

## Leapfrog Diffusion Mechanism for One-Dimensional Chains on Missing-Row Reconstructed Surfaces

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We analyze the in-channel diffusion of dimers and longer  $n$ -adatom chains on Au and Pt (110) ( $1 \times 2$ ) surfaces by molecular dynamics simulations. From our calculations it arises that, on the missing-row reconstructed surface, a novel diffusion process, called leapfrog, dominates over concerted jumps, thus becoming the most frequent diffusion mechanism. [S0031-9007(99)08441-0]

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Adatom diffusion plays an important role in the microscopic understanding of crystal growth, thin film formation, and other surface phenomena [1]. Even if some new diffusion processes have been recently discovered [2–4], the basic set of single-adatom diffusion mechanisms on the most interesting surfaces is now understood. The natural subsequent step is thus the study of small-cluster mobility, starting from the smallest, the dimer: as emphasized in Ref. [5], the role of dimer diffusion in affecting the growth kinetics is not yet fully understood and needs further investigation. In particular, it is of main interest to know how fast dimers and larger clusters can move, and by which mechanisms. In this paper we concentrate on Au and Pt  $n$ -chain ( $n \geq 2$ ) self-diffusion on the (110) ( $1 \times 1$ ) and ( $1 \times 2$ ) surfaces, in order to understand how the geometry influences diffusion. In the unreconstructed ( $1 \times 1$ ) geometry the fcc(110) surfaces are already characterized by channels along the  $[1\bar{1}0]$  direction. On the ( $1 \times 2$ ) surface channels are even deeper, so that in-channel diffusion might be thought of as a one-dimensional process. However, very recently, we showed [3] that for Au adatoms, an important contribution to diffusion (especially for long-jump events) comes from metastable walks (MW). In a MW, an adatom starts from a minimum in the channel reaching another in-channel minimum by an out-of-channel trajectory, passing through a metastable potential-energy region.

In this Letter we show, by molecular dynamics (MD) simulations, that a new mechanism, again involving an out-of-channel trajectory, occurs for dimers ( $n = 2$ ), trimers or longer chains ( $n \geq 3$ ), and that this mechanism [we shall call it leapfrog (LF), see below] has the lowest activation barrier, thus it becomes dominant at low  $T$ . To our knowledge, no works on dimer or chain self-diffusion on Au or Pt (110) are present in literature. Concerning dimers self-diffusion on fcc(110) surfaces, other metals have been already studied: Shiang and Tsong performed MD simulations of  $\text{Ir}_2$  and  $\text{Pt}_2$  [6] self-diffusion on Ir and Pt(110)-( $1 \times 1$ ). There, a great variety of diffusion processes was found, such as concerted jumps (CJ, i.e., a rigid dimer jump) and exchanges, but, due to the ( $1 \times 1$ ) geometry, no evidence for LF events could be

found. Recently, Linderoth *et al.* [7] observed Pt dimers diffusion on Pt(110)-( $1 \times 2$ ) by STM: again, there was no evidence for the LF event. However, in longer chains, LF diffusion events are now observed in Pt [8]. Here, inspired by the STM observations in Ref. [8], we analyze in detail the microscopic mechanism, the diffusion path, and the characteristic time scales of the LF process by total-energy calculations. We explain the reason why such processes are very hardly observable for dimers and, on the contrary, they can be observed for longer chains. We treat both Au and Pt. A comparison with the experimental results in Pt is made, with good results. We treat two metals in order to have some indications on the generality of the phenomenon.

Our calculations are based on the many-body RGL potentials [9], with a second-neighbor cutoff. Details about our MD simulations, and about the energy-minimization procedure (quenching) are in Refs. [3,10]. Rosato-Guillopé-Legrand (RGL) potentials correctly describe surface relaxations and reconstructions of noble metals [9], and predict the diffusion mechanism in agreement with experimental results, for transition and noble-metal surfaces [4,6,11]. A complete comparison between RGL potentials and other theoretical or experimental results is in Ref. [12]. In the following we make first a discussion of the results for Au. For Pt, results are qualitatively similar (see Tables I and II), and they are discussed towards the end of the Letter.

