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The fractal character of carbon surfaces determined by Fourier analysis of STM data

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The concepts of fractal geometry developed by Mandelbrot [1,2] have been applied successfully to the study of solid surfaces [3-5], where they provide a quantitative information on the topology.

Traditionally, the fractal dimension D is obtained from adsorption measurements, based either on the monolayer capacities of adsorbates with different molecular areas, or on adsorption models, as proposed by Fripiat [6] and Pfeifer [7]. The analysis of micrographs, as obtained in Donnet's laboratory by scanning tunneling electron microscopy (STM) [8,9] has also been applied recently to determine the fractal character of surfaces at the nanometer level. For example, the technique based on the ratio between the perimeter and the area of intergranular voids has been used by Gomez-Rodriguez et al. [10] to determine the fractal character of gold and platinum deposits. Ismail and Pfeifer [11], on the other hand, compared the fractal analysis of carbon fibers and carbon blacks, based on the adsorption technique, with the roughness of the surface observed by STM, but without quantitative analysis of the micrographs.

In the present letter, we show that the analysis of STM micrographs of a typical carbon black surface can provide direct information on its fractal character D, including the dispersion of this quantity. Our approach, based on the Fourier analysis of profiles and of patches of the surface, is similar to that described by Williams and Beebe [12], but it puts more emphasis on the statistical sampling. It also shows the good agreement with the fractal dimension derived from adsorption isotherms. The technique based on STM analysis applies only to open surfaces, since fine porosity and internal surface areas cannot be probed by this technique. Therefore, we limit ourselves to the case of a typical carbon black, but it is obvious that the present approach also applies to any type of irregular but open surface.

STM - or the related AFM technique - explores the surface at the atomic scale, and a typical micrograph, obtained with a Nanoscope-II, provides an array of 400 x 400 points for an area of 10 x 10 nm^2. This information corresponds to 400 profiles giving the change in height z along the x or y axes of the micrograph. A typical profile for carbon black XYL [13] is shown in Figure 1. As discussed by Williams and Beebe [12], we assume that such profiles, or even the entire surface, can be analyzed within the theoretical framework originally developed for fractal time signals of fractal brownian motion [1,4], later used to generate fractal surfaces [4,5]. We shall begin with the case of the STM profiles, which are functions of one dimension, x or y. Consider the Fourier transform (FT)

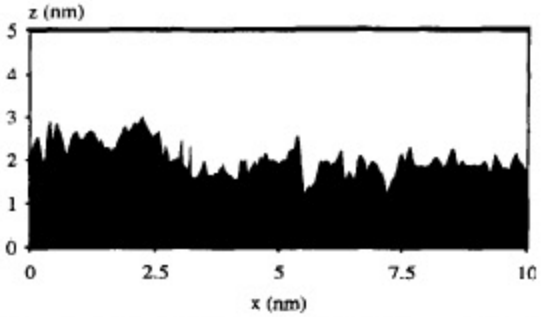

Figure 1. Typical STM profile Z(x) of micrograph No. 3 (see Table 1) for carbon black XYL [13].

$$Z(x) = \int_{-\infty}^{+\infty} F(f)\exp[2\pi i x f]\,df \qquad (1)$$

where $F(f) = |F(f)| \exp[i\phi(f)]$ and $\phi(f)$ represents the phase of F(f).

It has been shown, that Z(x) is a fractal curve if the power spectrum $F(f)\cdot F^*(f) = |F(f)|^2$ is proportional to $f^{-\beta}$, with $1 \le \beta \le 3$. Exponent β is related to the fractal dimension D of the curve [4,5] and

$$D = (5 - \beta) / 2 \qquad (2)$$

If the phases $\phi(f)$, i.e. the relative shifts of the contributions in the f space are random, it is possible to generate different profiles Z(x), but with the same underlying fractal dimension D. This property can be established by a suitable analysis of the profile. Eqn (1) shows that F(f), and consequently the power spectrum $|F(f)|^2$, can be obtained from the FT of Z(x). Provided that the $f^{-\beta}$ relation is satisfied, the fractal dimension D follows from eqn (2). In practice, the quality of the analysis depends on the number of points used in the discrete FT and on the extent of the domain on the x

axis. The latter will influence the lower bound f_o in the frequency (or reciprocal) space.

In this preliminary study, a fast FT [14] followed by the analysis of the power spectrum, was applied to a total of 3192 STM profiles obtained with a Nanoscope-II (courtesy Prof. J.B. Donnet, Mulhouse). In the present case, we considered 8 different-but typical-regions on the surface of carbon black XYL [13]. The magnifications corresponded to areas of 5 x 5 to 15 x 15 nm^2 and almost perpendicular to the z axis, which avoids the difficulties discussed in ref. [12]. The algorithms developed for the present study were tested with fractal profiles Z(x) generated by a standard procedure [5] and analyzed under the same conditions as the experimental data. These tests also provided useful information on the influence of a limited set of data on the quality of the FT analysis as discussed in [14].

The results shown in Table 1 were obtained from statistical samplings of the information and for each micrograph 399 profiles were analyzed, using in each case a random section of 256 consecutive points. This corresponds to 6.4 nm along the x axis for a 10 x 10 nm^2 micrograph. Fast FT also require sets of data corresponding to exact powers of 2 and 256 represents the maximum possible set for a profile of 400 points. As suggested by the tests on model profiles, it appears that 256 points are sufficient to provide good Fourier transforms of the individual profiles. The domain over which the power law $f^{-\beta}$ is determined, corresponds to $0\ nm^{-1} \le f \le 4\ nm^{-1}$ for a 10 x 10 nm^2 image.

