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Metal surface adsorbed clusters: Structure and dynamics

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Abstract

Extensive numerical simulation are reported for the structure and dynamics of large clusters on metal(1 0 0) surfaces. Different types of perimeter hopping processes makes center-of-mass of the cluster to follow a random walk trajectory. A *diffusion coefficient D* for the whole cluster can be defined as $\lim_{t\to\infty} D(t)$, with $D(t) = \langle d^2\rangle/(4t)$ and d the displacement of the center-of-mass from its initial position. The dependence of the diffusion coefficient on those perimeter hopping processes can be analyzed in detail, since the relations between different rates for the processes are explicitly considered as parameters.

Keywords: Monte Carlo simulations; Metal surface structure; Morphology; Roughness and topography

1. Introduction

The different diffusion processes that take place on surfaces have, clearly, an important role in many technological areas. Diffusion of individual atoms and clusters has been studied for a long time with different experimental techniques and, more recently, using scanning tunneling microscopy (STM) [1,2]. From a theoretical point of view, several lattice-gas kinetic Monte Carlo simulations [3] have addressed the question of the dependence of the cluster diffusion coefficient D on the cluster size in square [4,5] or triangular [6] lattice. Recently, the diffusion of metal clusters on metal surfaces has received extensive attention due to the fact that some experimental and theoretical studies have led to the expectation that only small, two-dimensional (2D) clusters were able to diffuse. The larger two-dimensional clusters, also observed on the surfaces, were not expected to diffuse. However, recent experimental evidence from STM studies [7] have became available showing that very large 2D Ag clusters clusters (containing $N = 10^2$–10^3 atoms) are indeed able to diffuse on Ag(1 0 0) substrates.

From the previous theoretical and experimental work, it is now clear that the movement of the cluster is a consequence of several atomic-scale processes, taking place at the periphery of the cluster, that makes the center-of-mass follow a random walk trajectory. For instance, for small clusters ($N < 20$) it has been proposed that the mechanism of diffusion is the short range motion of a single atom away from the periphery followed by a regrouping of the cluster around the peripheric vacancy [8]. Evidence of concerted gliding is also available [9]. In particular, the movement of very small clusters due to several peripheral hopping processes have been analyzed, both theoretically and numerically and the results can be well compared with experiments [10].

2. Theory

The movement of clusters composed of a large amount of atoms has been considered a consequence of two main mechanisms taking place at the boundary of the cluster: periphery diffusion (PD) and 2D evaporation–condensation (EC). In the PD process several types of atomic motions *along* the periphery of the cluster are responsible for the displacement of the center-of-mass. However, the atoms do not leave the cluster while executing those movements. In the EC process the cluster is considered to be in quasi-equilibrium with a dilute 2D gas of atoms, diffusing very quickly on the metal surface surrounding the cluster. Both types of process are non-exclusive and can take place at the same time. Of course, it can be

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anticipated that the energy barriers for the PD mechanism are much lower than the energy needed for an atom to leave the cluster and, in principle, the PD process can be expected to be primarily responsible for the movement of the cluster [11].

At this point, the question of the dependence of the diffusion coefficient on the number of atoms in the cluster (N) becomes relevant. The diffusion coefficient D of a cluster can be defined as

$$\lim_{t\to\infty} D(t) = \frac{\langle d^2\rangle}{4t}, \tag{1}$$

with d the net displacement of the center-of-mass from its initial position. It has been suggested that the value of the diffusion coefficient D behaves as $D \sim N^{-\alpha}$, while different values for the exponent α have been proposed depending on which diffusion mechanism is considered to facilitate the movement of the cluster [15,1]. In this sense, Monte Carlo simulations for cluster diffusion based on the PD mechanism are available, showing a variation of the exponent α from $\alpha \cong 1.5$ to 2.0 [12,13]. However, these values of α lead to a strong variation of the diffusion coefficient D as a function of the number N, which is not consistent with the experimental STM data available [7]. On the other hand, in reference [16] it is claimed that for *circular* clusters the diffusion coefficient behaves as $D \sim d^{-n}$, where d is the *diameter* of the cluster and the integer n identifies different diffusion mechanisms. When the center-of-mass motion occurs by adatom diffusion along the periphery of the cluster $n = 3$, while $n = 2$ or 1 when the cluster diffusion occurs by correlated or uncorrelated adatom evaporation and condensation, respectively.

2.1. Simulation theory

It is clear, then, that a deeper understanding of the way in which 2D large clusters move could be obtained by using numerical simulations. Following this idea, Monte Carlo simulations can be used for the kinetics in which each of the above described processes takes place at its own rate. Diffusion of atoms along the cluster perimeter proceeds at a rate r_e and evaporation–condensation at a rate r_c. Both are related by the detailed-balance relation

$$\frac{r_c}{r_e} = \exp\left(-\frac{\Delta E}{k_b T}\right), \tag{2}$$

where ΔE is the energy difference between the two processes. The relation between rates r_e and r_c is kept as a parameter in the simulations.

Monte Carlo simulation proceeds as follows. Starting with a 'square' cluster of N atoms at the center of a 1500×1500 lattice substrate [14], a site from the periphery of the cluster is selected at random and then two main events can take place.

