



3 May 1996

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 253 (1996) 223–229

Fractal dimension of disordered submonolayers: determination from He scattering data

D.A. Hamburger^{a,b}, A.T. Yinnon^b, R.B. Gerber^{b,c}

^a Department of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

^b The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

^c Department of Chemistry, University of California at Irvine, Irvine, CA 92717, USA

Received 22 November 1995; in final form 27 February 1996

Abstract

We propose a novel method to measure the fractal dimension of a submonolayer metal adatom system grown under conditions of limited diffusivity on a surface. The method is based on measuring the specular peak attenuation of He atoms scattered from the surface, as a function of incidence energy. The (Minkowski) fractal dimension thus obtained is that of contours of constant electron density of the adatom system. Simulation results are presented, based on experimental data. A coverage dependent fractal dimension is found from a two-decade wide scaling regime.

1. Introduction

Fractal dimension (FD) [1] has proved to be a very useful concept for the description of certain disordered systems [2,3]. The experimental determination of this quantity is therefore an important challenge. Scanning tunneling microscope (STM) studies of adsorption and homoepitaxial growth of metal atoms on metal surfaces have recently revealed the formation of fractal-like structures, under conditions of limited adatom diffusivity and low deposition flux [4–6]. The characterization of the structures formed during these growth processes is a major objective of surface science, and the determination of FD plays an important part in meeting this objective. At present, STM is virtually the only available method for measuring the FD of such 2D systems. This involves image analysis of the STM topograph, as performed, e.g., by Hwang et al. [5] for Au/Ru(0001) and Brune et al. [6] for Ag/Pt(111).

The STM method has, however, several experimental limitations. In particular, the method is inherently local, and the statistics for characterizing disordered surfaces, including fractal structures, may not be the best. In general, to probe these systems at the microscopic level requires resolution of several Å. Scattering techniques used conventionally for the measurement of fractal dimension at such high resolutions, such as X-rays and neutron diffraction [7], are not applicable, due to their penetration into the bulk. An attractive alternative is presented by He scattering, which is particularly well suited to the study of disordered surfaces [8] as it is not destructive, probes solely the surface, and provides excellent statistics: A single beam can cover an entire surface of close to a cm² at once, compared to merely several (10³ Å)² with STM.

In the present Letter, we propose a novel method (SIMF – specular intensity measurement of fractality) by which a He scattering experiment can be used

to measure the FD of submonolayer disordered surfaces. In sharp contrast to STM, which due to its inherent local nature observes individual clusters, the proposed method measures the FD of an entire disordered surface. Thus the fractal property observed by a SIMF experiment, differs significantly from the STM one. Another difference concerns the physical interpretation of what is actually measured: STM probes the electron density near the Fermi level. In the repulsive regime, He experiences an exchange interaction with other electrons: it is scattered from regions that represent typically the low density tail of the surface electrons. In a semi-classical picture, at a given incidence energy, He is scattered from contours of constant potential. Using the Esbjerg–Norskov–Lang [9] relation

$$V_{\text{rep}}(x, y, z) = \alpha \rho(x, y, z) \quad (1)$$

for the repulsive part of a He/metal interaction, where α is a system-dependent constant and $\rho(x, y, z)$ the surface electron density, it follows that it is the FD of constant electron density contours which is measured in a SIMF experiment. These two differences illustrate that SIMF, which offers a global view at the electron density tail level, is in fact complementary to the measurement of FD by STM, which measures locally the electron density at the Fermi level. More explicitly, since SIMF looks at contours of constant and low electron density, it observes an object which is quite different from the underlying geometrical set of adatom positions. This object is the “thickened set”, or Minkowski Sausage” [1] of the adatoms (see inset of Fig. 4). SIMF is simple to implement experimentally: All it requires is the measurement of specular intensities, over a wide range of incidence energies. This has to be performed for calibration on a very low coverage system (ideally a single adatom), and then on the system of interest itself. A straightforward analysis subsequently yields the FD. The method is based on the energy-dependence of the scattering cross section (CS) of He scattering by an adatom [8,10]. This dependence can be exploited to observe the adatom system at different resolutions, thus providing the variation of yardstick sizes necessary for FD measurements.

