Non-stochastic behavior of atomic surface diffusion on Cu(111) at all temperatures

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(Dated: March 22, 2022)

Abstract

Atomic diffusion is usually understood as a succession of random, independent displacements of an adatom over the surface’s potential energy landscape. Nevertheless, an analysis of Molecular Dynamics simulations of self-diffusion on Cu(111) demonstrates the existence of different types of correlations in the atomic jumps at all temperatures. Thus, the atomic displacements cannot be correctly described in terms of a random walk model. This fact has a profound impact on the determination and interpretation of diffusion coefficients.

PACS numbers: 68.35.Fx, 68.47.De, 71.15.Pd, 82.20.Db
Surface diffusion is a most influential process at the atomic scale, lying at the core of many relevant fields. In catalysis and surface chemistry the ability of the reactants to come together and/or reach the active surface sites controls the reaction rates [1]. Likewise, in epitaxial growth the adatom mobility decisively influences the nucleation probability and the average distance and size of the objects -islands- formed [2]; kinetic limitations result in the accumulation of roughness as growth proceeds [3].

Despite the many efforts devoted to studying this phenomenon, our current understanding is far from being complete [4]. The continuous advancements in both theory and experiments are unveiling a rich phenomenology unsuspected till now; even for the simplest self-diffusion case, new basic mechanisms are still being discovered. First it was site exchange, detected by means of FIM experiments [5] and theoretically demonstrated shortly afterwards [6]. Later, evidence was found on the existence of "long jumps", i.e., atomic displacements spanning several lattice constants [7, 8], lifting the restriction to nearest-neighbor hops. The last finding so far is subsurface diffusion, in which adatoms move below a loosely bound overlayer deposited on a given surface [9, 10].

Traditionally, diffusion was described as a random walk in which the adatoms occasionally acquire sufficient energy to jump from one lattice site to a nearby one where they attain again thermal equilibrium with the substrate; they would thus spend most of the time residing at the local minima of the potential energy surface and only a short fraction of it crossing the barriers. With these assumptions and applying Transition State Theory (TST) one gets for the diffusion coefficient [11]:

\[ D = D_0(T) \exp\left(-\frac{E_m}{k_BT}\right), \]  

where \(E_m\) is the difference between the saddle point and the minimum energy configurations along the most probable path. \(D_0\) is slightly temperature-dependent, but it can be safely taken as a constant [12, 13].

Using a different approach, the diffusion process can be described in terms of the so-called hopping frequency:

\[ \gamma = \gamma_0 \exp\left(-\frac{E_m}{k_BT}\right). \]

\(D\) and \(\gamma\) are geometrically related [13] only if the diffusion events are stochastic. When the thermal energy is higher than the diffusion barrier \((k_BT \geq E_m)\) the adatoms move rather freely over the surface and the definition of a hopping frequency loses sense. In this regime,
the diffusion coefficient is expected to follow a linear behavior, \( D = k_B T/mG \), where \( G \) is an appropriate friction coefficient for the unconfined Brownian motion of the adatom \[14\]. It is generally accepted that at temperatures of the order of \( E_m/2k_B \) most of the assumptions of TST fail, diffusion cannot be represented by a random walk anymore and long, correlated jumps become more and more important \[15\]. Hence at room temperature (RT, 300 K), an \( E_m \) not smaller than 50 meV is required to satisfy the above condition. For compact metallic faces such as Cu(111) the activation energy for monomer diffusion is clearly smaller \[16, 17\], and therefore correlated displacements are to be expected well below RT.

In this work, we demonstrate the existence of other correlated atomic movements even at low temperature, when single hops predominate, thus questioning many assumptions accepted so far. We draw our conclusions from analyzing the outcome of Molecular Dynamics (MD) simulations in which we follow the displacement of an adatom over a fully relaxed surface at different temperatures. Our MD code \[18\] uses interatomic potentials based on the Embedded Atom Model (EAM) \[19\]. The sample was a slab of 14 layers with 270 atoms in each, and vacuum on both sides; periodic boundary conditions were used in all directions. The three bottom layers were frozen to simulate the bulk. The evolution of a single adatom at the upper surface was followed for different temperatures. In order to obtain reliable statistics, the simulation was extended for up to 10 ns for the lower temperatures.

Surface diffusion is quantitatively described by means of the coefficient \( D \), which can be calculated from the adatom displacements through the Einstein relation in 2 dimensions:

\[
\sigma^2(t) = \frac{1}{N} \left[ \sum_{i=1}^{N} (x_i(t) - x_0)^2 + (y_i(t) - y_0)^2 \right] = 4 D t
\]

where \( x_i(t), y_i(t) \) are the surface coordinates at time \( t \) for \( N \) different initial conditions. As stated above, the diffusion coefficient may also be determined from the hopping frequency, \( \gamma \), as \( D = \gamma l^2/4 \) for (111) faces \[13\], \( l \) being the hop length (1.47 Å for Cu(111)).

