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Island Diffusion on Metal fcc (100) Surfaces

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We present Monte Carlo simulations for the size and temperature dependence of the diffusion coefficient of adatom islands on the Cu(100) surface. We show that the scaling exponent for the size dependence is not a constant but a decreasing function of the island size and approaches unity for very large islands. This is due to a crossover from periphery dominated mass transport to a regime where vacancies diffuse inside the island. The effective scaling exponents are in good agreement with theory and experiments. [S0031-9007(99)08824-9]

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Theoretical studies on island diffusion over the past two decades have led to expectations that even large islands may have substantial mobilities [1,2]. A seminal study of diffusion of large islands on metallic surfaces was done by Voter [2], where he was able to show that the diffusion coefficient D of islands with more than $s \approx 10$ atoms followed a simple scaling law with a constant scaling exponent α

$$D \propto e^{-\beta E_L} s^{-\alpha}, \quad (1)$$

where $\beta = 1/(k_B T)$ and E_L is an effective energy barrier for island diffusion.

Since then similar scaling law for large islands, with the scaling exponent α now depending on the diffusion mechanism, has been found in several simulation studies [3–5]. However, the experimental confirmation of the early theoretical predictions had to wait for the development of advanced scanning tunneling microscope (STM) techniques. Only recently the experiments have unequivocally confirmed that on metal surfaces even large islands of sizes up to 1000 atoms undergo diffusion and that the diffusion coefficient obeys Eq. (1) with α indeed depending on the diffusion mechanism [6,7]. Although the experiments and simulations have given strong support to the scaling law in Eq. (1), at least in a restricted region of sizes, the exact role of the various microscopic mechanisms in determining the value of α is still an open question.

On the theoretical side, Khare *et al.* [8,9] have explained island diffusion in terms of the shape fluctuations of the outer boundary, which makes it possible to relate the macroscopic motion of islands to the atomistic processes occurring on the boundary. The three basic mechanisms considered are as follows: particle diffusion along the periphery (PD); terrace diffusion (TD), where a particle can detach from and attach to the edge; and evaporation and condensation limited diffusion mechanism (EC). The effective exponent $\alpha(R) \equiv -\partial \ln(D)/\partial \ln(R)$ can be expressed as [8,9]

$$2\alpha = 2 + \frac{1}{1 + (R/R_{st})(R_{su}/R_{st})} - \frac{2 + (R/R_{st})(R_{su}/R_{st})}{1 + (R/R_{st})(R_{su}/R_{st}) + (R/R_{st})^2}, \quad (2)$$

where $R = \sqrt{s/\pi}$. The parameters R_{st} and R_{su} are related to periphery and terrace diffusion coefficients, respectively. Allowing only one of the mass transport mechanisms EC, TD, or PD at a time for large enough islands, the exponents 1/2, 1, and 3/2 are obtained, respectively (see Fig. 3 in Ref. [9]). When both the TD and the PD mechanisms are present, clear dependence of α on s should be observed, and finally one should always find $\alpha = 1$ for $s \rightarrow \infty$. However, the crossover regime towards this limit occupies a rather narrow region in the parameter space, and it has been assumed to be experimentally inaccessible [9,10].

In contrast, most simulations of island diffusion on metallic fcc surfaces indicate values $1.75 < \alpha < 2.1$ [2,4,11] that cannot be obtained from the theory of Khare *et al.* [8,9]. However, their approach is strongly supported by the recent experiments of Pai *et al.* [7], whose careful STM measurements on the diffusion of Cu and Ag islands on Cu(100) and Ag(100) surfaces yielded $\alpha \approx 1.25$ and $\alpha \approx 1.14$, respectively, at room temperature. According to their explanation, these values of α are due to the lack of the TD mechanism with $R_{su} = 0$, and $0.1 < R/R_{st} < 10$ in Eq. (2). The parameter R_{st} was interpreted as the average separation between adjacent kinks. However, the STM measurements were not able to directly confirm the nature of microscopic diffusion mechanisms for the islands.

