonrandom fractal (or mathematical fractal), an

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**Fig 5** Two examples of nonrandom fractals. (a) Demonstrates how one can generate a Koch curve by subsequent divisions of the original triangular bump. In (b) the growing Sierpinski gasket is constructed using an iteration procedure. In the \(k \rightarrow \infty\) limit the fractal shown in (b) becomes infinitely large, while the details of (a) become so fine that the picture can no longer be seen. Obviously, it is (b) which better approximates a real growth process. The fractal dimensions for (a) and (b) are given as \(\log 4/\log 3 \approx 1.2619\) and \(\log 3/\log 2 \approx 1.58\), respectively.
object which is self-similar on all length scales. Two examples are shown in Fig 5. Note that fractals in physics belong to the first category.

2.3. Multifractal scaling analysis

It is well known that the behavior of a system is frequently determined by the spatial distribution of a scalar quantity, e.g. electric potential, concentration, and probability. On the other hand, it is found that the distributions over fractals are quite different from those in ordinary Euclidean objects. In a Euclidean space or lattice, this distribution function and its derivatives are essentially smooth, and they usually contain no singularities, where the word ‘singular’ corresponds to a local power law behavior of the function. However, the measures associated with physical events occurring on the fractals may lead to a spatial distribution which possesses infinitely many singularities. The development of a formalism for the description of such situations, therefore, needs infinitely many dimension-type exponents to characterize these distributions, as was first recognized by Mandelbrot [42] in turbulence. This idea was later developed further by Hentschel and Procaccia [43], Benzi et al. [44], and Halsey et al. [45].

As an example, consider the growth probability distribution (GPD) of DLA. In a DLA simulation, one obtains the growth probabilities \( p_i \) by stopping at a given growth stage, and then sending many random walkers. Whenever a walker touches the aggregate, one increases a counter at that perimeter site by one, without letting the walker stick (the walker is then removed). Repeating this with many walkers yields the GPD with the normalized number of contacts regarded as the growth probability. The main disadvantage of this method is that it can only be used to obtain information in the regions where the measure is large enough. Places related to small growth probability are not visited by a sufficient number of walkers and the statistics is poor, fluctuates widely, and seems to be size dependent. More accurate data could be obtained by solving the Laplace equation direction [46]. The resulting measure is called the harmonic measure. The GPD is a very complex function changing rapidly in space due to screening. It is very different on the tips and inside the fjords. When we approach a tip in the outer region of the cluster, the growth probability sharply increases since a tip captures the diffusing particles with a large probability. On the other hand, when we get into a deep fjord which is almost completely screened by the surrounding branches, the growth probability is nearly equal to zero. Since an infinite number of tips is associated with a DLA cluster, it possesses infinitely many singularities of the growth probability. Moreover, tips at different positions generally have different local environments (configuration of the object in the region surrounding the given tip) which affect the strength of the singularity associated with that position. The above discussed distributions defined on a fractal substrate are called fractal measures. In general, a fractal measure possesses an infinite number of singularities of infinitely many types, i.e., a multifractal structure. However, it should be noted that it is not necessary to have a fractal structure to find multifractal phenomena [47]. There are further examples, such as turbulence, viscous fingering, voltage distribution in random resistor networks, reaction and adsorption probability distribution at interfaces, leading to distributions with an infinite number of singularities. Among these, the last will be discussed in Section 4.2.

In order to perform a multifractal analysis, we shall assume the measure is normalized so that its total amount on the fractal is equal to 1. Then, the fractal measure can be regarded as a probability distribution. The fractal substrate is divided into boxes of linear size \( r \) (note that \( r \propto 1/L \), where \( L \) is the linear size of the fractal object) and the probability associated with each box is measured. In the limit of small \( r \) values, the following scaling assumption is used:

\[
P_i(r) \sim r^{\alpha_i},
\]

where \( P_i \) denotes the probability at box \( i \). The physical meaning of the assumption of equation (2) is that in the local region \( i \), the probability scales with the size of that region, with a local exponent \( \alpha_i \). The exponent \( \alpha_i \) can take on a range of values depending on the given region of the measure and corresponds to the strength of the local singularity of the measure. Although \( \alpha \) depends on the position on the fractal, there are usually many boxes with the same exponent \( \alpha \). In general, the number \( n(\alpha)d\alpha \) of region \( i \) that obey equation (2) with an \( \alpha \) value in the interval \( [\alpha, \alpha + d\alpha] \) scales with \( r \) as

\[
n(\alpha)d\alpha \sim r^{-f(\alpha)}.
\]

Exponent \( f(\alpha) \) has been interpreted as the fractal dimension of the subset of boxes characterized with an \( \alpha \) in the interval \( [\alpha, \alpha + d\alpha] \) (the term multifractality, therefore, implies that points corresponding to a given type of singularity typically form a fractal subset whose dimension depends on the type of singularity [45,47,48]). However, this may be inconsistent with the fact that \( f(\alpha) \) can take on negative values [49].
The exponents $\alpha$ and $f(\alpha)$ are the characteristic scaling exponents for the fractal measures.

In principle, $\alpha$ and $f(\alpha)$ can be calculated directly from equations (2) and (3), but it is difficult to correctly estimate these two values [50]. To overcome these difficulties, Halsey et al. [45] suggested that it is useful to introduce a few quantities which are more directly related to a measurable property of the probability distribution in order to calculate the function $f(\alpha)$. Then, relations among these quantities and $f(\alpha)$ make it possible to obtain a complete description of a fractal measure.

For a given probability distribution, the $f(\alpha)$ might be related to the $q$th-order moments $M_q$ and to their scaling exponents $\tau_q$ defined as

$$M_q = \sum_i P_i^q = \sum_p n(P) P^q \sim \tau(q),$$  \hspace{1cm} (4)

where $n(P)$ is the number of boxes with probability $P$. In equation (4), as $q$ is varied, different subsets possessing different $P_i$ values and thus with different scaling exponents would become dominating in the sum. The logarithm of the maximum will provide a good approximation of the logarithm of the sum if the plot $n(P) P^q$ against $P$ shows a sharp peak. Then, for each value of $q$, the sum may be replaced by the element that takes the maximum value. According to the above arguments, $\alpha$ and $f(\alpha)$ can be expressed as functions of more practically measurable properties of the probability distribution as follows.

Firstly, substitution of equations (2) and (3) into equation (4) and, as an approximation, replacing the logarithm of the sum by the logarithm of the maximum element yields

$$\tau(q) = q\alpha(q) - f(\alpha).$$  \hspace{1cm} (5)

It is noteworthy that according to this approximation, exponent $\alpha$ can be determined in terms of $q$. Then, the value of $\alpha(q)$ that dominates equation (4) is given by the extremal condition

$$\frac{d}{d\alpha} [q\alpha(q) - f(\alpha)] = 0,$$  \hspace{1cm} (6)

so

$$q = f'(\alpha),$$  \hspace{1cm} (7)

$$f''(\alpha) < 0.$$  \hspace{1cm} (8)

It follows from equations (5) and (7) that

$$\frac{d}{dq} [\tau(q)] = \alpha(q).$$  \hspace{1cm} (9)

Equation (5) thus implies that $f(\alpha)$ is the Legendre transform of $\tau(q)$ and some analogies between multifractal functions and thermodynamics are given as: $q$ vs $1/kT$, $\tau(q)$ vs free energy, $\alpha$ vs internal energy, and $f(\alpha)$ vs entropy. Indeed, the function $\tau(q)$ has many properties which are similar to free energy. For example, it is a convex function of its argument and can even display a singularity or phase transition [51]. However, contrary to most critical phenomena problems in which the exponents describing moments of distribution functions are linear in their arguments, the multifractal behavior exhibits a nonlinear relation between $\tau(q)$ and $q$ [47]. From equation (4), one can express equation (9) as a function of the measured probabilities,

$$\alpha(q) = \frac{d}{dq} [\tau(q)] = \frac{\sum_i P_i^q \ln(P_i)}{\sum_i P_i^q \ln(r)}.$$  \hspace{1cm} (10)

In practice, the quantities $\tau(q)$, $\alpha(q)$ and $f(\alpha)$ might be computed as follows. Using an appropriate normalization of the observable quantities, the probability distribution is determined. Then for each $L$, $\tau(q)$ was calculated from equation (4). $\alpha(q)$ was then computed from equation (10). Having $\tau$ and $\alpha$, one can compute the $f(\alpha)$ from equation (5). The calculated results of $\tau(q)$, $\alpha(q)$ and $f(\alpha)$ are presented through two types of plots: $\tau$ vs $q$ and $f$ vs $\alpha(q)$. The analysis of these plots can yield information about the fractal measures.

The distribution of the measure $P_i$ is called multifractal if all of these moments (equation (4)) scale as power laws, with an infinite set of independent exponents $\tau(q)$. For $q = 0$, equation (4) reduces to the number of boxes which have a nonzero measure. If every box has a finite measure, $M_0$ coincides with $N$ (total amount of fractal objects), hence $\tau(0) = -D$. Also, the normalization $\sum_i P_i = 1$ requires that $\tau(1) = 0$. For a homogeneous distribution, $P_i = 1/N$ and $\tau(q) = D(q - 1)$, the $\tau(q) - q$ curve becomes linear (the slope is $D$) and then $f = \alpha = D$, i.e., $D$ is also the fractal dimension of all the subsets. Another linear relationship between $\tau$ and $q$ can also be held under the uniform distribution conditions, $P_i = 1/C > 1/N$, where $C$ is the number of sites having nonzero probabilities. In this case, the slope is smaller than the $D$ value, the fractal dimension of the fractal object. According to the above argument, it is useful to define $D_q$ via

$$\tau(q) = D_q(q - 1).$$  \hspace{1cm} (11)

$D_q$ is the so-called order $q$ generalized dimension and is larger than zero for all $q$. It can be shown that the $D_q$
values monotonically decrease with growing \( q \) and are not fractal dimensions. For a multifractal behavior, \( D_q \) exhibits a nontrivial dependence on \( q \).

