

## Diffusion of nanoclusters

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### Abstract

The diffusion of nanoclusters on various surfaces is investigated. It is shown that the misfit between the cluster and substrate is the main parameter determining the magnitude of the cluster diffusion on perfect surfaces. The motion of the cluster on non-ideal surfaces is also explored, and shows surprising results.

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### 1. Introduction

The behavior of nanometer-size clusters deposited on surfaces is potentially interesting for obtaining original nanostructures, which physicists hope are interesting for technological applications, e.g., micro-electronic, optoelectronic, and magnetic devices [1]. Diffusion is an important factor in the fabrication of thin films and self-organized structures by deposition of the clusters. It has been demonstrated experimentally that many metallic clusters diffuse on a graphite surface at a surprisingly high rate of about  $10^{-8}$  cm<sup>2</sup>/s at room temperature [2], quite comparable to the rates that would be achieved by single atoms. This was confirmed theoretically through molecular-dynamics simulations of Lennard-Jones clusters on a Lennard-Jones substrate [3]: clusters consisting of particles which are incommensurate with the substrate

exhibit very rapid diffusion. The cluster diffuses as “a whole”, and its path is akin to a Brownian motion induced by the internal vibrations of the clusters and/or the vibrations of the substrate. This is in striking contrast with other cluster diffusion mechanisms, whereby the motion results from a combination of single-atom processes (e.g., evaporation–condensation, edge diffusion, etc.). The latter are more appropriate to clusters which are in epitaxy with the surface, but are likely not significant in cases where the mismatch is large, such as in Refs. [2,4] (see Ref. [5] for a review).

In the present paper, we briefly review the results obtained for cluster diffusion on *perfect* substrates, and we investigate the diffusing properties on surfaces containing defects such as steps or vacancies. We focus here on gold clusters diffusion on a graphite surface because it has been the object of several experimental studies [5–8], and also because semi-empirical, many-body potentials are available for this material. The energetics of gold atoms is described in terms of the embedded-atom-method (EAM) [9], while carbon atoms are assumed to

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interact via Tersoff potentials [10]; the (generally assumed) weak interactions between gold and carbon atoms are modeled with a simple Lennard-Jones potential. A comparable model was used recently by Luedtke and Landman to study the anomalous diffusion of a gold nanocluster on graphite [11]; diffusion was found to exhibit a stick-slip mechanism resulting in an apparent Lévy-flight type of motion.

## 2. What determines cluster diffusion on perfect surfaces?

Fig. 1 shows the morphologies obtained after deposition of gold clusters containing 249 on (a) a graphite (highly oriented pyrolytic graphite) sur-

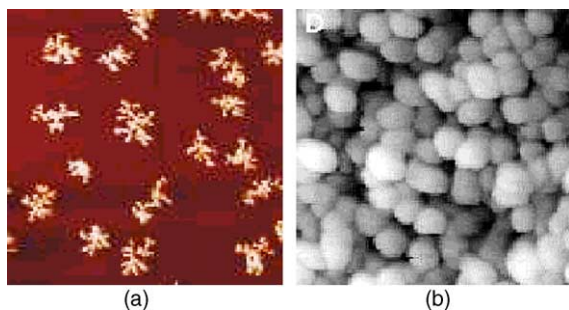


Fig. 1. Gold nanoclusters behave very differently on graphite (a, total width 1  $\mu\text{m}$ ) or gold surfaces (b, total width 150 nm). See Ref. [20] for experimental details.

face and (b) gold (111) surface. Clearly, on the graphite surface, deposited clusters are able to diffuse rapidly and aggregate into ramified islands. On the gold substrate instead, the clusters stick to their landing site and randomly fill up the substrate. This experimental result, together with many others presented in Ref. [5] confirms our main result obtained in molecular dynamics simulations of cluster diffusion on substrates, namely that the misfit is the main parameter determining the magnitude of the cluster diffusion speed [3]. Roughly speaking, diffusion coefficients of order  $10^{-8}$   $\text{cm}^2/\text{s}$  at room temperature are observed for nanoclusters on perfect surfaces when misfit is present, while much smaller coefficients (of order  $10^{-15}$   $\text{cm}^2/\text{s}$ ) seem to be the rule when clusters can epitaxially accommodate on the substrate [5].

