Atomic jumps during surface diffusion

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The characteristics of atomic displacements during surface diffusion of Cu on Cu(111) are studied by means of molecular dynamics simulations. It is found that even at very low substrate temperatures, the majority of the jumps are correlated, i.e., the displacement directions are not randomly chosen but rather keep some sort of memory from the previous moves and are influenced by them. Long jumps, spanning several surface unit cells, are observed at all temperatures. From an analysis of their length probability distribution information can be obtained about the mechanisms of friction and energy transfer between the diffusing adatom and the substrate. Both long jumps and recrossings (displacements in which the adatom moves back and forth between two adjacent adsorption sites) appear with a higher activation energy than normal diffusion. Finally, the influence of the instantaneous atomic configuration of the substrate on the adatom's trajectory is also highlighted.

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I. INTRODUCTION

In the traditional view of surface diffusion, an adatom is pictured drifting above the potential energy landscape created by the charge density of the substrate atoms. While trapped within an adsorption well, the atom may take up from the phonon bath the (thermal) energy needed to overcome the surrounding barriers, hence becoming capable of performing a successful hop to a nearby site. In the simplest model, these jumps are assumed to take place in random directions and only to nearest-neighbor positions.[1] However, this description has long been proved oversimplified: long jumps, spanning several surface unit cells, were first detected by means of numerical simulations,[2,3] and later confirmed experimentally by field ion microscopy (FIM) results, although only on W substrates.[4–7] Other studies have found evidence of long jumps during surface diffusion of molecules[8,9] and, indirectly, on Pb(110) close to its melting temperature.[10] Further details can be found in two excellent recent reviews.[11,12]

Nevertheless, experimental observations of single atomic movements are difficult, and in spite of calculations and numerical simulations[13] the nature of these events is not yet clearly established. For instance, it is not known whether such long jumps are actually different physical processes from the nearest-neighbor ones, with their own specific activation energy and pre-exponential factor. Field ion microscopy and scanning tunneling microscopy (STM) are the only techniques capable of directly imaging the positions of individual atoms, but they can only provide snapshots of the surface atomic configurations at finite time intervals. Analysis of these data thus yields information on the mean square atomic displacements, and to infer the details about the jump processes some kind of modeling must be used. Typically, the experimentally determined distributions of displacements have been compared to a statistical model[14] or to the results of Monte Carlo simulations,[6,7] from which the rates of the different jump processes can be estimated.

While the analysis of data in quasi-one-dimensional diffusion systems—like, for instance, on fcc-(110) faces—is somewhat simpler, further complications arise when dealing with compact faces such as the fcc-(111). There, a new type of atomic jumps has been identified recently.[15,16] In these so-called recrossing jumps an atom moves from its starting position to an adjacent site and immediately returns to its departure point. Although these movements are obviously long jumps, since they involve two surface cell crossings, they produce anomalous results because the net resulting displacement is zero.

In this work we use molecular dynamics (MD) simulations to carry out a detailed study of atomic jumps during self-diffusion of a single adatom on Cu(111). From a statistical analysis of the hops' directions and lengths we gain insight on the physics controlling the atomic displacements. We show that the jumps can be classified in two categories, correlated and random, depending on whether the choice of the hop direction is influenced by the previous trajectory or not. We also find that atoms performing correlated jumps—which include the long ones—possess a higher energy than when they are doing the usual random, nearest-neighbor moves. The jump lengths and types (as described in Sec. III) are determined by the mechanism of energy transfer from the diffusing adatom to the substrate, which seems to take place at specific times and due to scattering events of the adatom with the surrounding surface atoms.

