Size dependence of the diffusion coefficient for large adsorbed clusters

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We report systematic and accurate simulation studies of the diffusion coefficient (D) of two-dimensional clusters using a lattice model. For small cluster sizes, we observe a size dependence of D that is consistent with theoretical predictions for a periphery-diffusion mechanism. For larger sizes, we find a much weaker size dependence of D. This is in agreement with that seen in recent experimental studies of homoepitaxial, metal fcc(001) cluster diffusion. The weak size dependence of D for larger clusters correlates well with the concerted motion of kinks. We propose an expression to describe this behavior. [S0163-1829(99)16635-9]

Recently there has been a significant surge in interest in the study of diffusion in two-dimensional (2D) clusters using analytical approaches,[1–4] experiments,[5–10] and computer simulations.[11–18] This interest has, in part, been fueled by theoretical predictions that cluster mobility can influence the growth morphology in thin-film epitaxy.[19–21] Additionally, recent experiments[6,8] and computer simulations[12,13] indicate that large clusters can have significant mobility under typical film-growth conditions. Analytic theories[2–4] have been derived to describe the dependence of the cluster-diffusion coefficient D on the cluster size N. These theories predict that $D \sim N^{-\alpha}$, where α is an exponent that depends only on the diffusion mechanism.

Theoretical estimates for α are available for three different types of mechanisms that could mediate cluster diffusion. When $\alpha = \frac{1}{2}$, the cluster movement is aided by *random* attachment (condensation) and detachment (evaporation) of atoms at the perimeter of the cluster to a 2D gas, with which the cluster exists in a quasiequilibrium state. This is the evaporation-condensation (EC) mechanism. When the evaporation and condensation sites are spatially correlated, cluster movement occurs by correlated evaporation-condensation (CEC), which has the exponent $\alpha = 1$. If the cluster moves solely as a result of uncorrelated hopping of atoms along the island periphery (PD mechanism), then $\alpha = \frac{3}{2}$.

Recent studies[8,11,14] indicate that current analytic theories cannot accurately describe cluster motion in all cases. The convergence of α to one of the values above can be complicated as only *one* mechanism needs to be present in order to clearly observe an exponent. Also, mechanisms of cluster motion have been identified that do not conform to known theoretical exponents. For example, one study has suggested that at least for small cluster sizes, the motion of homoepitaxial fcc(001) clusters is aided by an elementary collective motion called dimer shear.[15] For relatively large clusters, embedded-atom method (EAM) molecular-dynamics simulations suggest a mechanism involving collective motion of dislocations that may facilitate diffusion of clusters on fcc(111) surfaces.[12,13] Experimental studies[10] indicate that homoepitaxial clusters on Ir(111) move via simultaneous gliding of each cluster atom. Due to the likely complexity of the diffusion process in real systems, there is a need to test under which limits the analytic theories are applicable. In

this paper, we report the results of large-scale simulation studies of two-dimensional cluster diffusion. We show that, even in a relatively simple model appropriate for metal homoepitaxial fcc(001) clusters, deviations from current theories can occur. We find that the size dependence of the cluster-diffusion coefficient exhibits two scaling regimes with exponents characteristic of the PD and EC mechanisms for small and large clusters, respectively. In the crossover between the two regimes, the size dependence of D does not adhere to current theoretical predictions and is consistent with that seen in a recent experimental study.[8] In the large-size regime, EC scaling is observed even though analysis shows that this mechanism does not significantly contribute to cluster motion. Our analysis indicates that the observed scaling for large clusters is consistent with the correlated motion of kinks at the cluster perimeter. We propose an expression to describe this behavior.

