

Diffusion of Clusters of Atoms and Vacancies on Surfaces and the Dynamics of Diffusion-Driven Coarsening

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We present Monte Carlo simulations and scaling theories for the size and temperature dependence of the diffusion coefficients of clusters of atoms and vacancies on surfaces. The mechanisms and rate-determining steps are found for a realistic model of the Xe/Pt(111) system. The coarsening of ensembles of clusters is also considered. By explicitly deriving the coarsening exponents, we show that the coarsening rate for systems dominated by coalescence due to cluster diffusion differs from the rates seen for Ostwald ripening.

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Recent experiments have demonstrated that two-dimensional clusters containing hundreds of atoms or vacancies are mobile on a variety of solid surfaces [1–3]. The motion of large clusters can play a significant role in processes such as surface diffusion and the kinetics of thin film growth. To model these phenomena, it is important to elucidate the mechanism(s) responsible for cluster diffusion and to develop techniques capable of following cluster diffusion on long time scales (>1 s). In this Letter, we investigate the diffusion of Xe islands and vacancy clusters on a Pt(111) surface using Monte Carlo (MC) simulations. We find that a simple activated process dominates the diffusion of both atomic and vacancy clusters, but that the diffusion coefficients scale differently with cluster size.

The simplest model for diffusion of a cluster is that of an uncorrelated random walk. For this model, the diffusion coefficient is $D \propto \langle k_h \rangle \langle \delta d_{c.m.}^2 \rangle$, where $\langle k_h \rangle$ is the rate of diffusion “events” and $\langle \delta d_{c.m.}^2 \rangle$ is the mean square displacement of the cluster’s center of mass per “event.” To make any use of this formulation it is necessary to define the nature of the diffusion events. Unlike single atom diffusion, cluster diffusion involves a multitude of distinct atomic hops between sites of various binding energies with a wide variety of rates. To devise a diffusion mechanism, it is necessary to identify the essential class of hops which control the motion of the cluster’s center of mass. A central goal of such an analysis is to obtain the dependence of the diffusion coefficient on the temperature, T , and the cluster size, N . Two principal ideas have been advanced to explain the diffusion of clusters of atoms: periphery diffusion (PD) and evaporation condensation (EC) [2,4,5]. In PD, mass transport occurs when atoms diffuse along the periphery of a cluster, while in EC, cluster diffusion is due to the exchange of atoms with a two-dimensional gas phase. For either scenario, a simple “random cluster scaling theory” (RCST) can be developed to predict the form of $D(N, T)$.

In a RCST, it is assumed that the rate-determining hops are uncorrelated, occur at random positions on the perimeter of the cluster, and are characterized by a well-defined activation energy, $E_a = E_{PD}$ or E_{EC} . Hence, the naive assumption is that $\langle k_h \rangle \sim \sqrt{N} e^{-E_a/kT}$, since the perimeter should scale like \sqrt{N} for compact clusters. The value of $\langle \delta d_{c.m.}^2 \rangle$ is mechanism dependent, since the basic PD or EC type events affect the center of mass differently. For PD, a hop by a perimeter atom gives $\langle \delta d_{c.m.}^2 \rangle \sim N^{-2}$ [2]. Thus, we expect that $D_{PD} \sim N^{-3/2} e^{-E_{PD}/kT}$. On the other hand, an evaporation (or condensation) event gives $\langle \delta d_{c.m.}^2 \rangle \sim N^{-1}$ [2]; thus, $D_{EC} \sim N^{-1/2} e^{-E_{EC}/kT}$. Below, we investigate whether either RCST can account for diffusion in the Xe/Pt(111) system. This work represents the first physically realistic simulations of cluster diffusion that examine both EC and PD.