Within the framework of TST both descriptions are equivalent. However, in the MD simulation the mean square displacement \( \sigma^2(t) \) of the diffusing particle can be obtained independently of \( \gamma \). The latter is calculated as the number of successful jumps divided by the total elapsed time. In Fig. \[\square\] we depict in the usual form of an Arrhenius plot the values of the diffusion coefficient \( D_{\sigma} \) obtained from the mean square displacement, and that found from the analysis of the hopping frequencies \( (D_{\gamma}) \). It is noteworthy that \( D_{\sigma} \) clearly deviates from the Arrhenius law at high temperatures. A similar phenomenon was
already observed by Kallinteris et al. [20], who ascribed this behavior to the onset of a new activated mechanism, namely the diffusion along the [110] direction by means of double jumps [8]. Besides, a fit to $D_\gamma$, which displays a more Arrhenius-like behavior, yields an activation energy of $30 \pm 1$ meV (solid line in Fig. 1), much larger than the theoretical predictions [16, 17].

Fig. 2 shows some representative atomic trajectories at different temperatures. In general they consist of displacements, which frequently extend up to several lattice sites, separated by periods of vibration within a single surface cell; the relative abundance of each type of event depends on the temperature. Similar trajectories have been reported previously, resulting from simulations with other sets of interatomic potentials [21] and also in experiments [22]. Evidently, adatom diffusion at high temperature can hardly be considered a random phenomenon; any thermally activated process, characterized by an attempt frequency (pre-exponential factor) and an energy barrier, should have the same occurrence probability for all equivalent paths. Quite on the contrary, clearly deterministic trajectories can be observed in Fig. 2(c); the path followed by the Cu adatom is reminiscent of surface channeling, where an energetic diffusing particle is steered along its trajectory by the interaction potential and its interactions with the surrounding atoms. The enhanced diffusivity at high temperature, above the expected Arrhenius behavior, is thus caused by these correlated movements. On the other hand, at low temperatures random processes based on single jumps separated by long stays at a given adsorption well seem to be dominant and no preferred trajectories are evident.

Further insight into the applicability of TST can be gained from a detailed study of the atomic trajectories. We split the surface into two sets of cells, corresponding to the fcc and hcp sites, and measure the time spent by the atom at every adsorption well by detecting the transitions from one cell to another one nearby. Fig. 3 shows histograms depicting the statistical distribution of such residence times for different temperatures. The appearance of large peaks at very short times is an evidence for the lack of randomness in the diffusion process. The average residence time for each substrate temperature is marked by the vertical line in the graphs of Fig. 3. The shift to lower times (i.e., higher jump frequencies) is clearly due to the disappearance of several types of processes, most significantly the recrossings, with their longer associated times, and not to a larger jump probability, as would be for a thermally activated process.
The stochastic nature of the diffusive process can be analyzed in full detail by sorting out the different kinds of jumps: all those that can be shown to be statistically non-independent will therefore be considered correlated. In Fig. 3, the solid circles take into account all the jumps detected in our simulations. A striking feature of this figure is the appearance of a double peak at short residence times for the lower temperatures. The first one corresponds to what we call *ballistic jumps*: rapid crossings making up the long displacements in which the adatom traverses several surface cells in a single impulse. This is obviously the shortest residence time observed and is related to the average velocity of the diffusing adatoms. We shall call this elementary time interval $\tau_0$; its magnitude decreases with increasing substrate temperature, from 0.6 ps at 100 K down to 0.38 ps at 650 K, reflecting the higher kinetic energy of the adatoms.

The curves marked with open squares in Fig. 3 depict the times associated with recrossing events [15], that is, two consecutive jumps that bring the adatom back to its former position. At 100 K this kind of processes completely accounts for the second peak in the general distribution. Significantly, this peak is centered at a time close to $2\tau_0$. Below 185 K yet another clear peak can be seen at about $3\tau_0$. As expected, this triple transition time appears after two frustrated jump attempts. Quite surprisingly, almost none of these hops is a recrossing, as demonstrated by the statistics in Figs. 3a and 3b; 1/3 of them would be expected if the process were truly random. We shall thus call this kind of jumps “double-bounces” for brevity.

Our statistical analysis of diffusion jumps is presented in Fig. 4. First, it is remarkable the large number of ballistic jumps observed even at low temperature; needless to say, they absolutely dominate the scene above 300 K. At low temperature the recrossings are more frequent than expected (1/3 of the total) for a random process. This is probably due to the geometric arrangement of atoms in the (111) face: The adatom jumping through the saddle point is directed in a collision trajectory toward the third atom in the threefold cell. If the energy is not enough to set the channeling effect in, the atom is backscattered preferently in a recrossing trajectory. Our results show that these processes occur before the adatom becomes thermalized again. Neither of them can be considered stochastic; rather, this behavior hints toward some participation of the substrate atoms. As for the double-bounces, their topological analysis is also shown in Fig. 4b: despite the rise at about 200 K, the percentage of them that are recrossings never reaches 1/3, implying that the choice
of directions is also non-random. We thus conclude that at least three oscillations within an adsorption well, or a residence time $\geq 4\tau_0$ is required to ensure the statistical independence of diffusion hops.