Since \( 0 \leq P_i \leq 1 \), it is clear that \( M_q \) decreases with \( q \), and therefore \( \tau(q) \) increases with \( q \) (note \( r < 1 \)). From equation (7) it follows that \( f(\alpha) \) has a maximum at \( q = 0 \). At that point, \( f(0) = -\tau(0) = D \). This can also be interpreted as the fact that a fractal cannot include any self-similar subset with fractal dimension larger than its own dimension. Thus \( f \) has the general shape described as follows: it grows for \( \alpha < \alpha(0) \) \((q > 0)\), reaches a maximum at \( q = 0 \), and decreases for \( \alpha > \alpha(0) \) \((q < 0)\). On the other hand, the value of \( P(q = 1) \) that dominates the sum in equation (4) is associated with the value of \( \alpha(q = 1) \) that makes the scaling exponent \( \tau(q = 1) \) smallest (note that \( r < 1 \)). Then \( \alpha_1 = \alpha(q = 1) \) is defined by \( df/d\alpha = 1 \).

We identify

\[
f(\alpha_1) = \alpha_1, \quad \left. \frac{df}{d\alpha} \right|_{\alpha_1} = 1,
\]

(12) and conclude that \( f(\alpha) \leq \alpha \), with equality only at \( \alpha_1 \), i.e., the curve of \( f(\alpha) - \alpha \) is below the line \( f(\alpha) = \alpha \) and is tangential to it at \( \alpha = \alpha_1 \). A general shape of the \( f(\alpha) - \alpha \) curve is demonstrated in Fig 6. Finally, we make a few remarks concerning the order \( q = 1 \) generalized dimension

\[
D_1 = a_1 = f(\alpha_1).
\]

(13) According to equation (10), one gets

\[
\sum_i P_i \ln P_i \sim D_1 \ln r.
\]

(14) \( D_1 \) tells us how the information on the distribution increases as the size of the boxes \( r \) decreases. This is why \( D_1 \) is called the information dimension.

The multifractal formalism has been successful in describing many phenomena of current interest to physicists and chemists ranging from turbulence [52], onset of chaos [53], fracture [54], and current distribution of percolation clusters [55] of GPD of DLA (for computer simulations and theoretical studies see [45,46,48,51,56]). Very recently, this approach has been applied to investigate the effects of fractal geometry on the heterogeneous catalysis processes. A more detailed description is given in Section 4.2.1. On the other hand, some effort has also been made in its application to the geometrical characterization of the microstructure of disordered heterogeneous materials. However, some warnings have been given concerning its applicability to real systems [57]. One difficulty is accurately obtaining the negative moments of the measures, which are dominated by the small probabilities. Since these rare measures are often missed in the counting process, large fluctuations are frequently observed for \( q < 0 \). On the other hand, they are often obtained by averaging over many fractals: thus, a numerical simulation may yield different results depending on the average used. Moreover, the assumption, used in multifractal formalism, that all the probabilities scale as powers of the size may be wrong for very small probabilities. Therefore, the behavior of \( f(\alpha) \) for large \( \alpha \) and \( \tau(q) \) for \( q < 0 \), which depend critically on the size dependence of these rare measures, should be interpreted with great care.

3. Characterization of solids

3.1. Basic concepts and properties used to describe surfaces and materials

Most real solids have a porous structure and are heterogeneous in nature. The porous structure of real solids is complex and may exhibit a wide range of pore dimensions from the micropore (<2 nm) to the mesopore (2–50 nm) and macropore (>50 nm). On the other hand, the heterogeneity of many solids comes from the complexity of crystallographical, geometrical structure and chemical composition. According to Jaroniec and Madey [58], the heterogeneities of solids might be roughly divided into three groups: surface, structural and energetic heterogeneity. The surface heterogeneity may be induced from some sources, such as different types of crystal planes, crystal edges and corners, various atoms and functional
groups exposed at the surface, irregularity structure of a surface, and impurities strongly bounded with the surface [58]. It generally occurs on crystalline solids and noncrystalline, nonporous, mesoporous and macroporous solids. On the other hand, the structural heterogeneity is encountered in microporous solids which contain micropores of different dimensions and forms (i.e., the distribution of micropore). As for energetic heterogeneity, it implies that energy is different at various points of the surface and can be represented by an energy distribution function, which characterizes a global energetic heterogeneity of solids but gives no information about the source of this heterogeneity or the arrangement of the active sites on the surface. In addition to those three types of heterogeneity, however, there is another disorder property existing in solids. The nonuniform micro-distribution of compositions or elements is quite often encountered in multicomponent solids and this may be defined as another type of heterogeneity. In principle, these four types of heterogeneity of solids might be lumped into two classes: geometrical and chemical heterogeneities. Although the two types of heterogeneity have some correlation, it is difficult to find a quantitative relationship between them and distinguishing one from the other may be purely conceptual. However, it is now realized that some new approaches may be employed to qualitatively or quantitatively identify those disorder properties of solids separately. Among these, percolation theory, fractal geometry and MSA will be discussed in this section.

General use of materials in science and technology requires the characterization of their physical and chemical properties. The physical properties used to describe a solid involve crystal and geometrical structure, surface properties and also their mechanical properties such as strength, compressibility, and shape and size distribution of the particles. Among these, the porosity (total pore volume), surface area and PSD are the most basic quantities to specify a porous material. The total pore volume of a solid is usually determined by the mercury-helium method. For solids with micropore, the micropore volume may be determined from the saturated adsorption amount using the simple Gurvitch rule [59] (assuming the pores are filled with liquids).

The common method for measuring surface area is based on the famous BET equation and utilizes the low-temperature nitrogen adsorption isotherm. The accuracy of surface measurement depends on several factors. Accurate adsorption data are essential. The correctness of the BET equation for the solid at hand is another factor. Basically, sorption occurs on the surface of nonporous solids, the surface of macropores and mesopores, and in the volume of the micropore. Therefore, for nonporous solids and for solids with large pores, the specific surface area has a real physical meaning. On the other hand, microporous solids may not follow the BET theory completely and the macroscopic concept of specific surface area loses physical meaning for such solids. Finally, for work with solids having a relatively low specific surface area (say <2 m² g⁻¹), krypton adsorption (at 77 K) should be adopted to reduce the uncertainty.

In characterizing the PSD, mercury porosimetry is recommended for determining the size distribution of macropore (see Fig 7), and nitrogen desorption for mesopores (see Fig 8). For still smaller pores, it is necessary to employ a range of probe molecules to obtain a reliable assessment of the size distribution of micropores. The distinction between the sizes of the admitted molecules and those not admitted has been termed the molecular sieving effect. The techniques of obtaining PSD from nitrogen adsorption and mercury porosimetry have been discussed in detail by others [60]. PSD determined from the nitrogen isotherm has many calculation schemes, most of which are based on variants of the Kelvin equation [61–64]. Some detailed and easy-to-follow calculation procedures can be found in [60,65]. More recently, density functional theory and statistical calculation [66,67] have been developed to better estimate the PSD. Although the PSD can be calculated using standard procedures, one must be aware of the assumptions behind these

![Figure 7: A schematic representation of typical mercury porosimetry data including intrusion and extrusion curves. Some mercury is retained after the initial extrusion cycle.](image-url)
3.2. More information about the complex structure of surfaces and materials

3.2.1. Sorption hysteresis and connection of pores: percolation analysis

PSD is just one of the characteristics that we can extract from the nitrogen adsorption isotherms or mercury penetration curves. It is also possible to acquire some structural information on the pore network (the way pores are connected) from the nitrogen sorption and mercury porosimetry data, particularly from the hysteresis of the isotherms or the penetration curves. As mentioned earlier, the natural language to describe phenomena related to the structure of the pore network is the percolation theory. Extensive effects based on percolation theory have been made to explain the hysteresis behavior observed in sorption and penetration experiments.

It is known that nitrogen does not condense in the network of macropores during the adsorption process. Therefore, the nitrogen adsorption isotherm gives only structural information about the network of micropores and mesopores. Mercury penetration curves are needed to obtain structural information about the macropore network. However, the percolation description of nitrogen sorption hysteresis is equivalent, from a mathematical point of view, to that of mercury penetration curves. We will therefore limit our discussion to the treatment of nitrogen adsorption data, with the understanding that all arguments apply equally well to mercury penetration curves. For more discussion of mercury porosimetry, readers are referred to [68–70].

A typical nitrogen adsorption isotherm is shown in Fig 8. The process in which the pressure increases from zero to its maximum value is called a primary adsorption process, and the isotherm generated by this process is called the adsorption boundary curve. Similarly, the process in which the pressure is decreased from its maximum value to zero is called the primary desorption process, and the isotherm generated is the desorption boundary curve.

Secondary desorption occurs if the previous adsorption step is terminated at a pressure lower than the maximum, so that nitrogen has not yet condensed in some of the pores (i.e., a pressure where the adsorption boundary curve is still increasing). The corresponding desorption isotherm, indicated in Fig 8, has been known as a desorption scanning curve. The difference between the desorption boundary curve and the scanning curve comes from the initial presence of vapor-filled pores in the secondary desorption process. Similarly, a secondary (scanning) adsorption refers to a process of gradually increasing

calculations. Otherwise, one may be misled by the seemingly 'direct' results. For example, the nitrogen adsorption technique only works for materials with large enough surface area. This technique may give a fictitious result if the amount adsorbed is not large enough.

Structural parameters mentioned above (total pore volume, BET surface area, and PSD) are essential to describe the structure of a material. However, a more realistic description should take into consideration both the geometry (shape and size) and the topology of the porous network, although we know that neither the pore shape nor the pore size will be uniform throughout the solid and the topology of pore connection is even more difficult to express quantitatively. In developing a theoretical model, simple shapes, such as slits, cylinders, spheres, prisms, cavities and windows, are often assumed. It is understood that none of them truly describes a real solid, but may be more suitable than the others for the solid at hand.

Since the pore space distribution exhibits spatial variations, one way to better treat it is based on the concept of multifractal scaling. Very recently, this new method has been employed to characterize the microstructure of some sedimentary rocks. The relationship between the multifractal characteristics of the rock pore space and its transport properties is then established. On the other hand, percolation theory describes how the connectivity of a system affects its macroscopic properties; it is thus a natural language to describe the hysteresis behavior observed in nitrogen isotherms and is a useful tool to offer a qualitative description of the pore network of solids.

