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Step fluctuations on Pt(111) surfaces

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Abstract

We have investigated the temperature dependence of equilibrium fluctuations of monatomic steps on Pt(111) surfaces using space and time correlation functions. From the spatial correlation function of steps we have determined a kink energy of 0.167 ± 0.005 eV for steps with (100) orientation. The same value was found for steps with (111) orientation. The time dependence of the correlation function obeys a $t^{1/4}$ power law, provided that the mean square of the fluctuations is in the macroscopic limit. The $t^{1/4}$ power law is indicative of mass transport along the steps. From the temperature dependence of the time fluctuations an activation energy of 1.0 ± 0.16 eV is determined for the hopping of atoms along steps of either orientation.

1. Introduction

Stimulated not least by the enormous technological impact of epitaxial growth, dynamic aspects of surfaces have moved more and more into the focus of research in recent years. A quantitative understanding of epitaxial growth and the ability to simulate growth perfectly, be it either near equilibrium or far from equilibrium, would in principle require the knowledge of a vast number of activation energies for the motion of atoms from one particular local atomic configuration into another. Even if all these activation energies were amenable to experimental investigation, one could hardly hope to produce all these numbers from experimental investigations within a reasonable time. Rather, one has to restrict oneself to the determination of the activation energies for a selected number of key processes and bridge the gap between experimentally available numbers and the simulation of

complex dynamic processes by invoking simple theoretical models. The diffusion of single atoms on flat surfaces has been studied quite frequently in this regard. The field ion microscope has been used for this purpose [1,2]. More recently, the scanning tunnelling microscope (STM) has also been successfully employed [3,4]. Quantitative information on the diffusion of atoms on flat surfaces can also be obtained from STM observations on the number of nuclei formed in epitaxial growth [5].

Epitaxial growth is not only determined by the diffusion of atoms on the flat terraces, but also by the hopping of atoms at or even more significantly across steps. A direct observation of the latter process is rather difficult, however. At high temperatures, where one might have a large enough concentration of single atoms at or near steps, the motion of atoms is far too rapid to be directly observable. Non-equilibrium situations with single atoms at steps could possibly be generated by evaporation on cold surfaces. The observable motions are then, however, restricted to motions

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down the energy scale. It has been established for some time now that the observation of equilibrium fluctuations of steps at elevated temperatures can likewise provide information on atomic hopping processes. It was established theoretically [6–8] and experimentally [9–15] that the mean square displacement of the step position with time obeys a t^α power law, where the exponent α depends on the prevailing type of mass transport causing the step fluctuations. The exponent α is equal to 1/4 when either the mass transport is restricted to a motion along the steps, or when atoms leaving the steps are reflected from a nearby neighboring step because of a large Schwoebel–Ehrlich barrier. In the latter case, the magnitude of the fluctuations depends on the distance between the steps. The exponent is 1/2 if atoms are exchanged between steps and the diffusion across the terraces serves as the “pipeline” which limits the fluctuations, or if the pipeline is the exchange of atoms from kinks with the terraces. An exponent 1/3 is also theoretically predicted, which should occur if the steps interchange atoms with the terraces and the pipeline is the diffusion on the terraces. For a detailed and very lucid explanation of the various cases, the reader is referred to Ref. [8]. Experimentally, only exponents of 1/2 and 1/4 have so far been observed, despite the fact that some investigations spanned a significant temperature range [6,9,14]. In this paper we report on yet another example for step fluctuations which obey the $t^{1/4}$ power law. The example presented here concerns steps on the Pt(111) surface. We have measured the fluctuations of both the (100) and the (111) steps oriented along the densely packed [110] direction in the temperature range 500–800 K. Within the limits of error, the fluctuations of these two different steps were found to be equal. From the spatial correlation function we have also determined the kink concentration of steps in thermal equilibrium, and the kink energy. With the kink energy and the help of a theoretical analysis of the fluctuations, we are able to determine the activation energy for the hopping of atoms along the steps. The paper is organized as follows. In Section 2 we describe experimental details as well as the basic method of data analysis. The results are presented in Section 3. Section 4 is devoted to

a discussion of the results, a comparison to previous experimental work, and a comparison to theoretical calculations of the kink energy and the activation energy for diffusion.