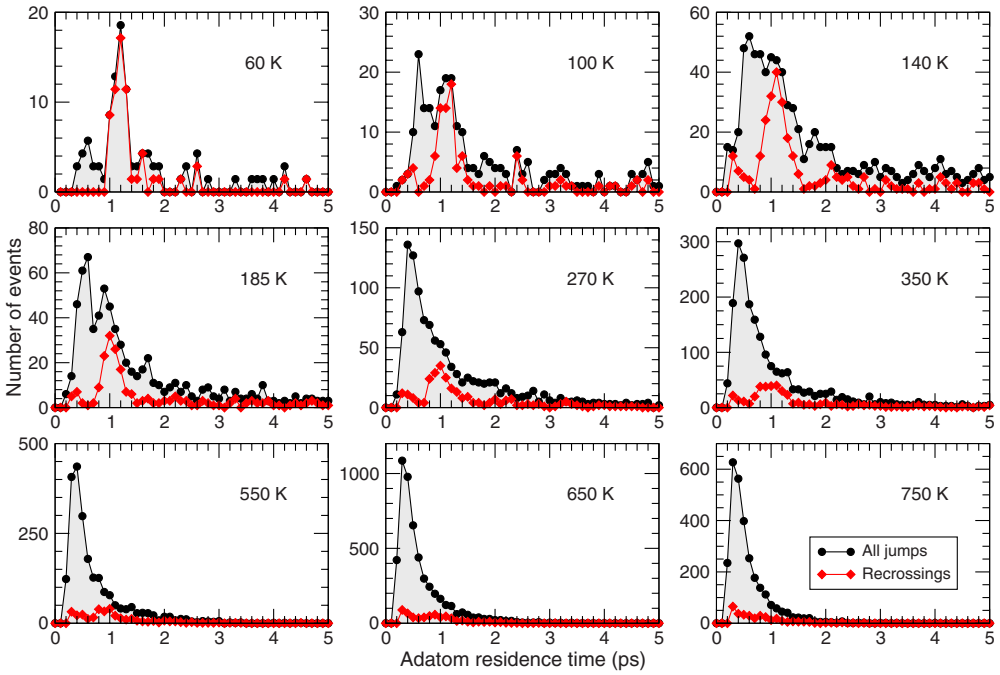

FIG. 1. (Color online) Statistical distributions of residence times of Cu adatoms, as a function of substrate temperature. Black dots: all types of jumps; red diamonds: recrossings.

II. METHODOLOGY

The simulations were carried out using the DYNAMO code.[17] The atomic interactions were accounted for by means of empiric potentials derived from the embedded atom model (EAM).[18] A single Cu adatom was allowed to diffuse on a Cu(111) substrate represented by a slab of 14 layers of 270 atoms each one, with vacuum on both surfaces and periodic boundary conditions in all directions. Before starting the simulations, the sample was fully relaxed to minimize its energy, except for the three deepest atomic layers that were frozen to simulate the bulk. The diffusing adatoms were deposited at random positions slightly above the upper surface and allowed to land and thermalize for several picoseconds before starting to record their displacements. The number and duration of simulation runs conducted at each temperature were extended until a sufficient number of jumps was accumulated to ensure good statistics (more than 1000) for the analysis described in Sec. III; for the lower temperatures this amounted to more than 20 ns.

Atomic jumps were detected automatically, in terms of barrier crossings, by using a double criterion. First of all, the ideal surface (without thermal agitation) was divided in two sets of cells, corresponding to fcc and hcp sites. Then, during the simulation the distances between the adatom and the surface atoms defining the occupied and the nearest-neighboring unit cells were continuously computed. A jump was considered successful when it satisfied both conditions, namely, that the adatom changes cell (it moves from an "ideal" fcc to an hcp or vice versa) and that the closest substrate atom (excluding those forming the bridge) also changes. This latter condition is essential to take into account the instantaneous changes in the surface atomic positions due to thermal vibrations. Furthermore, jumps with residence times within a surface cell shorter than 0.1 ps were discarded, as they usually correspond to atomic fluctuations when the adatom is close to the saddle point. All jumps detected by this method are thus of nearest-neighbor length, and the residence time of the adatom within a given cell is given by the time interval between two consecutive barrier crossings. Long jumps, which are dealt with in Sec. III B, thus consist of a succession of consecutive single-distance jumps along the same direction.

III. STATISTICAL ANALYSIS

A. Flight times of diffusing adatoms

We start our characterization by sorting out the atomic hops detected in the simulations at different temperatures according to the time spent by the moving atom to traverse a surface cell. Hence, for this analysis the long jumps are not considered as such, but rather as a succession of fast consecutive cell crossings. The resulting distributions are plotted in Fig. 1 as histograms. The graphs are truncated at 5 ps adatom flight time because we are mostly interested on the fast jumps, which are the ones that display a correlated behavior in disagreement with the classical random walk model.[15] Long residence times, on the contrary, correspond to atoms that have thermalized and undergone several vibrations within one adsorption well, thereby losing memory from previous displacements. Hence, their displacements when they finally cross to a nearby site are completely random.

The first outstanding feature of the histograms shown in Fig. 1 is the appearance of distinct peaks that can be directly correlated with specific jump types.[15] The first peak, appearing below 1 ps in all graphs, corresponds to what we have

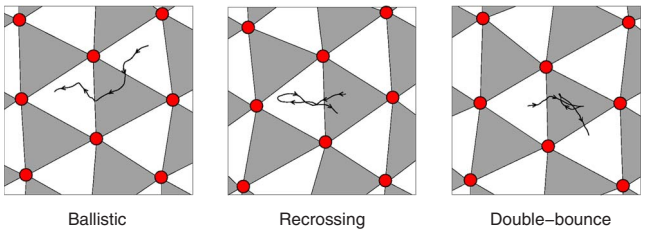

FIG. 2. (Color online) Schematic depiction of the different types of fast jumps, corresponding to the peaks visible in the histograms of Fig. 1. The solid red circles represent the surface atoms, and the shaded and white areas correspond to fcc and hcp subcells. The fragments of trajectories depicted are actual examples taken from the simulations.

called *ballistic* jumps, i.e., fast flights in which the adatom crosses one surface cell without stopping in it; a graphical example can be found in Fig. 2(a). The long jumps that will be discussed in detail in Sec. III B below thus consist of a succession of these rapid crossings. In the following we shall retain the term ballistic to refer to these fast crossings of a single surface unit cell, to distinguish them from the true long jumps, which involve several consecutive ballistic hops. We denote the temperature-dependent characteristic flight time of these ballistic jumps τ_0, and take it in the following as the reference unit time for surface diffusion processes.

