

## SURFACE DIFFUSION OF LARGE Ag CLUSTERS ON Ag(100)

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### ABSTRACT

Scanning tunneling microscopy has shown that large, two-dimensional Ag clusters undergo observable diffusion on Ag(100). The variation of the diffusion coefficient with cluster size in the range studied, 100 to 540 atoms per cluster, indicates that two-dimensional evaporation-condensation is the main mechanism of cluster diffusion. The experimental data consistently show evidence for a backward-correlation in the cluster motion. The meaning and origin of this correlation is discussed.

### INTRODUCTION

Diffusion of adatoms and clusters within metal films can control film morphology in two ways. First, the magnitude of the diffusion rate, relative to the deposition rate, determines the structures which develop in the film *during deposition*. Second, diffusion can control the *dynamics of equilibration* within a film, after deposition has stopped. In the second case, diffusion leads to coarsening, where the average size of surface structures (e.g. islands) increases and their density falls. For 2D metal-on-metal films, it is commonly accepted that a major mechanism for coarsening is Ostwald ripening (mediated by single-atom diffusion) at low coverages, or perimeter diffusion at higher coverages.<sup>1</sup> Another plausible mechanism is coalescence of (large) clusters mediated by cluster diffusion.<sup>2</sup> In this paper, we discuss a quantitative analysis of the diffusion of large 2D metal clusters. Elsewhere, we show that cluster diffusion is indeed the dominant mechanism for coarsening over a wide range of experimental conditions in our system.<sup>3</sup>

A great deal of work, mainly from the field-ion-microscopy (FIM) community, has indicated that diffusion of 2D metal clusters can be facile and interesting. Diffusion usually occurs less rapidly as cluster size increases, although there are special configurations of clusters which present exceptions to this trend.<sup>5-7</sup> For instance, dimers can diffuse more rapidly than monomers.<sup>4</sup> The mechanism of diffusion often is proposed to be short-range motion of a single atom away from the edge, followed by regrouping of the cluster around the departed atom.<sup>6,8</sup> In general, the FIM studies have dealt with clusters containing less than about 20 atoms.<sup>4</sup>

Simulations of cluster diffusion at surfaces<sup>9-14</sup> have dealt with a broader size range, up to  $N = 10^3$ . The simulations show that the diffusion coefficient,  $D$ , of large clusters decreases with the number of atoms per cluster,  $N$ , according to  $D \propto N^{-\alpha}$ . Here the exponent  $\alpha$  varies from about 1/2 to 2, depending upon the mechanism of diffusion. Hence, the simulations and the experimental studies

both show that the diffusion coefficient should generally decrease with increasing cluster size. This leads to an intuitive expectation that *very* large 2D clusters should be rather immobile. However, we recently reported that even very large 2D clusters of Ag ( $N \approx 10^2$  to  $10^3$ ) undergo measurable diffusion on a Ag(100) surface at room temperature.<sup>15</sup>

### Experimental Characteristics of Cluster Diffusion.

Some of the STM data, which led to the rather surprising conclusion that large clusters can diffuse, are shown in Fig. 1. Experimental details are available elsewhere.<sup>15</sup> The bright spots in the image are Ag clusters in the middle of a large, smooth terrace; the black streak at the right is a monatomic step edge. The Ag islands adopt an approximately square shape, although irregularities such as rounded corners and crooked edges are common. The Ag clusters in Fig. 1 range in size from 25 to 300 atoms ( $230$  to  $2500 \text{ \AA}^2$ ). Comparison of Fig. 1a with 1b clearly shows that the Ag clusters have moved in the interval between images, in this case 150 min. Over a period of several hours, the root mean square displacement of the clusters is on the order of  $10^2 \text{ \AA}$ .

The diffusion of these clusters did not appear to be an artifact of tip-sample perturbation, although such perturbations certainly can occur. For instance, efforts to obtain atomic-scale resolution on small islands ( $N < 30$ ) invariably perturbed the island. In order to avoid this problem, we limited examination to islands of  $N$

