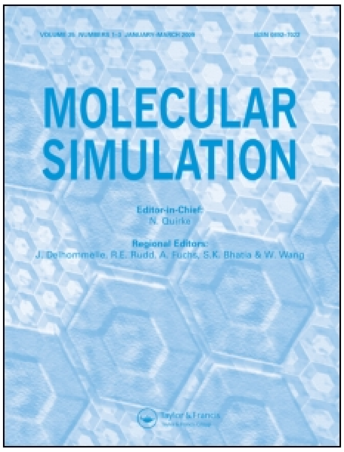

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On the limits of fractal surface behaviour in silica. A virtual adsorbates simulation

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On the limits of fractal surface behaviour in silica. A virtual adsorbates simulation

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A computer simulation technique, suited to replicate real adsorption experiments, was applied to pure simulated silica in order to gain insight into the fractal regime of its surface. The previously reported experimental fractal dimension was closely approached and the hitherto uncharted lower limit of fractal surface behaviour is reported herein.

Keywords: Surface; Silica; Fractal; Adsorption; Simulation

1. Introduction

Thanks to the pioneering adsorption experiments of Avnir *et al.* it is now well established that a wide range of powdered substances exhibit a rugged, or *fractal* (as opposed to smooth, or Euclidean) surface at the microscopic scale [1–8]. One distinctive principle behind fractality is that the value of the measured property is dependent on the size (and may also depend on the shape, [9]) of the measuring instrument or "yardstick" (the historical issue, put forth in the form of the celebrated question "How long is the coast of Britain?", was originally raised, as we know it, by Mandelbrot [10]). Since in surface-area determination experiments by adsorption, the yardsticks, or adsorbates, are usually small molecules, the surface area reported is different for every adsorbate species employed, and for all but the smoothest of surfaces.

The unifying concept of *fractal dimension* serves as a tool to characterise intrinsic surface intricacies in a quantitative manner, and it necessarily implies that the observed surface ruggedness remains invariant to changes of scale. In terms of adsorption experiments, it means that any adsorbed molecule will necessarily "see" a similar surface landscape, regardless of its size and of the original phase of the physisorption. In fact, topologic factors seem to take precedence over the former [4]. It is, therefore, possible to express the fractal dimension of the substrate surface as the fractal dimension of a uniform coverage of adsorbate molecules. The values reported range from close to 2 (purely Euclidean) for the smoothest surfaces, found, for example, for AEROSIL® silica spherules and graphite, to close to 3, for the most convoluted (hard-to-imagine, almost volume-filling) surfaces, found for some activated charcoals and silica gel [1,3,4] (the authors in Ref. [11], on the other hand, present an alternate view of what they call the "ultimate fractal", the one with a fractal dimension of 3).

The possibility of experimentally investigating with adsorption techniques the fractal behaviour of a given material surface ultimately depends on the size of the molecular probe employed. Therefore, adsorbates ranging from nitrogen to coiled polymer molecules have been successfully tested, covering a linear dimension range of about two orders of magnitude. However, the actual limits of such fractal surface behaviour are difficult to define. Since, the lowest experimentally known bound is the effective size of the nitrogen molecule, the purpose of this

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work is to explore around this lower limit by resorting to simulated silica samples and simulated—“virtual”—spherical adsorbates of adjustable, *ad hoc* radii.

2. Experimental details

The amorphous SiO2 sample (“particle”) used consisted of a computational box of cubic shape (165.5 Å per side) containing 300,000 atoms, prepared by a modified Montecarlo method [12]. (Figure 1 shows a representation of a smaller silica system from the same reference). This sample reproduces very well the structure of a real system (with an overall $T(r)$ discordance [13,14] of 4.0% between 1 and 10 Å). It is pertinent to mention that, whereas the above-simulated sample is in excellent agreement with the bulk material, the surface of the simulated particle was not specifically treated to achieve relaxation. Therefore, the surface of our sample is equivalent to a virtual cut in the bulk without any perturbation on the coordination and energetics of the individual atoms. This is clearly only a first order approximation to the real surface. The preparation of a more “physically correct” surface large enough for the meaningful simulation of adsorption processes is a lengthy task not devoid of complications. This is in fact the matter of our ongoing work.