A second and even a third peak can also be clearly resolved for the lower temperatures in the histograms of Fig. 1. Their origin can be determined from an inspection of the corresponding atomic trajectories. The curves labeled with diamonds in Fig. 1 represent sequences of two consecutive barrier crossings that bring the adatom back to the same departure site after having bounced back off the atom situated at the apex of the triangular (111) surface cell, as schematically depicted in Fig. 2(b). It is evident from Fig. 1 that, below 140 K, practically all the jumps in the second peak correspond to these *recrossings*.[15,16,19] This behavior clearly contradicts the assumptions of the random walk model, since the jump directions are not chosen by the moving adatom with the same probability. The same argument holds for the displacements making up the third peak: almost none of them leads the adatom back to the previously occupied cell. A representative trajectory for this type of jumps, which we have called *double bounces* because the adatom is deflected twice within the surface cell before exiting, is given in Fig. 2(c).

Based on this analysis, we concluded in our previous work that a minimum residence time of at least $4\tau_0$ (or equivalently, four oscillations of the adatom within the site's potential well) is required before an atomic displacement may be considered random.[15] These results are summarized in Fig. 3, where we plot the temperature evolution of the above described three types of jumps. With respect to our previous study, we have now added a new temperature, namely, 60 K. It can be seen how the new results nicely follow the trend set by the former data, in particular the steady decrease of the ballistic jumps as the system's temperature is progressively lowered and the parallel increase of recrossings, whose frequency stays clearly above the value

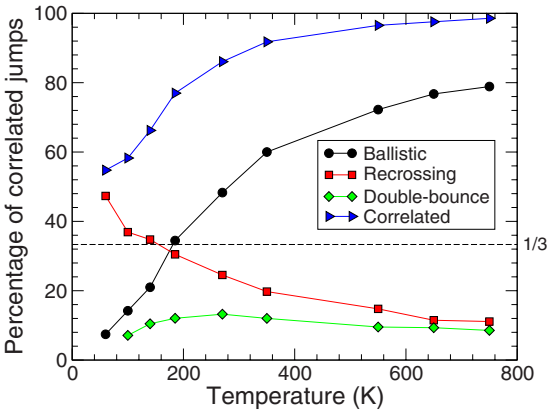

FIG. 3. (Color online) Temperature evolution of the different types of fast atomic jumps of a Cu adatom on Cu(111). The curve labeled "correlated" is the sum of the other three, and represents a lower limit estimate of the total number of nonrandom jumps.

of 1/3 that one should expect for random hops on the Cu(111) surface. The sum of the frequencies of these three types of jumps gives us a minimum estimate of the fraction of displacements that cannot be considered random, and for which the classical theory of diffusion would not be applicable. This magnitude is represented with triangles in Fig. 3, and it is noteworthy that even at a temperature as low as 60 K more than 50% of the jumps are correlated.

B. Long jumps

An adatom resting within an adsorption well starts moving when it captures from the surrounding phonon bath the thermal energy needed to overcome the adjacent barriers. Since the surface potential is periodic, this displacement can in principle continue until the atom loses enough energy so as to become trapped again within a different potential well. The existence of long jumps, and their length probability distribution, is therefore directly related to the efficiency of energy exchange between the diffusing adatom and the substrate.[5,20] In our simulations, long jumps manifest themselves as successions of consecutive ballistic displacements of the type described in Sec. III and characterized by their fast flight times τ_0. In a sense, thus, our description follows the model previously put forward by Antczak and Ehrlich,[6,7] in that a jump starts with the atom crossing to the nearest-neighbor site and once there the continuation of the trajectory is determined by the system configuration.

