Nanoparticles dynamics on a surface: fractal pattern formation and fragmentation

Veronika V. Dick, Ilia A. Solov’yov, Andrey V. Solov’yov
Frankfurt Institute for Advanced Studies, Goethe University, Ruth-Moufang-Str. 1, 60438
Frankfurt am Main, Germany
E-mail: solovyov@fias.uni-frankfurt.de

Abstract. In this paper we review our recent results on the formation and the post-growth relaxation processes of nanofractals on surface. For this study we developed a method which describes the internal dynamics of particles in a fractal and accounts for their diffusion and detachment. We demonstrate that these kinetic processes determine the final shape of the islands on surface after post-growth relaxation. We consider different scenarios of fractal relaxation and analyze the time evolution of the island’s morphology.

1. Introduction
The process of formation and post-growth relaxation of deposited structures is still not well understood (see e.g. [1–6] and references therein). The understanding of formation and post-growth relaxation processes would allow one to explore the self-organization processes of particles on the surface in obtaining patterns with predictable properties.

The conventional technique of thin-film growth by deposition of atoms [1, 2], small atomic clusters [1, 3] and molecules [2, 7, 8] on surfaces gives a possibility to construct materials with pre-defined properties. Recent experiments show that patterns with different morphology can be formed in the course of cluster deposition process on a surface [1, 3, 9]. Among other possible shapes, droplet-like and fractalic islands have been observed in various systems [1, 3, 9]. It was shown that the island morphology depends on various factors, such as the temperature [1, 3, 4, 10, 11], particle size [12], particle deposition rate [10, 13, 14], substrate roughness [15, 16], concentration of impurities in the system [3, 4, 17] and interparticle interaction energies [3, 10].

The formation of fractals provides a natural framework for studying disordered structures on surface because fractals are generally observed in far-from-equilibrium growth regime. During the last years fractal shapes have been observed for a variety of systems. For example, fractals consisting of Ag [4, 11, 17], Au [18], Fe-N [19] clusters and C_{60} molecules [20, 21] have been fabricated on different surfaces with the use of the cluster deposition technique [2, 7]. The self-organization dynamics of particles on a surface was also studied theoretically [5, 6, 16, 22]. An efficient theoretical tools for describing particle dynamics on a surface is the diffusion limited aggregation (DLA) method [23], which was used for the study of the fractal formation process on a surface [10, 13, 16, 22].

In the present paper we investigate further the process of fractal formation and also the post-growth fractal stability on a surface. For this we have developed a method describing the internal dynamics of particles in a fractal and accounting for their diffusion and detachment.
We demonstrate that these kinetic processes determine the shape of the islands on surface being formed in the course of island formation and the following post-growth relaxation. We consider different scenarios of fractal relaxation and analyze the time evolution of the island’s morphology. The results of our calculations are compared with experimental measurements of the post-growth relaxation of silver cluster fractals on a graphite substrate [4, 11, 17].

2. Theoretical methods
In this section we discuss the theoretical methods used for studying the dynamics of particles on a surface. Computations were performed with the use of the MBN Explorer computer package, which is developed for structure optimization, simulation of dynamics and growth processes in various nanosystems [5, 6, 24–33]. Below we describe the computational method used in our work and explain how the internal dynamics of particles in a fractal has been accounted for.

To study the diffusion of particles on surface we used a version of the kinetic Monte Carlo (KMC) method [34–36]. The idea of the KMC method is as follows. The time-evolution of a molecular system is modeled stepwise in time. With a certain probability, at each step of the simulation, the system undergoes a structural transformation. The new configuration of the system is then used as the starting point for the next simulation step. The transformation of the system is governed by the kinetic rates, input into the KMC method. Note, that at each simulation step the system can be transformed into one of several states. Thus, in the KMC method, the probability for the system to attain a certain configuration is proportional to the corresponding kinetic rate. Due to its probabilistic nature, the KMC method allows to study dynamical processes on time scales significantly exceeding the time scales of the conventional molecular dynamics simulation. Therefore, this method is ideal for studying dynamical processes involving large ensembles of particles, in which the details of single particle dynamics are not so important, and it can be parameterized by a few relatively simple kinetic rates.