To perform these simulations, we have used an efficient kinetic Monte Carlo (KMC) method based on exact implementation of the N-fold way algorithm.[22,23] We use a lattice model with periodic boundary conditions, and nearest-neighbor interactions on a square lattice. The rate of hopping from an occupied site i to a nearest-neighbor vacant site j is given as $r^{\mathrm{hop}}(i \to j) = \nu \exp[-\Delta E(i,j)/k_B T]$, where $\Delta E(i,j) = E_0 - (J/2)(n_j - n_i)$, $n_{(i,j)}$ is the number of lateral nearest neighbors at sites (i,j), E_0 is the barrier for diffusion for an isolated atom, and J is the lateral bond strength. We assume that $E_0 = 0.52$ eV, $J = 2E_0/5.5$, and $\nu = 10^{12}$ s^{-1}. Despite its simplicity, our model should capture the essential features of hopping diffusion on metal fcc(001) surfaces that are shown by semiempirical potentials, such as EAM and effective-medium theory (EMT). Recently, Merikoski *et al.*[24] have shown that interactions are short ranged in these systems and that the hopping barriers can be accurately expressed as a linear function of the change in the number of neighbors that occurs upon hopping. Since both of these features are included in our model, we should observe realistic behavior that is generally representative for these systems. Our model can also be contrasted to those in recent simulation studies of the diffusion of large clusters on surfaces.[16,17] Here, a major difference is that adatom detachment from the cluster perimeter is forbidden in those studies,[16,17] while it is allowed here. Also, in Ref. 17, diffusion is mediated by the motion of

vacancies inside the cluster. This type of process does not occur to any appreciable extent in our model.

To implement the algorithm, we first categorize all *types* of moves characterized by the same rates r^{hop}. The probability P_k for a move of type k is $P_k = n_k r_k^{hop}/\Sigma_j n_j r_j^{hop}$, where $n_{\{k,j\}}$ is the number of moves of *type* $\{k,j\}$ and the sum runs over all possible move types. A move *type* is first chosen based on its probability, and then a particular move is chosen randomly within that move type. Once a particular move is chosen, the particle position is updated and time is incremented according to the rule $t_{new} = t_{old} + 1/\Sigma_j n_j r_j^{hop}$,[23] where t_{old} and t_{new} are old and new times, respectively. With this implementation using the N-fold way algorithm, typically systems can be studied from several minutes to hours at room temperature (300 K) using moderately large clusters. Note that the manner in which time progresses depends on the temperature and the interactions. With the interactions used here, the diffusion coefficient at 300 K for a cluster with size $N = 100$ is about 30 times larger than in experimental studies of Ag clusters on Ag(001).[6]

Cluster sizes ranging to 1024 atoms have been studied in our simulations. The diffusion coefficient D is obtained from $D = \lim_{t \to \infty} \langle \Delta r_{cm}^2(t) \rangle / 4t$. To estimate the diffusion coefficient accurately, we use the instantaneous mass of the cluster to calculate the center of mass. An adatom that has moved away more than one lattice unit from the cluster periphery is not included in the diffusion coefficient calculation. The random numbers were generated using a combination of shift register and RAN2 (Ref. 25) to obtain high-quality numbers. Many independent runs were made with new random number seeds and new starting configurations. The runs were then averaged such that a long plateau in the D versus t data is visible, where D fluctuates around an average value. Typically $> 10^6$ Monte Carlo steps were performed for each cluster size. The largest run was for $N = 625$, where 4×10^6 steps were performed. For $N = 1024$, only one long run to 3×10^6 steps was performed to estimate D. This corresponds to roughly 12 h of experimental time at 300 K. The number of total data points used in the averaging was at least 5×10^3.