For each micrograph one obtains a Gaussian distribution for the fractal dimensions D of the individual profiles, which can be written in the normalized form

$$\left(1/\sigma_D\sqrt{2\pi}\right)\exp\left[-\left(D-\overline{D}\right)^2/2\sigma_D^2\right]$$

A typical example, corresponding to the data obtained from micrograph no 3, is shown in Figure 2. As seen in Table 1 the average values $\overline{D}$ and the standard deviations σ_D obtained from the profiles of the various micrographs are similar, but not necessarily identical. This confirms that a sampling of the surface is necessary, in order to derive statistically reliable information from the STM data. The overall average for the typical regions of carbon black XYL, corresponding to a total of 3192 profiles, is $\overline{D} = 1.32 \pm 0.06$. It follows, that the fractal dimension of the surface itself should be approximately $\overline{D} = 2.32 \pm 0.06$, since moving to a higher space

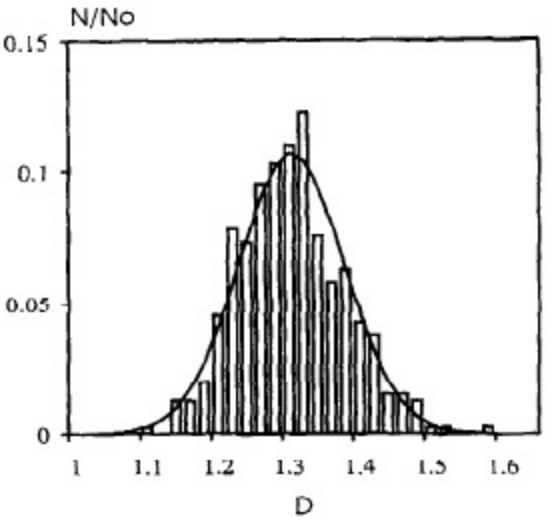

Figure 2. Normalized Gaussian distribution of the fractal dimensions D obtained from the 399 profiles Z(x) of micrograph no. 3. See also Table 1.

corresponds to an increase of 1 in the fractal dimension. [1,4].

The Fourier analysis applied to the profiles Z(x) can be extended to selected areas, by generalizing eqns. (1,2) and using two-dimensional FTs. Variable f is replaced by u and v in reciprocal space and for a fractal surface, the power spectrum should be proportional to $(u^2 + v^2)^{-\beta}$. The corresponding fractal character is now given by [5]

$$D = (7 - \beta)/2 \qquad (3)$$

As shown in Table 1, the sampling carried out for each micrograph on 30 random areas of 64 x 64 points leads to relatively consistent results. Following the general properties of discrete FTs [14], the power spectrum is determined over the frequency domain between 0 and p/n, where p represents the number of points (4096 = 64 x 64) and n is the dimension of the patch. One also obtains Gaussian distributions of the fractal dimensions D. As before, differences exist between the data obtained for the different micrographs and the overall average of the fractal dimension of the surface (240 patches on 8 different micrographs) is

Table 1. Average fractal dimensions obtained by Fourier analysis of STM profiles and selected areas on carbon black XYL.

Micrograph		Profile analysis		Selected area analysis	
No	size (nm^2)	$\overline{D}$	σ_D	$\overline{D}$	σ_D
1	15 x 15	1.41	0.06	2.29	0.12
2	10 x 10	1.32	0.06	2.21	0.10
3	10 x 10	1.27	0.06	2.16	0.10
4	10 x 10	1.37	0.06	2.23	0.09
5	10 x 10	1.38	0.06	2.28	0.09
6	5 x 5	1.25	0.06	2.19	0.06
7	5 x 5	1.23	0.06	1.85	0.08
8	5.65 x 5.65	1.29	0.06	2.27	0.10

$\bar{D} = 2.23 \pm 0.10$. It is somewhat smaller than the value suggested by the profiles Z(x) and has a larger standard deviation. The latter is due to the smaller sampling and illustrates its importance.

As summarized in Table 2, the results obtained from the Fourier analysis also agree with the fractal dimension $\bar{D} = 2.25 \pm 0.05$, derived from the adsorption isotherms of N_2 (77 K) and CH_2Cl_2 (293 K), following the procedure proposed by Fripiat [6].

The present study suggests that it is possible, in principle, to derive useful information on non-porous surface, by analyzing STM or AFM data by fast Fourier transform techniques, provided that a sufficiently large sampling of the surface is considered. It also appears that the two-dimensional FT of selected areas is more reliable, but it requires more computing time. This approach leads to an average fractal dimension $\bar{D}$ and its dispersion σ_D, two parameters which may be regarded as "fingerprints" of the surface. It is possible that the fractal dimension D changes with the scale at which the surface is examined, but the region below 10 nm is probably the most significant. The advantage of the technique described here lies in the fact that the topology of a surface and its evolution can be described by two parameters which have a precise physical and mathematical meaning (the surface can be modeled by using these parameters in standard algorithms). This approach will be illustrated later for series of carbon blacks of different origins or subjected to various physico-chemical treatments, such as graphitization and/or oxidation.

Table 2. Average fractal dimension of carbon black XYL

Method	profile FT	selected area FT	gas adsorption
$\bar{D}$	1.32 ± 0.06	2.23 ± 0.10	2.25 ± 0.05

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