For our studies we use a modification of the conventional KMC method. For each particle on surface we first determine the number of its possible diffusion directions. Thereby, a particle can either diffuse freely on surface, or diffuse along the periphery of the already pre-formed structure on surface (see Fig. 1). A diffusion direction of the particle is chosen randomly in such a manner that all possible diffusion directions are equally probable. For the chosen diffusion direction the probability for particle diffusion is then calculated, and the particle is translated in this direction with the calculated probability. To speed up the calculation, we simulate particle dynamics on a two-dimensional hexagonal grid, on which a particle has up to six neighbors, as illustrated in Fig. 1. The size of a single grid cell in this case is defined by the particle radius.

To simulate the growth process the following procedure has been adopted. At every step of the simulation new particles are deposited on the surface according to the deposition rate and occupy some of the free cells in the grid. Simultaneously, the already deposited free particles diffuse on the surface with the rate

\[ \Gamma = \frac{1}{\Delta t} = \nu_1 \exp \left[ -\frac{E_a}{kT} \right], \]  

(1)

where \( E_a \) is the activation energy, \( \nu_1 \) is the attempt escape rate, \( T \) is the temperature of the system, \( k \) is the Boltzmann constant, and \( \Delta t \) is the simulation time step, which defines the characteristic time for particle diffusion on surface. As follows from Eq. (1) the values of \( E_a \) and \( T \) define the characteristic time scale of the fractal growth. In this paper we focus on the study of silver cluster fractals on a graphite substrate, and therefore, assume \( E_a \) fixed.

The simulation time step \( \Delta t \) is related to the particle diffusion coefficient \( D \) on surface as follows [6]

\[ \Delta t = \frac{d_0^2}{4D}, \]  

(2)
Figure 1. Arrangement of deposited particles on the hexagonal grid. The important processes which govern pattern formation on surface are indicated by arrows: $\Gamma$ is the free particle diffusion rate, $\Gamma_d(m, n)$ is the diffusion rate along the periphery of an island, and $\Gamma_e(l)$ is the particle detachment rate from an island. The diffusion along the periphery depends on the number of broken bonds ($m$) and the number of maintained neighboring bonds ($n$). The particle detachment rate depends on the number of broken bonds ($l$). In the depicted example $m = 3$, $n = 1$, $l = 2$.

where $d_0$ is the particle diameter. The experimental value of the diffusion coefficient of an Ag$_{500}$ cluster on graphite at room temperature is equal to $2 \cdot 10^{-7}$ cm$^2$/s [17]. Substituting this value in Eq. (2), one obtains $\Delta t = 78$ ns.

The relaxation of an island on surface is driven by diffusion of particles along the island’s periphery and particle detachment from the island. Both processes are schematically illustrated in Fig. 1. The diffusion and the detachment rates depend on the activation energy and the particle-particle interaction. In the Arrhenius approximation, the diffusion rate of a particle along the periphery of the fractal reads as:

$$\Gamma_d(m, n) = \nu_2 \exp \left[ -\frac{mE_b}{kT} - \frac{n\Delta \epsilon}{kT} - \frac{E_a}{kT} \right],$$

where $m$ is the number of bonds that are broken due to the particle motion, $E_b > 0$ is the binding energy barrier of two particles, $n$ is the number of maintained neighboring bonds between two particles and $\Delta \epsilon \leq E_b$ is the diffusion energy barrier [11, 22], $\nu_2$ is the attempt escape rate. Equation (3) describes the probability of a particle to overcome a potential energy barrier,
which for a particle diffusing along the fractal periphery is parameterized by the energies $E_b$, $\Delta \epsilon$, and $E_a$. Parameters $E_b$ and $\Delta \epsilon$ define the potential energy barrier for particle diffusion along the fractal periphery, while $E_a$ characterizes the time scale of particle diffusion [6].