(1) With probability r_c/r_e, an evaporation or condensation event is selected. If the evaporation event is going to take place, an atom is detached from the cluster and goes into the surrounding two dimensional gas of fast, diffusing atoms. If the condensation event is going to take place, an atom is attached to a randomly selected place on the periphery of the cluster since it is considered to come from the surrounding two-dimensional gas. In this way, the average number of atoms in the cluster in maintained equal to N.
(2) With probability $1 - (r_c/r_e)$, an atom is relaxed to the nearest-neighbor or next-nearest-neighbor empty site where it finds that more bonds are saturated. This is the mechanism that makes the cluster stay connected (i.e. not to dissolve) in the $r_e \gg r_c$ limit and, in order to avoid dissolution, we restrict ourselves within such limit by letting r_c/r_e to be less than 0.2.

After a certain thermalization time, we start to record the position of the center-of-mass of the cluster with respect to the origin of coordinates considered to be at the center of the lattice representing the substrate. Time is being measured in Monte Carlo steps per atom.

3. Results

The simulational results are shown in Figs. 1–4. Results presented have been averaged over 100 independent runs and for 10 different cluster sizes containing from 121 to 961 particles.

Fig. 1 is a representative plot of the overall behavior of the diffusion coefficient. It can be seen that, in agreement with the available experimental results [7], the simulations show a fast decay in the value of the diffusion coefficient at early times, for $(r_c/r_e) = 0.1$ and $121 \le N \le 961$. After this fast decay the cluster reaches a diffusive random-walk-like behavior,

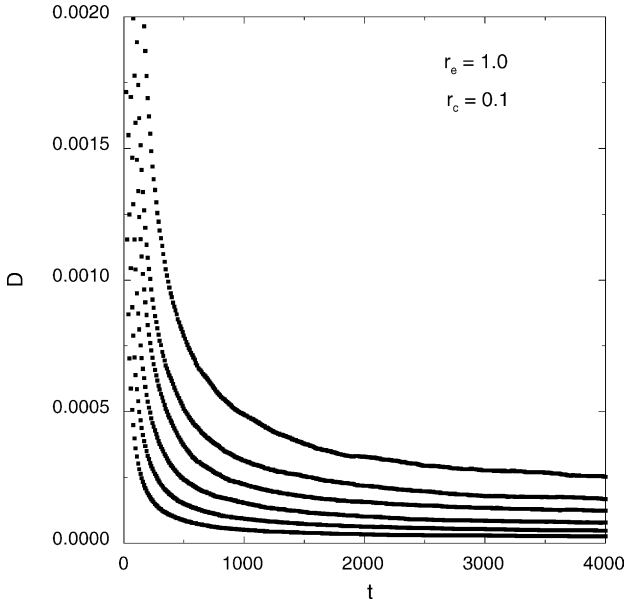

Fig. 1. The behavior of the diffusion coefficient along the total simulation time for $N = 121$ (top curve) to $N = 961$ (bottom curve). The very fast decay at early time is in correspondence with the experimental results.

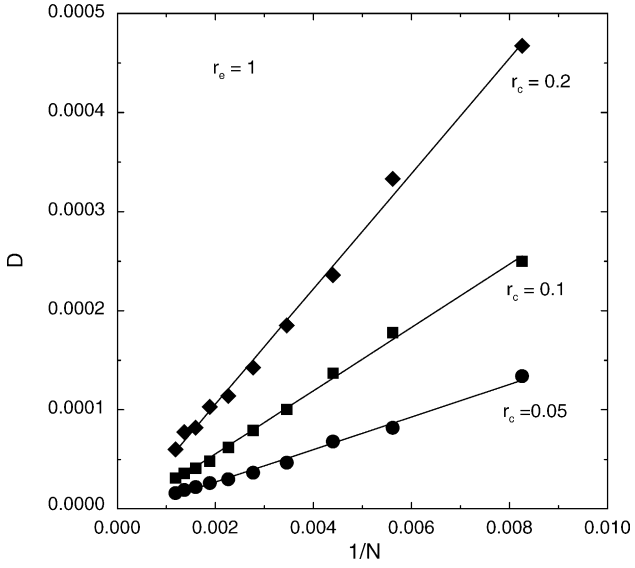

Fig. 2. The diffusion coefficient D vs. $1/N$. Different slopes for different values of r_c indicate that the pre-factor D_0 depends on the r_c/r_e relation.

demonstrated by the plateau at $t \to \infty$. This figure confirms that the main characteristics of the movements of the cluster are well reproduced in the simulations. In particular, the very fast decay at early times has been associated with a certain *back correlation effect*, and it has been observed in previous cluster diffusion simulations where it was considered to be related to the cluster connectivity [12].