From the theoretical point of view, the diffusion problem is most frequently formulated in terms of a Brownian motion described by means of a Langevin equation[21] with a constant friction term. This assumption implies that the diffusing adatom would be continuously losing energy during its displacement.[22–24] A different approach considers that the adatom interaction with the substrate takes place only at specific times, by instantaneous collisions that drain the excess energy of the former and leave it in thermal equilibrium with the system. This behavior is described by the Bhatnagar, Gross, and Krook (BGK) model.[25] Such different treatments naturally yield different probabilities for the jump lengths,

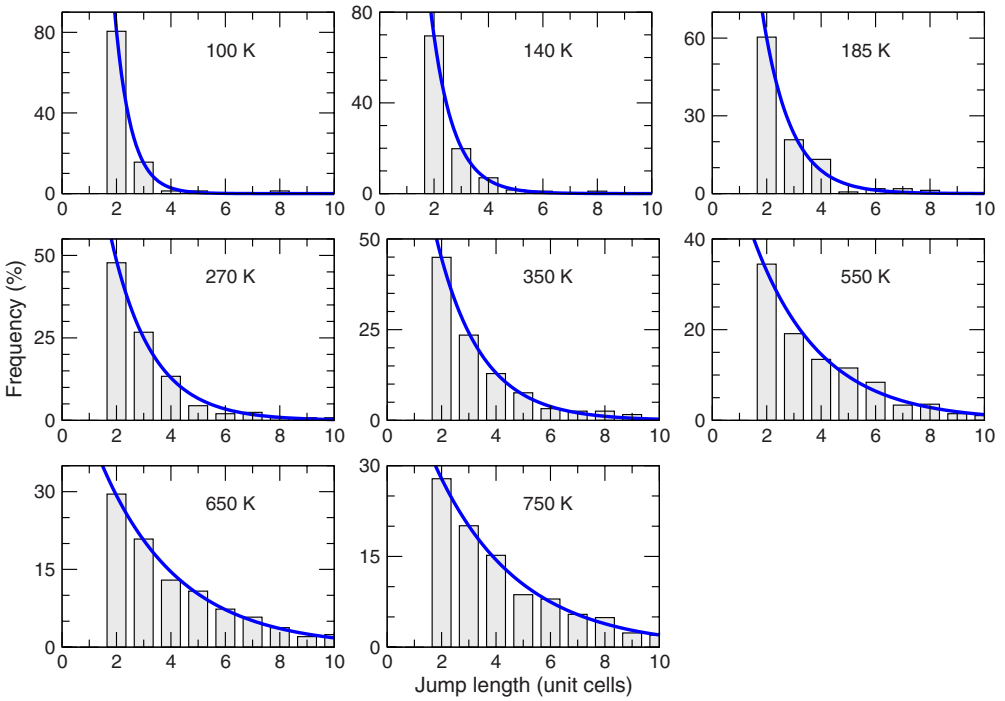

FIG. 4. (Color online) Jump length probability distributions as a function of temperature for Cu/Cu(111). The solid lines are exponential fits to the data.

and in particular for the longest ones;[26] hence, information can be gleaned on the thermalization mechanism by studying the distribution of jump lengths and their evolution with temperature. While such a study is extremely difficult to accomplish experimentally, computer simulations are much simpler to do and they can provide valuable insight into this problem.

The histograms displayed in Fig. 4 show the jump length probability distributions (JLPD) derived from our MD simulations at different temperatures; the data at 60 K have been excluded due to the scarcity of jumps longer than two unit cells. The solid line in each graph is a fit to the data with an exponential law, $f(L)=C\exp(-L/L_0)$. Here, L_0 is the characteristic amplitude of the long jumps, and it increases roughly linearly with temperature as graphically summarized in Fig. 5. According to previous theoretical studies,[26,27] the strictly exponential behavior of the jump length probability distribution is a fingerprint of BGK behavior; in the Langevin model, the JLPD deviates from the exponential, particularly at short lengths. This means that, in our simulations, friction takes place by discrete events rather than as a continuous process. Let us now briefly analyze the possible implications of this observation.

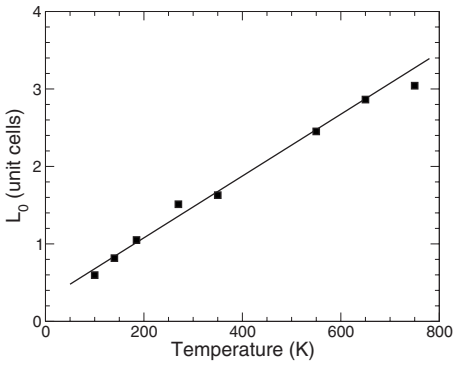

FIG. 5. Temperature dependence of the characteristic length L_0 of the long jumps, as derived from the exponential fits in Fig. 4. The solid line is a guide to the eyes.

In general, the friction η between the adatom and the substrate consists of two contributions, electronic and phononic one: $\eta=\eta_{el}+\eta_{ph}$,[11] the latter term being about 2 orders of magnitude larger than the electronic part.[28–30] One can therefore assume that the diffusing adatom thermalizes basically via interaction with the surface phonons. It should be kept in mind that there are no straight line diffusion channels on the Cu(111) surface, and therefore an adatom performing a long jump must follow a zigzag path alternating fcc and hcp threefold hollow sites. These ballistic trajectories seem to be steered by the surface potential,[15] an effect reminiscent of ion channeling. Thus, once the adatom has gained from the thermal bath enough energy to start crossing barriers, it will continue to do so until it loses that energy, most likely in a single scattering event with a surface phonon.