In this Letter we will show through extensive simulations of a realistic model of Cu islands on the Cu(100) surface that these open questions can be resolved. First, our simulations show that there exist a long crossover towards $\alpha = 1$ for this system. This indicates that large *effective* values of α may be obtained if only relatively small island sizes are considered. This may explain some of the large

values reported in the literature in cases where there are no unusual diffusion mechanisms present [3]. Second, we show that this crossover is actually due to PD dominated diffusion changing over to TD dominated case, where the microscopic mechanism for the TD process comes from *vacancy diffusion* within large islands. In this way, the values of α obtained in Ref. [7] can be explained with the existence of *both* PD and TD mechanisms for Cu islands, with vacancy diffusion now accounting for the latter. We also discuss the origin of persistent oscillations in D for small island sizes, and vacancy island diffusion on the Cu(100) surface.

The model system we consider here is based on kinetic Monte Carlo simulations of Cu adatoms on the Cu(100) surface, with energetics obtained from molecular dynamics simulations with the effective medium theory (EMT) potential [12]. As discussed in detail in Refs. [12], the EMT barriers are in good agreement with available experimental data for this case. The hopping rate ν of an atom to a vacant nearest neighbor (NN) site can be well approximated by [12,13]

$$\nu = \nu_0 e^{-\beta[E_S + \min(0, \Delta_{NN})E_B]}, \quad (3)$$

where the attempt frequency $\nu_0 = 3.06 \times 10^{12} \text{ s}^{-1}$ and the barrier for the jump of a single adatom $E_S = 0.399 \text{ eV}$. When there is at least one atom diagonally next to the saddle point the barrier $E_S = 0.258 \text{ eV}$. The change in the bond number $-3 \leq \Delta_{NN} \leq 3$ is the number of NN bonds in the final site subtracted by the number of NN bonds in the initial site. The bond energy $E_B = -0.260 \text{ eV}$. We note that within the EMT, barriers on the Ag(100) and Ni(100) surfaces are very similar to the barriers on Cu(100) up to a scaling factor [12]. We therefore expect that the features observed here may describe island diffusion on some other fcc(100) metal surfaces, too.

In this work we prevent detachment of adatoms from the island; however, an adatom can still go around the corner so that the PD mechanism is operational [2,5]. It thus follows that $E_S = 0.258 \text{ eV}$ for all the allowed jumps. Therefore, the energetics in Eq. (3) for the adatom islands is equivalent to the ferromagnetic Ising model with Metropolis transition rates and Kawasaki dynamics.

We create the initial island of s particles by adding atoms one by one to the nearest and the next nearest neighbor sites with the probability $\propto e^{-\beta z E_B}$, where $0 \leq z \leq 4$ is the number of nearest neighbors. It is important to start the simulation with a well thermalized island configuration since the relaxation times for larger islands can become very long. After thermalization, we compute the tracer diffusion coefficient of the island defined through $D = \lim_{t \rightarrow \infty} \frac{1}{4} d\langle r^2 \rangle / dt$ where $\langle r^2 \rangle$ is the mean square displacement of the island [2]. An efficient way of computing D is given in Ref. [14].

We implement our Monte Carlo program by the Bortz-Kalos-Lebowitz algorithm [2,15] using a binary tree struc-

ture [16]. In the algorithm, every trial leads to a jump. At low temperatures, a large number of unsuccessful trials inherent in the traditional Metropolis algorithm can be avoided. This allows very long simulation times in our system.

We first simulate adatom island diffusion with sizes $1 \leq s \leq 10^4$ at high temperature $T = 1000 \text{ K}$ [17]. Our data together with a fit of D from Ref. [9] [Eq. (36)] are shown in Fig. 1. For $s \geq 10$ we clearly observe a crossover region where the effective scaling exponent behaves as predicted by Eq. (2) (see the inset of Fig. 1). For large islands, α finally approaches the limit $\alpha = 1$ as predicted by theory [8,9]. Because of the crossover, it is evident in Fig. 1 that for a limited window of sizes, an effective exponent between $1 < \alpha < 3/2$ can be obtained. A similar type of crossover region persists at lower temperatures, and we find that, for example, using the size window $100 \leq s \leq 1000$ we obtain values of α that only weakly depend on temperature, i.e., $1.12 \leq \alpha \leq 1.23$ at $T = 400, 500, 700,$ and 1000 K . In particular, the overall behavior of D for large values of s at 300 K is in very good agreement with the behavior found in the experiments of Pai *et al.* [7] at room temperature where $80 \leq s \leq 440$ (see Fig. 2) ($60 \leq s \leq 870$ for Ag).

