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Title: Role of concerted atomic movements on the diffusion of small islands on fcc(100) metal surfaces

Year: 2001

Version: Final published version

**Please cite the original version:**

Salo, P. & Hirvonen, J. & Koponen, I. T. & Trushin, O. S. & Heinonen, J. & Ala-Nissilä, Tapio. 2001. Role of concerted atomic movements on the diffusion of small islands on fcc(100) metal surfaces. *Physical Review B*. Volume 64, Issue 16. P. 161405/1-4. ISSN 1098-0121 (printed). DOI: 10.1103/physrevb.64.161405.

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## Role of concerted atomic movements on the diffusion of small islands on fcc(100) metal surfaces

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(Received 6 July 2001; revised manuscript received 21 August 2001; published 5 October 2001)

The master equation formalism is used to analytically calculate the center-of-mass diffusion coefficient for small two-dimensional islands on fcc(100) metal surfaces. We consider the case of Cu on Cu(100) containing up to nine atoms, with energetics obtained from semiempirical interaction potentials. In the case where only single-particle processes are taken into account, the analytic results agree well with previous Monte Carlo simulation data. However, when recently proposed many-particle processes are included, in some cases the diffusion coefficients increase by an order of magnitude at room temperatures. Qualitatively, the oscillatory behavior of diffusion as a function of the island size is not affected by the many-particle processes.

DOI: 10.1103/PhysRevB.64.161405

PACS number(s): 68.35.Fx, 36.40.Sx, 68.55.-a

Island diffusion on surfaces has recently received attention not only because of its importance for surface growth<sup>1-3</sup> but also because there are theoretically interesting issues regarding the dependence of the center-of-mass (CM) diffusion coefficient  $D_s$  on the number of atoms  $s$  in the island.<sup>4-7</sup> The limit of large islands where  $s \gg 1$  for simple metal surfaces is understood to a large extent (see, e.g., Refs. 4-7). For small islands [with  $s \approx O(1) - O(10^2)$ ] the situation is more complicated since continuum theories are obviously not valid. One indication of this is the fact that there are pronounced oscillations in the size dependence of  $D_s$  (Refs. 6-8) as seen in experiments on Rh(100) surfaces<sup>9</sup> (see also Ref. 10). The oscillations can be qualitatively explained by the geometry of the islands and by the relative stability of small square and rectangular configurations.<sup>6,9,11</sup> Typically, one expects that  $D_s \propto e^{-\beta E_s}$  at low temperatures, and thus the oscillations are most pronounced there because the rate limiting step (RLS) barriers  $E_s$  can be very different for islands of different sizes.

Another challenge is that in addition to the single-atom events that control the shape fluctuations of large islands,<sup>4</sup> for small islands there are concerted *many-particle processes* which are in some cases of equal importance for island mobility.<sup>8,12-14</sup> For fcc(100) metal surfaces Shi *et al.*<sup>8</sup> found in their embedded atom model (EAM) calculations a new mechanism for island diffusion through concerted dimer shearing. Most recently, Trushin *et al.*<sup>14,15</sup> used sophisticated saddle-point search methods combined with EAM and showed that there are additional mechanisms such as *trimer shearing* at the periphery, and dimer and trimer shearing *inside the island* which control the RLS in some cases.

In this work it is our purpose to quantitatively study the role of many particle processes in diffusion of adatom islands on fcc(100) metal surfaces. In particular, our aim is to compare the diffusion coefficients at various temperatures with and without the inclusion of many particle processes. To this end, we calculate  $D_s$  for small islands using the analytic master equation (ME) formalism by Titulaer and Deutsch,<sup>16</sup> as modified by Sanchez and Evans (SE).<sup>17</sup> This method is

based on the Markovian approximation of independent transitions between different configurations. With all the relevant transition rates known,  $D_s$  can be obtained explicitly at all temperatures where the Markovian approximation holds. The exact enumeration of configurations within the ME formalism allows us to discuss the role of concerted motion on small-island diffusion in detail. In this work we consider the case of Cu adatom islands on the Cu(100) surface. In the previous work of SE,<sup>17</sup>  $D_s$  was calculated up to  $s=5$  including transition processes in which single atom jumps occur, and also dimer shearing was considered for tetramers. In this work, we consider dimer and trimer shearing processes for islands from five up to nine atoms as suggested by the energetics of Trushin *et al.*<sup>14</sup> These results can be directly compared to the analytic formula of SE for  $s=5$ , and the Monte Carlo (MC) data of Heinonen *et al.*<sup>6</sup> which is based on single-particle processes only.