In addition to the structural heterogeneities of pore, the surface irregularity and nonuniform chemical distribution over solids are also important quantities for characterizing the heterogeneity of adsorbents and catalysts. As mentioned earlier, the degree of surface irregularity may be characterized by the fractal geometry with noninteger dimensions taking values between two and three. As for the chemical heterogeneity, which represents the spatial distribution of compositions or energy being different at various points of the solids, one appropriate way to describe it is in terms of multifractal distribution, which requires not one but an infinite number of fractal dimensions for their description. This is given in Sections 3.2.3 and 4.2.2, respectively.

In what follows, we review these new approaches to see how they can provide more information about the heterogeneous properties of solids.
pressure that starts from any point on the primary desorption isotherm.

On the adsorption process, pore condensation happens when the pressure is above the value prescribed by the Kelvin equation. Pore condensation is a first-order phase transition, where the density of the pore fluid changes abruptly. However, condensation occurs only in pores above a critical size. In pores smaller than the critical size, the first-order phase transition disappears and pores fill rapidly, but con-

tinuously, with nitrogen at a ‘filling pressure’. This is frequently observed in the sorption of vapors in zeolites, and is called a micropore pore filling process. The isotherm generated by such a process is classified as type I isotherm.

In some cases, a type I isotherm is nearly horizontal above the filling pressure. This suggests that essentially all the micropores have already been filled by nitrogen at this point. The small positive slope beyond the filling pressure can be attributed to the compressibility of the condensed pore fluid. If, on the other hand, a positive slope persists even close to the normal saturation pressure of nitrogen, one would conclude that capillary condensation is still occurring in large mesopores at this pressure. This would suggest that there may be still larger pores in which nitrogen has not condensed.

During the primary desorption process, the liquid-like pore fluid vaporizes from the pores. Initially, vaporization happens only in pores connected to the surface of the solid. This may result in a linear decrease of the desorption isotherm. However, the decompression of the pore liquid may also result in an almost linear decrease of sorption amount. It is difficult to separate one effect from the other.

As a rule, the desorption isotherm does not retrace the adsorption one but rather lies above it over a range of relative pressures, forming a hysteresis loop, before eventually rejoining the adsorption isotherm. The International Union of Pure and Applied Chemistry (IUPAC) has classified the various

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Fig 8 Typical nitrogen sorption isotherms including (A) adsorption boundary curve, (D) desorption boundary curve, (B) desorption scanning curve and (C) secondary (scanning) adsorption curve

Fig 9 The IUPAC hysteresis loop classification
Fig 10 Schematic sorption isotherm for a single pore [75]

hysteresis loops that are observed experimentally as types H1, H2, H3 and H4 (see Fig 9).

The observed hysteresis may be the result of two basic mechanisms. Firstly, it was found that even in a single idealized pore a metastable phase may persist beyond the vapor–liquid coexistence pressure during the adsorption and desorption processes [71–74]. This is an intrinsic property of the phase transition, where a vapor phase may be present at pressures above the condensation, and a liquid phase below the condensation pressure. The extent to which the metastable phase persists depends on the nucleation rate of the stable phase. This is called the ‘single-pore’ mechanism for the hysteresis behavior (see Fig 10).

The second mechanism is related to the topology of the pore network. One simple example which clearly exhibits the effects of the connectivity of pore on the hysteresis is demonstrated in Fig 11. During the adsorption process, pore condensation happens anywhere in the pore network, as long as the pressure is above the local Kelvin pressure. The vapors needed to fill the pore can be transported either through the liquid or through the vapor phases. However, during the desorption process, the desorbed vapors must be transported to the outside through the vapor phase. Vaporization therefore occurs only in pores connected to the bulk vapor phase, not in pores surrounded by other liquid-filled pores. Once vaporization has occurred in some of the pores near the external surface, the adjacent pores now have contact with the vapor phase, and will vaporize when it becomes thermodynamically favorable, i.e., when the pressure falls below the condensation pressure for that particular pore size. In such a way, clusters of vapor-filled pores grow from the surface until enough pores are open so that a large cluster that spans the solids is formed. The growing of clusters is exactly what the percolation theory is concerned with. The transition point from finite size clusters to a spanning cluster corresponds to the ‘knee’ of the desorption isotherm identified in Fig 8. Once a spanning cluster is formed, there is a rapid increase in the slope at which desorption occurs, until most of the pores have access to the vapor phase and the hysteresis loop closes. Accordingly, the structure of the pore network (its connectivity and accessibility), while irrelevant for adsorption, is very critical in the desorption processes. A more detailed schematic illustration of the role of the connectivity of the pore network in the nitrogen desorption process is shown in Fig 12 for the two-dimensional case.

The first direct observation of percolating transition during desorption was made very recently by Page et al. [78]. They detected the formation of a spanning cluster exactly at the knee of the desorption isotherm by ultrasonic attenuation and light scattering measurements. The fractal dimension of 2.6 was determined for this spanning cluster.

The relative contributions of the single-pore and
network effect to the hysteresis loop are difficult to ascertain, and certainly vary from one solid to another. Nevertheless, it is noted that pore blocking effects may lead to hysteresis even in the absence of nucleation kinetic effects [79]. The effect of pore blocking should also increase with a broad pore size distribution. Ball and Evans [74,80] have compared the shape of the hysteresis loops generated by different mechanisms, and have concluded that the network mechanism is likely to be more important, unless the PSD is very uniform. By comparison between the predicted and experimental scanning curves, Liu et al. [75] suggested that the pore blocking (network) effect dominates when few of the pores have access to the vapor phase, but the single-pore contribution becomes important when most of the pores have access to the vapor phase.

It is known that both the size of the network and the degree of interconnection between the pores affect the extent and shape of the hysteresis loop [75–77,81–84]. For porous solids possessing bidispersed structure, the sharpness of the desorption isotherm knee is a measure of the size of the solids. The smaller the solid particle, the more ‘smoothed out’ is the percolation transition. It is easy to understand that if the solids are small, a significant amount of nitrogen can vaporize via the surface clusters before a spanning cluster is formed and this also leads to a more gradual change of slope at the knee. On the other hand, the measured isotherm is the aggregate of the isotherms of the individual solid particles. Fluctuation in the percolation threshold among the solids leads to a diffuse overall transition. Such fluctuation is larger for smaller solids and disappears in the limit of infinite size.

The extent of hysteresis also depends on the connectivity of the network. In a highly connected network, each pore has a very large number of possible routes to the surface of the solids. Once some pores become open, other pores have more chances to access the vapor phase if the connectivity is high. Thus the percolation threshold is decreased and the hysteresis loop narrowed.

A number of workers have analyzed sorption hysteresis using pore network models [75–77,79–99], and some attempts have been made to infer structural information such as the PSD [79,81,85–89,96] and the pore network connectivity [75–77,82,84,86] from the extent of hysteresis.

Instead of completing the primary adsorption–desorption cycle, a family of desorption scanning curves can be measured, with each curve corresponding to a different starting pressure. Because the initial number of vapor-filled pores depends on the pressure at which the secondary desorption process begins, the desorption scanning curves contain further information about the pore network. For this reason, the desorption scanning curves have also been widely studied [71,75,79,81,82,85–92].

In the above description, the mapping of adsorption hysteresis into the percolation process is given in a qualitative manner. To carry out practical percolation analysis of porous solids from nitrogen isotherms, much more work is needed. Since this review concentrates on fractal and multifractal analysis, these detailed procedures are not given here.
and can be found in a recent review [100]. However, a few remarks must be given before we conclude this section:

1. Although the mean coordination number obtained from this analysis may be used in the interpretation of properties such as effective diffusivity, conductivity, etc., no information about the distribution of coordination number within the pore network is available.

2. There is always a chance that the results are model-dependent. One should be careful when making conclusions about one model being better than the other.

3.2.2. Fractal analysis

The model used in the percolation theory, a random network of pores with different shapes, fits our intuitive understanding about a porous material. However, something is missing when one focuses on just the averaged coordination number of the structure. Even though one may describe the desorption branch of the sorption isotherms very well with this parameter, the size distribution of the pores still has to be calculated from the adsorption branch. Yet, there is no reason why one should only use the nitrogen sorption isotherms for the percolation analysis. On the other hand, it is well known that different vapors produce different isotherms on the same solid. Then, one may be faced with different sets of pore size distribution and connectivity parameters when the theory is applied to the adsorption of different vapors.

What was missing was the relation to size scale. It is well known that when one is dealing with phenomena confined to a scale much smaller than the correlation length of the network, a fractal dimension appears. Fractal geometry has been applied to describe the structural heterogeneity of solid surfaces by several authors since 1983 [101–107]. At the molecular size range, the surfaces of most materials are fractals. That is, at this size scale, surface irregularities and defects are characteristically self-similar upon variations of the resolution.

Significant progress in fractal geometry has been made during the past decade. Theoretical and experimental studies of adsorption on fractal geometry showed that a fractal dimension is very handy in describing the irregular structure of porous solids. For instance, it has been found that the fractal dimension of carbon changes gradually from $D = 3$ (microporous disordered carbon black) to $D = 2$ (graphite) when it is heated under aerobic conditions [102]. Therefore, it might be an alternative to reveal the complex structure of porous material.

The ability to describe a complex geometric structure with one fractal dimension is truly a theoretical triumph. However, the key problem left is to determine the fractal dimension of the geometry. Various methods have been proposed to evaluate the fractal dimension of a porous solid. They are all based on the power law derived from the self-similarity of a fractal geometry:

$$ \text{measured property} \propto (\text{resolution of measurement})^D.$$  \hspace{1cm} (15)

In the study of a porous solid by an adsorption experiment, the measured properties could be the monolayer adsorption or the pore volume. The corresponding change in resolution is then achieved by changing the size of the adsorbate or the Kelvin radius. By suitably expressing and modifying the above equation, fractal analysis has been applied to other experimental methods, in addition to adsorption, especially to small angle X-ray and neutron scatterings (SAXS and SANS), image analysis, NMR, and flows. However, the focus of this article will be on the fractal analysis of adsorption experimental data from which the surface fractal dimension $D$ of a solid can be determined and serves to characterize its surface roughness or irregularities. Readers interested in more detailed treatments of SAXS and SANS from fractals can consult reference [108]. As for NMR, it is a new approach and still not in wide use: see [109] for details.