Let us first consider dimers. We have calculated CJ barriers for Au dimers, finding  $E_{\text{CJ}} = 0.47$  eV in the ( $1 \times 1$ ), and  $E_{\text{CJ}} = 0.52$  eV in the ( $1 \times 2$ ). Then we have performed very long high- $T$  MD simulations [at 450 K on both geometries and at 550 K on the ( $1 \times 2$ ) only]. On the ( $1 \times 1$ ), we have found the statistics of events (see Table I) to be in agreement with the above energy barriers: only the CJ mechanism is present, and its rate  $r_{\text{CJ}}$  is roughly obtained with an Arrhenius form,  $r_{\text{CJ}} = \nu_{\text{CJ}} \exp(-\beta E_{\text{CJ}})$ , where  $\beta = (k_B T)^{-1}$  and  $\nu_{\text{CJ}}$  frequency prefactor (here and after, in all quantitative estimates, all prefactors will be of  $10^{12} \text{ s}^{-1}$ ). On the other hand, in the ( $1 \times 2$ ) geometry, we have found a new event, clearly dominating at both 450 and 550 K (see Table I),

TABLE I. MD simulations results for Au and Pt  $n$ -chains. In the case of trimers and tetramers, in the last column, besides the number of successful leapfrog events, we report also in parenthesis the number of events in which the adatom reaches the position  $C$  in Fig. 4, but after that it descends again to the side of departure and not on the opposite side

Metal and geometry	$n$	$T$ (K)	Simulation Time ( $10^5$ ps)	CJ	LF
Au( $1 \times 1$ )	2	450	1.5	5	...
Au( $1 \times 2$ )	2	450	3.5	3	21
Au( $1 \times 2$ )	2	550	1	18	40
Au( $1 \times 2$ )	3	550	0.5	0	4(+5)
Pt( $1 \times 2$ )	3	1000	0.7	8	34
Pt( $1 \times 2$ )	3	1000	0.5	0	20(+24)
Pt( $1 \times 2$ )	4	1000	0.15	0	4(+7)

the LF event. Its nature is understood from Fig. 1, where a typical LF event at 450 K is shown. Our 0 K energy calculations give an energy barrier  $E_{up} = 0.45$  eV (in Figs. 2–4 this is the energy required to jump from a site  $A$  to a site  $B$ ). Thus  $E_{up} < E_{CJ}$ , and at typical FIM or STM experimental temperatures, the LF event should dominate. When trimers (or longer chains) are considered, one of the two side adatoms can climb out of the channel [see Fig. 4 and notice that the energy barrier for such an event is in good approximation the same found for the dimer (0.45 eV) and this is still true for longer chains], and diffuse over the other two ( $n - 1$ ) adatoms, finally falling again in the channel, but on the opposite side of the trimer (chain). We shall call this mechanism LF once again, but always specifying the chain length. Trimers (or longer  $n$ -chains) CJ have to be considered extremely rare events (the barrier for a CJ of a trimer is of about 0.7 eV, and even larger for longer chains; in the high- $T$  simulation trimer CJ were never observed, see Table I), so that, for all Au chains with  $n \geq 2$  the LF event is, by far, the most favorite mechanism.

An important question arises: is it possible a direct experimental observation of such events? A LF causes

TABLE II. Energy barriers (in eV).  $E_{AB} = E_{up}$  is the energy barrier for the promotion above the chain (dimer) by jump,  $E_{down}$  is the descent by jump,  $E_{up}^{exch}$  and  $E_{down}^{exch}$  are the promotion and descent energies by  $E_{diss}$  is the dissociation energy. The latter is practically independent on the chain length for  $n > 3$ .

Metal	Dimer			
	$E_{AB} = E_{up}$	$E_{BA} = E_{down}$	$E_{diss}$	$E_{CJ}$
Au	0.45	0.14	0.51	0.52
Pt	0.84	0.21	0.96	1.06
Metal	Trimer			
	$E_{AB} = E_{up}$	$E_{BA} = E_{down}$	$E_{diss}$	
Au	0.45	0.37	0.52	
Pt	0.84	0.64	0.97	

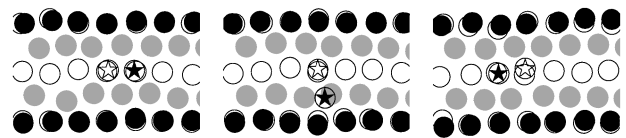


FIG. 1. A typical LF event, at 450 K. Left: The dimer (black and white stars) lies inside the channel. Center: The black-star adatom is climbing on the metastable channel. Right: The black-star adatom falls again down into the channel, but on the opposite side.