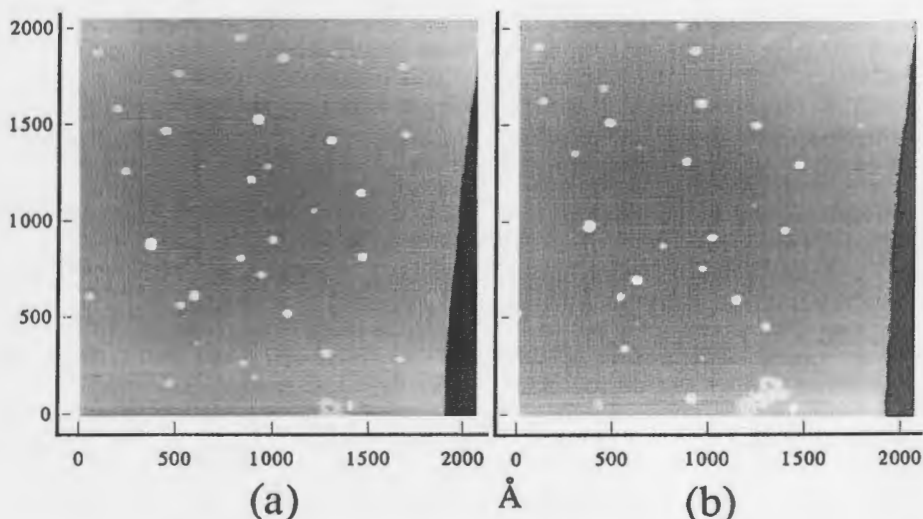


Figure 1. STM images obtained following deposition of 0.015 monolayers (ML) Ag on Ag(100) at room temperature. Deposition rate is  $3 \times 10^{-3}$  ML/s. (a)  $t = 0$  min. (b)  $t = 150$  min.

$\geq 100$ ; further, we sacrificed spatial resolution to minimize perturbation. We also examined the effect of different raster conditions on the measured diffusion coefficient, and could find no effect.<sup>15</sup>

Examples of the key experimental data quantifying cluster motion are given in Fig. 2a. It shows the mean value of the ratio of the square of the displacement, divided by the time interval between observations,  $\langle r^2/t \rangle$ , as a function of the mean time between observations,  $\langle t \rangle$ , for 5 different clusters. In Fig. 2a,  $r$  is taken to be the *total* displacement,  $d$ , of the cluster's center-of-mass from its point of origin after a time,  $t$ . Diffusion coefficients were extracted from data such as those