The details of the formalism can be found in Ref. 17. Here we only give an outline of the procedure. For any island with  $s$  atoms the number of possible configurations connected by nearest-neighbor (NN) bonds can be exactly enumerated, but this number grows very quickly with  $s$ . However, it turns out that in most cases of interest, only part of all the accessible configurations are of importance. The number of NN and next-nearest-neighbor (NNN) bonds characterizes the configurations here. The one with the largest number of NN and NNN bonds is usually the equilibrium configuration according to bond-counting arguments, as demonstrated by energetics based on semiempirical potentials on fcc(100) metal surfaces.<sup>14,18</sup> Among the set of configurations one can transform one configuration into another with specific transition mechanisms, characterized by transition rates  $h_i$ . As usual, we make the assumption that any rate  $h_i$  can be written in the Arrhenius form  $h_i = \nu_i e^{-\beta \Delta_i}$ , where  $\nu_i$  is a prefactor and  $\Delta_i$  the activation barrier of the process  $i$ . To solve the problem of having too many such transitions, one has to consider the relative magnitudes of the barriers  $\Delta_i$ . In many cases, some of the configurations can be put together in a single *quasiconfiguration* (QC). This is the case

TABLE I. Processes and activation energies listed first for the equilibrium shapes (configurations at the upper left corners) and for other shapes of small Cu islands of sizes  $s = 5-9$ . The corresponding rates are put in brackets. The energies of RLS for CM motion are shown in boldface. When the energy is in italics, the corresponding process is not included explicitly in the transition matrix of many-particle processes because (i) the process is so fast that it takes place immediately (with very low energy), (ii) the process is so slow that it does not occur at the relevant temperatures (with very high energy), or (iii) there is a process with a considerably lower energy that takes place before the one considered.

$s$	Processes	$\Delta_i$ (eV) [rate symbol]
5		$0.21 [h_e], 0.42 [h_{s1}], 0.51 [h_k], \mathbf{0.53} [h_{si}], 0.55 [h_r], 0.71 [h_s]$
		$0.82 [h_3], 0.15 [h'_k], 0.20 [h'_{si}], 0.39 [h'_s], 0.65 [-]$
6		$\mathbf{0.70} [h_{si}], 0.71 [h_s], 0.83 [h_c], 0.90 [h_3], 0.08 [h'_{si}], 0.15 [h'_k]$
		$0.27 [-], 0.39 [-], 0.41 [h'_s], 0.44 [-], 0.55 [h_r], 0.71 [-]$
7		$0.45 [h_{s1}], 0.84 [h_c], 0.43 [h_{si}], 0.44 [h'_{s1}], \mathbf{0.50} [h_{3i}], 0.55 [h_r]$
8		$0.45 [h_{s1}], 0.54 [h_k], \mathbf{0.63} [h_{3i}], 0.76 [h_s]$
		$0.84 [h_c], 0.94 [h_3], 0.31 [h'_{3i}], 0.62 [h'_3]$
9		$\mathbf{0.81} [h_{3i}], 0.82 [h_c], 0.95 [h_3], 0.18 [h'_{3i}], 0.18 [h'_k]$
		$0.37 [h_{3a}], 0.46 [h_{s1}], 0.54 [h_k], 0.62 [-], 0.64 [h'_3]$

when transitions between different configurations inside the QC can be considered as infinitely fast processes as compared to the other transitions.<sup>17</sup> A good approximation for the fcc(100) metals is to construct the QC from configurations which have the same number of NN bonds, but the number of NNN bonds varies, as will be shown below.

Once all the possible configurations and the transition processes between them with  $\Delta_i$  less than a given limit have been gathered together, the corresponding displacement vectors of the CM between these configurations are calculated. After that  $D_s$  can be calculated from the acoustic eigenvalues of the corresponding transition matrix  $\mathbf{M}$ .<sup>17</sup> The size of this square matrix equals the number of configurations included. This means that in practice, the method is useful only for rather small islands,<sup>16,17</sup> but systems with about less than ten different real and quasiconfigurations are still manageable with symbolic algebra programs. Even if explicit analytic formulas were not required, the construction of the transition matrix would become very tedious if the number of configurations included were much larger than that.

An important role in the construction of the QC's and the transition matrix is played by the actual energetics. For the fcc(100) metal surfaces considered here, semiempirical methods such as the effective medium theory (EMT) (Ref. 19) and EAM (Ref. 20) should give a good approximation of the relative ordering of the barriers  $\Delta_i$ . In the case of Cu(100), EMT has been used to calculate the energetics of single-particle events for island diffusion.<sup>18,21</sup> These energetics were subsequently used in the MC studies of Heinonen *et al.*<sup>6</sup> In Table I we show some important single and many-particle processes as calculated using the EAM potential (see also Ref. 14). From Table I, it is immediately obvious that many-particle processes are important and will affect island

diffusion for many cases. Although many-particle processes have not been calculated using the EMT, the ordering of the single-particle events is in good agreement with EAM. In particular, single atom processes along the edge of the island for EMT (EAM) are given by 0.26 eV (0.21 eV) for edge hopping (rate  $h_e$ ), 0.52 eV (0.51 eV) for kink escape (rate  $h_k$ ), 0.52 eV (0.55 eV) for corner rounding (rate  $h_r$ ), and 0.78 eV (0.82 eV) for core breakup (rate  $h_c$ ). These processes are illustrated in Fig. 1 of Ref. 17 (see also Table I).