2. Experimental

The step fluctuations on Pt(111) were analyzed using a variable temperature STM of the Besocke type. The Pt(111) single crystal was cut by spark erosion and polished to the desired (111) orientation to within 0.2°. Prior to mounting in the UHV chamber, the platinum crystal was cleaned by heating in an O₂ atmosphere at a temperature of 1000°C for 24 h. This procedure serves to burn off common impurities like C and S, or to segregate impurities such as Ca or Si to the surface, from where they are easily removed by ion sputtering in the UHV chamber. This final cleaning in situ was achieved by cycles of 3 keV Ne sputtering for 15 min followed by annealing to 950°C for 15 min and a cooling period of 10 min. After a few cycles, no traces of impurities were found in Auger spectra, which were obtained using a cylindrical mirror analyzer. It is well established, however, that the sensitivity of Auger spectra to common impurities is not sufficient to secure sufficient cleanliness for a quantitative investigation of step fluctuations. Cleaning cycles were therefore continued significantly beyond the number of cycles necessary for a clean Auger spectrum. The final qualification of the surface was by inspection of the STM images. In the temperature range of interest here, the only persistent impurity on platinum (apart from the aforementioned impurities Si and Ca) is C. Carbonaceous deposits on Pt are formed from hydrocarbons in the residual pressure of the vacuum chamber. These carbonaceous deposits are quite easily seen in STM images.

Step fluctuations are measured as the mean square deviation of a step position using STM images of 512 × 512 pixels. The scan widths of the STM were calibrated in situ with the help of atomically resolved images of the Pt(111) terraces. In the following, we denote the coordinate along the densely packed step direction, which is the [110] direction, as y , and the coordinate perpen-

pendicular to the step direction as x . We choose the metric such that y and x are measured in units of the atomic distances, which are the diameter of an atom and the length of a single kink measured along the x -direction, respectively. Rather than measuring the mean square deviation in the position of a single step with reference to the [110] direction, it is easier to determine the deviation in the difference between the position of two steps [14], and hence the quantity.

$$2F(y,t) = \langle (\Delta x(y - y_0, t - t_0) - \Delta x(y_0, t_0))^2 \rangle. \quad (1)$$

Here, Δx denotes the difference in the position of two steps, measured at the same y and t , and the bracket denotes the average over a large ensemble of data. For uncorrelated fluctuations of the two steps, the mean square deviation in the difference between the position of two steps is twice the quantity of a single step. Uncorrelated motion can be safely assumed as long as the distance between the two steps is large compared to the fluctuations. Since it requires a finite time to take an STM image, the y coordinate in an STM image is also a time coordinate. It is therefore not possible to determine the function $F(y,t)$ completely from STM data. In the limit of very small fluctuations, i.e. at sufficiently low temperatures, the time dependence of the fluctuations can be neglected, and steps in ordinary STM images can be analyzed as if the STM image were an instantaneous image. In that case, the mean square deviation $F(y)$ is

$$F(y) = b^2 y, \quad (2)$$

with b^2 being the “diffusivity” of the step [16]. In this work we have $b^2 \ll 1$. The diffusivity is then equal to the concentration of kinks of one atomic unit length and also

$$b^2 \approx 2 e^{-\beta \epsilon} \quad (3)$$

with ϵ being the kink energy and $\beta = 1/k_B T$.

If the two steps do not fluctuate randomly, but have a systematic slope with respect to each other, then the space correlation function $F(y)$ has a contribution proportional to y^2 . Such a quadratic contribution is easily visible in plots of $F(y)$. Non-random fluctuations of steps can arise from a pinning of the steps by impurities. Since even a small quadratic contribution eventually wins

over the linear random term as y becomes larger, the residual systematic misorientation of the steps sets an upper limit to the range in y over which the function $F(y,t)$ can be analyzed.

The time dependence of the mean square deviation can be determined by measuring the difference in the step positions Δx at the same y_0 at different times.

$$2F(t) = \langle (\Delta x(y_0, t - t_0) - \Delta x(y_0, t_0))^2 \rangle. \quad (4)$$

Technically, this is performed by repetitively scanning across the steps at a fixed position y_0 perpendicular to the step direction along the x -coordinate, and by assembling the data in the form of an image. Hence, in these “time images” the ordinate is the time, while the abscissa remains the spatial x -coordinate.