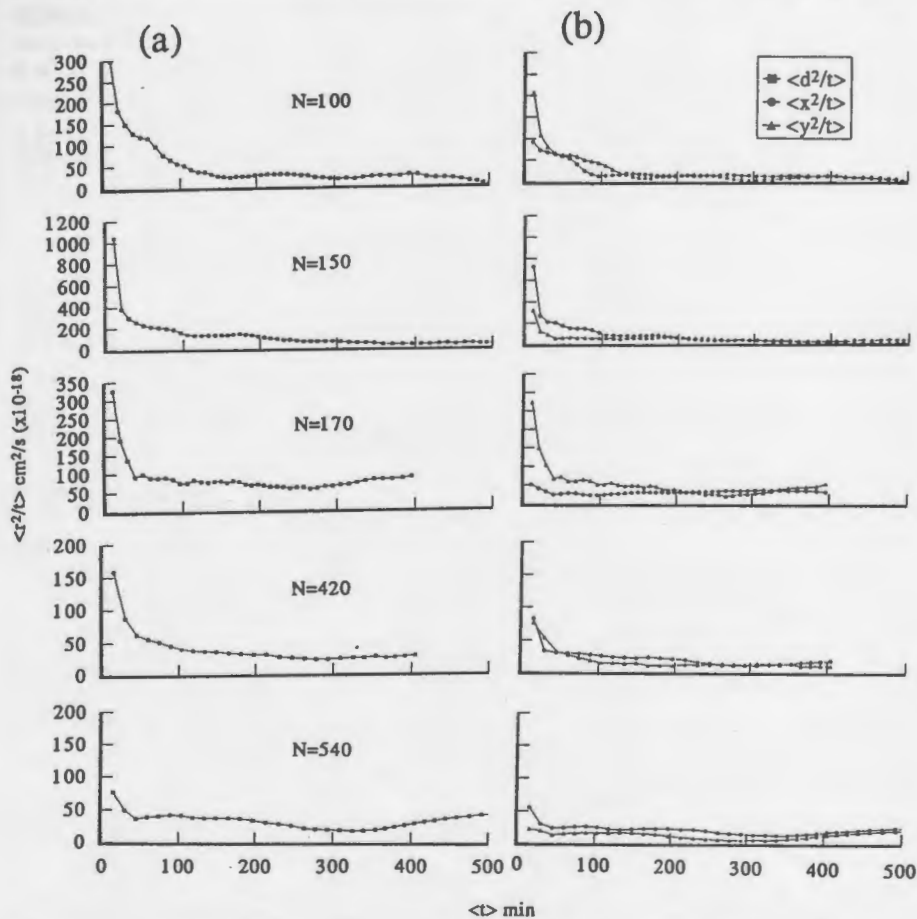


Figure 2.  $\langle r^2/t \rangle$  vs.  $\langle t \rangle$ , for a variety of cluster sizes ( $N$ ) as indicated. For the panels on the left-hand side,  $r = d$ , the total displacement. For the panels on the right-hand side,  $r = x$  or  $y$ , the components of displacements along the respective Cartesian coordinates. The  $x$ -axis is parallel to the scan direction.

of Fig. 2a, using only data where the clusters remained constant in size to within  $\pm 15\%$ , and where the clusters remained at least  $300 \text{ \AA}$  (and more typically,  $500\text{--}600 \text{ \AA}$ ) away from a step edge, and at least  $220 \text{ \AA}$  away from each other. By definition, the diffusion coefficient is the value of  $1/4\langle d^2/t \rangle$  in the limit as  $\langle t \rangle \rightarrow \infty$ . Thus,  $D$  was extracted from the value of the plateau in  $\langle d^2/t \rangle$  at long  $\langle t \rangle$  in Fig. 2a. The value of  $D$  thus obtained at room temperature was on the order of  $10^{-17} \text{ cm}^2 \text{ s}^{-1}$ . Its variation with cluster size was very weak, dropping by a factor of two at most, as  $N$  increased from 100 to 720 atoms.<sup>15</sup>

As a final test for tip-sample perturbation, we examined another characteristic of the cluster trajectories. If significant tip-sample perturbation occurred, one might expect to find different motion in the scan ( $x$ -) direction than in the orthogonal ( $y$ -) direction. The mean-square displacement shown in Fig. 2a is further broken down into its  $x$ - and  $y$ -components,  $\langle x^2/t \rangle$  and  $\langle y^2/t \rangle$ . The result is shown in Fig. 2b. It can be seen that the mean-square displacements in the  $x$ - and  $y$ -directions are not significantly different. All of these results together suggest that the tip does not induce or affect motion of the clusters.

### Mechanism of Cluster Diffusion.

We considered two main possible mechanisms by which such large 2D clusters might diffuse.<sup>15</sup> One mechanism was periphery diffusion (PD), in which motion of atoms at the cluster edges leads to motion of the cluster's center-of-mass. The other was evaporation-condensation (EC), where the cluster is in quasi-equilibrium with a dilute two-dimensional gas of single atoms on the terraces; these atoms leave and re-attach to the cluster edges, again leading to displacements in the center-of-mass. The two mechanisms predict much different variations of  $D$  with  $N$ .<sup>9-15</sup> The weak or nonexistent variation of  $D$  with cluster size, observed in experiment, served to rule out periphery diffusion, and was interpreted as strong evidence for evaporation-condensation. One might have expected PD to be the dominant mechanism for cluster diffusion, since the activation barrier for the fastest edge diffusion processes is much lower than the effective barrier for evaporation. However true long-range diffusion via PD is controlled by breakup of the central rectangular "core" of the cluster, which has a much higher barrier, thus making PD and EC energetically comparable.<sup>15</sup>

### Correlations in Cluster Motion.

In Fig. 2, and in *all* of our other data, the value of  $\langle d^2/t \rangle$  showed a sharp decline at small values of  $\langle t \rangle$ . If the cluster center of mass (CM) underwent a perfect random walk, the value of  $\langle d^2 \rangle$  would increase linearly with  $\langle t \rangle$ ; hence, the ratio  $\langle d^2/t \rangle$  would be exactly constant, for all  $\langle t \rangle$ . Below we show that the consistently observed decline in  $\langle d^2/t \rangle$  corresponds to a slight tendency for clusters to move opposite the direction of recent motion--a "back-correlation". Then, we discuss this behavior in more detail.

For simplicity, we describe cluster diffusion with a "discrete time" correlated walk model. This applies better to the PD rather than the EC diffusion mechanism.