## 3. Cluster diffusion on non-ideal surfaces

### 3.1. Experimental motivation

Fig. 2 shows the experimental motivation behind our computer simulations of cluster diffusion on non-ideal surfaces. One of the most important aims in the field of nanostructure growth is the ordering of nanoislands on a surface. Many approaches have been suggested, among which atomic deposition on strained surfaces or the use of self-organized molecular structures (see for exam-

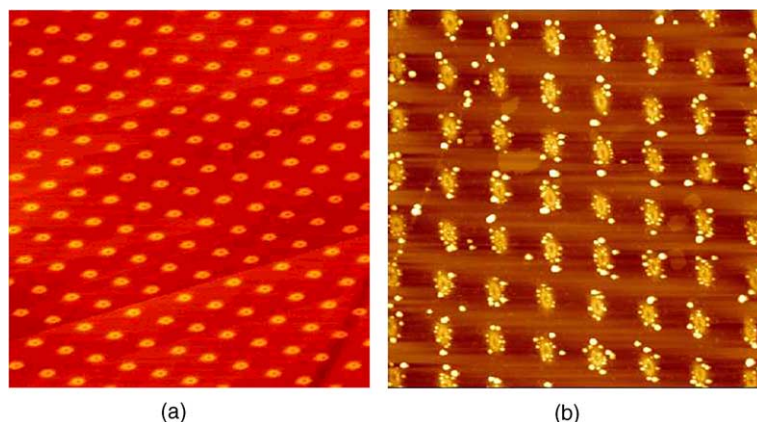


Fig. 2. One way of ordering clusters that are initially randomly deposited on a substrate is to prepare it by creating an ordered array of defects (a, width 3.4  $\mu\text{m}$ ) which then act as “traps” for the diffusing clusters (b, width 2  $\mu\text{m}$ ). See Ref. [13] for details.

ple Ref. [12]). Here we take a different approach: the bombardment of a perfect graphite surface by an ion beam, to produce an ordered array of defects which are supposed to serve as traps for diffusing clusters. Experimentally, the idea seems to work [13]. We would now like to understand why clusters are trapped by these defects. For this, we perform molecular dynamics simulations of gold cluster diffusion on graphite surfaces containing defects such as vacancies or steps.

### 3.2. Computational details

Diffusion coefficients for clusters can only be obtained at the expense of very long MD runs: there exists numerous possible diffusion paths, and there is therefore not a single energy barrier (and prefactor) characterizing the dynamics. These systems, further, do not lend themselves readily to fast MD algorithms [14,15]. Brute-force simulations—long enough for statistically significant data to be accumulated—therefore appear to be the only avenue. This rules out ab initio methods, which can only deal with very small systems (a few tens of atoms) over limited timescales (tens of picoseconds at best): empirical or semi-empirical potentials *must* be employed.

As mentioned above, we describe here the interactions between Au particles using the embedded-atom method (EAM) [9], an  $n$ -body potential with proven ability to describe reliably various static and dynamic properties of transition and noble metals, in either bulk or surface configurations [16]. The model is “semi-empirical” in the sense that it approaches the total-energy problem from a local electron-density viewpoint, but using a functional form with parameters fitted to experiment (equilibrium lattice constant, sublimation energy, bulk modulus, elastic constants, etc.).

The interactions between C atoms are modeled using the Tersoff potential [10], an empirical  $n$ -body potential which is known to account well for various conformations of carbon. The Tersoff potential for carbon is truncated at 2.10 Å, which turns out to be smaller than the inter-plane distance in graphite, 3.35 Å. Thus, within the Tersoff potential, there are no interactions between neighbouring graphite planes. This is of course an

approximation, but not a bad one since basal planes in graphite are known to interact weakly. (This is why it is a good lubricant!) A pleasant consequence of this is that the substrate can be assumed to consist of a single and only layer, thus reducing formidably the (nevertheless heavy) computational load of the calculation.