a one-site move of the chain, as well as a CJ event, so that if only the initial and the final position are considered, LF and CJ are not distinguished. So, in order to observe a LF, one should be able to collect images of the system during the event itself, i.e., while the adatom is walking on the chain. Now, there is an important difference between dimers and longer chains: for instance, in the case of a trimer, the potential energy surface for an adatom along the metastable diffusion path has a deep minimum (see Fig. 4), when the diffusing adatom lies exactly in the middle above the other two adatoms of the chain. This situation does not change for  $n > 3$ . So, during its trajectory, the adatom can thermalize in one of these deep metastable minima. Let us calculate the average time spent by an adatom along such trajectories. Two conditions must be satisfied: at the experimental  $T$  the frequency of the LF (or of the MW for the adatom) should be appreciable, and the average duration of the permanence in the metastable region should be long enough.

First, we consider the single-adatom case (see Fig. 2): at the initial time the adatom is in a  $B$  position, then it makes a random walk on the metastable channel, and it is finally trapped again at the channel bottom, after  $2N + 1$  steps with  $N = 0, 1, 2, \dots$ . If  $p$  is the probability to jump

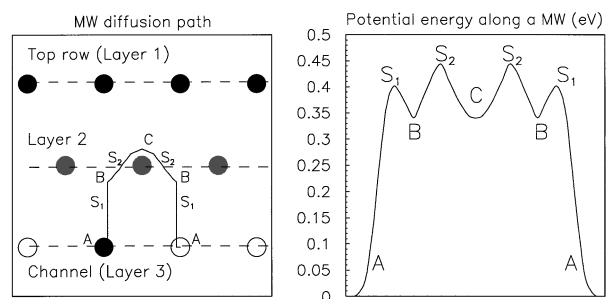


FIG. 2. Left: Adatom MW diffusion path. An adatom (full circle in the channel), starting from  $A$ , climbs on the (111) facet, passes the saddle  $S_1$ , and goes to a minimum  $B$ . From  $B$ , it can fall again into the channel, or it can move to  $C$  from where it can only go to another  $B$  site. Right: The energetics of this path is shown. This energetics (and the corresponding ones in the next figures) are obtained by interpolation from a full sampling of a lattice cell by quenched MD. We fix the  $x$  and  $y$  coordinates of the adatom and let all other degrees of freedom in the slab relax. This has been done on a grid of  $50 \times 50$  points per lattice cell.

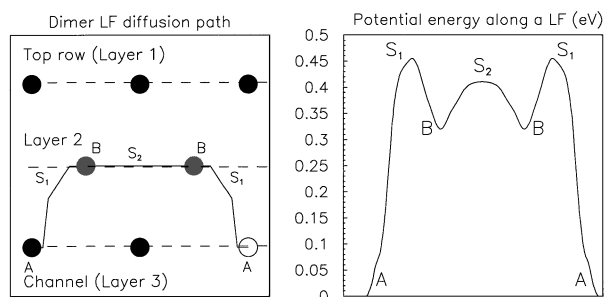


FIG. 3. Left: Dimer LF diffusion path. The left adatom of the dimer (full circle in the channel), climbs out of the channel, passes a saddle point  $S_1$ , and goes to a metastable minimum  $B$ . From  $B$ , it can jump to the other symmetric  $B$  minimum (through  $S_2$ ), or it can fall again in the channel. Right: The energetics along this path is shown.

from  $B$  to  $C$ , and  $(1 - p)$  the corresponding probability to fall down into the channel, then

$$p = \frac{2\nu_{BC} \exp(-\beta E_{BC})}{2\nu_{BC} \exp(-\beta E_{BC}) + \nu_{BA} \exp(-\beta E_{BA})}. \quad (1)$$

In Eq. (1),  $E_{BC}$  and  $E_{BA}$  are the energies needed to go from  $B$  to  $C$  and from  $B$  to  $A$ , while  $\nu_{BC}$  and  $\nu_{BA}$  are the corresponding frequency prefactors. It turns out that  $E_{BC} \approx E_{CB}$  (see Fig. 2, and Ref. [3]), thus the average time  $\tilde{\tau}$  spent on a MW is

$$\tilde{\tau} = \sum_{N=0}^{\infty} [(N+1)\tau_B + N\tau_C] p^N (1-p); \quad (2)$$