To investigate the diffusion mechanism and size scaling for a realistic system, we have performed MC simulations for a model of Xe/Pt(111) derived from an interatomic potential function [6]. Xe/Pt(111) has been heavily studied (see [6–9] and references therein), and for $62 < T < 99$ K, Xe forms a $\sqrt{3} \times \sqrt{3} R30^\circ$ commensurate phase with Xe atoms separated by 4.8 \AA [9]. We define the Xe coverage, θ , to be unity when the surface is completely covered by this phase. Only surfaces with $\theta \leq 1$ are treated. Our MC model employs the pair potential due to Rejto and Andersen [6], which reproduces a number of important experimental observations. The potential predicts that Xe atoms bind at the threefold sites on the Pt(111) surface, which form a hexagonal lattice with adjacent sites separated by 1.6 \AA . The transition sites lie at the twofold site of the Pt surface. The potential energy of a Xe atom due to other Xe atoms is found by summing the contributions from all Xe atoms separated by between 4.0 and 8.0 \AA (since repulsions constrain Xe atoms to be at least 4 \AA apart and the potential beyond 8 \AA is negligible). Thus, 48 sites must be included to evaluate the energy of a Xe atom, and a wide range of

binding energies and barrier heights are obtained. In our model, an isolated Xe atom on Pt(111) exhibits a diffusion barrier of 0.500 kcal/mole [7,8].

We assume that Xe atoms move on the surface by hops between adjacent sites. This model neglects multisite hops that occur in this system but are not dominant at the temperatures considered [8]. An MC event consists of choosing a Xe atom and an adjacent site at random. If the Xe atom is not blocked from entering the latter site by another Xe atom, the atom is moved into the new site with probability $e^{(E_{\min} - \Delta E)/kT}$. ΔE is the difference in energy between the original binding site and the transition site. The binding and transition site energies are independently calculated by adding the contributions of all Xe atoms within 8 Å to the potential due to the Pt surface. A wide range of potential barriers exist in the model. Typically, $0.1 < \Delta E < 1.0$ kcal/mole. E_{\min} is the smallest energy barrier in the model. We fixed $E_{\min} = 0.1$ kcal/mole. Regardless of the success of this attempted transition, another Xe atom and neighbor are chosen randomly. Our choice for the transition probability yields the same microscopic rates as transition state theory with the assumption that the vibrational frequencies of adsorbed Xe atoms are constant. The physical time associated with one MC event is $\delta t = e^{-E_{\min}/kT}/N_{\text{Xe}}\nu_0$, where ν_0 is the hopping attempt frequency of adsorbed Xe atoms and N_{Xe} is the total number of Xe atoms. We set $1/\nu_0 = 2.5$ ps [7,8]. The efficiency of the algorithm is greatly enhanced if transitions to blocked sites are explicitly omitted and the time variable is rescaled accordingly. Simulations for 1–10 μs of physical time can be routinely performed in this way. This MC method cannot be used to address diffusion mechanisms that involve the collective motion of many atoms, such as large scale dislocations, although there may be systems in which such mechanisms are important.

Atomic cluster diffusion was measured by evolving a lattice configuration in which all the Xe atoms were initially contained in one cluster. In the initial stages of evolution, some Xe atoms evaporate from the cluster and form a 2D gas phase. Once equilibrium has been established between the gas and cluster phases, the mean square displacement of the cluster's center of mass, $\langle \Delta r_{\text{c.m.}}^2(t) \rangle$, is measured. We have verified that the same equilibrium is reached if other initial conditions are used. After averaging $\langle \Delta r_{\text{c.m.}}^2(t) \rangle$ over multiple simulations (typically 20–50), the diffusion coefficient is defined by the long time limit of $\langle \Delta r_{\text{c.m.}}^2(t) \rangle / 4t$ [2,4,8]. The convergence of this function to a constant value at large t indicates the cluster motion is indeed diffusive. The results of this analysis are shown for various cluster sizes and temperatures in Figs. 1 and 2, respectively. Applying linear regression to these data shows that $D \sim N^{-\alpha} e^{-E_{\text{EC}}/kT}$ with $\alpha = 0.989 \pm 0.056$ and $E_{\text{EC}} = 1.18 \pm 0.11$ kcal/mole. E_{EC} agrees with the experimentally observed activation energy for macroscopic diffusion [7]. This correspondence shows

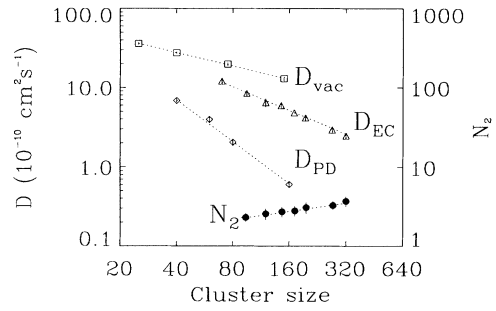


FIG. 1. The N dependence of D for PD and EC diffusion of atomic clusters at 75 K, and for vacancy cluster diffusion at 95 K. N_2 for EC diffusion at 75 K is also shown.

that the rate-determining steps for macroscopic diffusion and the motion of single clusters are the same.