Last—and most problematic—is the Au–C interaction. One way of determining this would be to fit an ab initio database to a proper, manageable functional potential. However, since Au–C pairs conform in so many different ways in the present problem, this appears to be a hopeless task, not worth the effort in view of the other approximations we have to live with. We therefore improvised this interaction a little bit and took it to be of the Lennard-Jones form, with  $\sigma = 2.74$  Å and  $\epsilon = 0.022$  eV, truncated at 4.50 Å. The parameters were obtained rather loosely from Ref. [17].

Overall, we therefore expect our model to provide a qualitative, rather than quantitative, description of the system. Our model is *realistic*, however, in that the most important physical characteristics are well taken into account, but is not expected to provide a *precise* description of the particular system we are investigating.

We consider here a gold nanocluster comprising 249 atoms, close to the clusters deposited in the experiments [5,8]. The graphite layer has dimensions  $66.15 \times 63.65$  Å<sup>2</sup> and contains 1500 atoms. Calculations were carried out for several temperatures in the range 500–600 K. It should be noted that a free-standing 249-atom Au cluster melts at about 650 K in this model [18]. This temperature is not affected in a significant manner by the graphite substrate as the interaction between Au and graphite-C atoms is weak. However, the dynamics of the cluster is expected to be different in the high-temperature molten state from the low-temperature solid state. The equations of motion were integrated using the velocity form of the Verlet algorithm with a timestep of 1.0 and 2.5 fs for dynamic and static substrates, respectively [19]. (Carbon being a light atom, a smaller timestep is needed in order to properly describe its dynamics.) All calculations were performed using the program `groF`, a general-purpose MD code for bulk and surfaces developed by one of the authors (LJL).

### 3.3. Results

#### 3.3.1. Vacancies

We naively thought that the ion bombardment would create “holes” (i.e. islands of atomic vacancies) in the first graphite layer, these holes being able of trapping clusters which would “fall” into them. Our MD simulations suggest exactly the opposite situation: the cluster seems to *avoid* the holes, never approaching from the hole center more than a minimum distance of 9 Å (Fig. 3). Instead, a histogram of the center to center distances shows a clear maximum for 20 Å, showing a “repulsion” effect between the cluster and the hole. We discuss this effect in the next section.

#### 3.3.2. Steps

A more careful examination of the experimentally created defects shows that these are not really

holes but more like “craters” or bumps [13]. Previous experimental results [8] had already shown that clusters can be trapped by monoatomic steps on a graphite surface at room temperature. We therefore decided to study the interaction of a gold cluster with a step.

Fig. 4 shows the trajectory of the center of mass at two different temperatures. Clearly, the cluster is attracted by the *ascending* step (on the right) and repelled by the *descending* one (left). Moreover, we have checked that the cluster never crosses any of the steps, which suggests a *Schwobel* effect [21] acting on the whole cluster, and not only on single adatoms as has usually been assumed. Work is in progress on this point. The attraction of the cluster to the ascending step suggests that at lower temperatures the cluster can be effectively trapped by the step, thus explaining the experiments cited above. We are now