$\tau_B = [2\nu_{BC} \exp(-\beta E_{BC}) + \nu_{BA} \exp(-\beta E_{BA})]^{-1}$ , and  $\tau_C = [2\nu_{BC} \exp(-\beta E_{BC})]^{-1}$  are the average residence times in  $B$  and  $C$ , respectively. Equation (2) gives

$$\tilde{\tau} = (\tau_B + \tau_C) \frac{p}{1-p} + \tau_B. \quad (3)$$

At low  $T$ ,  $\tilde{\tau} \approx 2\tau_{BA}$  so the leading time scale is  $\tau_{BA}$ . Since  $E_{MW} = 0.44$  eV [3], in order to collect about ten events in one hour (typical STM observation time), one

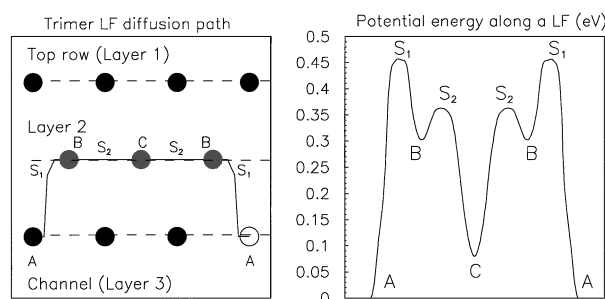


FIG. 4. Left: Trimer LF diffusion path. The left adatom of the trimer (full circle), climbs out of the channel, passes a saddle  $S_1$ , and goes to a minimum  $B$ . From  $B$ , it can fall back in the channel, or it can jump to a deeper minimum ( $C$ ). By jumping from  $C$  on the symmetric  $B$  minimum, it can reach the channel again ( $A$ ). Right: The energetics along this path is shown.

finds that a  $T$  around 150 K is needed. But at that  $T$ , Eq. (3), with  $E_{BC} = 0.1$  eV,  $E_{BA} = 0.06$  eV, and  $E_{AB} = 0.4$  eV, gives  $\tilde{\tau} \approx 10^{-9}$  s, clearly too short for a MW to be directly observed.

Now we repeat the same calculation for dimers, and evaluate  $\tilde{\tau}$  for a LF event. We begin with one of the two adatoms of the dimer in a  $B$  position, the other being at the bottom of the channel. By random walk considerations it follows that  $\tilde{\tau} = \tau_{BA}$  for a dimer LF. Being  $E_{AB} = E_{up} = 0.45$  eV and  $E_{BA} = 0.14$  eV one finds that the LF event is again too fast to be directly observed ( $\tilde{\tau} \approx 10^{-7}$  s at 150 K).

Now we consider trimers. From Fig. 4, it is evident that the situation is now qualitatively different. Indeed, a deep minimum along the metastable path is present. If one of the side adatoms of the trimer gets to a  $B$  position, it can make  $2N + 1$  ( $N \geq 0$ ) jumps to return down to the bottom of the channel;  $N$  of such jumps are from  $B$  to  $C$  sites, and  $N$  from  $C$  to  $B$  sites. In this case, the probability  $p$  to jump from  $B$  to  $C$  is

$$p = \frac{\nu_{BC} \exp(-\beta E_{BC})}{\nu_{BC} \exp(-\beta E_{BC}) + \nu_{BA} \exp(-\beta E_{BA})} \quad (4)$$

$\tilde{\tau}$  for a trimer LF is again given by Eqs. (2),(3) with  $\tau_B = [\nu_{BC} \exp(-\beta E_{BC}) + \nu_{BA} \exp(-\beta E_{BA})]^{-1}$ , and  $\tau_C = (2\nu_{CB})^{-1} \exp(\beta E_{CB})$ . At low  $T$ , we have:  $\tilde{\tau} \propto \exp[\beta(E_{CB} + E_{BA} - E_{BC})]$  so the adatom stays long on the metastable channel. Since  $E_{up} = E_{AB} = 0.45$  eV, while  $E_{down} = E_{CB} + E_{BA} - E_{BC} = 0.375$  eV, there is the possibility of a direct observation of trimers LF. For example, at 160 K, in one hour about 80 times a side adatom should jump up to a  $B$  site, so that  $\sim 40$  LF should occur, with a duration of 0.3 s each; so, it should be possible to observe these events in Au. Finally, for longer  $n$  chains, we have  $n - 2$  metastable minima and the LF mechanism should be even easier to observe.