3.2.2.1. Surface fractal dimension and monolayers of different adsorbates

The term ‘surface fractal’ has been extensively used by Avnir and co-workers [101–103] to identify the fractal dimension $D_s$ derived from monolayer adsorption measurements. Essentially, the adsorbed molecule serves as a yardstick that defines the resolution (see Fig 13). In what follows, a brief review of their approach will be given.

Based on the fractal power law, Avnir and co-workers [101] proposed the following relationship between the monolayer capacity $n$ (usually determined from the BET plot) and the molecular area $\epsilon$ of the adsorbate:

$$ n \propto \left( \frac{\xi}{\sqrt{\epsilon}} \right)^{D_s}.$$  \hspace{1cm} (16)

where $\xi$ is a characteristic length of the solid. Since $\xi$ is fixed for the same solid, and the BET surface area $A$
equals \( n\epsilon \), we have

\[
A \propto \epsilon^{(2-D_s)/2}.
\]

(17)

\( D_s \) is called the surface fractal dimension. The adsorption isotherms of various adsorbates with different molecular areas (usually estimated from models, liquid densities, viscosities, etc.) can then be used to determine \( D_s \). A plot of adsorption data according to equation (17) gives \( D_s \) and the pre-factor. The \( D_s \) value gives the surface irregularity but the pre-factor provides further information on the adsorbent structure. This can be clearly shown by the following relation:

\[
\log n = \log k - D_s/2 \log \epsilon,
\]

(18)

which implies \( k \) is the monolayer value for unit \( \epsilon \). Therefore, material with higher \( k \) is more porous. For example, two carbon surfaces [105], Vulcan 3G and carbon black, both have a low degree of surface irregularity with \( D_s = 2.07 \pm 0.01 \) and \( 2.04 \pm 0.04 \), respectively. The value of the pre-factor \( k \) reveals the difference between the two materials: the values are 12.5 and 174.2 \( \text{Å}^D \text{g}^{-1} \text{mmol} \), respectively. According to the \( k \) values, it is concluded that the carbon black sample is much more porous than the Vulcan 3G graphite because of intra-particle porosity.

The results of this approach suggest that most solids with high surface area have a surface fractal dimension between 2 and 3 [102,103,110,111]. However, for use as a routine practice, this method has still many problems, such as the precise definition of monolayer capacity, what molecular sequence is the best yardstick, the possible effect of adsorbate–adsorbent interactions, and above all, the evaluation of the cross-sectional area \( \epsilon \). One example is the fractal dimension of sol–gel derived silica being deduced to be close to 3.0 or 2.2 depending upon the precise method of estimating the sizes of the C\(_5\)–C\(_8\) \( n \)-alkane adsorbates [112]. A detailed discussion of these problems and their implications for the apparent surface fractal dimension has appeared in [107,113].

3.2.2.2. Surface fractal dimension and monolayers on adsorbent particles of different size

If the solid to be analyzed can be sieved to different size fractions, another route to determine the surface fractal dimension may be applied [101]. The power law described in equation (15) is again employed. However, the characteristic length of the solid is now taken as a variable, with a fixed adsorbate surface area. Assuming each sieved fraction can be characterized by the averaged radius \( R \) of an equivalent sphere, the monolayer capacity per unit bulk volume scales as

\[
n \propto R^{D_s-3}.
\]

(19)

In practice, the solid powder under study is sieved into several fractions. For each fraction, the apparent monolayer value is determined with the same probe molecule by any convenient method. If the surface is fractal in nature, \( D_s \) can be obtained from the slope on a log–log plot of the above quantities.

Notice that the notion of self-similarity is associated with the quantity in question and with its range. If a fractal dimension has been found for average particle radius from \( R_{\text{min}} \) to \( R_{\text{max}} \), with the monolayer capacity of a probe molecule having a cross-sectional area \( \epsilon_0 \), then the range of self-similarity is

\[
\epsilon_0 \leq \epsilon \leq \epsilon_0 (R_{\text{max}}/R_{\text{min}})^2.
\]

(20)

It is clear that to extract more information about the geometry at the molecular level, one should use a probe molecule with a cross-section as small as \( \epsilon_0 \).

Some further remarks should be made on equation (19) [114,115]. This equation has been given, assuming the monolayer capacity has been measured with a fixed apparent volume \( V \propto R^3 \). If, on the other hand, the monolayer capacity was measured with a constant mass, then the exponent should be changed to \( D_s - D_m \), where \( D_m \) is the mass fractal dimension of the particles. An additional knowledge of \( D_m \) is
then required. In principle, $D_m$ can be measured from the particle size dependence of the apparent density, $\rho_a$, which scales as $R^{D_m-3}$. It has been found [114,115] that $D_m \approx 3$ for a wide class of solids ranging from compact particles to very porous materials. Only those materials formed by kinetically controlled growth processes possess $D_m$ values significantly lower than 3. (There is now a growing recognition that surface fractals comprise the most diverse type of fractal objects, and a very wide class of materials in common use in the industry and in the laboratory have a mass fractal dimension $D_m \approx 3$. Materials which are formed by some kinetically controlled growth process, such as DLAs, possess $D_m$ values significantly lower than 3 and are of low mechanical stability. Because of mechanical weakness, one actually does not find real catalysts that are DLAs: while aggregation processes in catalyst synthesis do occur, the catalysts actually used in the laboratory and in industry are broken DLAs and their small fragments. Real catalysts are surface fractals with $D_m = 3$. DLAs only exist when they are supported.)

The variation of particle size is obviously much easier than the change of molecular probe. The second approach has an additional advantage in that one does not need to redefine the probe size as long as the same molecule is used. Therefore, this method has been the favorite one for many studies [102,116,117]. In many cases this model works well. However, it is shown that errors may result if it is applied to samples with specific particle size distributions [118].

Usually, but not always, a surface fractal dimension $2 < D < 3$ is found from the above methods [107]. A $D = 2$ surface indicates that the surface is regular and smooth. $D$ values deviating slightly from 2 are indicative of lightly defected surfaces. Intermediate $D$ values represent a fairly rough surface. A higher $D$ value suggests that the surface is more wiggly and space filling. When the $D$ value is close to 3, we are faced with an extremely irregular surface. One may even claim that $D \approx 3$ stands for a pore-filling phenomenon, not related to the details of the surface roughness. This is practically the Gurvitch law [59], which states that pore filling is independent of the size of the adsorbed molecule, as long as it can enter the pores.

A low $D$ value surface need not be flat, as long as the typical radius of curvature is large compared to the size of adsorbate molecule. For a low $D$ surface, it is suggested that the monolayer capacity is not sensitive to the adsorbate size. To put it another way, this means that all the surface area is accessible to adsorbates of varying sizes. At the other extreme, a sharp drop in surface area could be observed for solids with $D = 3$ when the adsorbate molecule becomes larger.

A rough surface might be considered either as a crumpled surface or as a porous one. For the latter, two possibilities arise [119]. Roughness may come from the presence of uniform pores, or it may be the result of a distribution of pore sizes. Uniform pores are identified whenever a steep riser appears in the adsorption isotherm, corresponding to the sudden filling of all pores of the same size. However, fractal analysis of samples with high porosity and uniform pore size (such as some zeolites) does not lead to a high surface fractal dimension [102,120]. A distribution of pore size, in particular the self-similarity of structure from one scale to the other, is needed for a highly fractal surface.

### 3.2.2.3. Surface fractal dimension and pore size distribution

It has been shown [101,102] that the pore volume distribution $J(x)$ scales as

$$J(x) \propto x^{2-D_p},$$

(21)

where $x$ is the pore dimension and $D_p$ takes noninteger values between 2 and 3. One can also write

$$-dV/dx \propto x^{2-D_p},$$

(22)

where $V$ is the total volume of pores with diameter larger than 2x. If a porous solid has a fractal dimension, a log–log plot of the pore size distribution $J(x)$ should be linear, where the slope $s = D_p - 2$ gives the fractal dimension. When $D_p \approx 3$, the distribution $J(x)$ approaches a hyperbolic function, whereas a uniform distribution is observed for $D_p$ close to 2. It has been shown [8] that some calculated adsorption thermodynamic properties also increase with the fractal dimension of the porous adsorbent. This has been taken as an indication of increasing contributions from smaller micropores when the solid has a higher $D_p$ value.

This equation has been combined with the Washburn equation by Friesen and Mikula [121] to give

$$dV_p/dP \propto P^{D_p-4},$$

(23)

where $V_p$ is the volume of mercury intruded under an external pressure $P$. It was then employed to analyze the mercury intrusion data of coal and coal char. On the other hand, a modified power law relationship between cumulative pore volume and pore radius,

$$\left(\frac{V_{\text{max}} - V}{V - V_{\text{min}}}\right) = \left(\frac{x - x_{\text{min}}}{x_{\text{max}} - x}\right)^{3-D_p},$$

(24)
was proposed by Tam et al. [122] to characterize membrane morphology, where \(x_{\text{max}}\) and \(V_{\text{min}}\) represent a maximum pore size and its corresponding cumulative pore volume; \(x_{\text{min}}\) and \(V_{\text{max}}\) represent a physical limit to the size of the probe to measure the size of the pore and its associated cumulative pore volume. It was found that the fractal dimensions of several synthetic membranes having pore radii 1 to 50 nm range from 0.80 to 2.3 and are independent of the type of membrane materials or the method used to obtain the pore size and pore size distribution. The fractal nature of membranes was explained as a direct consequence of their formation mechanism and the configuration of the polymer chains in the casting solution.

Several authors have applied pore volume distributions, obtained from mercury porosimetry or nitrogen adsorption measurements on silica [123,124] and carbonaceous adsorbents [121,125–128], to evaluate their fractal dimension \(D_p\). We must point out that the \(D_p\) obtained from the pore size distribution is not the same as the surface fractal dimension \(D_s\) discussed above. On the other hand, since the mercury porosimetry and nitrogen adsorption isotherm reveal only size information about the macropores and mesopores, respectively, the fractal dimensions obtained will be limited to the respective size range.