In Fig. 2 the diffusion coefficient D is plotted versus $1/N$. From the plot it can be seen that D depends on N as $D = D_0(r_c/r_e)N^{-\alpha}$ with $\alpha = 1$. The most notable characteristic is the dependence of the pre-factor D_0 on the evaporation–relaxation relation r_c/r_e. This dependence can be observed only by a numerical simulation that allows full control of the relation. It can be seen that the cluster has a greater D for greater values of the relation r_c/r_e. This result is a little bit surprising. It tell us that, although the predominant processes at the periphery is the PD process, the EC process has a greater effect on the *mobility* of the cluster. Then, the simulations favor the EC mechanism as the primary one responsible for the movement of the cluster, in accordance with the available experimental data.

From Fig. 3, it can be seen that the exponent α does not depend on the ratio r_c/r_e. By linear fitting the points of the plot, an average [17] value for the exponent α is obtained. This value is $\alpha = 1.092 \pm 0.123$ and differs from the value obtained from the experimental data, reported in reference [7]. However, the experimental measurements of D as a function on N have been adjusted within a certain experimental error and cannot be considered to be conclusive. On the other hand the value of $\alpha \sim 1.0$ is in accordance with the theoretical predicted value of [16] ($n = 1$) when the evaporation–condensation process is uncorrelated.

Finally, in Fig. 4 the behavior of the diffusion coefficient versus time (at early evolution times) is plotted in log–log plot for $r_e = 1.0$ and three different values of r_c. From this plot a very new characteristic of the movement is identified. The diffusion coefficient behaves as $D(t) \sim t^{-\beta}$ with $\beta = 0.812 \pm 0.021$, showing a non-trivial scaling behavior at early times. In principle, it could be anticipated that the scaling behavior should be in close relation with the above mentioned back correlation effect. But, the explanation of this characteristic from a physical point of view needs more experimental and theoretical work.

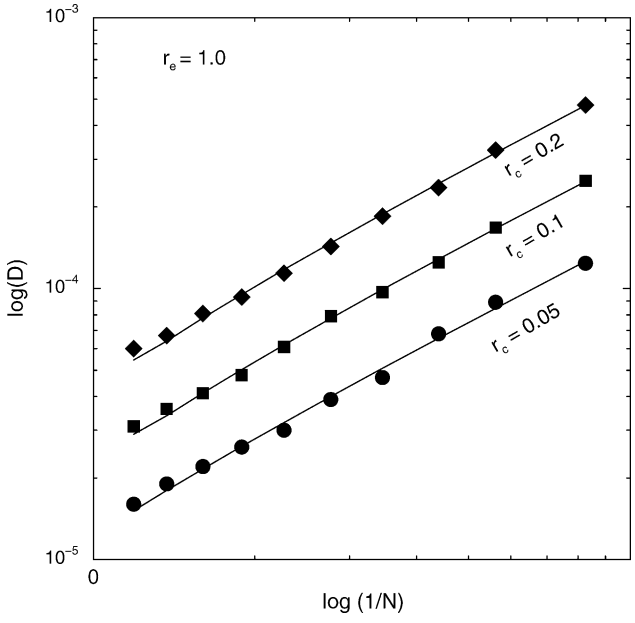

Fig. 3. Log–log plot of D vs. $1/N$. The average slope of the three plots gives the value for the exponent $\alpha = 1.092 \pm 0.123$.

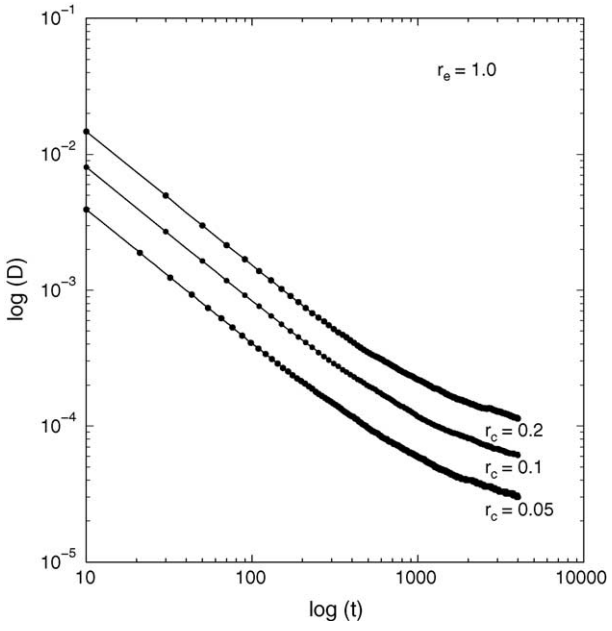

Fig. 4. Log–log plot of the diffusion coefficient vs. time (at early evolution times) for $r_e = 1.0$ and different values of r_c. The straight decay indicates a scaling behavior $D(t) \sim t^{-\beta}$, with $\beta = 0.812 \pm 0.021$.

4. Conclusions

Results for the simulation of the diffusion of large Ag clusters over Ag(1 0 0) surfaces have been presented. The simulations reproduce very well the main characteristic of the movement of the cluster according to the available experimental results. The dependence of the diffusion coefficient on the number of atoms in the cluster has been explored, as well as other features of the mechanisms by which the large clusters diffuses. Also, from the simulations new characteristics of the movement have been identified and suggest new experimental and theoretical work. A deeper understanding of the basic cluster diffusion mechanisms will have important consequences on the techniques that make possible the epitaxial growth.

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