In addition to measuring D, we also quantified the individual atomic movements mediating cluster diffusion. By monitoring the movement of each atom, noting the initial and final environments, it is possible to classify all movements. When an adatom reattaches to the cluster within six hops after breaking away from the cluster perimeter, we call it CEC, otherwise it is categorized as EC. For large clusters we find that for $\sim 70\%$ of CEC events, atoms reattach to the cluster perimeter within two hops, while for about 6% of CEC events atoms reattach within six hops. If an adatom moves along the cluster periphery without any change in the number of neighbors, it it characterized as a PD event. In this mechanism one bond is broken, and one bond is formed when the adatom moves to a nearest-neighbor site, as shown in Fig. 1. We introduce another mechanism for movement (KD denotes kink detachment), shown in Fig. 1, in which an adatom breaks away from a perimeter site where it had two lateral bonds and hops to a nearest-neighbor site where it gets only one lateral bond. The inverse process of movement from one to two lateral neighbors is termed KA (kink attachment). When a kink detaches, another mechanism becomes
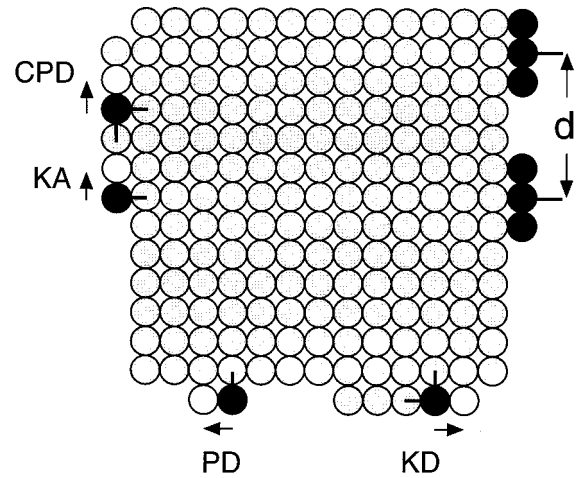

FIG. 1. Schematic representation of four elementary diffusion mechanisms. Filled circles represent atoms in their initial state, while empty circles are nearest-neighbor sites to which the atoms hop. Bonds at the initial site are indicated by lines. The different mechanisms shown are for (i) elementary hop KD of a kink atom; (ii) periphery diffusion (PD) of an adatom to a nearest-neighbor site; (iii) kink attachment (KA) of an isolated atom; (iv) the mechanism CPD where two bonds are broken, and two bonds are formed when the adatom hops. Also, a group of three periphery atoms is shown to move a distance d during a time interval δt.

important: an atom hops from a site where it has two bonds to a neighboring site where it gets two bonds, as shown in Fig. 1. This is a variant of the simple PD process, which we denote CPD. The results are averaged over multiple data points to accurately estimate the mechanisms present during cluster motion.

Figure 2 shows the diffusion coefficient for various cluster sizes. An apparent power-law behavior is seen for different regions in N. For small cluster sizes, α is close to 1.5, as would be expected for the PD mechanism.[2] However, deviations in α begin to appear for $N \gtrsim 100$. A linear fit through the data points in the region ($100 \leqslant N \leqslant 1024$) gives a slope of -0.49. Also note from Fig. 2 that there are oscillations in
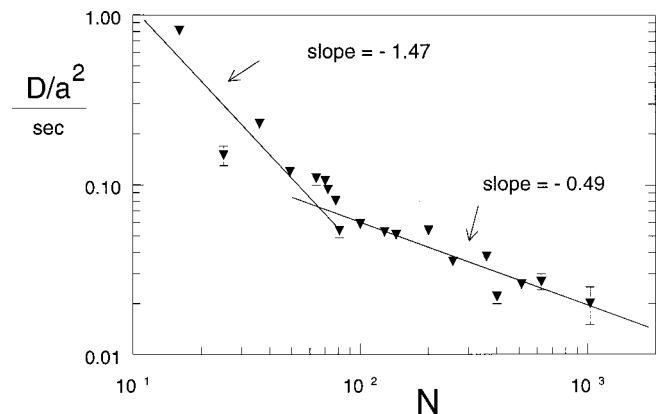

FIG. 2. The diffusion coefficient $(D/a^2)s^{-1}$ as a function of N on a log-log scale, where a is the lattice constant. The error bar is within the symbol size where not indicated. A linear fit through the data points for the four smallest clusters has a slope -1.47. In the region $100 \leqslant N \leqslant 1024$, a linear fit through the data points gives a slope -0.49.
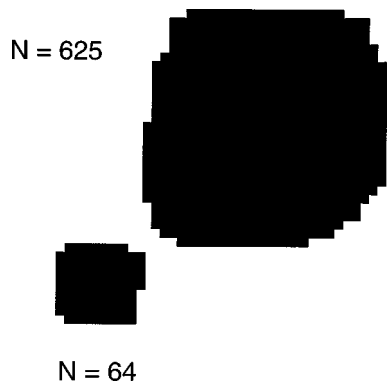
FIG. 3. Typical equilibrated configurations of clusters at 300 K.