For solids such as activated carbons, active carbon fibers, zeolites and molecular sieves, a PSD in the micropore range is essential. To obtain such information from nitrogen adsorption is however difficult, although significant progress has been made in the past decade. A promising method can be found in [129]. Another way to evaluate \(D_p\) of microporous solids is to derive an isotherm equation for fractal material directly, without going through an intermediate step of finding the PSD. This will be discussed in the next section.

### 3.2.2.4. Surface fractal dimension and adsorption isotherms

A variety of theoretical models for adsorption on fractal surfaces have recently been suggested [15,16,130–132]. They are all generalizations of the classical theories for adsorption in a medium with flat surfaces. Pfeifer et al. have presented a detailed study on adsorption on fractal surfaces. The Brunauer-Emmett-Teller (BET) equation for adsorption with a finite number of layers is employed and integrated over a fractal pore size distribution [130]. The resulting expression is denoted the fractal BET theory and is given by

\[
N/N_m = [(D - 1)c x / ((1 - x)(1 - n_m^{-D}))]
\times \int_1^{n_m} n_l^{-D} f_n(x) dn,
\]

where

\[
f_n(x) = \frac{(1 - (n + 1)x^n + nx^{n+1})}{(1 + (c - 1)x - cx^{n+1})}.
\]

\(N\) is the number of adsorbed molecules, \(N_m\) is the number of molecules in a monolayer, \(x = P/P_0\) is the normalized pressure, \(c\) is the BET constant, \(D\) is the fractal dimension, and \(n_m\) is the maximum number of adsorbate layers. The fractal BET theory should be applicable at least in the range of validity \((x < 0.4)\) of the original BET theory and can be fitted with experimental results to determine the three adjustable parameters \(N_m\), \(c\) and \(D\). However, since other effects might affect the adsorption isotherm (e.g. capillary condensation), it should be fitted to complete experimental isotherms with caution.

On the other hand, by a mean-field approximation, Pfeifer and Cole [131] have shown that the adsorption isotherm on a fractal surface, in the multilayer range, depends on the surface fractal dimension. The controlling forces in this range are the van der Waals attraction between the solid and the adsorbates, and the capillary force. Under the van der Waals forces, the adsorption isotherm follows the fractal FHH (Frenkel, Halsey, Hill) equation:

\[
n \propto \left[\frac{\ln(P_0/P)}{v}\right]
\]

with

\[v = 1 - \left(D_{\text{FHH}}\right)/3\].

Beyond a certain thickness of the adsorbed film, capillary force sets in, and capillary condensation occurs. Then the exponent becomes

\[v = 3 - D_{\text{FHH}}, \text{ with } v < 1\].

Avnir and Jaroniec [15] have previously arrived at a similar relation from a fractal generalization of the Dubinin-Radushkevich (DR) isotherm, which is well known for the description of micropore filling. However, the exponent obtained by Avnir and Jaroniec is \(v = 3 - D_{\text{FHH}}\), similar to the case with capillary condensation.

In another paper, Yin [16] presented an alternative derivation of the exponent from the Kelvin capillary condensation equation and a fractal pore size distribution. Essentially, the amount adsorbed is the volume of pores that vapor has condensed. This volume is equal to \(V_{\text{total}} - V\). Since we have

\[
\frac{d(V_{\text{total}} - V)}{dx} \propto x^{2-D_p}
\]

from the fractal PSD, and \(\ln(P_0/P) \propto x^{-1}\) from the Kelvin equation, the exponent \(v = 3 - D_p\) can again be achieved.

Note that \(v = 1 - (D_{\text{FHH}})/3\) is required in the limit
of a flat surface \((D_{FHH} = 2)\) to coincide with the nonfractal multilayer FHH theory. On the other hand, a \(v\) value larger than 1/3 is usually found [72] for microporous solids. Since the fractal dimension of a surface must be larger than 2, this would suggest that an exponent \(v = 3 - D_{FHH}\) is more appropriate. The disagreement was later reconciled by Pfeifer et al. [132] upon considering the surface tension in their analysis. Effectively speaking, the adsorbed film thickness is independent of \(D_{FHH}\) only when it is very close to 2 (smaller than 2.0001), and only in this range does the exponent reduce to \(v = 1 - \frac{D_{FHH}}{3}\). For most cases, surface tension and capillary condensation have to be considered, and the exponent \(v = 3 - D_{FHH}\) should be used. The validity of equation (27) with exponents \(v = 1 - \frac{D_{FHH}}{3}\) and \(v = 3 - D_{FHH}\) have been examined by using adsorption data for some solids [133–137]. Plots of adsorption data according to the fractal FHH equation frequently exhibit strong curvature below or near monolayer coverage, with a linear portion at higher coverages. However, it is quite clear that the \(D_{FHH}\) values must be obtained at low values of adsorption potential. Hence, the data in the multilayer region of the isotherm should generally be most relevant to the fractal dimension [135]. The application conditions of the fractal FHH equation to the nitrogen adsorption isotherm, and how to choose the suitable fitting adsorption data from the whole isotherm in order to evaluate the fractal dimension, have been examined [134]. It was found that the values of \(D_{FHH}\) depend on the range of the fractional filling and that the fractal FHH equation is applicable near completion of bilayer micropore filling. However, a consistent conclusion has still not been arrived at and some further studies are needed to clearly define the limits of applicability of the fractal FHH equation and the reliability of surface fractal dimension obtained from that equation.

The fractal FHH equation is attractive because it yields a fractal dimension without \textit{a priori} assumptions regarding the molecular surface area of the adsorbate and the monolayer capacity. However, one should realize that this isotherm equation does not comply with the Henry law at the limit of zero coverage. To put it differently, the exponent is a constant only above certain coverage [134,135].

The structure of a porous solid is so complicated that the conventional parameters, such as BET surface area, porosity and tube bundle pore size distribution, are not enough to fully characterize its behavior. However, with new developments in percolation theory and fractal geometry, some new parameters have been defined to add to our understanding of the complex solid structure (not all materials are fractal, of course, but the fractal materials can be regarded as generic examples of disordered materials, and the development of a kind of unified description that encompasses all materials should serve as an inspiration for further studies). These methods need no extra data except the sorption isotherms and mercury penetration curves. Such analysis may very soon become standard techniques and be packaged with the original software of these equipments. Before that happens, however, people may have to write their own software and make their own interpretations of the results. This review serves as a starting point for those who like to be in advance of the equipment vendors. If more people are willing to do so, and more data are published on the connectivity and fractal dimension of porous solids, we may eventually arrive at a common understanding of these new characteristics, as we have done for such parameters as BET surface area.

Finally, since there are many methods to obtain surface fractal dimension, and basically the surface fractal dimensions are empirical, some further comments concerning the use of molecular yardsticks for finding the fractal dimensions, the meaning and significance of these numbers, and the difficulties of applying the fractal concepts experimentally are in order:

1. The use of molecular yardsticks reflects the surface irregularity as 'seen' by the set of adsorbates used to derive it (i.e. a relative heterogeneity). This is contrast to other modern techniques, e.g. SAXS and SANS, which see all the surface, including closed voids and bottleneck pores (i.e. absolute heterogeneity). Therefore, attempts to equalize the fractal dimension obtained from adsorption experiments with that obtained from another technique should be treated with caution.

2. As mentioned earlier, the vast majority of experimentally derived surface fractal dimensions fall within the limits 2 and 3, which can be explained from the point of view of purely fractal geometry considerations. However, many cases with \(D < 2\) (chemisorptions on metal surfaces) and a few with \(D > 3\) are known [105]. For the former, they are still interpretable in terms of a fractal dimension (one explanation is a subset of all surface points). On the other hand, \(D > 3\) may be found either in materials with a very narrow pore size distribution (sieving effects), or if the distribution of active sites is nonfractal. It is noteworthy that for \(D > 3\) cases, interpretation with a geometrical dimension is inappropriate since the value is
larger than the dimension of the embedding space, 3.

3. The fractal theory, which can give additional information on the structure of the material or its mode of formation, is based on the self-similarity concept. Therefore, the central problem is linked to the legitimacy of applying self-similarity. The mathematical concept of fractality which is valid for an infinite range of similitude must be restricted to a finite range of similitude in the case of physical systems. It was found that a number of experiments reveal difficulties of practical application of the self-similarity concept, mainly because of the small fractality range [138]. The structure determination as well as the experiments to characterize the physical properties of materials clearly show the importance of the limiting length scale. The presence of these limits complicates the analysis of the experimental data and much of the controversy over the values of the fractal dimension stems from such difficulties. Therefore, one of the aims of the continuing work in this field is to develop better overall models that allow for the inclusion of the cutoff effects in the analysis of the experimental results.

3.2.3. Multifractal scaling analysis

The internal texture or morphology of materials is largely responsible for most of their physical properties, and any correlation between internal structure or morphology and the physical properties is of considerable practical importance. As mentioned in Section 3.2.2, the concept of surface fractal dimension has been found to be useful for the characterization of the disorder structure of materials. Recently, however, it has been realized that in many cases a more detailed characterization can be obtained using the multifractal formalism (i.e. the geometrical multifractality). In this case, the structure is described by a \( D_q - q \) plot or by a spectrum of scaling indices \( f(\alpha) - \alpha \). Such characterizations may be useful for the study of relationships between the microstructure and the macroscopic properties of such materials. This method has been recently applied to a variety of disordered heterogeneous materials.

In disordered materials the local properties, e.g. mass distribution and porosity, often exhibit spatial variations. These variations depend on the location and the size of the subregion considered within the disordered material, and they can be used for its detailed description. These variations can be characterized by a multifractal formalism if suitable scaling features are present. In what follows, we briefly introduce the concepts of geometrical multifractals which may be useful for the investigation of complex geometrical objects.