The linear increase in the characteristic long jump length L_0 depicted in Fig. 5 indicates that adatoms thermalize more rapidly at low temperature. No significant change in the adatom height over the substrate has been detected as a function of temperature, and thus this effect cannot be explained in terms of different separations between the diffusing and the surface atoms. We do observe that at high temperatures the adatoms' trajectories increasingly deviate from the path connecting the potential energy minima through the saddle points. This indicates that the adatoms have enough energy to fly almost freely above the surface. Since the characteristic feature of the BGK model is that thermalization takes place

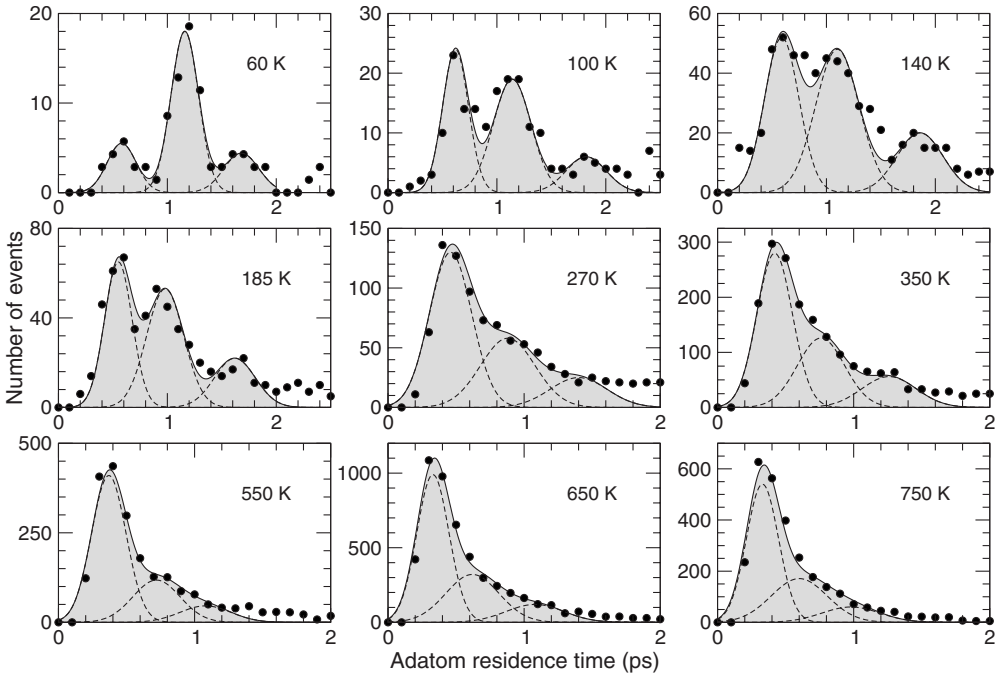

FIG. 6. Fits (—) to the histograms data of Fig. 1 (represented with black dots) using three Gaussians (- - -) that account for the characteristic flight times of ballistic, recrossing and double-bounce jumps, respectively.

by a single, instantaneous event, we suggest that the long jump trajectories are terminated by a collision with a surface atom that drains all the excess kinetic energy from the diffusing adatom. As Fig. 9 shows and we shall discuss in detail in Sec. IV below, the adatoms performing long jumps have a larger kinetic energy than the normal, random ones. Thus, the reduced thermalization probability at elevated temperatures must result from this increased kinetic energy dominating over the effect of the larger amplitude of the surface atomic vibrations.

C. Recrossings

We now turn in our discussion to the recrossing jumps. As Fig. 3 demonstrates, their probability shows a temperature dependence approximately inverse to that of the ballistic or long jumps. This fact suggests that the two types of processes may be somewhat related. Further insight can be gained through a detailed study of the adatom's flight times. For a more accurate analysis we have fitted the peaks in the histograms of Fig. 1 with Gaussians; these fits are shown in Fig. 6.

The characteristic flight times of the three types of jumps (ballistic, recrossings, and double bounces), determined from the centers and widths of the Gaussians, are plotted in Fig. 7. It is clear from this figure that the typical time employed by the adatoms performing a recrossing jump is almost exactly twice the ballistic time ($2\tau_0$). Since the average path covered by the atom within the surface cell during a recrossing is also very approximately twice that of a ballistic jump (see the trajectories depicted in Fig. 2), this implies that the average speed, and hence also the kinetic energy, of the adatoms is about the same for both kinds of processes. The same argument can be applied to the double bounces, for which a three times longer path is covered in a time interval close to $3\tau_0$. The data in Fig. 7 have been plotted as a function of $T^{-1/2}$ to emphasize their linear behavior; this issue will be discussed in more detail in Sec. IV below.