FIG. 4. The percentage of diffusion mechanisms for cluster sizes N. The error in the data points is within the symbol sizes. The mechanism KA is not represented in the figure. Other mechanisms account for less than 4% of observed events.

the diffusion coefficient with cluster size and, over a small-size scale, larger clusters do not necessarily diffuse more slowly than smaller ones. Because we have compiled extensive statistics to procure our averages, we believe that this is a real effect. Possibly, this phenomenon has similar origins to the oscillations in D with cluster size observed experimentally with field-ion microscopy for small clusters.[5] Currently, there is no theory capable of predicting oscillations in D with cluster size for large clusters.

Recently the diffusion and coarsening of homoepitaxial islands on Ag(001) has been studied experimentally with scanning-tunneling microscopy (STM) by two different groups.[6,8] Neither of the groups observed the predicted[2–4] integer scaling exponents. In addition, the observed scaling exponents and the final conclusions in these studies were different, despite the fact that the experimental conditions were similar. Wen *et al.*[6] observed a slow variation of D with N (although there was large uncertainty in the data) and suggested that EC is the dominant mechanism for cluster diffusion on Ag(001), while Pai *et al.*[8] found larger exponents and concluded that PD is the dominant mechanism instead. Our simulations reconcile these seemingly contradictory results: for smaller cluster sizes, we observe exponents that are somewhat less than those predicted for PD and consistent with those reported in Ref. 8. As the cluster-size range increases, we observe a much weaker size dependence of D. This weak dependence is consistent with that observed by Wen *et al.*,[6] who studied larger clusters. We also point out that our model reproduces cluster shapes that are squarelike, with rounded corners, that are consistent with those seen experimentally[6,8] (cf. Fig. 3). Below, we discuss the origins of the observed dependence of D on cluster size.

To better understand cluster motion, we have calculated the relative occurrence of various atomic moves involved in cluster diffusion. These are plotted for different cluster sizes N in Fig. 4. For small clusters, clearly the PD process is the dominant one. Small clusters tend to have straight sides, which makes it very easy for an atom to hop along the cluster edges. Larger clusters tend to have more kinks at the perimeter due to thermal fluctuations (see Fig. 3). Because of the presence of kinks, in turn it becomes progressively difficult to have simple PD as the cluster size is increased, as is evident from Fig. 4. We also find that the relative occurrence of EC and CEC is not very pronounced at room temperature. The mechanisms that dominate for large cluster sizes are KD and KA. Statistically, the number of occurrences of KD and
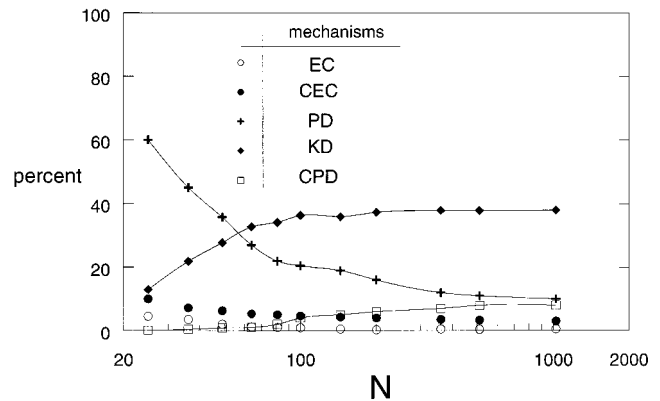
KA are the same, i.e., $\langle KD \rangle = \langle KA \rangle$. As shown in Fig. 4, PD decays with increasing N and appears to saturate for $N > 300$. Similarly, KD increases and saturates for $N > 300$ where clearly it is the dominant process. Around $N = 100$, CPD increases rapidly from its value of 0% for smaller clusters and then finally appears to saturate at about 8% around $N = 1024$. The changes in KD and CPD correlate to the onset of the slow variation of D with N. Other complex diffusion mechanisms account for less than 4% of the total number of events. Some of these mechanisms, although present in small numbers, can induce other mechanisms to follow.