To measure the separate contribution of periphery diffusion, we repeated the simulations above while setting the transition probability of any transition that creates a 2D gas atom to zero [4]. The N and T dependence of D_{PD} are shown in Figs. 1 and 2. The data yield $D_{\text{PD}} \sim N^{-\alpha} e^{-E_{\text{PD}}/kT}$ with $\alpha = 1.75 \pm 0.07$ and $E_{\text{PD}} = 1.46 \pm 0.13$ kcal/mole. Thus, it is clear that EC is the dominant cluster diffusion mechanism in this system.

As in previous simulations of PD [4,10], the size scaling exponents obtained above for EC and PD do not conform to the predictions of the simple RCST. At least part of the discrepancy can be traced to the character of the rate-determining diffusion event. Examination of Xe clusters shows that almost all perimeter atoms have either 2, 3, or 4 nearest neighbors (NN). In Fig. 3 we show a typical cluster of $N = 80$ where the perimeter atoms with 2 NN's (NN₂ atoms) are indicated. The cluster diffusion is controlled by NN₂ atoms. Examination of animations made from the MC simulations reveals the vast majority of evaporation events occur with NN₂ atoms. We have also measured the kinetics of cluster evaporation by repeating the simulations above with absorbing boundary conditions that remove Xe atoms once they become well separated from the cluster. The cluster evaporation rate is extremely well described

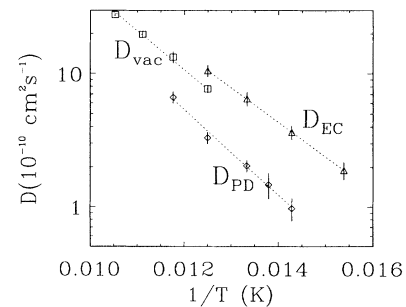


FIG. 2. The T dependence of D for PD with $N = 80$ and EC diffusion with $N = 120$ of atomic clusters, and for vacancy cluster diffusion with $N = 40$.

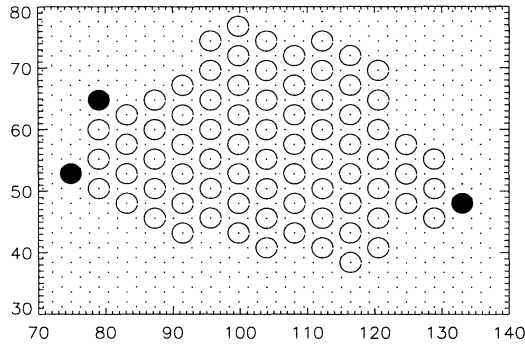


FIG. 3. A cluster of 80 Xe atoms (\circ) with the NN_2 atoms indicated (\bullet). The points show the underlying lattice of binding sites on the Pt surface. The axes are in Å.

by $k_{ev} \sim N_2(N)e^{-E_{ev}/kT}$, where $N_2(N)$ is the number of NN_2 atoms in a cluster of size N and E_{ev} is an activation energy very close to E_{EC} . Furthermore, E_{ev} (and hence E_{EC}) are found to correspond to the potential barrier for the escape of an NN_2 atom. In addition to the 0.500 kcal/mole diffusion barrier presented by the Pt surface, the atom must overcome an attractive energy of 0.761 kcal/mole due to its NN's. However, E_{ev} cannot be found simply by adding these energies, because during evaporation the atom must pass over multiple barriers before escaping completely from the cluster. E_{ev} can be calculated exactly for a Xe atom escaping from a half plane of the commensurate phase. In this case the rate equations for this process are a coupled set of linear differential equations [11]. The result is that the observed energy barrier is slightly less than the sum of the barriers above and decreases weakly as T is increased. As $T \rightarrow 0$, $E_{ev} \rightarrow 1.261$ kcal/mole. This is entirely consistent with the observed diffusion activation energy barrier.