To summarize our findings, we find evidence in our simulations showing that most of the atomic jumps in surface diffusion are biased, i.e., the process is not stochastic: the correlated jumps exceed 95% of the total above 500 K and even at 100 K amount to more than 50%. The kind of correlations, however, is not the same, and they have different effects on the determination of diffusion coefficients. Below $\sim 200$ K recrossing events dominate, they compute as jumps but do not produce an effective displacement and therefore cause an overestimation of $D_\gamma$ in this temperature range. On the contrary, at high temperatures the predominance of long jumps in the forward direction results in the longer net displacements responsible for the deviation in the values of $D_\sigma$. Clearly then, the simple, intuitive connection between the diffusion coefficients and the activation energy for nearest-neighbor atomic hops can only be established if all correlated jumps are excluded. This can easily be done with our simulation results: recalculating $D_\gamma$ in this way yields the results depicted in Fig. 5, with a preexponential $D'_0 = 0.44 \, \text{Å}^2/\text{ps}$ and an activation energy $E_m = 22 \pm 1$ meV which, although still higher than the calculated static barriers, approaches much more closely their values. In any case, these results must be taken with care since at high temperatures the statistics is poor due to the small number of uncorrelated jumps.

The physical picture that emerges from this work is the following: due to thermal fluctuations the adatom gains energy and momentum. The former allows it to overcome the diffusion barriers, while the latter establishes a privileged movement direction [23]. Due to the symmetry of the (111) face, the diffusing adatom is propelled in a collision trajectory toward the surface atom situated directly across the nearest-neighbor three-fold site. If the adatom has enough energy, the surface potential steers its trajectory along the [110] direction, initiating the ballistic movement. On the other hand, if its kinetic energy is not high enough the adatom will be backscattered by the surface atom, and may perform a recrossing. In any case, the truly statistically independent jumps seem to be a minority at all temperatures of interest. Obviously, the key point here is the rate at which the adatom transfers its energy to the substrate to become thermalized again. Further work is in progress on this subject. All these effects influence the relationship between the atoms displacements and the hopping frequencies, and therefore also the experimental determination of diffusion...
barriers [24]. We expect that our findings may shed some light onto these controversies.

Acknowledgments

This work has been financed by the CICyT through project BFM2001-0174 and by CONICET through PIP 2553/99. J.F. thanks Fundación Antorchas for financial support.

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FIG. 1: Diffusion coefficient for Cu atoms on Cu(111), calculated either by measuring the atomic displacement as a function of time ($D_\sigma$, solid squares) or from the hopping frequency ($D_\gamma$, open circles). The solid line is an Arrhenius fit to $D_\gamma$, with $D_0 = 1.56 \times 10^{-4}\text{cm}^2\text{s}^{-1}$ and $E_m = 30 \pm 1$ meV.

FIG. 2: Some typical examples of atomic trajectories of Cu adatoms self-diffusing on Cu(111) at diverse temperatures. Notice the different sizes of the regions exposed.

FIG. 3: Statistical distribution of residence times of the diffusing Cu monomers as a function of substrate temperature. Solid circles: all kinds of jumps; open squares: recrossings. The vertical lines mark the average residence time at each particular temperature; at 100 K the corresponding value of 10.6 ps falls outside the graph range. The inset within the last graph illustrates the definition of the surface cells with a typical ballistic trajectory and the determination of residence times: the solid circles are surface atoms, while the smaller grey and open dots mark the hcp and fcc sites, respectively.
FIG. 4: Statistical analysis of correlations in atomic jumps. (a) Percentage with respect to the total of: ballistic or long jumps (open circles), recrossings (squares) and “double-bounces” (diamonds). The dotted line is the 1/3 mark, the expected probability of recrossings for purely random hops. (b) Percentage of “double-bounces” (jumps after a residence time $3\tau_0$) that return to the previous adsorption site. The total fraction of correlated jumps, after our analysis, is given by the solid triangles in (a); even at 100 K this figure exceeds 50%, reaching nearly 100% at the higher temperatures.

FIG. 5: Diffusion coefficient $D_\gamma'$ (filled diamonds) obtained from the hopping frequency $\gamma$ after excluding all correlated jumps. The solid line is an Arrhenius fit to these data, yielding $D_0 = 4.44 \times 10^{-3} \text{cm}^2 \text{s}^{-1}$ and $E_m = 22 \pm 1 \text{meV}$. The open circles are the uncorrected $D\gamma$ values from Fig. 1 shown for comparison.