Since we observe a characteristic exponent of $\alpha \sim \frac{1}{2}$ for $N \geq 100$, it is natural to inquire as to whether EC is the underlying mechanism responsible for this behavior. Our simulations indicate that this is not the case. We ran a second set of simulations for a few selected cluster sizes in which the EC mechanism (but not CEC) was suppressed. For each of the clusters, the diffusion coefficient was essentially the same as that in simulations for which the EC mechanism was allowed. Thus, the scaling exponent of $\frac{1}{2}$ is not unique for the EC mechanism and some other characteristic mechanism is responsible for the observed dependence of D on N for large clusters.

It has been pointed out that cluster diffusion cannot occur if the motion is mediated solely by periphery-atom hopping.[6,16] Atoms must be transferred from the cluster core to the perimeter to achieve net motion of the cluster center of mass. In our classification scheme, these ''core break-up'' events fall either under the CEC or EC category (e.g., corner breaking involves an atom leaving and rejoining the cluster) or under the category of more complex diffusion mechanisms. Since there is no significant change in the relative frequencies of these mechanisms with increasing N, it is difficult to correlate these mechanisms with the change in α. Instead, we observe a significant increase in KA/KD with increasing N, with a concomitant 8% increase in CPD. These findings suggest that KA/KD, in combination with CPD, leads to the concerted motion of kinks and that this is the dominant mechanism underlying cluster motion.

In light of the discussion above, we present a simple, analytical model for cluster diffusion. We argue that if the center of mass for a group of M atoms has moved a distance

d (see Fig. 1) along the periphery during a time interval δt, then the motion should appear to be a simple periphery diffusion of an adatom of mass M. We assume that the distance d traveled by the block of atoms of combined mass M depends as $d \sim 1/M^{\delta}$, where δ characterizes the motion of the group of atoms. A positive δ implies that the distance traveled by the group decreases with increasing mass, which is normally expected. For uncorrelated hopping around the perimeter, $\delta = 1$. However, there is a possibility of zero or negative δ, in which the traveled distance is independent of or increases with M. We speculate that concerted motion of the M atoms can cause δ to become zero or negative. If, for example, the motion of the block is limited by KD, and rapid CPD of many atoms follows, we imagine that $\delta = 0$. The diffusion coefficient is given by $D \propto \Gamma \langle (\Delta \mathbf{r}_{cm})^2 \rangle$, where Γ is the total edge-hopping rate and $\langle (\Delta \mathbf{r}_{cm})^2 \rangle$ is the mean-square displacement of the cluster center of mass. For a block of M perimeter atoms that has moved a distance d,

$$(\Delta \mathbf{r}_{cm})^2 = (Md/N)^2. \tag{1}$$

If M is proportional to the cluster perimeter, i.e., $M \propto \sqrt{N}$, the diffusion coefficient is given as

$$D \sim N^{-(\delta + 1/2)}. \tag{2}$$

Here we also assume that $\Gamma \propto \sqrt{N}$.[6] Note that the analysis gives $D \sim N^{-3/2}$ for $\delta = 1$, as expected for the PD mechanism. Combining the above analysis with Fig. 2, we deduce that since α is approximately $\frac{1}{2}$ for $N \gtrsim 100$, δ is close to zero. For the special case of $\delta = -\frac{1}{2}$, the diffusion coefficient becomes independent of cluster size. This interesting effect of the very weak dependence of the diffusion coefficient on cluster size N has been observed in experiment.[6] In our study, D shows little or no variation over small regions in N for large N (cf., Fig. 2). Only over a larger range $\delta \sim 0$ appears to be visible.

Together with the observations in Figs. 2, 3, and 4, our analytical model suggests that collective motion of periphery atoms occurs via single elementary hops of KD, combined with CPD. Note that the scaling we report here reflects, to some extent, our model Hamiltonian, which has been constructed to be generally representative of homoepitaxial fcc(001) metal-atom clusters. We expect our model to describe similar systems, in which cluster diffusion is mediated by the motion of periphery atoms.

In conclusion, using large-scale computer simulations, we have shown that periphery diffusion is a dominant mechanism in cluster diffusion as suggested in a recent experiment.[8] In large clusters, a variant of the periphery-diffusion process, along with the movement of kink atoms, dominates. This leads to a different behavior of D with N than is predicted by conventional theories.

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