The multifractal formalisms discussed in Section 2.3 are for the general case where the measures defined on the support are not uniformly distributed. In the special case that we assume the measure to be homogeneously spread over the growing cluster, it is the number of particles which contributes to the amount of measure within a given region on the object. This is the concept of geometrical or mass multifractality concerning the multifractal properties of the geometry of the objects [139]. In this case, the scaling of the mass within such objects can be expressed in terms of an infinite hierarchy of exponents corresponding to different scalings of the mass distribution. Similar to ordinary multifractal formalism, the generalized dimension \( D_q \) for the mass distribution is defined by

\[
\sum_i \left( \frac{m_i}{m_0} \right)^q \sim r^{(q-1)D_q},
\]  

where \( m_i \) is the number of particles in the \( i \)th box and the normalization factor \( m_0 \) is the total mass of the cluster. The knowledge of \( D_q \), therefore, allows the determination of the multifractal spectrum \( f(\alpha) \) as a function of the local mass exponents \( \alpha \) as previously described. Since the measure generating the spectrum is the uniform mass distribution (the Lebesgue measure), the \( f(\alpha) \) characterizes the pure geometry of the system and is called geometrical multifractal if there exists a set of different mass indices in the growing structure. It has been shown that the mass distribution in various asymmetric nonrandom models is geometrically multifractal [139–141]. On the other hand, a similar result has also been obtained for a randomly growing cluster. Vicsek et al. [142,143] have reported that DLA clusters have multifractal geometry and the commonly used methods for the determination of the fractal dimension of DLA clusters yield \( D_{q=2} \) which is smaller than the true fractal dimension \( D_{q=0} \). It is important to note that for growing fractals, one can obtain the true multifractal scaling behavior only if the condition

\[
a \ll r \ll L
\]  

is satisfied, where \( a \) is particle diameter (or the lattice constant), \( r \) the linear size of boxes used to cover the cluster, and \( L \) the extensive linear size of the cluster. This means that the clusters must be extremely large in numerical simulations and the mass multifractal behavior can be observed on a length scale which is much larger than the particle size, but is much smaller than the cluster size. It has been found that the \( f(\alpha) \)
curve for a regular Cantor set may converge to a single point only after an extremely large number of iterations [57]. One should therefore be very careful in interpreting data based on small ranges of $L/r$ and $r/a$. On the other hand, geometrical multifractality should be most pronounced in heterogeneous growth processes because it is a consequence of local density fluctuations.

The concept of mass multifractals has been applied to the geometrical characterization of zinc electrodeposition clusters [144], polymer alloys [145,146], granular films [146], sedimentary rocks [147], and paper formations [148]. For examining the self-similar structure of zinc electrodeposition clusters, the values of $D_q$ are estimated using a box-counting algorithm. In this case, the normalized probability is the relative portion of the cluster boundary in the box. It was found that in the limit of small ionic concentration and small voltage the two-dimensional zinc electrodeposition clusters are self-similar with generalized dimensions $D_q = 1.66 \pm 0.08$. On the analysis of morphology of polymer alloys, which are a blend of low-density polyethylene and polystyrene (20 wt% PE, 80 wt% PS) containing 2 and 5 wt% of two hydrogenated polybutadiene-polystyrene block copolymers, the normalized probability $P_i$ represents a measure of the mass of one of the components of the blend. The different degree of homogeneity and different morphological structures of these multicomponent polymer systems are reflected in the $f(a)$ spectrum of singularities which are obtained by a box-counting method. A correlation between the $f(a)$ curves and the mechanical properties of the corresponding samples is then suggested. The application to sedimentary rocks focuses on the microdistribution of elements in those materials. The quantification and description of the distribution of Si, Fe, and Al in bioactive siliclastic marine sediments have been reported using images from scanning electron microscopy and energy dispersive X-ray spectrometry. The relationship between the nonuniformity of the distribution of elements within the sediment and certain diagenetic processes and various properties such as permeability is then discussed.

On this analysis, some problems arise which might also occur when applying the multifractal analysis to another real system. Basically, the multifractal formalism is applicable if the quantities $M_q$ for all values of $q$ and $P_i$ for all $i$ are power laws of $r$ in the limited range $a < r < L$. For real systems, this is not always the case due to experimental white noise contributions or the wrong scaling assumption for the highest or lowest probability regions. On the other hand, it is difficult to measure small values of probabilities experimentally. Therefore, one may have to consider smaller scaling regions and a limited range of values of $q$. In that way, one obtains a limited $D_q-q$ plot and $f(a) - \alpha$ spectrum (i.e. the top part). In practical application, it was found that these restrictions have no serious consequences and one may need only a very limited subset of $D_q$ or $f(a)$ in order to describe the important physical consequences of particular distributions.

Another type of geometrical multifractal is based on the scaling behavior of a measure defined by the volume of a set, e.g. the pore space volume in the case of porous materials [149]. The $\tau(q)$ can be defined as

$$\sum_i (P_i(r))^q = \sum_i \left( \frac{v_i}{v_0} \right)^q \sim r^{\tau(q)}, \quad (30)$$

where $v_i$ denotes the pore space volume contained in the $i$th box with size $r$ and the normalization factor $v_0$ is the total pore space volume. If $\tau(q)$ is a nonlinear function of $q$, we shall say that the measure is multifractal. Since the spatial variations of $P_i(r)$ reflect the spatial fluctuations of the pore space geometry, the spatial change of the local porosity can be characterized by a multifractal spectrum, i.e., by a function $f(a)$ or equivalently by the $\tau(q)$ curve. This concept has been adopted in the analysis of the complex geometry of sedimentary rocks [150–155]. In practice, pictures of a porous rock are obtained at a finite resolution by digitizing micropore images of two-dimensional thin sections [156]. Such analysis may give us a better understanding about the flow property of rocks, relationship between permeability and porosity, fingering etc.

Finally, it should be noted that there are important differences between geometrical multifractals and multifractals in general. For instance, the values of $D_q$ and $\alpha$ for geometrical multifractals must obey some bounds to make them physically meaningful. Moreover, some other specific constraints must be also obeyed by geometrical multifractals and they will affect these bounds. A detailed discussion about these problems may be found in [149].

The multifractal formalism has been applied to a variety of different phenomena. However, much less effort has been paid to its application to material science problems. In particular, relatively little experimental work has been carried out to test these formalisms and generate new ones. The reasons are that it is difficult to obtain well-characterized fractal substrates on which experiments can be carried out and to obtain accurate experimental results to compare with the multifractal formalism. However, some encouraging
results have been obtained and this will prompt more people to apply the same type of approach to a number of important heterogeneous systems.

4. Heterogeneous phenomena on surfaces and materials

As mentioned earlier, heterogeneous phenomena play a key role in most parts of natural and artificial processes, many of which occur at the border of interfaces and in pores. Fractal approaches are being used more and more in interface science. With a few exceptions, most published papers have dealt mainly with the geometrical fractal interface. Various effects of fractal geometry on reaction kinetics, adsorption, diffusion, and other transport phenomena behavior of the interfaces have been analyzed. It is our aim in this section to show how fractal and multifractal analysis can be used to characterize heterogeneous processes and, in particular, to point out the influence of the surface geometry on some specific processes. There are many types of heterogeneous phenomena but we shall concentrate on catalytic reactions and adsorption.

4.1. Fractal approach to heterogeneous processes

Heterogeneous chemistry plays a key role in a large variety of natural and man-made chemical processes. A major example of such a process is the field of catalysis. In all heterogeneous catalytic systems, the reaction rate and performance are determined not only by the details of the chemistry involved, but also by the geometry of the environment in which the catalytic process takes place. For instance, the geometrical structure of the catalyst may have a vital influence on the selectivity of catalytic reactions. Therefore, a quantitative treatment of reaction kinetics of such systems requires an understanding of the effects imposed by the complex geometrical and topological features associated with most porous solids. In some cases, structural effects can be easily described, such as in the study of catalytic processes on specific metal crystal planes or in the regular and repetitive structures of zeolites. But for most catalysts, the catalytic surface is usually irregular, convoluted and fractured, and there are considerable discrepancies between the theoretical predictions and the experiment, especially when the kinetic order is a fraction. The reason for the difference is that either the nature of the catalytic surface is ignored or an ideal surface is adopted in the theoretical treatment. As mentioned above, structural information on materials is usually described by empirical parameters such as BET surface area, PSD, particle sizes and recently connection of pores and formalisms involving fractal dimensions. The realization that many of these sophisticated geometrical structures are fractal-like has provided an appropriate approach to the study of chemical and physical processes taking place in such environments. Recent works have shown that materials which are frequently used as catalyst supports or adsorbents exhibit self-similarity over at least some range of length scales [18] and have demonstrated the applicability of the fractal theory to a variety of problems in surface science, from which some new insights on the relation between geometry and characteristics of process are provided.

Basically, applications of fractal geometry to problems of structure sensitivity studies in catalysis might be divided into interpreting experimental observations, theoretical studies, and direct computer simulations. For explanations of experimental observations, several papers have been published on the relation between heterogeneous reactions and fractality [157–165]. It was found that in many cases, such as hydrogenation, hydrogenolyses, oxidations, isomerizations and photochemical reactions, the relation between catalytic activity \( a \) (mol time\(^{-1}\) particle\(^{-1}\)) and the particle size \( 2R \) of the catalyst obeys the simple scaling law

\[
    a \sim R^{D_r},
\]

in which \( D_r \) is defined as the reaction dimension and is quite often interpreted as the fractal dimension of the subset of reactive sites of the surface [157–161]. Thus, \( D_r \) carries information on the structural sensitivity of the process and in some cases also on the actual distribution pictures of the active sites on the surface. A value of \( D_r \neq 2 \) indicates that there is a certain degree of structure sensitivity. For \( D_r > 2 \) this implies that the number of active sites increases faster with particle size than the total number of surface sites. The value \( D_r < 2 \) is indicative of reaction sites involving principally edge/corner atoms and a small fraction of active plane atoms. It also indicates that structure sensitivity exists and the number of reaction sites increases more slowly than the total number of surface sites. It was found that the relation between \( D_r \) and the surface fractal dimension \( D \) is controlled by one or more of the following effects: (a) screening (b) chemical selectivity (c) roughing and smoothing (d) trapping and reactions in pore volume [159].

Other experimental investigations are the effects of surface geometry (average pore size and surface
fractality) on diffusion-limited reactions on porous silicas [162,163] and photocatalytic cleavage of water [164] as well as fractal-like kinetics in solid–gas reactions [165]. Note that the concept of fractal-like chemical kinetics is advanced by Kopelman and co-workers [166–168]. When a reaction obeys fractal-like kinetics, the reaction orders are noninteger and the rate constant $k$ is a function of time of the form

$$k = k_1 t^{-h},$$

where $0 \leq h \leq 1$ is a constant. In a 3D homogeneous space, $h = 0$. If a system is well stirred, then again $h = 0$. For a diffusion-limited reaction, $h$ lies between 0 and 1.