In real adsorption experiments, adsorbate molecules cover the surface of a powdered substance usually in form of a monolayer. We have simulated this process by randomly positioning spheres (the *virtual adsorbates*) of a given radius on the surface—in fact, in any part of the volume, as will be discussed below—of the amorphous silica sample (figures 2 and 3). In order for a virtual adsorbate to be accounted as part of the monolayer two conditions need to be met, namely that the adsorbate is not

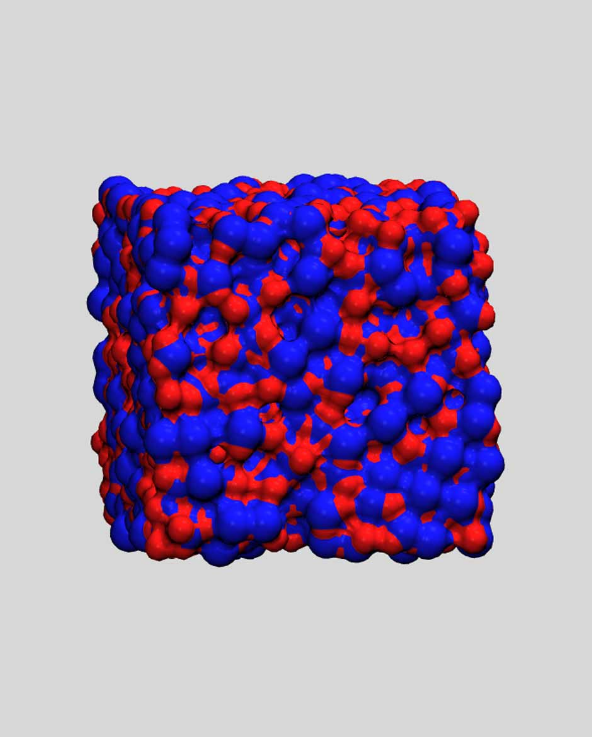

Figure 2. Arbitrary representation of the outer surface of the SiO_2 cubic particle from figure 1.

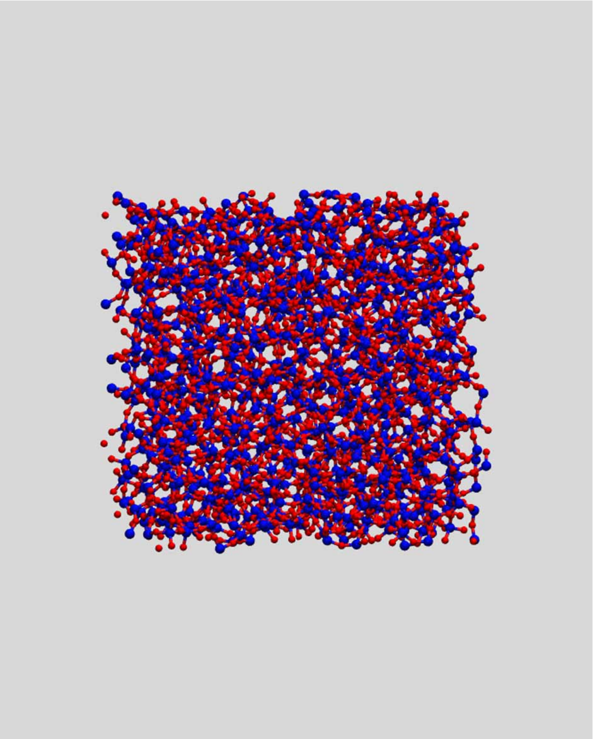

Figure 1. Representation of a 3000-atom vitreous SiO_2 cubic particle [12].