One can thus conclude from the above analysis that the special processes that we have called recrossings and double bounces are nothing but *frustrated long jumps*. Hence, the

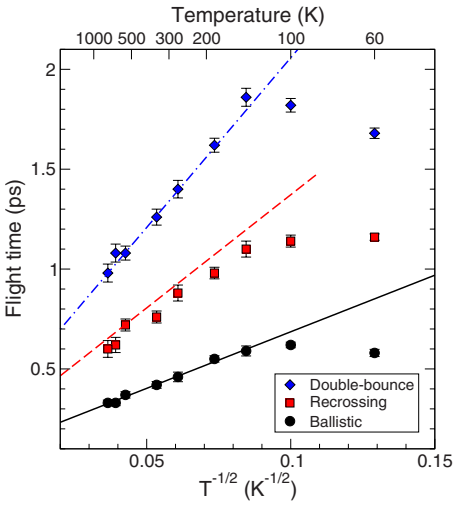

FIG. 7. (Color online) Characteristic time interval spent by the adatoms crossing one surface cell during ballistic (black dots), recrossing (red squares), and double-bounce jumps (blue diamonds). The values of τ and their error bars are determined from the Gaussian fits depicted in Fig. 6. The black straight line is a linear fit to the high-temperature ballistic data; the red-dashed and blue-dot-dashed lines result from multiplying this fit by 2 and 3, respectively (more details in Sec. IV).

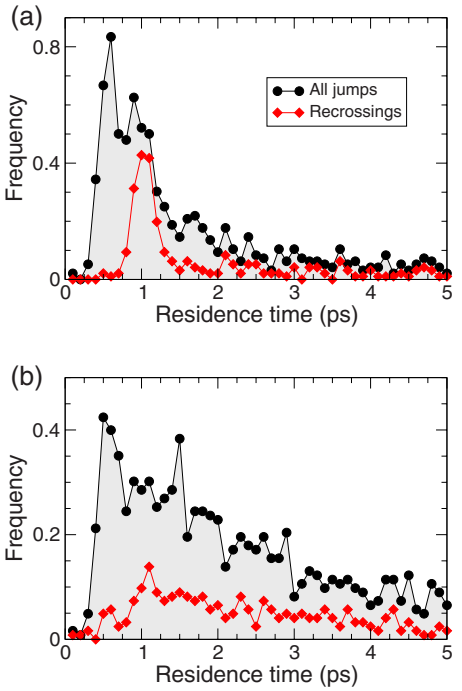

FIG. 8. (Color online) Flight time distributions at 185 K in (a) unperturbed MD simulations and (b) after forced periodic randomizations of all atomic velocities except that of the diffusing adatom. All correlated jumps are suppressed in the second case, and the choice of jump directions becomes completely random as evidenced by the curve representing the recrossings (marked with red diamonds).

jump characteristics must be defined by other factors. The trajectories depicted in Fig. 2 may give us some clues to understand this behavior. While in a ballistic displacement the atom follows a meandering path seeking one saddle point of the surface potential after another, a recrossing takes place when the diffusing adatom collides head on with the surface atom situated right ahead of it after crossing the barrier at the bridge position. It thus appears that the type of jump is decided not by the adatom energy, but rather by the detailed system's configuration, i.e., the spatial coordinates and momenta of both the diffusing and substrate atoms.

The influence of correlated atomic configurations on the jump characteristics has been checked by performing some special simulations in which we introduce a periodic forced randomization of the velocities of all substrate atoms (but not of the diffusing adatom) every few simulation steps, conserving the distribution dictated by the system temperature. The results of this test are presented in Fig. 8, where we compare the jump histograms obtained at 185 K in the "unperturbed" mode, in panel (a), and after velocity randomization, panel (b). Clearly, in the second case all peaks have disappeared, leaving a continuous distribution of flight times. Furthermore, the distinction between different jump types also disappears: the fraction of recrossings now amounts to 1/3 of the total (as expected for purely random displacements) for all residence times except for the shortest ones that obviously correspond to the fastest crossings of a single atomic cell and therefore cannot be matched by jumps covering a double distance.

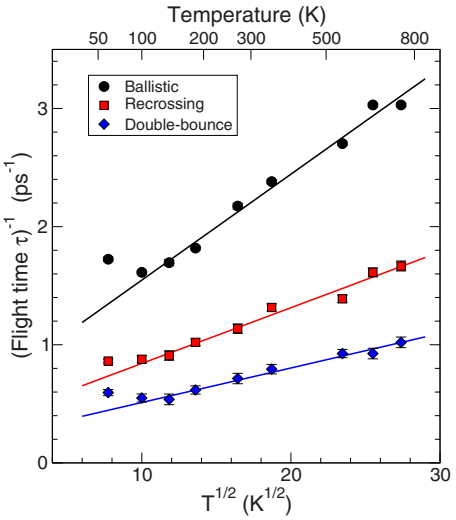

FIG. 9. (Color online) The inverse of the adatom flight times (proportional to its average velocity) previously depicted in Fig. 7 are plotted now as a function of $T^{1/2}$, to demonstrate the linear relationship of the adatoms' kinetic energy with temperature. The straight lines are linear fits to the high-temperature data.