We assume that the cluster CM hops a fixed distance  $\delta d_{cm}$  in one of the four directions (for an fcc(100) geometry), at "discrete" times separated by  $\delta t=1/H$ . Thus the total CM hop rate is  $H$ . Let  $\delta d_i$  denote the displacement at the  $i$ th hop, so the total displacement after  $n$  hops is given by  $\underline{d}(n=Ht)=\sum_{i=1}^n \delta d_i$ . For a correlated walk, one must also specify the correlation between the direction of the hops at different times,  $\langle \delta d_i \cdot \delta d_j \rangle = (\delta d_{cm})^2 A(|i-j|)$ , where trivially  $A(0)=1$ . Specifically, we consider walks either with a backward correlation, where  $A(m>0)<0$ , or with a forward correlation, where  $A(m>0)>0$ . The key quantity of interest, the mean-square displacement after  $n$  hops, corresponding to time  $t=n\delta t=n/H$ , satisfies:<sup>16</sup>

$$\langle d(n=Ht)^2 \rangle = \langle \sum_{i=1}^n \delta d_i \cdot \sum_{j=1}^n \delta d_j \rangle = (\delta d_{cm})^2 [n+2 \sum_{m=1}^n (n-m)A(m)]. \quad (1)$$

Assuming that the correlation extends over many hops, one can replace the sum in (1) by an integral, and then after some suitable rearrangement, we obtain:

$$\langle d^2/t \rangle = H (\delta d_{cm})^2 C(t), \text{ with } C(0)=1 \text{ and } C(t) \sim C(\infty)[1 \pm t_c/t], \text{ as } t \rightarrow \infty. \quad (2)$$

In (2), the upper (lower) sign for  $C(t)$  corresponds to backward (forward) correlation,  $C(\infty)=1+2\int_1^\infty A(m)dm>0$  determines the diffusion coefficient,  $D=H(\delta d_{cm})^2 C(\infty)/4$ , and the characteristic time,  $t_c$ , satisfies  $Ht_c=2\int_1^\infty m|A(m)|dm/C(\infty)$ .<sup>17</sup>

Of particular significance here is that this theory predicts  $\langle d^2/t \rangle \propto 4D [1+t_c/t]$  is a *decreasing* function of  $t$  for *backward* correlation, matching the experimental data for cluster diffusion, but that  $\langle d^2/t \rangle \propto 4D [1-t_c/t]$  is an *increasing* function of  $t$  for *forward* correlation, contrasting the experimental data. The plateau value of  $\langle d^2/t \rangle$ , and thus  $D$ , is determined by the asymptotic value of  $C(\infty)<<1$ , for back correlations, and hence is lower than its value in the absence of correlations.

The origin of one type of back-correlation,--albeit probably not that apparent in the experimental data,--can be explained as follows. We imagine the cluster to be composed of a rather stable rectangular "core", together with much more mobile periphery atoms. The latter include single atoms which diffuse very rapidly along the cluster edge, as well as less mobile atoms at kink sites. Most of the hopping or movement of the cluster CM is associated with rapid hopping of these periphery atoms for which  $\delta d_{cm}=1/N$ , with total hop rate  $H$ . However, as noted above, true long-range cluster diffusion requires core breakup, which occurs at a much lower rate than periphery atom diffusion due to its much higher activation energy.<sup>15</sup> Thus, for very short times,  $\langle d^2 \rangle \sim H (\delta d_{cm}=1/N)^2 t$  increases quickly until the cluster "realizes" that it is tethered by a relatively immobile core. At this stage, the rate of increase of  $\langle d^2 \rangle$  with  $t$  declines dramatically, the final value reflecting the rate controlling effect of either core breakup (for PD) or evaporation (for EC) on cluster diffusion.

Actually, it is likely that the observed decline in  $\langle d^2/t \rangle$  or  $C(t)$  is due to other more subtle effects producing correlations in the cluster's walk, rather than the above dramatic tethering effects which must be manifested for rather short times. For the PD mechanism, we have previously performed extensive

simulations<sup>13</sup> which show back correlation occurs even for the case where all perimeter atoms hop at the same rate. These correlations cannot be explained by tethering to a relatively immobile core, but rather are associated with the more general "connectivity requirement" that the atoms in the diffusing cluster must stay together. No such detailed simulations are currently available for cluster diffusion via the evaporation-condensation (EC) mechanism which, we believe, dominates 2D Ag cluster diffusion. Here the situation is more complicated since, certainly, many edge diffusion events (for which  $\delta d_{cm}=1/N$ ) occur for each evaporation or condensation event (for which  $\delta d_{cm}=N^{-1/2}$ ). We plan such studies to characterize in detail the nature of these correlations in the cluster's walk both due to tethering by the core on a short time scale, and perhaps due to more subtle connectivity effects on a longer time scale.

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