The behavior of D for smaller island sizes where Eq. (2) is not valid is interesting. There are clear size dependent oscillations present as also reported by Fichthorn and Pal [18] in their simulations. However, in the experiments such oscillations are easily smeared out by size fluctuations [7] as can be seen in Fig. 2 where the experimental data for D follow closely the *average* behavior of D in the same regime. At low temperatures there is a

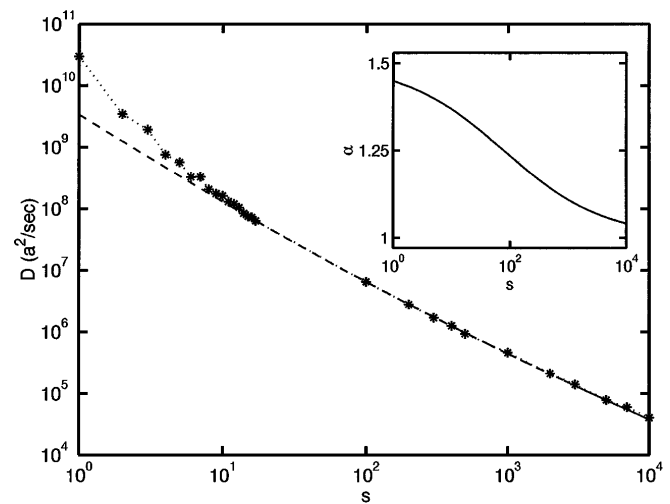


FIG. 1. Adatom island diffusion coefficient D vs s for $1 \leq s \leq 10^4$ at $T = 1000 \text{ K}$ ($a \approx 3.5 \text{ \AA}$ is the lattice constant of copper). Stars denote the results of our simulations, and the dashed line is a fit to Eq. (36) from Ref. [9] ($R_{st} = 5.0 \times 10^{-2}$ and $R_{su} = 5.0 \times 10^{-4}$). Error bars are of the size of the symbols or smaller. The inset shows the effective exponent α from Eq. (2) using this fit.

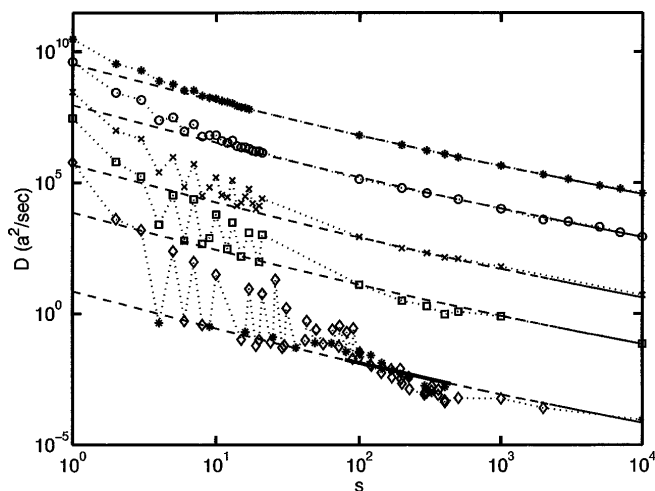


FIG. 2. Adatom island diffusion coefficient D for $1 \leq s \leq 10^4$ at $T = 1000, 700, 500, 400,$ and 300 K (from top to bottom). For $T = 300$ K, the n^2 configurations are shown with stars. The dotted lines are just guides to the eye. The dashed lines indicate fits to Eq. (36) of Ref. [9] (R_{st} and R_{su} are almost independent of T). Error bars are of the size of the symbols or smaller except at $T = 300$ K for $s \geq 100$ where the scatter in the data indicates the errors. The thick line at $T = 300$ K shows the experimental results of Ref. [7] for Cu. See text for details.

difference for D between small islands of sizes n^2 and $n^2 \pm 1$, where n is an integer, in particular, that $D(n^2)$ is much smaller than $D(n^2 + 1)$. This is consistent with the notion that the square configurations are very stable and therefore move slowly [2]. However, for larger island this is oversimplified since entropy must be taken into account. In equilibrium, the probability for a given configuration to occur $P(s, E) \propto \omega(s, E)e^{-\beta E}$, where $\omega(s, E)$ is the number of states of the island with size s and energy E . There is no degeneracy at $T = 0$ for an n^2 configuration, while the degeneracy of an “excited state” with one bond broken (e.g., an adatom moving along the edge) grows rapidly as a function of the island size. Thus, for n^2 islands the contribution of the low-mobility configuration to D becomes less important when n grows. Eventually, the oscillations dampen out and the continuum theory becomes valid [19]. At higher temperatures, this naturally occurs for smaller islands already.