As the first case, we consider pentamer islands ( $s=5$ ). From Table I it is immediately evident that there is a large number of different configurations and possible transition mechanisms. An analytic solution for this problem was presented by SE (Ref. 17) where all the single-atom processes were considered by using four different QC's as shown in Fig. 7 of Ref. 17. For a more accurate analysis including dimer shearing we have chosen the QC shown in Fig. 1 which contains 21 configurations. These configurations are taken into the same QC because any of them can be transformed to another configuration inside the QC via a slide along the edge of the island with rate  $h_e$  which has a relatively low activation barrier ( $\Delta_e \approx 0.2$  eV), and thus we set

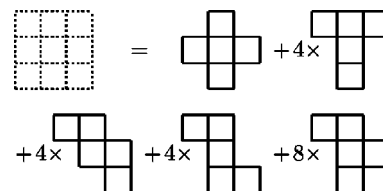


FIG. 1. The 21 configurations in the QC for pentamer diffusion. The multipliers represent the degeneracy of the corresponding configurations.

$h_e = \infty$  here. The configurations in the QC have approximately the same energy, with four NN and at least two NNN bonds, and they are all unbroken. The QC shown in Fig. 1 is included between each transition considered by SE.<sup>7</sup>

The additional two-particle transitions and their rates are shown in Table I. Transition rates  $h_{si}$  and  $h_s$  have different inverse rates  $h'_{si}$  and  $h'_s$  while the transition rate  $h_{s1}$  equals its reverse rate. The corresponding barriers for each transition are in Table I. The transition processes that are included in the present calculation have  $\Delta_i < 0.65$  eV. With this description, the size of  $\mathbf{M}$  with dimer shearing included becomes five-by-five and the diffusion coefficient can be shown to be

$$D_5 = \frac{2[h'_{si} + 2(h'_s + h_r)]}{[2(h_{s1} + h_{si}) + h_r]} \times \frac{[2h_{si}(h_{s1} + h_{si}) + h_r(h_{s1} + 2h_{si})]}{(8h'_{si} + 16h'_s + 21h_{si} + 16h_r)}. \quad (1)$$

It is interesting to analyze the limiting behavior of this somewhat complicated expression. Assuming that the Arrhenius form holds with energetics according to Table I and  $\nu_i = \text{const}$ , at low temperatures  $D_5 \approx h_{si}/4$  which is the expected RLS form for diffusion. It is also straightforward to obtain the single-particle limit by setting  $h_{s1} = h_k/2$  and the other rates for dimer shearing to zero, which gives  $D_5^{\text{sp}} = h_k h_r / [8(h_k + h_r)]$ . This is exactly the same result as that of SE.<sup>17</sup> Finally, we note that with EMT energetics,  $h_k = h_r$  and thus  $D_5^{\text{sp}} \approx h_r/16$  at low temperatures, while with EAM,  $h_k > h_r$  and thus  $D_5^{\text{sp}} \approx h_r/8$ . This shows the sensitivity of the  $s=5$  case to the details of the energetics.

The diffusion of a six-atom island is rather similar to the pentamer case. The transitions can be considered with two two-by-three configurations and one three-by-three QC (with 24 internal configurations) and thus the transition matrix is only three-by-three. Internal and edge dimer shearing are included (see Table I). The diffusion coefficient is given by

$$D_6 = \frac{(h'_s + h'_c)(h_{si} + 2h_s)}{4(h'_s + h'_c + 3h_{si} + 6h_s)}, \quad (2)$$

where  $h'_c = h_r$ . The low-temperature limit gives the expected RLS form  $D_6 \approx h_{si}/4$  (see Table I). It is interesting to note that the diffusion of hexamer does not require a core break-up process since there are dimer-shearing processes that lead to the CM motion without the core break-up. Thus, it is the lowest energy process left out in the present case, with  $\Delta = 0.83$  eV.