2. Theory

Consider first the measurement of the CS of a single adatom adsorbed on an otherwise flat surface (as is the case to a good approximation for Pt(111)). Assume also that the surface is perfectly rigid. Any off-specular intensity must be attributed to scattering by the adatom [8], which allows for a convenient measurement of the CS as

$$I(k_z) = I_0 e^{-n\theta \Sigma_s(k_z)}. \quad (2)$$

Here I and I_0 are, respectively, the specular intensities for scattering from a surface with a single adatom and a flat surface; n is the number of sites per unit-cell; θ is the coverage; Σ_s is the adatom CS; and k_z is the incoming He wavenumber, assumed for simplicity to strike the surface at normal incidence. One can accordingly associate a scattering radius, $R_s(k_z) = (\Sigma_s(k_z)/\pi)^{1/2}$ with a single adatom. (Formally Bragg scattering must be counted along with specular scattering, but this effect is negligible for the flat metal surfaces considered here. We have shown elsewhere [10] that Eq. (2) is rigorously equivalent to the formal definition of the scattering cross section of a single adatom.) Next consider the CS measurement of a disordered submonolayer of adatoms. Suppose that every collision with an adatom results in off-specular scattering. This may be the case if the coverage is sufficiently low, so that no large compact regions have formed; or if the ad-islands are “dendritic” (fractal), so that the width of their “arms” is only several atoms across; or if the adatoms are non-metallic (e.g., CO), so that they present a highly corrugated surface to the incident He beam. Then the probability of hitting the adatom system is just the off-specular intensity. But this is also clearly the fraction of surface occupied by the adatom system. Thus

$$A_s(k_z) = 1 - I(k_z), \quad (3)$$

where I is now the specular intensity for scattering from the adatom system, and A_s is the total CS of the diffusely scattering adatoms, normalized to the total available surface area. Thus A_s cannot be considered the total CS of large compact metallic islands, which scatter diffusely only from their rim. This should, however, not be regarded as a limitation of SIMF: The method is designed to be applied

foremost to fractal structures, and these are known to have “arms” that rarely exceed 4–5 atoms across [5,6]. If specular scattering from the interior of ad-islands is important, the adatom system is likely to contain large compact regions and should probably be viewed as a “fat fractal” [11], i.e., a fractal with non-zero Lesbegue measure. Such fractals are characterized by their “exterior dimension” [12], i.e., the fractal dimension of the rim of the islands. But since it is the rim which accounts for the off-specular intensity, one can still apply SIMF, and find that it measures to a good approximation just this exterior dimension. Thus the method is seen to naturally provide the proper characterization of fat fractals as well. A point of concern regarding Eq. (3) is that it implicitly employs the “geometric overlap principle” [8] of adatom CSs. This has been criticized for adatom pairs [13]. For other systems¹ [8,14] it is strongly corroborated by test cases. We accepted it here, by assumption, as a method valid for all systems, for sufficiently low coverages. For some systems, at high coverage, systematic higher-order corrections to Eq. (3) may be necessary, which in our belief can be introduced. However, in this study we shall not deal with these complications.

3. Results and discussion

We proceed to present the results of our analysis of combined experimental and simulation data. To simulate (presently unavailable) experimental data, we performed He scattering calculations within the sudden approximation (SA) [16] on configurations of Ag/Pt(111) generated by kinetic Monte Carlo (KMC) simulations [17], in accordance with the deposition, diffusion and aggregation (DDA) scheme [18]. This scheme has been very successful in modeling thin-film-deposition experiments. A typical configuration generated by our simulations at a relatively high coverage of 27% is shown in the inset of Fig. 4, and is reminiscent of the STM topographs of Refs. [5,6]. Experimental CS data was available for

¹ Preliminary calculations show strong evidence for the success of the geometric overlap approach for systems of up to at least 5% randomly adsorbed Xe atoms on Pt(111) [15].