For theoretical studies, transport phenomena with chemical reaction in fractal porous media have been examined by several authors [169–173]. Some predictive theories for transport and reaction rates in catalysis, taking place in the environment of fractal surfaces and fractal subsets, have been developed. It is found that the geometry of the catalytic surface is a crucial parameter in determining the reaction rate in catalytic systems. As for computer simulation, some interesting simulation studies are catalytic oxidation of CO (see [174,175] and references therein), fractal clustering of reactants on a catalyst surface [176,177], selectivity behavior of multistep reaction systems [178–180], Eley–Rideal mechanism and its modified versions over fractal surfaces [181–187], kinetics of diffusion-limited adsorption on fractal surfaces [188], and decomposition of N$_2$O on fractal surfaces [189]. Computer simulation results have indicated that it is a powerful and successful tool in this field and indeed could qualitatively identify the important trends although it is difficult to mimic in full a real catalytic process.

For adsorption processes on surfaces, the concept of surface heterogeneity in the theory of physical adsorption has a rich history (see [190] and references therein). The complex geometrical structure of many solids and their complex chemical composition are the main sources of adsorbent heterogeneity. Structural parameters, such as BET surface area, PSD, connection of pores, and surface fractal dimensions, used to describe structural heterogeneity can give information about surface phase capacity and adsorbent geometrical structure but do not provide information about distribution of adsorption sites with respect to their adsorption energies. In the adsorption studies, the energy distribution is often determined by adsorption data measured at low equilibrium pressure, in which the interaction between adsorbates may be neglected. For adsorption on heterogeneous solid surfaces the topology of adsorption sites on the surface plays a key role. Traditionally, two models of heterogeneous surfaces are quite often used (see Fig 14). The patchwise model assumes a surface having several types of adsorption sites which are present in sufficiently large patches so that the adsorption on each patch can be treated independently and behave as if each is a separate crystallite or crystalline face. The random model, on the other hand, assumes a random configuration of adsorption heterogeneities. The random model seems to better approximate the majority of real adsorbents. It is found that isotherm equations based on these two models are frequently very complex and mathematically unmanageable.

For microporous solids (e.g., zeolites) the main source of heterogeneity is their complex porous

Fig 14 Schematic illustration of the (a) patchwise and (b) random models for surfaces with energetic heterogeneity.
structure containing micropores of different dimensions and forms. One recent active investigation on this phenomenon is the aromatics/silicalite adsorption system. Silicalite is a pure silica zeolite having a structure similar to that of the well-known ZSM-5 zeolite. There are two types of intersecting channels in the structural framework of silicalite, both defined by ten-membered oxygen rings. The first type of pores comprises the small, circular zig-zag channels along the $a$ direction with a diameter of about 5.4 Å. The second group includes the larger elliptical straight channels along the $b$ direction with a cross-section of $5.75 \times 5.45$ Å. For every unit cell ($a = 20.02$, $b = 19.80$, $c = 13.36$ Å) there are two large pores each 19.80 Å in length (including intersections) and four small pores each 6.6 Å in length. A schematic illustration of the channel structure of silicalite is shown in Fig 15. Unlike most zeolites, silicalite is hydrophobic in nature, and has no exchangeable cation. Many organic molecules, such as benzene and xylenes, are comparable in size to the channels in silicalite. Due to the strong guest–host interaction under a tight fit, the adsorption of these molecules in silicalite becomes very unique. Several investigators [191,192] have reported abnormality in the adsorption of aromatics in silicalite (or ZSM-5). For instance, the isotherm might change from type I to type IV with decreasing temperature (one example is shown in Fig 16). Furthermore, the adsorption heat was found to rise sharply at some intermediate loading (see Fig 17). Several attempts have been made to explain, both qualitatively and quantitatively, these heterogeneous adsorption equilibria with comparable molecular and pore size. One of them uses a simple lattice gas model having three types of lattice sites to describe the adsorption of benzene in silicalite [193].

So far, on applying fractal theory to adsorption processes the main concern is the morphological disorder. The influence of the surface fractal character on the physical adsorption isotherms has been studied using different approaches, such as a fractal description of the pore volume, or a progressive smoothing of a rough surface as the multilayer adsorption builds up [194]. As already mentioned in Section 3.2.2.4, they all belong to generalizations of the classical theories for adsorption on flat surfaces.

### 4.2. Multifractal approach to heterogeneous processes

On applying the fractal approach to those heterogeneous physical and chemical processes, some interesting phenomena were found which seem to require not one but an infinite number of exponents for their description, i.e., in addition to the single fractal dimension of the cluster itself, singular distributions of various physical and chemical quantities defined on the fractal determine an infinite set of fractal dimensions each corresponding to the distribution of a given kind of singularity of the measure. For instance, in growth phenomena of DLA, the sites which are most likely to grow are at the tips of the
aggregate; these sites are a subset with a fractal dimension less than the fractal dimension of the entire aggregate. Multifractality is related to the decomposition of the fractal object into many fractal sets, each with its own fractal dimension, and different distributions define different multifractal spectra on the same fractal object. Such multifractal phenomena reflect the heterogeneity of surface and materials and have recently become an extremely active area of investigation.

As mentioned earlier, surface heterogeneity is a consequence of the multiplicity of exposed crystallographic faces, structural defects and the presence of chemisorbed impurities. In practice most surfaces are both geometrical and chemical heterogeneities. Needless to say, both kinds of disorder can be related and distinguishing one from the other may be purely conceptual. However, the study of the effects of both complex geometries and chemical heterogeneities separately should provide insight into the physical and chemical behavior of these more realistic surfaces.

In what follows, we take the analysis of reaction probability distribution (RPD) over fractal surfaces and adsorption (or reaction) on multifractal lattices as examples to illustrate how the multifractal analysis permits the characterization of complex phenomena in a fully quantitative fashion, from which the high sensitivity of adsorption and reaction to structure may be manifested. It is noteworthy that for reactions over fractal surfaces, the structures are geometrically heterogeneous but energetically homogeneous, while the multifractal lattice is a geometrically homogeneous but energetically heterogeneous substratum.

4.2.1. Multifractal approach to reactions over fractal surfaces

In a steady state regime, the reaction rate at each active site is proportional to the active site reaction probability. This property may be determined by Monte Carlo simulations of particles undergoing a random walk and released from an equal-event boundary, i.e., a diamond-shaped boundary. Particles are released one at a time and each then undergoes a random walk until it either reaches the surface site of the fractal cluster or goes out of the outer perimeter. When this random-walking particle enters a site occupied by the fractal, it gets adsorbed with probability \( p \), which is given by various forms. The acceptance/rejection check can be achieved by generating a random number when the particle visits the fractal site and checking whether it is less than \( p \). If it is less than \( p \), then the reaction counts on that surface site are added by one or the particle continues its random walk (with probability \( 1 - p \)).

When the probability of reaction of a fractal set with diffusing particles is measured, RPD curves for the fractal object are obtained. A typical result shown in Fig 18 was taken as an example from simulation of a decay-type Eley-Rideal diffusion-limited reaction.
mechanism over a DLA cluster. In this auto-poisoned system, a decay function defined as \( P(n_i) = P_{ini} \exp(-n_i/m) \) for every surface site is used to describe the changes of sticking probability as the reaction proceeds, where \( P_{ini} \) is the initial sticking probability, \( n_i \) are the reaction events occurring over active site \( i \) and \( m \) is a parameter used to regulate the decay rate. Accordingly, the two parameters \( P_{ini} \) and \( m \) control the properties of the decay function and thus the reaction dynamics. Another useful parameter is the total number of reaction events which could affect the values of \( n_i \) over every active site and the decaying behavior. In principle, factors that could accelerate the rate of decay would lead to more homogeneous RPD profiles. The reason is that after some reaction events the sticking probability is reduced quickly to a very low value and the RPD is similar to that of the fixed low sticking probability case, namely, a nearly uniform RPD. According to the decay function, both lower \( P_{ini} \) and \( m \) values can prompt the decay rate, and lead to more uniform RPD pictures. The total number of reaction events may also produce a homogeneous RPD, and a high enough number of reaction events would eventually compel the sticking probability over active sites to become very low and again yield a homogeneous RPD.

In Fig 18, the RPD was obtained from simulations with \( P_{ini} = 1.0 \) and different \( m \) values, which are 5, 30, 150, and 300, respectively, after \( 10^3 \) reaction events. Note that a lower \( m \) value corresponds to a faster decay rate. In order to understand the position sensitivity of the reaction probability, the reaction probability was plotted as a function of active site position, where the active sites were numbered from the inner part of the DLA outwards. For active sites of the same radius, they are numbered clockwise. Note that the inactive sites and the screened active sites were not included in this plot. Valleys between the spikes in the RPD profile arise mainly from the screening effect, i.e., the inner active sites are screened by the outer ones, showing that the deep inner sites are rarely visited. As the value of \( m \) increases, the reaction probability has a wider distribution showing a higher position sensitivity. It can also be seen in Fig 18 that the number of low reaction probability sites gradually increases as \( m \) decreases.

A natural question that one can ask then is what formalism could provide the function that characterizes the scaling form of probability distribution on the fractal set, i.e., are there scaling exponents that tell us how these probability distributions depend on the yardstick used to measure them? The MSA answers this question.