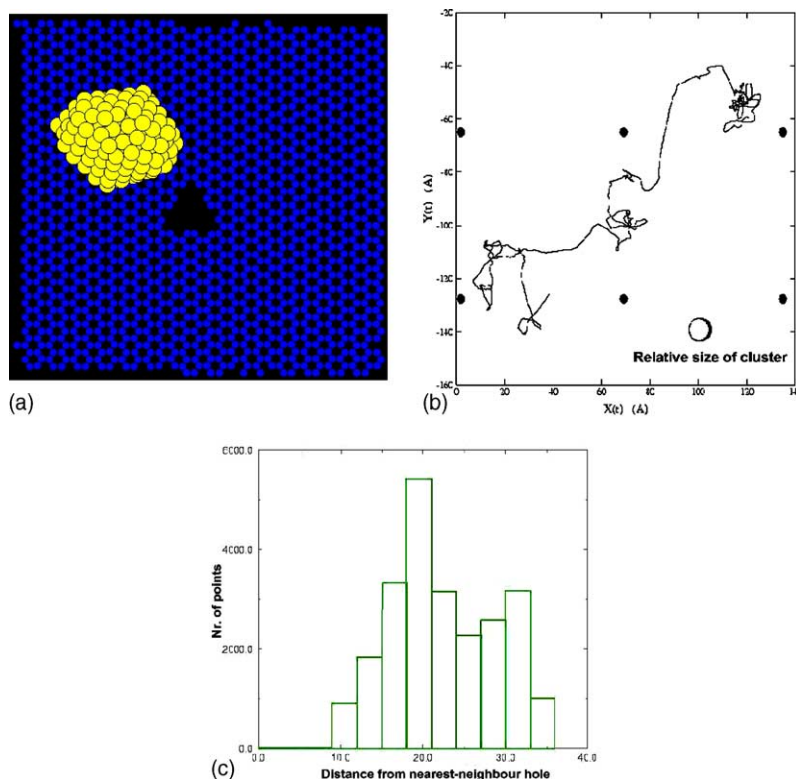


Fig. 3. A gold nanocluster diffusing on a surface seems to avoid the hole (obtained by removing 15 carbon atoms from the surface, (a)). The trajectory shown here (b) corresponds to a diffusion of 7 ns at  $T = 500$  K. The circle on the lower left of the figure indicates the diameter of the cluster. The inset (c) shows the histogram of the center-to-center distances.

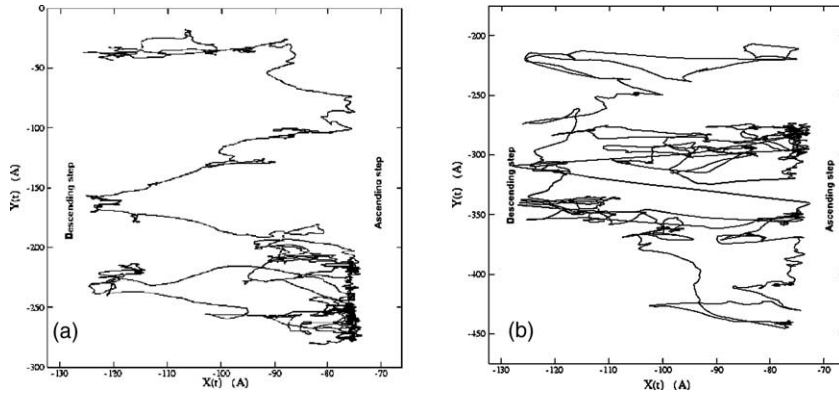


Fig. 4. Effect of monoatomic steps on the diffusion of a gold nanocluster. The descending step is on the left, and the ascending one on the right. The trajectories shown here correspond to a diffusion at  $T = 500$  K (a) and  $T = 600$  K (b) for 20 ns. Clearly, the cluster is trapped by the steps. The inset shows an example of the atomic configurations obtained during the runs.

working to quantify the trapping energy at this barrier.

#### 4. Concluding remarks

We have studied the diffusion of nanoclusters on different kinds of surfaces: epitaxial (gold on gold, for which diffusion is very slow), non-epitaxial (gold on graphite, with a very rapid diffusion) or on surfaces with defects (vacancies, which show a repulsive effect) or steps (which are never crossed by the cluster at the studied temperatures). These simulations shed light on the mechanism by which clusters can be trapped by defects on surfaces, thus allowing for the preparation of ordered arrays of nanoclusters on prepared substrates.

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