Heinonen, J.; Koponen, I.; Merikoski, J.; Ala-Nissila, T.

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Island Diffusion on Metal fcc (100) Surfaces

J. Heinonen, I. Koponen, J. Merikoski, and T. Ala-Nissila

1Helsinki Institute of Physics, University of Helsinki, P.O. Box 9, FIN-00014 Helsinki, Finland
2Department of Physics, University of Jyväskylä, P.O. Box 35, FIN-40351 Jyväskylä, Finland
3Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02150 HUT Espoo, Finland

and Department of Physics, Brown University, Providence, Rhode Island 02912-1843

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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.

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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 = 10 atoms followed a simple scaling law with a constant scaling exponent α

\[ D \propto e^{-\beta E_L} s^{-\alpha}, \]

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 \( \alpha \) 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 \( \alpha \) 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 \( \alpha \) 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 atomic 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 \( \alpha(R) = -\partial \ln(D)/\partial \ln(R) \) can be expressed as [8,9]

\[ 2\alpha = 2 + \frac{1}{1 + (R/R_{st})(R_{su}/R_{st})} - \frac{2 + (R/R_{st})(R_{su}/R_{st})}{1 + (R/R_{st})(R_{su}/R_{st}) + (R/R_{st})^2}, \]
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 $\alpha$ 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 $\nu$ of an atom to a vacant nearest neighbor (NN) site can be well approximated by

$$\nu = \nu_0 e^{-\beta(E_S + \min(0, \Delta_{NN}) \epsilon_b)},$$

where the attempt frequency $\nu_0 = 3.06 \times 10^{12}$ s$^{-1}$ and the barrier for the jump of a single adatom $E_S = 0.399$ eV. When there is at least one atom diagonally next to the saddle point the barrier $E_S = 0.258$ 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 $E_B = -0.260$ 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 $E_S = 0.258$ 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 $\epsilon e^{-\beta \Delta \epsilon_b}$, 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 $D = \lim_{s \to \infty} \frac{1}{4} \frac{d<r^2>/dt}{d}$ 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 structure [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 $T = 1000$ K [17]. Our data together with a fit of $D$ from Ref. [9] [Eq. (36)] are shown in Fig. 1. For $s \approx 10$ 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, $\alpha$ 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 $\alpha$ 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
Moreover, we have explicitly checked the role of the PD which indicates that the TD mode must be involved \([8,9]\). 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...
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*Author to whom correspondence should be addressed. Email address: jarkko.heinonen@helsinki.fi


[17] We note that the lattice-gas model used here is not expected to be valid at high temperatures. However, for the present case simulations of diffusion over a large temperature range are important in order that the relevant low temperature mechanisms be correctly identified (see also Ref. [18]).


[19] From our data, we can estimate the limit $s_m$ where the oscillations become negligible by finding the largest island size for which $D(s - 1) < D(s)$ still applies. Using this definition we find in temperature range $300 \leq T \leq 1000$ K that $s_m \approx gT E_w$, where the effective barrier $E_w \approx 0.26$ eV. This is very close to the energy barrier needed to excite an adatom from an $n^2$ configuration.

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