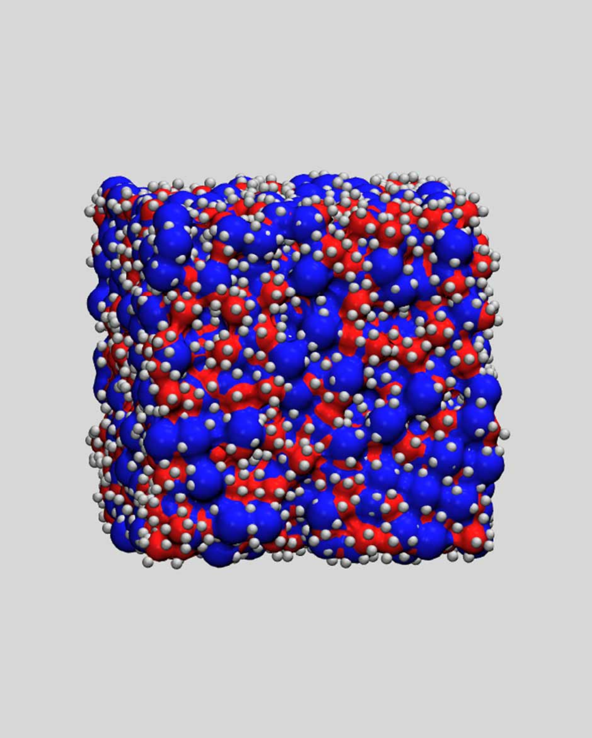

Figure 3. Representation of the (as shown still incomplete) adsorption process on the surface of the SiO_2 particle from figure 1.

allowed to overlap with other adsorbates and that it is not allowed to overlap with any atom. (However, in order to save considerable calculation time, the former—quite severe—restriction was forgone in favour of a maximum overlap of 0.5% between neighbouring adsorbates).

If a simulation is to reproduce the results of a real adsorption experiment, it is important to assess the number of random trials large enough, at any radius value within the explored range, to assure that the silica particle under examination becomes fully covered, or *saturated* with virtual adsorbates. Failure to achieve surface saturation will nonetheless yield a fractal dimension, although not that of the underlying surface, since it is well known that the fractal dimension of a random array of spheres depends on the occupation fraction of the array with respect to the Euclidean space of the experiment [15]. Figure 4 shows the saturation behaviour of the simulated adsorption process. Saturation is achieved when an increased number of random trials is not able to increase the number of virtual adsorbates on the surface. It is evident that even a rather small number of random trials, 10^6, is able to produce a saturated surface at radius values greater than around 0.3 Å (for a small silica particle). A much larger value, 10^{10} (equivalent to 2200 random trials per Å^3), was chosen for all production runs.

One of the strengths of this method is that, once the particle surface is saturated, the statistical error among several production runs is rather small, at least in our range of interest. Figure 5 shows this behaviour. However, statistical error increases with particle radius, merely as a consequence of the growing *r*/*L* ratio (the ratio between adsorbate radius and particle edge length). In other words, adsorbates become increasingly too big to accommodate on the particle surface. This trend would eventually preclude a precise determination of the upper cutoff of the fractal surface behaviour for this particle size under the same conditions.

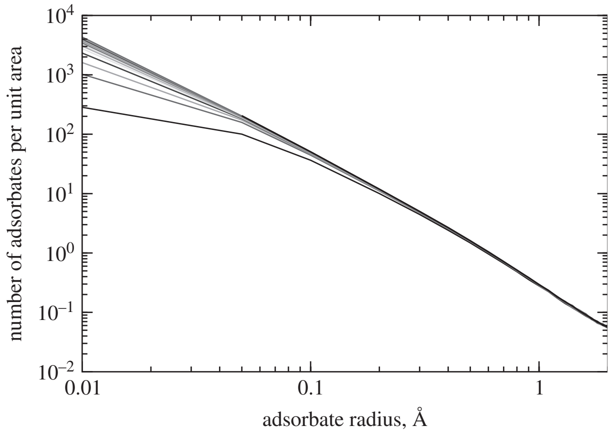

Figure 4. Surface saturation curves for a 648 atom silica conglomerate. The lower curve corresponds to 10^6 random trials (equivalent to around 100 random trials per Å^3). The upper curve corresponds to 10^9 random trials (10^5trials/Å^3). Intermediate values are also shown. *Unit area*, on the *y* axis, refers to the surface of the computational box.