![Fig 19 Multifractal characteristics of RPD of Fig 18: (a) \( \tau(q) \)-q curves and (b) \( f(\alpha) \)-\( \alpha \) curves [187] ]

As mentioned in Section 2.3, the RPD pictures may be transferred into a useful compact form through the multifractal formalism, namely, through the \( \tau(q) \) and \( f(\alpha) \) plots. In Fig 19a, \( \tau(q) \) is plotted against \( q \) for the above RPD profiles. As can be seen in Fig 19a, deviation from linearity indicates multifractality, representing that simple single-valued fractal scaling does not apply in this condition. The difference among four different \( m \) values can also be observed in the parts with high positive \( q \) values, and there is a bigger deviation from a full superposition of the \( \tau-q \) curve as \( m \) decreases. This result can be interpreted by the fact that the number of active sites with highest reacting probability, which dominates the sum in equation
(4) in the large positive q region, is quite different for different m values. Another important feature in Fig 19a is the curve curvature, which implies the degree of heterogeneity and is also quite different for the four m values. The trend is that a larger m value corresponds to a greater curvature in the τ(q) curve. These results agreed with RPD profiles for different m values, i.e., inhomogeneity in RPD increases as the m value increases. Note that the τ−q curve in Fig 19a for m = 5 exhibits a nearly linear relationship, representing a homogeneous RPD, and the slope almost equals the D value, implying that the heterogeneity is distributed over almost every active site. The effect caused by faster decay rate on RPD can also be analyzed through the f(α) dispersion of the RPD profiles, which allows a quantitative evaluation of the degree of RPD inhomogeneity: high non-linearity of the τ(q) curves is translated into wider distribution in the f(α) plots.

In Fig 19b, f(α) is plotted as a function of α to further explore the properties of RPD for different m values. As can be seen in Fig 19b, the f(α) profiles show that the RPD is characterized by a wide range of α values, indicating the existence of multifractality. Also shown is that the range of the α value decreases as the m value decreases and this can be connected to the RPD shown in Fig 18. As demonstrated in Fig 18, the larger value of m leads to a much higher position sensitivity than the smaller one. For smaller m, a great number of low reaction probability sites would level out the distribution and thus lower the position distinction.

Owing to anisotropic screening of DLA studied, the RPD profiles observed appear to be asymmetric (Fig 18) and the f(α) figures are also asymmetric with respect to α, in contrast to the symmetric f(α) profiles of Cantor sets and Devil's staircases obtained by Gutfraind et al. [181,182]. The key feature is that the curve contracts upwardly at high α value and the number of lowest reaction probability sites and the number of large reaction probability sites are not even.

Finally, one may observe that the right part of the f−α plot (q < 0) does not coincide markedly. This is inconsistent with the τ−q curves for q < 0. The f−α curves seem to scale up the difference. It is noteworthy that the scaling of the moments of the distribution (equation (4)) does not imply the scaling of the singularities of the probability distribution (equation (2)) and the scaling behavior of the sets associated with each singularity (equation (3)).

Multifractal analysis is a useful tool in the study of processes in environments of complex geometry. Avnir and coworkers [181,182] used the multifractal scaling techniques to analyze the diffusion-limited reactions over two mathematically made fractal surfaces, the Cantor set and the Devil's staircase, indicating that multifractals exist for RPD on both surfaces.

Lee and Lee have performed simulations of the Eley-Rideal (ER) diffusion-limited reaction mechanism and its modified versions over surfaces of different fractal objects using a Monte Carlo random walk algorithm [185–187]. Effects on reaction probability distribution (RPD) were examined by employing various sticking probability functions. Other effects also studied included cluster size effects and noise reduction. Multifractal analyses were then carried out on the reaction probability distribution to study the effects of those factors on model chemical reactions.

Their analyses manifest the high sensitivity of catalysis to structure even in a basic reaction like the ER mechanism. The multifractal formalism is also useful in examining the heterogeneity effects on the performance of other chemical processes. An application is to analyze the sensitivity of selectivity of multistep catalytic reactions to catalyst structure. In this case, the selectivity for each surface site is first determined from the simulations. Then, P_i is defined as the normalized selectivity

\[ \frac{S_i}{\sum_i S_i} \]  

where S_i is the selectivity of surface site i. This has been performed by Lee and Lee using Monte Carlo simulations of a three-step catalytic reaction over fractal surfaces [180]. The effects of varying probability of reaction steps, rate constant, and cluster size on the catalyst selectivity were analyzed with multifractal scaling techniques. It was found that because of the screening effects, macroscopic average selectivity and normalized selectivity distribution of fractal catalyst behave differently from those of a smooth surface.

Before leaving this section, some remarks may be made on the simulation results of Lee and Lee [187]. According to multifractal scaling formalism, in the limit of infinite large system size the measure can be well characterized by size-independent multifractal functions. However, it was found that the convergence of multifractal scaling with respect to size is relatively slow compared to the rather fast convergence of the fractal dimension of the object that supports the probability measure. One example may be seen in Fig 20, which represents the multifractal analysis of RPD for simulations over 3 × 10^3, 6 × 10^3, and 10^4 particle DLA clusters with sticking...
probability equal to one (i.e., diffusion-limited Eley-Rideal reaction mechanism). The difference of RPD among the three different sizes can be observed in the parts with high negative $q$ values and it shows a bigger deviation from a full superposition of the $\tau-q$ curve as the radii increase. This result implies that the number of active sites with lowest reacting probability, which dominate the sum in equation (4) in the large negative $q$ region, are quite different for DLAs of different sizes. One reason for the existence of finite size effects may be the intrinsic difficulty in calculating small values of reaction probability numerically. However, the averaging procedures used to obtain the moment $M_q$ and the wrong scaling assumption for small reaction probability may also render this ambiguous result.

In addition to checking the multifractal assumptions with different cluster sizes, Lee and Lee also examined the fractal dimension effects under fixed cluster size condition on RPD shapes. Basically, in order to probe fractal dimensionality effects on RPD curves, one must first obtain a set of size-independent RPD profiles. However, according to their simulation results the size effect always exists and renders the comparison more difficult, and no concrete conclusions can be drawn. On the other hand, it should be noted that the clusters generated by their model for diffusion-limited aggregation with drift may not be self-similar fractal with a fractal dimensionality that varies from $\approx 1.70$ at small drifts to 2.0 at large drifts. Instead the clusters may have a DLA-like structure on short length scales $l \ll \xi$ with a crossover to a uniform $D = 2$ structure on long scales, with a crossover length $\xi$ that decreases with increasing drift [195–197]. Therefore, one should be aware of the possibility that the small range of length scales explored and the crossover effects may exaggerate the uncertainty in the multifractal analysis results.

4.2.2. Reaction and adsorption on multifractal lattices

The fractal structures used above are characterized by geometrical heterogeneities on all scales. For particle diffusion on these media it is assumed that all the sites of the structure have the same time residence probability. Therefore, in this sense, the structures are geometrically heterogeneous but energetically homogeneous. On the other hand, the spatial distribution of site residence or adsorption probabilities may be described in terms of multifractal distribution, i.e., with an infinite family of scaling exponents and fractal dimensionalities. This is called a multifractal lattice.

A multifractal lattice may be obtained as follows [198]. On square lattices of size $L \times L$, four normalized probabilities $P_i$ ($i = 1, \ldots, 4$) are selected. In the first stage, the lattice is divided into four equal quadrants and these four probabilities are randomly assigned to the four quadrants. In the second generation, each quadrant is divided into four smaller quadrants and the probabilities associated with each of the subquadrants is then multiplied by $P_1, P_2, P_3$, and $P_4$ in random order. After $n$ generations, each lattice site is associated with a probability (or measure) with the form $P_1^a P_2^b P_3^c P_4^d$, where $a + b + c + d = n$. In the limit $n \to \infty$ the procedure outlined above defines a
fractal measure on the two-dimensional space which determines an infinite set of fractal dimensions \( f(\alpha) \) each corresponding to the distribution of a given kind of singularity of the measure \( \alpha \). Models of this type have been used to describe the distribution of energy dissipation in turbulent fluids [23,42,44,199–201].

Since the multifractal lattice represents another type of heterogeneous effect, it is interesting to compare some physical and chemical phenomena on such lattices with those on the perfect lattice. Accordingly, Eden growth [198,202], random walks [203], and self-avoiding random walks [204] on the multifractal lattice were investigated using computer simulation and renormalization group methods. It was found that the multifractal disorder could have important effects on the scaling behavior of these processes. On the other hand, to study the effect of heterogeneity on the scaling property of the DLA, Meakin investigated the DLA on a two-dimensional multifractal lattice by using computer simulation [205]. It was shown that the effective fractal dimensionality of the DLA patterns was decreased as the magnitude of the heterogeneity was increased. The multifractal structure of the GPD in the DLA on the multifractal lattice was investigated by Nagatani using a renormalization group approach and the multifractal heterogeneity was found to have important effects on the multifractal structure of the GPD [206].

As mentioned above, the probabilities of each lattice may correspond to time residence or adsorption probability. Therefore, the multifractal lattice is a geometrically homogeneous but energetically heterogeneous substratum. Reaction and adsorption processes on these multifractal lattices have been studied [207,208] and it was found that the spatial distribution of measures plays a fundamental role in these processes. One similar approach has been adopted by Vlad [209] to investigate the influence of size and energetic heterogeneities on patchwise adsorption, in which a Markovian scenario is introduced to generate a broad distribution of patches and the probability \( P(N) \) that \( N \) molecules are adsorbed on a patch has a multifractal behavior.

In Section 4.2, we have presented various applications of MSA. It has proved to be useful in the study of processes in environments of complex geometrical and energetic heterogeneities. The beauty of multifractal concepts is that they provide a means for organizing often complex and bewildering phenomena. However, although some attempts have been made to measure \( \tau(q) \) and \( f(\alpha) \) of GPD for a few specific experimental situations including viscous fingering [210], crystal growth [211], and electrochemical deposition [212,213], so far most investigations have concentrated on theoretical study and computer simulations. It is clear that the implications of the use of multifractal concepts in many fields of experimental surface science have not yet been fully explored. It should serve as a challenge to experimentalists to complement the current theoretical progress with carefully thought-out experiments under controlled conditions. In this manner multifractal analysis will become more applicable in practice and this field of science will continue to flourish.

5. Conclusions

The heterogeneity of surfaces and materials plays a key role in most natural and artificial chemical processes. The heterogeneous structure of porous solids is so complicated that the conventional parameters, such as BET surface area, porosity and tube bundle pore size distribution, are not enough to fully characterize it. However, with new developments in percolation theory, fractal geometry, and MSA, some new parameters have been defined to add to our understanding of the complicated solid structure. Among these methods, percolation theory and fractal analysis need no extra data except the sorption isotherms and mercury penetration curves. On the other hand, the fractal approach and MSA may manifest the high sensitivity of processes to complex geometries and chemical heterogeneities.

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