From these results we conclude that the appearance of the special types of atomic jumps described above (ballistic or long jumps, recrossings and double bounces) is directly related to the existence of some particular configurations in phase space (that is, taking into account both positions and velocities) of all the atoms involved in the diffusion process, which includes the moving adatom and at least those defining the departure and destination surface unit cells. A consequence of this extreme sensitivity of the system's behavior to the initial conditions is that, under some circumstances, it should show chaotic behavior.[31,32]

IV. ENERGETICS OF ATOMIC JUMPS

Let us now concentrate on what our simulations allow us to learn about the energies of the diffusing adatoms. A first piece of information can be obtained from the temperature dependence of the flight times, already presented in Fig. 7. For the sake of clarity we have replotted these data in Fig. 9 showing now the inverse of the flight time (which should be proportional to the average adatom velocity) as a function of $T^{1/2}$. The linearity of all three graphs above 100 K demonstrates that the kinetic energy of all these correlated jumps scales with sample temperature in that range, with the same proportionality factor in all cases. Below 100 K, on the contrary, there seems to be a lower limit to the energy required to perform one of those correlated jumps. With a minimum of ~ 0.6 ps for an average hop length of 1.46 Å, one thus finds ~ 20 meV for the minimum kinetic energy required to perform a long jump on the Cu(111) surface.

A central question of debate concerning the nature of long jumps is whether they constitute a specific process, with a characteristic energy different from that of the "normal," nearest-neighbor hops. A higher activation energy for double-length jumps was first reported from STM experi-

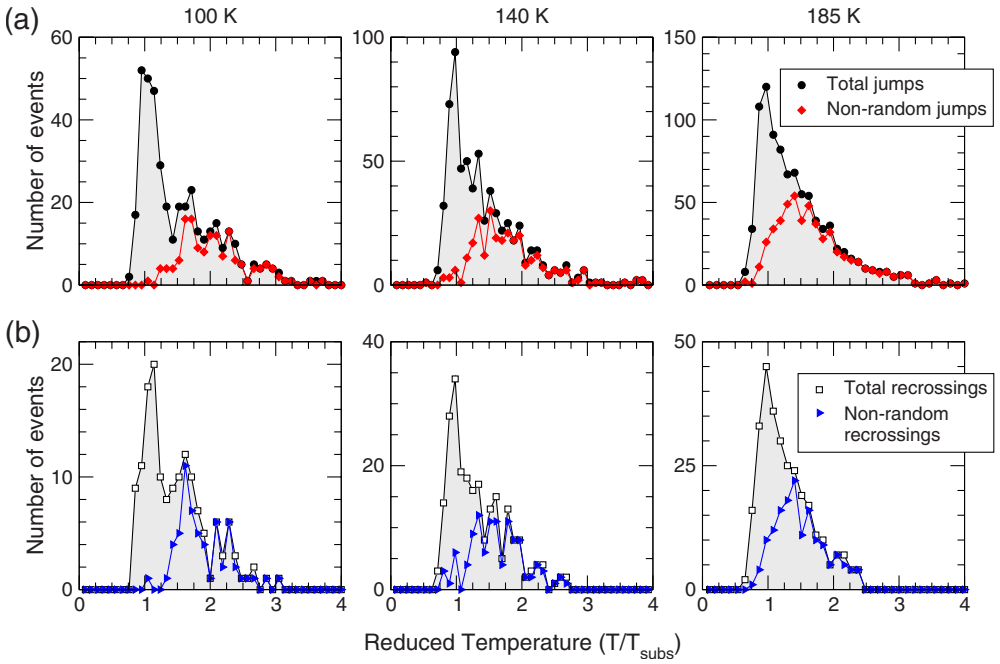

FIG. 10. (Color online) Histograms showing the abundance of jumps as a function of the adatom kinetic energy, expressed in terms of its reduced temperature $t=T/T_{\mathrm{subs}}$ for different substrate temperatures T_{subs}. (a) Total jumps (black circles) and total correlated jumps (red diamonds). (b) Total (open squares) and correlated (blue triangles) recrossings.

ments on self-diffusion on Pt(110)-(2×1) (Ref. 33), nevertheless, it was soon afterward demonstrated that the observed displacements corresponded to a special diffusion mechanism along the facets of the missing row reconstruction.[34,35] Finally, FIM experiments confirmed some time later the higher activation energy of double jumps, although so far only for W (Ref. 6) and Ir (Ref. 7) atoms on W(110).