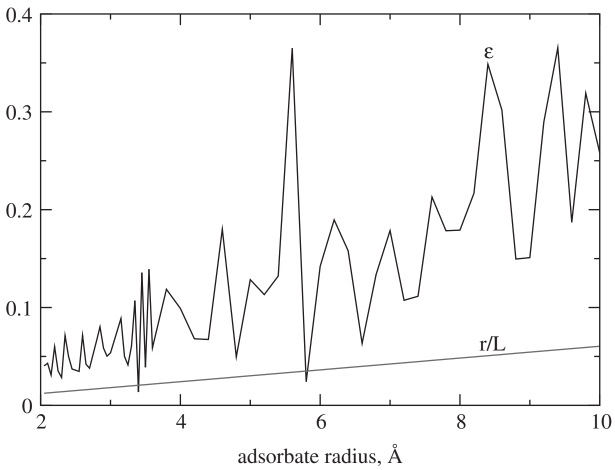

Figure 5. Relative error, $(n_{\max} - n_{\min})/n_{\text{avg}}$, between four runs of the simulated adsorption process. Here, *r*/*L* is the ratio between adsorbate radius and computational box (particle) edge length.

The fractal dimension of the surface is calculated once a series of points representing the number of adsorbates vs. adsorbate radius is available, so that the trend can be accurately described, within a definite range, by $n \propto r^{-d_f}$, where *n* is the number of adsorbates on the surface, *r* is the adsorbate radius and d_f is the fractal dimension of the surface.

It is pertinent to note that this method relies on the fact that, as pointed out before, geometrical factors seem to predominate over the nature of the interaction energetics between the adsorbate and the substrate. Therefore, no provision was made to account for the energetics involved.

In the simulation, the Shannon & Prewitt's atomic radii (0.4 Å for Si and 1.2 Å for O) were used [16,17].

3. Results and discussion

3.1 Fractal surface dimension

Figure 6 shows the adsorption behaviour of our silica particle. A linear trend is evident in most of the range studied (see inset). This is precisely where a *surface* fractal behaviour takes place, that can be succinctly described by the slope of this line, which is in fact the fractal dimension of the surface ($2 < d_f < 3$).

Since, it is not easy to assign merely by sight a lower cutoff value of the linear trend (inset, figure 6), we resorted to statistical multivariate analysis. Results are shown in figure 7.

It is clear that every statistical measure of fit presented (minimum standard deviation, maximum coefficient of determination and maximum Fisher's *F*-test value), is best at $r_c = 2.55$ Å. This is, therefore, the lower cutoff of the fractal surface behaviour. Our determination of the surface fractal dimension of amorphous silica yields a value of 2.093 ± 0.011 ($R^2 = 0.996241$, $F = 29{,}949$). In order to stabilize the growing variance of the data (visible on figure 5) we deemed suitable to run the analysis excluding

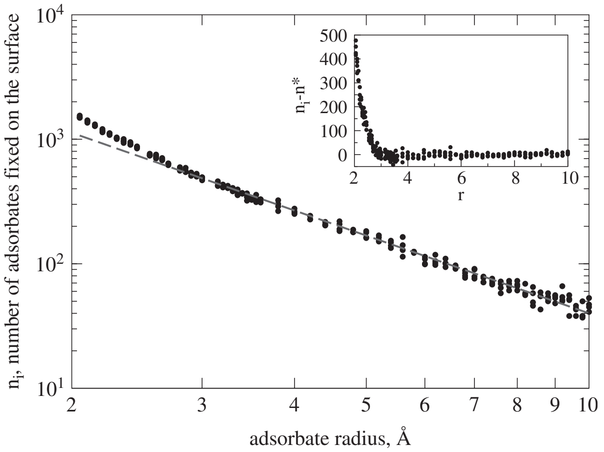

Figure 6. *Virtual adsorption curve*, log–log plot of the $n(r)$ vs. r relationship for the virtual adsorption experiment. A surface fractal behaviour is present wherein the linear relationship holds. Here, the best fit is represented by the dashed line. The fractal dimension, d_f, has herewith a value of 2.093 (after outlier exclusion, see text; the real experimental value is 2.15 ± 0.06 [4]). *Inset*: departure from linearity—the lower cutoff value of surface fractal behaviour (see text)—, shown in linear scale. N_i is the number of adsorbates attached to the surface during the computer experiment at a given radius, r_i, and n^* is the (best) fitted value corresponding to such radius.