The value of N_2 as a function of N is shown for diffusing clusters at 75 K in Fig. 1. Applying linear regression to these data shows that $N_2 \sim N^{0.35 \pm 0.12}$, so it is clear that N_2 is not proportional to \sqrt{N} . Thus, the assumption of the RCST that $\langle k_h \rangle \sim \sqrt{N}$ does not hold for this system. This counterintuitive result arises because the perimeter of the cluster is comprised of various energetically distinct sites, and the equilibrium cluster configuration is determined by the interplay between various processes taking place at these sites. Heuristically, this result suggests that cluster "roughness" decreases as N is increased. We expect the deviation of the scaling of $\langle k_h \rangle$ from \sqrt{N} to be a quite general result.

There are also other effects that contribute to the size scaling of D_{EC} . For example, examination of the Xe cluster structure shows that when an NN_2 atom evaporates, the new cluster is unlikely to have another NN_2 atom in the immediate vicinity of the departure point. Thus, the evaporation events are not entirely uncorrelated, as was assumed in the RCST. Similarly, a small number of evaporation or condensation events may be followed by

a local rearrangement of the cluster. These phenomena all affect the N dependence of $\langle \delta d_{c.m.}^2 \rangle$.

Our PD simulations can also be interpreted in terms of a simple rate-determining step. The observed value of E_{PD} corresponds to the energy necessary for a Xe atom to break out of the "core" of the cluster. There are some perimeter diffusion events with lower activation energies, but core breakup events are necessary to allow long-range mobility [2,4]. This system provides an example where $E_{EC} < E_{PD}$.

Now we consider the diffusion of clusters of vacancies, which has been observed experimentally on a number of surfaces [1,3]. As with atomic clusters, there are two principal mechanisms that could account for the mobility of vacancy clusters: PD and EC diffusion. PD occurs in the same way as for atomic clusters: the RCST predicts $D_{PD} \sim N^{-3/2}e^{-E_{PD}/kT}$ [1,3]. For vacancy clusters, EC diffusion occurs when adsorbates detach from the edge of the cluster, move across the cluster, and reattach to the cluster perimeter. When the typical time for an atom to diffuse across the cluster is much greater than the period between evaporation events, a RCST gives $D_{EC} \sim N^{-1}e^{-E_{EC}/kT}$ [3]. However, the Xe/Pt(111) system lies in the opposite limit, where the evaporation events occur much more slowly than the passage across the cluster. In this case, assuming that the evaporation and condensation sites are randomly distributed about the cluster perimeter and that $\langle k_h \rangle \sim \sqrt{N}$ yields $D_{EC} \sim N^{-1/2}e^{-E_{EC}/kT}$. As with atomic cluster diffusion [2], if the activation energies and the frequencies of the rate-determining steps for PD and EC are comparable, the latter should be the dominant mechanism.

We investigated the mobility of vacancy islands using methods entirely analogous to those used for atomic clusters. On the time scales of our simulations, the number of vacancies in a cluster was conserved. The N and T dependence of the vacancy cluster diffusion coefficient, D_{vac} , is shown in Figs. 1 and 2. These data show that $D_{vac} \sim N^{-\alpha}e^{-E_{vac}/kT}$ with $\alpha = 0.562 \pm 0.031$ and $E_{vac} = 1.34 \pm 0.12$ kcal/mole.

The N dependence of D_{vac} does not correspond exactly to any version of the RCST, although it is reasonably close to the RCST for EC diffusion in the limit of slow evaporation. We have established that the EC mechanism is the dominant mode for diffusion and the rate-determining step is the evaporation of NN_2 atoms. Simulations were run with absorbing boundary conditions in the central region of the cluster to remove the evaporating atoms. It was found that the subsequent cluster growth rate was proportional to $N_2(N)$. One significant difference between atomic and vacancy diffusion is the size scaling of N_2 . We find for vacancies, $N_2 \sim N^{0.75 \pm 0.15}$, compared to the result for atomic clusters, $N_2 \sim N^{0.35 \pm 0.12}$. Thus, under the assumption that D is proportional to N_2 , the difference in the size scaling of the diffusion coefficients can be wholly attributed to the relative concentration of NN_2 atoms for the concave

vacancy clusters and the convex atomic clusters. It is an important result that the mechanism and rate-determining step are the same for the diffusion of both types of clusters and that neither phenomenon is accurately described by the naive RCST.