Note that Eq. (3) does not account for the bonds which may be created in the system when a particle diffuses. This feature of Eq. (3) is easy to understand. Indeed, in our model the particle diffusion process is considered stepwise, i.e., at each step of the computation a particle is displaced with a certain probability on the distance equal to its diameter in a random direction (see Fig. 1). But prior the particle is displaced to its new location there is no information about the newly created bonds in the system. Therefore only those bonds which the particle forms in its neighborhood prior the displacement influence its diffusion dynamics.

The evaporation (detachment) rate of a particle from the island in the Arrhenius approximation is given by

$$\Gamma_e(l) = \nu_3 \exp \left[ -\frac{lE_b}{kT} - \frac{\Delta \mu}{kT} - \frac{E_a}{kT} \right],$$

(4)

where $l$ is the number of bonds broken after particle detachment from the island, $\Delta \mu$ is the chemical potential of particle detachment [3,11,22,37], $\nu_3$ is the attempt escape rate of a particle from its equilibrium position. For the simulations of the fractal fragmentation presented below we assume:

$$\nu_2 \approx \nu_3 = \nu.$$

(5)

This approximation is valid when the characteristic attempt escape rate of a particle leading to its diffusion or detachment are close. From Eqs. (1)-(4) one derives that the probability of different kinetic processes in the system depends on the values of $E_b$, $\Delta \epsilon$, $\Delta \mu$, which are called below as the kinetic parameters. For the convenience, in this paper we define all the kinetic parameters in the units of $kT$ ($1 kT = 0.026$ eV) at room temperature (300 K).

3. Results

3.1. Fractal growth

Using the methods described in the pervious section we consider particle dynamics on a $500 \times 500$ nm$^2$ substrate with periodic boundary conditions. According to the periodic boundary conditions every particle which reaches a boundary of the substrate is removed to the opposite boundary. This method allows to keep the surface density of deposited particles constant when no new particles are added into the system. Periodic boundary conditions provide a useful tool for studying processes on a small surface fragment with particle surface density as in experiment. Thus, the periodic boundary conditions allow to study formation of a single (or several fractals), as if it was surrounded by many similar fractals on a macroscopically large substrate.

To illustrate the process of particle selforganization on surface we consider two different scenarios shown in Fig. 2. We deposit the particles on surface with the rate $F = 1.026 \times 10^9$ particle/cm$^2$s being close to the experimental value [4]. The diameter of a particle in the simulations is taken 2.5 nm, i.e. as in the Ag$_{500}$ cluster [4,11,17]. It is known from experiment that particles nucleate more efficiently in the vicinity of point defects [16]. Therefore, to speed up the nucleation process we have introduced five immovable point defects on surface that become the fractal growth centers as illustrated in Figs. 2a-b.

The variation of the kinetic parameters $E_b$, $\Delta \epsilon$ and $\Delta \mu$ results in the formation of different patterns on surface. Figure 2 shows the morphology of fractals on surface during the particle deposition process simulated for $E_b = 30 kT$, $\Delta \epsilon = 10 kT$, $\Delta \mu = 100 kT$ (plot a), and for $E_b = 60 kT$, $\Delta \epsilon = 20 kT$, $\Delta \mu = 100 kT$ (plot b) after $t = 50$ s of simulation. The comparison of the fractal morphologies shown in Fig. 2a and Fig. 2b shows that the thickness of fractal branches
Figure 2. Formation of fractals on surface during the particle deposition process simulated for $E_b = 30\, kT$, $\Delta \epsilon = 10\, kT$, $\Delta \mu = 100\, kT$ (a) and for $E_b = 60\, kT$, $\Delta \epsilon = 20\, kT$, $\Delta \mu = 100\, kT$ (b). Plots (a) and (b) show the morphology of the formed structures after $t = 50\, s$ of simulation. Contour plots (c) and (d) show the time evolution of the size distribution calculated for the emerging fractals on surface at room temperature for the kinetic parameters introduced in (a) and (b) respectively.