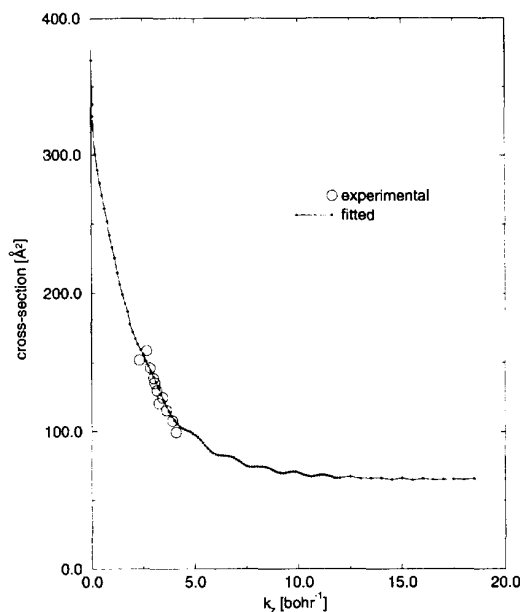


Fig. 1. Cross section of single Ag atom on Pt(111) as a function of incidence wavenumber. Circles are experimental results [19], accurate to within 20%. Dots connected by solid line are calculated CS values, using an LJ 6–12 potential with parameters fitted to the experimental data. The CS saturates at $k_z^m \approx 10 \text{ bohr}^{-1}$. Small interference oscillations due to particles striking the flat surface and the adatom tops can be observed. These measurements and simulations constitute step 1 in the SIMF algorithm.

scattering from a single Ag/Pt(111) adatom [19]. The He/Ag/Pt potential (to be published separately in Ref. [20]), unavailable at present from other sources, was obtained by fitting SA-CS calculations to this data. (To test its reliability, the same potential was used independently to reproduce an experimental angular intensity distribution for scattering from a system of polydispersed, small Ag/Pt(111) clusters, which it did with impressive accuracy [20]). The fit is shown in Fig. 1. Clearly, this potential is approximate only. However, we believe it is realistic enough for the purpose of simulating scattering data. In any case, the method does not depend on any specific potential: The ultimate test of SIMF will have to be experimental. The single-adatom CS, $\Sigma_s(k_z)$, shown in Fig. 1, was extracted from the specular intensity according to Eq. (2), yielding $R_s(k_z)$. As seen, beyond $k_z^m \approx 10 \text{ bohr}^{-1} \approx 10^3 \text{ K}$, $\Sigma_s(k_z)$ tends to a minimal limiting value $\Sigma_s^m = \pi R_m^2$, with $R_m = 4.55$

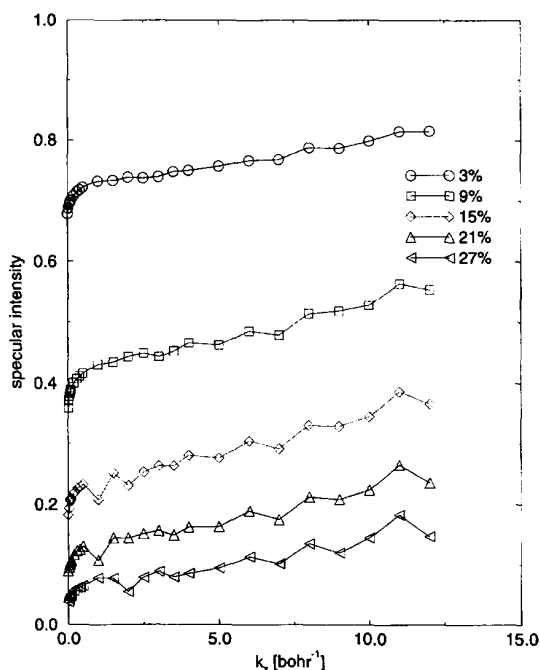


Fig. 2. Specular intensity of He scattered by fractal adatom islands of Ag/Pt(111), for coverages of 3%–27%, averaged over 30 configurations at each coverage. Interference oscillations increase in magnitude with the coverage. The specular intensity overall increases with wavenumber, reflecting the decrease in total cross section of the Ag islands. These simulations constitute step 2 in the SIMF algorithm.

Å. The Pt(111) lattice constant is 2.77 Å, thus the CSs of nearest-neighbor Ag adatoms always overlap, and the set appears as a continuum to the incoming He. This is shown in the inset of Fig. 4, where a circle of radius R_m is drawn around each nucleus, and the resulting contour is shown. This is an approximate view of the contour of constant electron density observed by He atom incident at $k_z > k_z^m$, and of the fractal whose dimension is measured by SIMF. The adatom system CS, $A_s(k_z)$, was found according to Eq. (3) from the specular intensities calculated at various coverages, shown in Fig. 2.