The diffusion of a seven-atom island is less trivial. We have included two real configurations and four QC's, making the transition matrix six-by-six, with dimer shearing at the periphery, and internal dimer and trimer shearing included (see Table I). With this,  $D_7$  is of a relatively simple form

$$D_7 = \frac{h_{s1} h_{3i} (h_{si} + h'_{s1})}{(h_{si} + 2h'_{s1} + 12h_{s1})(h_{si} + h'_{s1} + h_{3i})}. \quad (3)$$

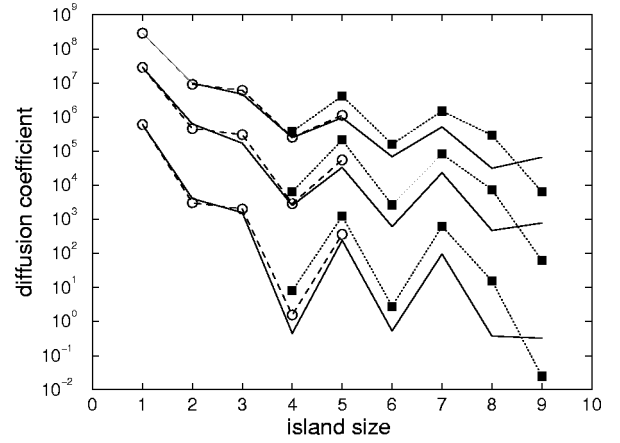


FIG. 2. Size dependent oscillations of the diffusion coefficient (in units  $a^2/\text{sec}$ , where  $a$  is the lattice constant) for small islands. MC simulations (solid line), analytic results with single-atom (open circles) and many-particle (filled squares) processes with temperatures 300, 400, and 500 K from bottom to top, respectively.

However, the low-temperature limit does not give the expected RLS barrier 0.50 eV, but there is an extra term that gives a small additional energy. This is due to the fact that the RLS does not operate to the equilibrium configuration. Thus, there has to be a transition before the RLS can operate which slightly increases the activation barrier. This indicates that this method is rather sensitive to the choice of configurations in a QC on the grounds of the energetics of the system. The transition processes that are included here have  $\Delta_i < 0.55$  eV which is the energy for corner rounding.

The diffusion of an eight-atom island can be considered with a six-by-six transition matrix, consisting of four real and two QC's. Dimer shearing at the edge, and trimer shearing both at the edge and in the island are included. The diffusion coefficient is then

$$D_8 = \frac{h_{3i}(h'_{3i} + h'_3)(2h_{s1} + h_{3i})}{4(h_{s1} + h_{3i})(2h'_{3i} + 2h'_3 + 9h_{3i})}. \quad (4)$$

At low temperatures  $D_8 \approx h_{3i}/4$  which is the expected RLS. The transition processes that are included have an energy less than 0.76 eV which corresponds to dimer shearing at the periphery (see Table I).

Finally, for  $s=9$ , using a five-by-five transition matrix the diffusion coefficient is

$$D_9 = \frac{2h_{3a}h'_3h_{3i}}{3(2h_{3a} + h'_3)(h'_3 + 4h_{3i})}, \quad (5)$$

and at low temperatures  $D_9 \approx h_{3i}/3$  which is the expected RLS. The lowest rate not included is  $h_c$ .

In Fig. 2 we show a comparison between the single-particle MC simulations<sup>6</sup> (with energetics based on EMT), analytic ME results of SE (Ref. 17) with single-particle processes only (EMT), and our analytic ME results with dimer and trimer shearing included as explained above (EAM). As expected, the MC data and results from the equations of SE are in very good agreement with each other. For  $s \geq 5$  where

we have included the many-particle processes, two important conclusions can be drawn. First, the qualitative behavior of the oscillations in  $D_s$  is not affected by the new processes. The relative energetic stability of the compact  $s=4, 6, 8,$  and  $9$  islands is still the dominant factor in determining  $D_s$  in good agreement with the experiment.<sup>9</sup> However, the quantitative values of  $D_s$  are greatly influenced by the many-particle processes.<sup>22</sup> Dimer shearing allows rapid transformation of islands to open configurations and therefore it opens up several new favorable kinetic pathways for diffusion. The inclusion of trimer shearing for septamer and octamer diffusion further increases the values of  $D_7$  and  $D_8$  as compared to the single-particle MC data.<sup>24</sup> As seen in Fig. 2, this difference can easily be one order of magnitude at  $T=300$  K. The discrepancy between EMT and EAM results for  $D_9$  is

due to the more favorable core-breakup process for EMT than for EAM.

In summary, by a comparison of results based on a variety of methods including microscopic semiempirical calculations, MC simulations, and analytic results, we have been able to obtain a rather complete picture of adatom island diffusion for small Cu islands on Cu(100) surfaces. There exist several previously overlooked many-particle mechanisms that play an important role. This means that the CM motion of islands up to size ten and even larger can be activated more easily than previously assumed.

This work has been in part supported by the Academy of Finland through its Center of Excellence program. O.S.T. acknowledges partial support from the Russian Foundation for Basic Research (Grant no. 98-02-16581).

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