increases at smaller values of kinetic parameters. This observation can be easily understood. The morphology of fractals is mainly governed by the time needed for a newly deposited particle to reach the growth region, and by the time needed for a particle to find an optimum position within the fractal (rearrangement time). The later process is governed by the parameter $\Delta \epsilon$. For $\Delta \epsilon = 10\, kT$ (see Fig. 2a) the rearrangement time becomes shorter than for $\Delta \epsilon = 20\, kT$, as seen from Eq. (3), leading to an increase of the fractal branch thickness. If $\Delta \epsilon = 20\, kT$ (see Fig. 2b), the particles within the fractal need much time to hop, and therefore, the fractals with less optimized particle structure, i.e. with thinner branches, are formed. Note that the thickness of fractal branches is related to the cluster mobility on surface, which is also determined by the
The thickness of the fractal branches influences the compactness of the structures formed on surface. Figures 2c-d show the time evolution of the size distribution calculated for the fractals shown in Figs. 2a-b respectively. It is clear from Figs. 2c-d that the average radius of a fractal grows nonlinearly with time. At each time frame the distribution of fractal sizes for the fractals with thicker branches (see Fig. 2c) has a smaller width than that for the distribution of the fractals with thinner branches (see Fig. 2d). This happens because in the case of fractals with thicker branches the peripheral particles have enough time to rearrange and form a more compact structure, while in the case of fractals with thinner branches the inner dynamics of particles in the fractal is almost frozen. The fact that fractals with thinner branches grow almost without any rearrangements leads to the formation of larger size structures, as compared to the more compact fractals with thicker branches during the same simulation time interval.

An important characteristic of a structure on surface is the fractal dimension $d_f$. The Hausdorff fractal dimension is generally defined as \[ [39, 40] \]

\[
d_f = \lim_{l \to 0} \frac{\log[N(l)]}{\log[1/l]}. \tag{6}
\]

Here $N(l)$ is the number of self-similar structures of linear size $l$ needed to cover the whole structure. In practice, the fractal dimension is usually calculated by the box-counting method or using the mass-formula for dimension introduced in [41]:

![Figure 3. Time evolution of the average fractal dimension calculated using Eq. (7) for the structures shown in Fig. 2. Curves (a) and (b) illustrate the time evolution of the fractal dimension for the fractalic islands shown in Fig. 2a and Fig. 2b respectively.](image)
\[ N = \rho \left( \frac{2R}{d_0} \right)^{d_f}, \]  

(7)

where \( N \) is the number of particles in the system, \( R \) is the radius of the minimal circumscribed circle of the structure, \( d_0 \) is the diameter of a particle and \( \rho \) is the ratio of the covered surface to the entire surface area (packing density). In the case of the hexagonal grid \( \rho = \pi/2\sqrt{3} \).

The time evolution of the average fractal dimension calculated using Eq. (7) for the structures shown in Fig. 2 is presented in Fig. 3. Here the averaging is performed over the five structures which are formed during the growth process. Figure 3 shows that the fractal dimension calculated for fractals with thicker branches is higher than the fractal dimension calculated for the structures with thinner branches. This happens because the morphology of a fractal with thicker branches is closer to a compact droplet for which the fractal dimension is equal to 2.

Figure 3 illustrates that the fractal dimension for the structures with thicker branches experiences more significant fluctuations in the beginning of the simulation. This happens, because the structure of small fractals with thicker branches experiences more significant rearrangements due to the formation of compact droplets in the core of the fractal (see Fig. 2a). This results in an increase of the fractal dimensionality. When the number of particles attached to the fractal core reaches a critical value, the time needed for the particle rearrangement becomes larger than the characteristic period for a new particle attachment and the fractal branches are getting formed. This fixes the fractal dimension at a certain value.

3.2. Fractals fragmentation

The structures shown in Figs. 2a-b experience further transformation after the particle deposition has finished. Depending on the kinetic parameters the time after which a noticeable change in the fractal morphology can be detected is different. To illustrate the difference in the post-growth relaxation processes we considered fragmentation of a single fractal by varying the kinetic parameters of our model. The initial structure of the fractal used to study the fragmentation process is different from the structures presented in Fig. 2, and is shown in Fig. 4a. This fractal was grown with the method described above and has a diameter of \(~ 638 \text{ nm}\), which is close to the diameter of the experimentally grown structures discussed in [4, 11, 17].