Once the functions $R_s(k_z)$ and $A_s(k_z)$ are known, the FD can be found. The algorithm we propose is based on the Minkowski [1] definition. The Minkowski cover $M(R)$ of a set X is obtained by placing circles of radius R centered at every point in X . One then calculates the area $A(R)$ of the union of

all circles. The FD is found in practice as the slope at small R values of the log–log plot,

$$\left\{ \log \frac{1}{R}, \log \frac{A(R)}{R^2} \right\}, \quad (4)$$

which presumes that a constant slope (i.e., scaling) is observed over at least one decade [21]. In the present context, a natural choice of the set X is the union of adatom CSs at the high k_z /minimal radius (R_m) limit, shown in the inset of Fig. 4. Since in this limit the CS is determined by the repulsive part of the potential, semi-classically, the CS circumference corresponds, through Eq. (1), to a contour of constant electron density. Therefore, this choice yields the FD corresponding to such contours of the Ag system, where a high-energy He atom would be stopped. This is an inherent property of the adatom system, uniquely accessible to He. Other probes (e.g., STM) would measure the FD of another feature of the adatom system. The remarkable property of He scat-

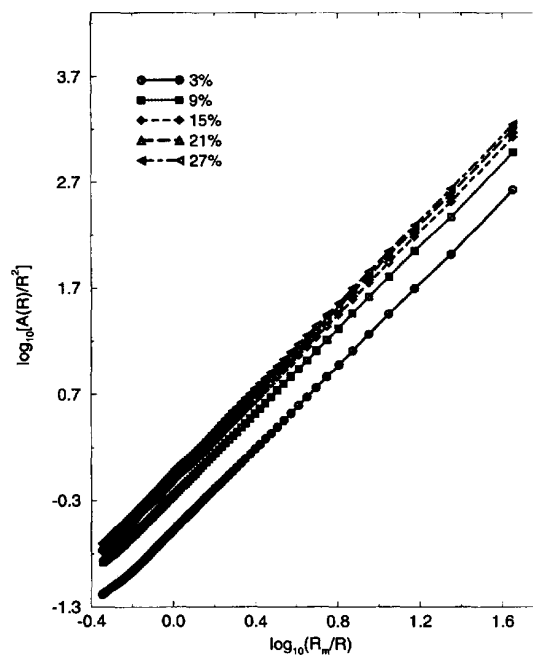


Fig. 3. Plots of $\log[A_s(R_s)]/R^2$ versus $\log(R_m/R)$, for various coverages, used to determine the FD (note that the oscillations from Figs. 1,2 have cancelled out). Two decades of scaling behavior are observed, indicating that He is indeed capable of measuring the FD of the scattering object.

tering, is that it is capable of providing the Minkowski cover of the adatom set, through a variation of the incidence energy, which is equivalent to a change of the scattering radius R_s . Thus, the process summarized by Eq. (4) can be carried out in an He scattering experiment in two steps: First, the CS of an individual Ag adatom is measured over a wide range of incidence wavenumbers, at least as far as the saturation point k_z^m . This then yields $R_s(k_z)$, with

the minimal radius measured as $R_m = R_s(k_z^m)$. Second, $A_s(k_z)$ is measured under the same conditions of variable incidence wavenumbers. Eliminating k_z between A_s and $R_s = R_m + R$ yields the scattering-determined area of the Minkowski-cover, $A_s(R_s)$. From here the calculation of the FD proceeds according to Eq. (4). (Note that it is the “Minkowski-radius”, R , and not the full cross-sectional radius R_s , which appears in Eq. (4)). We applied this