We now turn into discussion about the microscopic mechanisms for island diffusion. Most importantly, our simulation results indicate that there is a TD type of process involved in the island motion in contrast to what was suggested in Refs. [7,20]. This process in the present case is due to *vacancy diffusion* inside the island. This conclusion is supported by the observation that the effective scaling exponent α approaches unity as the island size increases even at room temperature which indicates that the TD mode must be involved [8,9]. Moreover, we have explicitly checked the role of the PD and TD mechanisms at 1000 and 700 K with $s \leq 1000$.

We modified our model by first disallowing atoms to diffuse around corner sites to prohibit the PD mechanism. In the second modification, we disallowed the creation of vacancies in the island to prevent the TD mechanism from operating. Simulations of the two modified cases gave the scaling exponents $\alpha = 1.02$ and $\alpha = 1.48$, in complete agreement with the theoretical values for the TD ($\alpha = 1$) and PD ($\alpha = 3/2$) dominated island diffusion.

We have also measured the effective Arrhenius barriers for island diffusion for $s = 100, 300, 500,$ and 1000 , and find that there is virtually no size dependence. Interestingly enough, whether the PD or TD mechanism is present also makes very little difference. We have measured the barriers between 700 and 1000 K for the PD and the TD dominated cases with one of the mechanisms suppressed as discussed in the section above, and obtain 0.77 and 0.79 eV, respectively. The Arrhenius barrier for the nonmodified case at $400 \leq T \leq 1000$ K is 0.79 eV. All these values are very close to the corresponding rate-limiting process with $\Delta_{NN} = -2$. This can be easily explained by microscopic considerations. In the PD process, two bonds are broken when a particle goes from a kink to a corner site [2]. Symmetrically, in the TD process, the rate-limiting step is the creation of a vacancy where an atom having three neighbors becomes a one-neighbor particle; i.e., a vacancy jumps into the island. Therefore, jumps with $\Delta_{NN} = -2$ dominate the vacancy creation.

An interesting question for (100) metal surfaces concerns *vacancy island* diffusion. In our model, the energetics for vacancy islands is very similar to the adatom case. Symmetrically to adatom islands, vacancies are prevented to detach from a vacancy island, but atoms can detach from the edge to the pit. According to Eq. (3) the barriers for vacancies are then equivalent to the barriers for the adatoms, except that the jumps inside the vacancy islands for adatoms have $E_S = 0.399$ eV in contrast to 0.258 eV for vacancies inside the islands. However, this difference is not important in practice. We have simulated vacancy island diffusion at various temperatures, and the diffusion coefficients are the same as for the adatom islands within the statistical errors. This is because the diffusion inside either an adatom or vacancy island is *not* the rate-limiting process.

To summarize, our model gives results in very good agreement with experiments and theory and demonstrates that, for at least Cu(100) surfaces, vacancy diffusion within the islands contributes significantly to the island mobility for larger islands [2]. Another interesting feature not easily seen in the experiments are the persistent oscillations in D at low temperatures that are due to entropic reasons; in fact, this is yet another example of the compensation effect seen in many other systems. Our model predicts that vacancy island diffusion on the Cu(100) surface is essentially similar to adatom island diffusion since the rate-limiting mechanisms are

symmetric for both cases. Finally, we note that the present model is somewhat idealized in the sense that the effect of other islands, surface steps, etc., is neglected. It would be of great interest to study these issues, as well as island and vacancy diffusion on (100) surfaces of other metals to further study the role of various microscopic mechanisms.

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- [20] We have measured the average number of kinks and find that it scales as $\propto s^\gamma$, where $\gamma = 0.49$ at $T = 1000$ K, and larger than ≈ 0.43 down to 400 K. Therefore, the average separation between adjacent kinks is nearly constant as suggested by Pai *et al.* [7].