We present several scenarios of fractal relaxation. The rate of fractal decay depends on chosen parameters of our model, which define the morphology of fragments emerging during the relaxation of a fractal. The snapshots of the structures which emerge on the surface after different time intervals are shown in the Fig. 4 and give an illustrative example of three different fragmentation scenarios of a fractal. Figure 4b corresponds to the “explosion” of a fractal and is the fastest fragmentation scenario. In this case the interaction energy \( E_b \) between particles is weak and the probability of a particle to evaporate from the fractal is of the same order of magnitude as the probability of a particle to diffuse along the fractal periphery. This fragmentation scenario can be realized in experiment if the temperature of the system is rapidly elevated after the fractal formation. Figures 4c and 4d illustrate the fragmentation into a group of compact and non-compact islands respectively. The possibility of compact droplets formation depends on the ratio between \( E_b \) and \( \Delta \epsilon \) as follows from Eqs.(3)-(4). At higher value of the barrier energy \( \Delta \epsilon \) the diffusion rate of a particle along the periphery of an island is comparable with the rate of particle detachment, leading to the formation of highly disordered droplets. These fragmentation scenarios shown in Figs. 4c-d are expected to occur in experiments in which impurities are added to the system, causing the fractal to break apart [4].

The important quantity characterizing the fractal fragmentation process is the number of fragments at a given time. The minimum size of a fragment corresponding to a single particle is equal to one. The time evolution of the number of fragments calculated for different sets of kinetic parameters is shown in Fig. 5a-b. Lines 1 and 2 in Fig. 5a show the time evolution of
Figure 4. Evolution of the fractal structure during the post-growth relaxation process. Plot (a) shows the initial structure of a fractal. Plots (b)-(d) show the snapshots of the system at different fragmentation stages: (b) rapid fragmentation of a fractal after \( t = 0.02 \) s with \( E_b = 1 \) \( kT \), \( \Delta \epsilon = 0.2E_b \), \( \Delta \mu = 2 \) \( kT \); (c) the diffusion of particles along the branch of a fractal is a more preferable process, fractal fragments into a group of compact islands after \( t = 0.05 \) s with \( E_b = 4 \) \( kT \), \( \Delta \epsilon = 0.1E_b \), \( \Delta \mu = 2 \) \( kT \); (d) slow diffusion of particles along the branch causes the fractal to fragment into a group of dispersed islands after \( t = 0.05 \) s with \( E_b = 4 \) \( kT \), \( \Delta \epsilon = 0.8E_b \), \( \Delta \mu = 2 \) \( kT \).

The number of fractal fragments in the case of relatively weak binding energy between particles being equal to 1 \( kT \) and 2 \( kT \) respectively. The number of fragments rapidly approaches the asymptotic value, equal to the total number of particles in the fractal.

Figure 6 shows the distributions of island sizes calculated after 0.78 s of simulation for the fractal shown in Fig. 4a. The calculations were performed on a 2.5 \( \times \) 2.5 \( \mu \)m\(^2\) substrate with
Figure 5. Time evolution of the number of fragments $N_{fr}$ calculated for the fractal structure shown in Fig. 4a on a substrate $2.5 \times 2.5 \mu$m$^2$ with periodic boundary conditions. The fractal fragmentation in this example is considered for $\Delta \mu = 2 kT$ for different values of the binding energy $E_b$ and the barrier energy $\Delta \epsilon$. Plots (a) show the results of calculation obtained for $\Delta \epsilon = 0.2E_b$ by varying the binding energies between two particles. The lines 1-6 correspond to $E_b = (1, 2, 3, 4, 5, 6) kT$ respectively. Plots (b) represent the results obtained for $E_b = 4 kT$ with varying $\Delta \epsilon$. The lines 1-6 correspond to $\Delta \epsilon = (0, 0.1, 0.2, 0.5, 0.8, 1)E_b$ respectively.