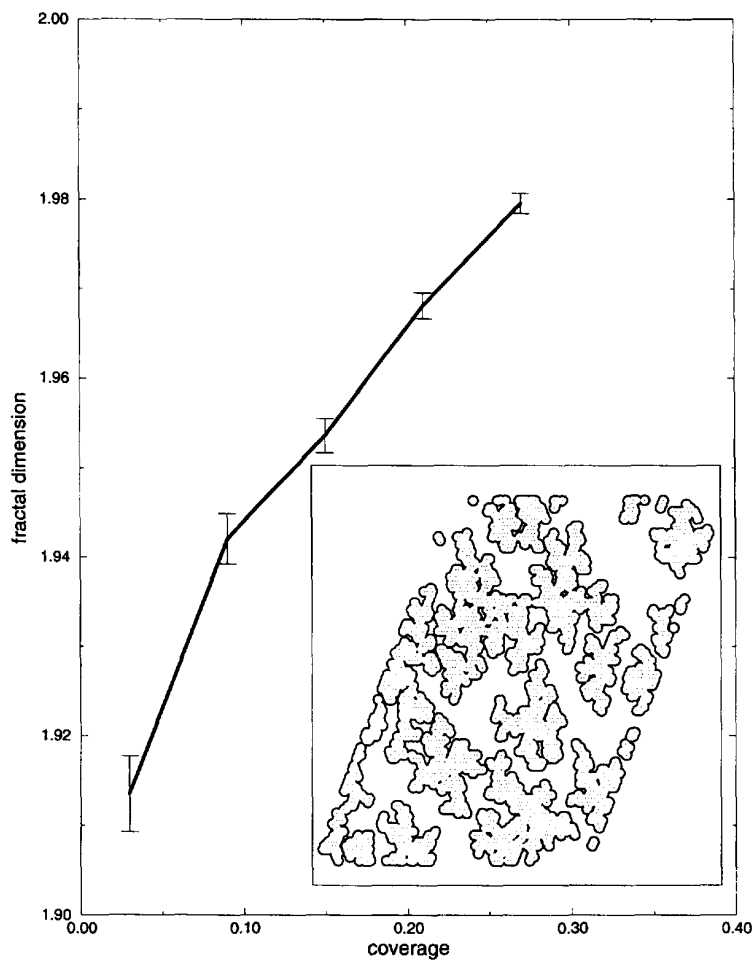


Fig. 4. He scattering prediction of fractal dimension as a function of coverage, obtained from the log–log plots in Fig. 2. Error bars are due to linear regression. Inset: Dots are nuclei positions in typical configuration obtained by KMC simulations on a P(111) hexagonal surface (periodic boundary conditions apply). Coverage is 27%. Contour represents view of electron density by He atom incident with $k_z > k_z^m$. That is, each adatom is drawn to scale with a cross-sectional radius of $R_m = 4.55 \text{ \AA}$. According to SIMF, this fractal has a dimension of 1.98.

procedure, for step 1, to the CS fitted to the experimental Ag/Pt(111) data (Fig. 1), and for step 2, to our scattering simulation data at various coverages. The results are shown in Fig. 3. It is noteworthy that two decades of linear, scaling behavior are observed. The existence of a large scaling regime is an “empirical” proof of the fractality of our systems, and the ability of He scattering to measure it. It is tempting to compare the scattering results to a simple geometrical model, where the Minkowski procedure is applied to circles of radius R_m , centered at the adatom positions. However, such a naive approach is misleading: The quantum CS has no simple geometrical counterpart. The CS is “fuzzy”, i.e., a He atom is scattered off-specularly from within the CS only with a probability. Work incorporating a distribution of geometrical radii, allowing a comparison with the CS, is currently in progress.

The corresponding slopes, or FDs, are displayed as a function of coverage in Fig. 4. The FD rises monotonically with coverage and is close to the embedding-space dimension of 2. This high FD is expected, if the large value of the individual CS (Fig. 1) is taken into account: As seen in the inset of Fig. 4, due to this large CS the contour has a rather smooth structure (compared, e.g., to a typical, highly ramified, DLA cluster), thus enclosing an almost “ordinary” 2D set. The non-universality of the FD (i.e., its dependence on coverage) is a definite prediction of the theory, and differs significantly from the well-known result for individual DLA clusters, the only fractal systems observable so far by STM [5], whose $FD \approx 1.7$ [22] is universal. However, it does agree with the results obtained by Jensen et al. [18] for the DDA model: There too, a strong dependence of the FD on coverage is observed. More importantly, as previously mentioned, $R_m > a$, the Pt(111) lattice constant. This implies that the geometry probed by the He beam is much less porous than that of DLA clusters. Gaps in the latter can easily be smoothed out by overlapping CSs, and disjoint DLA clusters may in fact become one from the He point of view. The rise in FD can be understood as an increasingly larger portion of the surface being covered by overlapping CSs, as the coverage is increased. Taken together, these observations should explain why the geometry of constant electron density contours, probed by a He beam, has a very

different fractal nature from that of DLA clusters. We expect actual He scattering experiments to produce similar result to Figs. 1–4.

4. Concluding remarks

In summary, a simple new procedure for the measurement of FD of disordered submonolayers by He scattering has been proposed. First the specular intensity as a function of incidence wavenumber k_z for a single adsorbate must be measured, from which the scattering-radius R_s is determined according to Eq. (2). Then the specular intensity is measured over the same incidence wavenumber range for the adatom system of interest, and its CS, A_s , is found according to Eq. (3). Eliminating the wavenumber between these two quantities, the function $A_s(R_s)$ is plotted on a log–log scale according to Eq. (4). The slope of this plot is the FD. If the adatom system contains large compact regions, the calculated FD should be interpreted as the exterior dimension of a fat fractal.