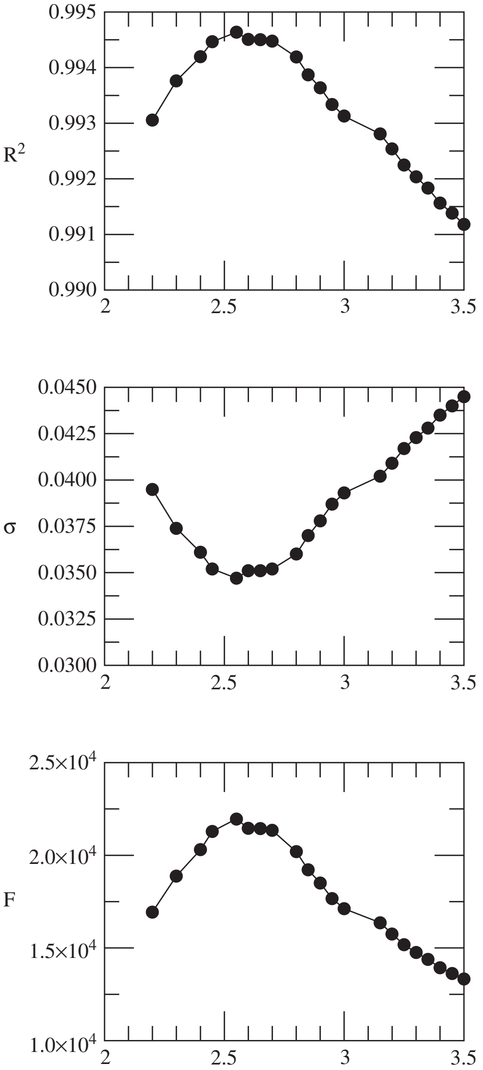

Figure 7. Location of the surface fractal behaviour lower cutoff radius by use of the determination coefficient, R^2, the standard deviation, σ, and the Fisher F-test value, respectively, from top to bottom. According to these figures of merit the lower cutoff value is situated at 2.55 Å.

some of the most discrepant points, or *outliers*, with a standard rejection criteria of $\pm 2\sigma$. In Ref. [4], a value of 2.15 ± 0.06 is reported for ground Belgian quarz glass of high purity, which is seemingly the closest physical match of our simulated substance. The agreement is quite good, in spite of the fact that our results refer to an *unrelaxed* surface. Preliminary surface fractal trial determinations of quartz make us suspect that the fractal dimension is not very sensitive to the structural differences between the surface of these silica varieties, and perhaps less so between a relaxed and an unrelaxed surface. Studies are underway in order to clarify this point.

On the other hand, the fractal dimension reported for crushed Corning lead glass in Ref. [4], 2.35 ± 0.11, rather than being an imprecise experimental determination or a figure our present data should come close to, most likely suggests a yet-unexplored correlation between fractal dimension and glass composition. Perhaps a matter of future work.

As regards the upper limit of the fractal surface behaviour, it is evident that, if there is one, it seems not to be within the range of our experiment. However, if the results from Ref. [4] are recalled at this point, it is reasonable to overlap the ranges covered by both sets of data. These authors have determined the fractality of their silica in the range of yardstick cross-sectional areas of 16–10,600 Å^2. However, since it is difficult to convert molecular cross-section values to effective radius values [8], a precise lower cutoff radius value cannot be readily extracted. Our data, on the other hand, refer exclusively to spherical adsorbates, and therefore, the cross-sectional area range can be directly obtained; thus, we find that it spans roughly from 20 to 300 Å^2 (corresponding to 2.55–10 Å). Due to the good agreement between both sets of results, it can be inferred that the fractal surface behaviour covers a yardstick cross-sectional area range of *at least* 20–10,600 Å^2, which implies that there is still surface fractality in silica at adsorbate radius values of around 58 Å, considering a spherical experimental molecule.

3.2 Lower fractal limit and percolation onset

Avnir and collegues [15,18–20] have collected profuse theoretical and experimental evidence of the finite range of fractal behaviour in many systems. On these grounds it is well established that many—if not most—experimental systems present a intrinsical—that is, not experimentally bound—fractal range of around two decades in span. Fractal surface behaviour of silica is, most likely, no exception to this rule. However, to our knowledge, existing experimental evidence is not enough to substantiate this claim.