Let us now discuss in detail the microscopic mechanisms of the promotion of a side adatom to the metastable region, and its descent down into the channel from the metastable region. Both going up and descent may happen either by jump or by exchange, and the experiments are not yet able to discriminate which mechanism prevails indeed. In the case of the descent, the adatom in  $C$  (see Fig. 4) could fall down into the channel by pushing aside one of the two atoms below and taking its place at the channel bottom. In order to determine whether this exchange process would be favorable, we have first estimated its energy barrier by quenched MD. We put the adatom in  $C$  and then displace one of the two chain adatoms below along the in-channel direction, fix its  $x$  coordinate, and let all other coordinates of the system relax. The quenching procedure is done after letting the constrained system evolve by some time at rather high  $T$  by microcanonical MD, in order to avoid trapping in spurious metastable configurations. By letting  $x$  take different values we are able to estimate the following barrier

for exchange descent:  $E_{\text{down}}^{\text{exch}} = 0.55$  eV, much larger than  $E_{\text{down}}$ . We estimate also a barrier of  $E_{\text{up}}^{\text{exch}} = 0.64$  eV, much larger than  $E_{\text{up}}$ . In order to be sure that these exchange processes are really unfavorable in our system (as should follow by the above estimates of the barriers), we have also made several high- $T$  simulations. At 550 K, the promotion into the metastable region happened always by jump, and of 9 descents, 8 were by jump and one by exchange. At 450 K we made simulations starting directly from the promoted position, and then we observed always jump descent.

Finally, we repeat the above calculations for Pt dimers, trimers, and chains on Pt( $1 \times 2$ ) and compare our results with those in the experiments by Linderoth *et al.* [8]. Qualitatively, the energetics along the metastable paths resemble closely what is obtained for Au (see Figs. 2–4), but with higher barriers (see Table II). As observed with other potentials [14], RGL potentials underestimate the barrier for single-adatom diffusion (0.60 eV against the experimental value of 0.81 eV [13]). However, in the case of Pt chains, we obtain an energy  $E_{AB} = E_{\text{up}} = 0.84$  eV, and an energy  $E_{\text{down}} = 0.64$  eV. Again, our results somewhat underestimate the experimental barriers [8], but the differences are within 10%, and therefore the agreement can be considered quite good. Also in Pt dimers (and chains) we obtain that LF is favored over CJ (see Tables I and II). We obtain that chains are stable, and that the promotion and descent processes happen mainly by jump, the exchanges being rare (again, this has been verified both by static energy calculations and high- $T$  simulations).

In conclusion, our results indicate that the LF mechanism for chains diffusion should be common in (110) missing-row surfaces, its occurrence being related more to the geometry of the surface than to the specificity of the metal.

In this Letter, we studied Au dimers and longer chains self-diffusion on Au and Pt (110) surfaces, both in ( $1 \times 1$ ) and in the ( $1 \times 2$ ) geometries. A new diffusion mechanism (leapfrog) has been found, which has a fundamental role in chains diffusion on missing-row surfaces. Indeed, LF events dominate at low  $T$ , and cause a very different diffusion scenario with respect to the ( $1 \times 1$ ) surface, where, due to the geometry, this mechanism cannot take place, and thus  $n$ -adatoms-chains moves will be hardly observed. The role of out-of-channel trajectories in determining in-channel diffusion was already remarked by the present authors [3] for

single-adatom diffusion on Au(110)-( $1 \times 2$ ). In such a system, these trajectories were mainly theoretically interesting, contributing to a small fraction of single jumps, to the 25% of the double jumps, and showing a tendency to dominate the rare long-jump events. In chains diffusion, on the other hand, the LF becomes the dominant diffusion mechanism. Because of the energetics, we show that dimer LF events can very hardly be experimentally detected. But the same kind of events can happen also in longer chains, and in this case, the moving adatom spends on the average a rather long time above the chain. This makes possible a direct observation of the process, as it is now experimentally demonstrated for Pt chains in Ref. [8].

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