One very important use for the scaling form of the diffusion coefficient is to model the motion of clusters for very long time scales. Since the cluster as a whole diffuses without reference to its constituent atoms, the simulation of diffusion can be greatly accelerated. To illustrate this approach, we have modeled the long-term coarsening of an adlayer. The process of coarsening has often been discussed as an example of Ostwald ripening where immobile clusters grow and shrink due to atom exchange through a 2D gas phase. The late stages of this process are characterized by a scaling form of the cluster size distribution, $f(r, t) = f(r/\bar{r})$, and a power law scaling of the average cluster size, $\bar{r} \sim t^\beta$ [12]. Under the usual assumptions of Ostwald ripening, $\beta = 1/3$. Here, we consider coarsening in the limit where clusters diffuse with $D \propto N^{-\alpha}$ and the only change in cluster sizes occurs when two (or more) diffusing clusters collide and coalesce. Our main result is that the scaling exponents that characterize coarsening under these conditions can be explicitly derived as a function of α and that they are not the same as for Ostwald ripening.

As an illustration of the increased computational efficiency allowed by use of a diffusion scaling relation, we have performed very long-term MC simulations of the coarsening kinetics. The clusters were assumed to be circular, and coalescence to a single cluster occurred instantaneously when a pair of clusters touched. Each cluster was allowed to undergo a spatially continuous random walk with a fixed hopping frequency and a step size chosen to endow each cluster with $D \propto N^{-\alpha}$. Simulations using up to 10^5 clusters were carried out for durations on the order of 1 s for several choices of α . These computations would not be feasible using a conventional atomic-scale MC simulation. Our simulations suggest that α and β are related by $\beta = [2(\alpha + 1)]^{-1}$. Thus, if $\alpha = 1/2$ (as in our RCST for EC diffusion of vacancy clusters), $\beta = 1/3$, in agreement with the Ostwald ripening result. On the other hand, if $\alpha \neq 1/2$, the coarsening exponents differ from those of Ostwald ripening. For example, if $\alpha = 3/2$ (the RCST prediction for PD), $\beta = 1/5$. We emphasize that these results are independent of the total coverage of clusters on the surface. We are currently using these simulations to investigate several related issues, such as the cluster size distribution functions and the correlations that develop between clusters.

It is noteworthy that the relationship between α and β can also be derived analytically. We assume that $\bar{r} \sim t^\beta$ and that the cluster size distribution function, $f(r, t)$, has the scaling form $f(r/\bar{r})$. Denote by T_1 the time taken for the system to evolve from $\bar{r} = r_0$ to $\bar{r} = kr_0$. The addi-

tional time required for \bar{r} to grow to k^2r_0 is $T_2 = k^{1/\beta}T_1$. The spatial structure at these two times is identical if length is rescaled by a factor of k . Now consider the mean square displacement of a cluster with radius r_0 in time T_1 , $\langle \delta r_0^2(T_1) \rangle$. If the cluster does not coalesce with any other clusters in this period, its displacement is given by the Einstein relation to be $\langle \delta r_0^2(T_1) \rangle \propto 4(\pi r_0^2)^{-\alpha}T_1$. Similarly, a cluster of radius kr_0 has $\langle \delta(kr_0)^2(T_2) \rangle \propto 4(\pi kr_0^2)^{-\alpha}T_2$. By using the spatial rescaling mentioned above, we see that $\langle \delta(kr_0)^2(T_2) \rangle = k^2\langle \delta r_0^2(T_1) \rangle$. Combining this expression with the relationship between T_1 and T_2 above shows β is given by $\beta = [2(\alpha + 1)]^{-1}$.

The main results of this work can be summarized as follows: (1) For a physically realistic model of the Xe/Pt(111) system, atomic and vacancy cluster diffusion occur through the EC mechanism. The rate-determining step in both cases is the evaporation of atoms with 2 NN's. (2) The size scalings for D do not conform to the simple RCST and may prove to be system dependent. Nevertheless, the RCST is very useful for providing an approximate size scaling, and it does correctly predict that D_{PD} depends more strongly on N than D_{EC} . This qualitative result means that if the frequencies of the rate-determining steps for PD and EC diffusion are similar (as seems likely in general), EC diffusion will be the dominant mechanism for cluster diffusion [2]. (3) The scaling form of D allows large scale modeling of cluster diffusion.

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