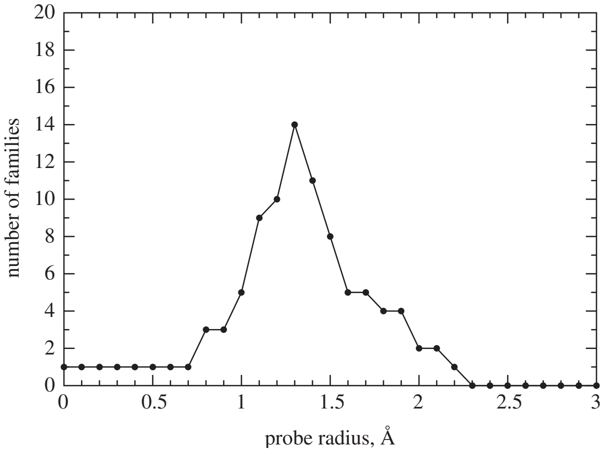

Figure 8. Number of probe families in terms of probe radius. *Probe* is a spherical molecule inserted in an interatomic cavity of the solid. *Family* is an overlap of at least two individual probes [21]. Percolation is achieved when all probes are connected, forming one big family. This graph is better understood reading it from right to left.

We will next concentrate on the lower cutoff radius in order to correlate it with a specific material characteristic of silica, namely its percolation radius.

Figure 8, originally from Ref. [21], shows the percolation behaviour of a simulated silica sample in terms of the radius of "probes" inserted in cavities of the proper size in the bulk of the material. In terms of physical experiments these probes would be Argon atoms or nitrogen molecules, for example.

It is pertinent to mention that the probe location algorithm from Ref. [21] is essentially similar to the one presented here: while the former looks for overlapping (rather, connecting [21]) probes within the structure, and the latter counts adsorbates on the surface, both algorithms have a common core that looks for places where to locate a virtual atom *in the bulk*. In the latter case, however, virtual adsorbates attach to outer atoms merely because of size constraints and the absence of periodic boundary conditions. As adsorbate size decreases, adsorbates start penetrating in the bulk, and this is readily reflected in the slope of the n vs. r curve (figure 6). If this figure is now compared to figure 8 above, it is evident that the changes observed in both cases correspond to the onset of percolation, at around 2.55 Å (keeping in mind the limitations of the former experiment), which seems to become complete close to the value of 0.7 Å.

Owing to the fact that the computing time required to continue the experiment to even lower radii increases very abruptly with decreasing radii, the adsorption experiment was finished at 2 Å. As was outlined above, this value falls within the percolation transition and, furthermore, the slope of the virtual adsorption curve at this point is close to 3. However, it is to be expected that, at even lower radii, another linear regime will be ultimately met, but now with $d_f = 2$, corresponding to the surface of the spheres representing the atoms themselves (if not flat, indeed smooth, therefore, the Euclidean value will be reached). It has been shown, on the other hand [15], that d_f is expected to take on the value of the underlying Euclidean space of the experiment. Therefore, a transition from d_f, corresponding to the fractal surface, to 3, where the adsorbates fill up the internal cavity volume, and ultimately to 2, would probably be encountered with decreasing probe radii.

4. Conclusions

In order to gain some insight into the fractal regime of the pure vitreous silica surface, we implemented a technique, a computational analogue of real powder adsorption experiments. Our experiments produced successful results compared with their real counterparts.

A fractal dimension of 2.093 ± 0.011 was found, close to the experimental value but with lower data dispersion, the latter being a desirable and often-found characteristic in computer experiments. With the help of statistical multivariate analysis, the existence of a lower surface fractal behaviour cutoff was ascertained, and its precise value, 2.55 Å, was determined. It was, therefore, possible to correlate this figure with the onset of percolation behaviour in this material. The excellent agreement of our determination of the fractal dimension of an unrelaxed simulated surface with the fractal dimension of the real material might relate to the insensitivity of the fractal dimension to surface relaxation.

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