Our simulations can also contribute to the understanding of this subject. For this purpose, we have plotted in Fig. 10 the number of jumps as a function of their kinetic energy, expressed in terms of their reduced temperature, $t=T/T_{\mathrm{subs}}$. The graphs in row (a) display, for several substrate temperatures, the total number of jumps with black dots, and with red diamonds those that we have considered correlated or nonrandom, that is, the sum of ballistic, fast recrossings and double bounces. Clearly, the correlated events account for practically all high-energy hops, whereas the peak centered about $t=1$ corresponds to jumps that have succeeded after a long residence time at the adsorption site: only these ones result in displacements that can be described with the traditional random walk model.

The plots in row (b) of Fig. 10 are limited to recrossing jumps: the open squares list all events, while the solid blue triangles display only the fast ones, those forming the peak about $2\tau_0$ in Fig. 1. Again, it can be seen that only those with the lowest energy (corresponding to long residence times at the same site) can be deemed truly uncorrelated displacements. Furthermore, by comparing the graphs within each column of Fig. 10 one can see that the energy dependence of the correlated recrossings—row (b)—and the global nonrandom jumps—row (a)—is the same. Since a large fraction of the latter consists of long, ballistic flights, these data further confirm that the long jumps and the recrossings are basically the same type of event, performed by adatoms possessing a similar energy, higher than that required for normal, random nearest-neighbor hops.[36]

It should also be mentioned that the data plotted in Fig. 10 also confirm our previous conclusion regarding the existence of a minimum energy cutoff for the existence of correlated jumps. It can be readily seen that at 100 K there is a clear gap in temperature between the onsets of the random and nonrandom jumps. This gap becomes progressively smaller with increasing substrate temperature, indicating that the correlated jumps appear more easily under those conditions.

One last interesting point deserving mention is the fact that all the JLPD's depicted in Fig. 4 display a similar exponential behavior. This seems to imply that the same friction scheme is operative throughout the whole temperature range explored in our simulations. Since for the highest temperatures analyzed in our study the adatom's thermal energy is substantially higher than the activation barrier for surface diffusion, which is of the order of 40 meV for Cu on Cu(111),[37–40] dynamical analysis of the correlated jumps based on transition state theory (TST) should be performed with caution.

V. SUMMARY AND CONCLUSIONS

To summarize this work, our MD simulations on the self-diffusion on Cu(111) reveal a variety of atomic jumps; only a small fraction of them, those for which the adatom kinetic energy is lowest, can really be considered independent as required by the usual interpretation of diffusion in terms of a random walk model. On the other hand, several types of correlated hops have been identified: in them the choice of displacement directions seems to be determined by certain

details of the trajectory since the initial impulse, resulting for instance in either a long or a recrossing jump. The likelihood of each of these events evolves differently with temperature. We call ballistic jumps the fast crossings of a surface unit cell that are part of the so-called long jumps already observed in other systems. Our simulations show these long jumps already at temperatures well below one tenth of the Cu bulk melting temperature (T_m), in agreement with previous experimental results for the diffusion of another relatively light atom (Ni) on W(211).[41] Furthermore, an analysis of the kinetic energy of the adatoms performing long jumps confirms that these are distinct events, different from the low-energy hops in which the atoms thermalize at nearest-neighbor positions losing memory of their previous positions and hence resulting in a true random walk.

Recrossings are another special type of atomic hops. These are sequences of two consecutive crossings of the same barrier that leave the adatom at the same site of departure. They show the same energetic characteristics of the long jumps, which leads us to hypothesize that both classes of events are in fact manifestations of one and the same physical process. The trajectory of the diffusing adatom would be determined by the details of the surrounding atomic configuration and dynamics,[15,36] which could eventually give rise to chaotic behavior.

The analysis of the probability distributions of the long jumps reveals a decreasing exponential dependence with jump length, consistent with a discrete mechanism of atomic friction. The characteristic jump length determined from these data increases linearly with temperature. The same exponential behavior is observed in the whole temperature range studied, which ranges between 7% and 55% of the bulk Cu melting temperature.

The variety and complexity of jumps observed in this work could affect the long-term atomic displacements, eventually resulting in anomalous diffusion.[5,42,43] With long jumps predominating at elevated temperatures, the average distance covered by the moving atom increases with time faster than expected from a typical random walk with nearest-neighbor hops and should rather be described in terms of Lévy walks.[44] Nevertheless, a diffusive motion following a truly exponential JLPD such as the ones presented in Fig. 4 should still display a linear dependence of the mean square displacement with time, according to Einstein's relation. On the other hand, recrossings dominate at low temperature and result in reduced diffusional lengths, since they represent an accumulation of jumps that leave the adatom position unaltered. Work is in progress to accurately test the long-time dependence of the average atomic displacements.

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