SIMF measures the FD of constant electron density contours of an adsorbed metal system. This observation raises some interesting questions for future research, which is beyond the He scattering context: For example, what is the effect of this fractality on bulk properties, such as surface conductivity and elasticity?

Finally, the present article does not deal with the effect of adatoms adsorbed near step edges. These adatoms have different CSs from those adsorbed on terraces, and hence require a separate calibration of $\Sigma_s(k_z)$. This issue is currently under investigation. An initial experimental effort to implement SIMF for Ni/Cu(111) is under way [23].

Acknowledgement

This research was supported by the German–Israeli Foundation for Scientific Research (G.I.F.), under grant number I-215-006.5/91 (to RBG). Part of this work was carried out with support from the Institute of Surface and Interface Science (ISIS) at UC Irvine. The Fritz Haber Center at the Hebrew University is supported by the Minerva Gesellschaft für die Forschung, Munich, Germany. We are grate-

ful to Professor G. Comsa and Dr. P. Zeppenfeld for stimulating discussions, and thank Professors D. Avnir, O. Biham and G. Vidali, and D. Thimor for helpful comments.

References

- [1] B.B. Mandelbrot, *The fractal geometry of nature* (Freeman, San Francisco, 1982).
- [2] T. Vicsek, *Fractal growth phenomena* (World Scientific, Singapore, 1989);
A. Bunde and S. Havlin, eds., *Fractals and disordered systems* (Springer, Berlin, 1991).
- [3] D. Avnir, ed., *The fractal approach to heterogeneous chemistry: surfaces, colloids, polymers* (Wiley, Chichester, 1992).
- [4] M. Bott, T. Michely and G. Comsa, *Surface Sci.* 272 (1992) 161.
- [5] R.Q. Hwang, J. Schröder, C. Gunther and R.J. Behm, *Phys. Rev. Letters* 67 (1991) 3279.
- [6] H. Brune, C. Romainczyk, H. Röder and K. Kern, *Nature* 369 (1994) 469.
- [7] J. Teixeira, in: *On growth and form*, eds. H.E. Stanley and N. Ostrowsky (Martinus Nijhoff, Boston, 1986) pp. 145–162.
- [8] B. Poelsema and G. Comsa, *Springer tracts in modern physics*, Vol. 115. *Scattering of thermal energy atoms from disordered surfaces* (Springer, Berlin, 1989).
- [9] N. Esbjerg and J.K. Norskov, *Phys. Rev. Letters* 45 (1980) 807;
N.D. Lang and J.K. Norskov, *Phys. Rev. B* 27 (1983) 4612.
- [10] D.A. Hamburger and R.B. Gerber, *J. Chem. Phys.* 102 (1995) 6919.
- [11] D.K. Umberger and J.D. Farmer, *Phys. Rev. Letters* 55 (1985) 661.
- [12] C. Grebogi, S.W. McDonald, E. Ott and J.A. Yorke, *Phys. Letters A* 110 (1985) 1.
- [13] G. Petrella and L. Cassidei, *Chem. Phys. Letters* 212 (1993) 512; *Chem. Phys.* 191 (1995) 203.
- [14] A.T. Yinnon, R. Kosloff, R.B. Gerber, B. Poelsema and G. Comsa, *J. Chem. Phys.* 88 (1988) 3722.
- [15] G. Petrella, private communication.
- [16] R.B. Gerber, A.T. Yinnon, J.N. Murrel, *Chem. Phys.* 31 (1978) 1;
R.B. Gerber, *Chem. Rev.* 87 (1987) 29.
- [17] D.A. Hamburger, A.T. Yinnon, I. Farbman, A. Ben-Shaul and R.B. Gerber, *Surface Sci.* 327 (1995) 165.
- [18] P. Jensen, A.-L. Barabási, H. Larralde, S. Havlin and H.E. Stanley, *Phys. Rev. B* 50 (1994) 15316.
- [19] P. Zeppenfeld, private communication.
- [20] A.T. Yinnon, D.A. Hamburger, I. Farbman, R.B. Gerber, P. Zeppenfeld, M.A. Krzyzowski and G. Comsa, in preparation.
- [21] P. Pfeifer and M. Obert, in: *The fractal approach to heterogeneous chemistry: surfaces, colloids, polymers*, ed. D. Avnir (Wiley, Chichester, 1992) p. 16.
- [22] T.A. Witten Jr. and L.M. Sander, *Phys. Rev. B* 27 (1983) 5686.
- [23] G. Rosenfeld and B. Poelsema, private communication.