Figure 6. Distributions of island sizes after the fractal fragmentation obtained for different sets of the kinetic parameters: (a) $E_b = 4 kT$, $\Delta \epsilon = 0.1 E_b$, $\Delta \mu = 2 kT$; (b) $E_b = 3 kT$, $\Delta \epsilon = 0.2 E_b$, $\Delta \mu = 10 kT$. Insets show the results of the experimental measurements: (a) for perturbed silver fractals after annealing, and (b) after adding of oxide impurities to silver clusters [4].
periodic boundary conditions for the kinetic parameters \( E_b = 4 \, kT \), \( \Delta \epsilon = 0.1E_b \), \( \Delta \mu = 2 \, kT \). In this case the diffusion of particles along the fractal periphery is the dominating process. The increased rate of particle peripheral diffusion leads to the higher probability of island rearrangement and to the formation of a broad distribution of island sizes, as seen in Fig. 6a. The inset in Fig. 6a shows the results of experimental observations for silver fractals after annealing at 600 K. The size distribution of the silver cluster islands has a broad width with the most probable radius of silver islands \( \sim 25 \, nm \). The same value follows from the theoretical calculation.

Figure 6b shows the distribution of island sizes calculated for \( E_b = 3 \, kT \), \( \Delta \epsilon = 0.6 \, kT \), \( \Delta \mu = 10 \, kT \). The result of the numerical calculation is compared with the experimental observation on silver fractals grown from oxidized silver nanoparticles [4] shown in the inset. The most abundant radius of silver cluster island in this case is 18 nm, being in good agreement with the results of our calculations as seen from Fig. 6b.

Note that in Fig. 6 the width and the position of the maximum in the theoretical distributions are close to experiment while the absolute value in the distributions differs significantly. This happens because in our calculation we consider a single fractal, while the experimental measurements deal with many fractals on a surface. A similar shape of the calculated distributions and the measured ones shown in Fig. 6 allows one to conclude that for \( N_{fractals} \) fractals on surface the number of islands formed after fragmentation is equal to

\[
N_{tot} (R) = N_{fractals} \cdot \langle N_{isl} (R) \rangle, \tag{8}
\]

where \( \langle N_{isl} (R) \rangle \) is the average number of islands formed after fragmentation of a single fractal.

4. Conclusion
We have performed a theoretical analysis of the growth and post-growth processes occurring in nanofractals on a surface using the method, which describes the internal dynamics of particles in a fractal and accounts for their diffusion and detachment. We demonstrated that these kinetic processes are responsible for the morphology of the islands created on a surface.

The developed method includes three kinetic parameters, which are determined by interatomic interactions in the system. The kinetic parameters can be also obtained from experiment and are specific for different types of substrates and deposited materials. We have analyzed the fractal stability on surface by varying the kinetic parameters over a wide range of values and revealed three principally different fragmentation scenarios of a fractal.

5. Acknowledgments
This work was supported by the European EXCELL project. The possibility to perform complex computer simulations at the Frankfurt Center for Scientific Computing is also gratefully acknowledged.

References
[1] Meiweis-Broer K H (ed) 2000 Metal Cluster at Surfaces: Structure, Quantum Properties, Physical Chemistry (Berlin: Springer-Verlag)
[2] Drexler K E 1992 Nanosystem (USA: Willey)
[3] Bréchignac C, Houly P and Lahmani M (eds) 2007 Nanomaterials and Nanochemistry (Cambridge University Press)
[4] Lando A, Kébaâli N, Cahuzac P, Masson A and Bréchignac C 2006 Phys. Rev. Lett. 97 133402–(1–4)
[5] Dick V V, Solov’yov A and Solov’yov A V 2009 AIP Conf. Proc. 1197 76–88
[6] Dick V, Solov’yov A and Solov’yov A V 2010 http://arxiv.org/abs/1001.3992
[7] Rubahn H G 2004 Basics of Nanotechnology (Denmark: Weinheim)
[8] Solovyeva V, Keller K and Huth M 2009 Thin Solid Films 517 6671–6676
[9] Jensen P 1999 Rev. Mod. Phys. 71 1695–1735