The step positions in spatial images or time images were determined using special-purpose computer codes. Since studies on step fluctuations for the purpose of retrieving information on surface dynamics are becoming more commonplace, it may be useful to document briefly the features of the computer codes which we have used in this study. Prior to the analysis of an individual image, the program requests the initial input of left and right boundaries in the image in which the step positions are to be determined. Further inputs are the number of steps n within these boundaries, and a statement as to which of the steps within these boundaries one wishes to analyze. The program then runs a smoothing spline [17] through 100 data points which are assembled as an appropriate average from the original 512 (or less, if left and right boundaries were set) pixels in each scan line. The position of the steps are determined with a resolution of 1/1000 of the distance between the left and right boundaries by marking the n points of largest slope in the splines. After ordering the step positions according to the sequence of their x -coordinates, the position of the pre-selected steps are displayed and stored. In STM images, one has frequently an instability of the tip, causing noise in a particular scan line. As a result of such noisy scan lines, the step positions, as determined by the program, may jump by an unphysically large amount from one scan line to another. These unphysical jumps can be eliminated by an inter-

active routine which restricts the maximum step jump from one scan line to another, if necessary. In order to be able to use the difference between the positions of two steps as described above, one step in each image is selected as the reference step, and the mean square deviation as a function of the difference in the y or t coordinate is then determined with reference to this particular step. The maximum value for y or t typically corresponded to 100 of the 512 pixels. Averaging of the data for $F(y)$ or $F(t)$ is first performed along each pair of steps, then over all pairs within one image, and finally over all images taken at a particular temperature. A typical measurement of $F(y)$ or $F(t)$ at a particular temperature involved about 10^4 step positions.

An important question which has been raised quite frequently in connection with quantitative studies on the step fluctuation is that of tip–surface interactions. Tip–surface interactions have been reported for example for steps on Ag(110) surfaces [18], and in the investigation of the hopping of single atoms [5] on Pt(111). In general, one should expect the tip effects to depend on the tunnelling voltage and current. A comparison of results obtained under different voltage and current conditions is therefore useful. However, tip–surface effects which are largely independent of the voltage and current have been also reported [5]. In studies involving surface diffusion processes, the best check for possible tip surface interactions is to vary the time scale of the experiment and look for possible inconsistencies in the experimental results. In the following we describe an experiment of this type with reference to the issue of interest here. We have measured the fluctuations as a function of time, i.e. $F(t)$ according to Eq. (4) using two different scan times of 52 s and 114 s per image. In Fig. 1 the result for $F(t)$ is plotted versus time for the two cases. Within the limits of error, the two curves fall on top of each other. This is the evidence that the step fluctuations on Pt(111) are not caused by or influenced by the STM tip: each data point $F(t)$ for the image with the higher scan speed corresponds to a measurement where the step has been crossed by the tip about twice as many times (exactly 114/52 as many times). If the fluctuations were caused by or significantly influenced by the

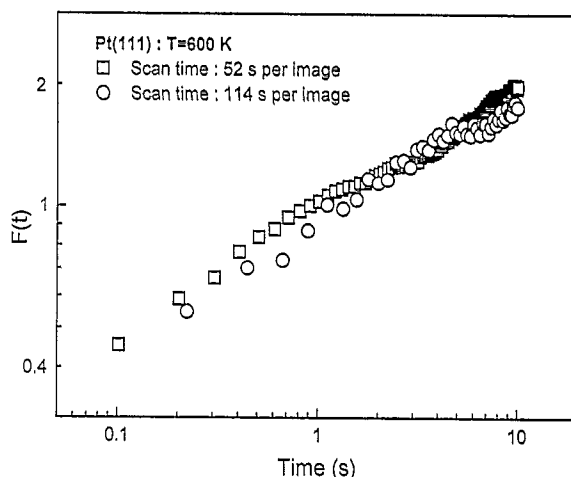


Fig. 1. Time dependence of the step fluctuations on Pt(111) measured with two different scan times per time image. Within the statistical error, the result is the same. This proves that the fluctuations are not significantly affected by tip–surface interactions.

tip, the results for $F(t)$ would be systematically different for the two scan speeds.

3. Results and data analysis

3.1. Spatial fluctuations

We first present the results on the spatial fluctuations. The spatial fluctuations can be measured in conventional STM images, provided that the temperature is sufficiently low so that the time contribution to the fluctuations is small compared to the spatial part. On the other hand, the temperature should not be too low. The time fluctuations must be still large enough so that the diffusivity, measured at a particular temperature, corresponds to the genuine equilibrium concentration of kinks at this temperature. We have measured the diffusivity at several nearby temperatures in order to establish that the diffusivity has the correct (exponential) temperature dependence. Three such results are shown in Fig. 2. In all cases we find the expected linear dependence of $F(y)$ (Eq. (2)) and the slopes (equivalent to the diffusivities and the kink concentrations) increase with the temperature. The slopes are converted into the kink energies ϵ

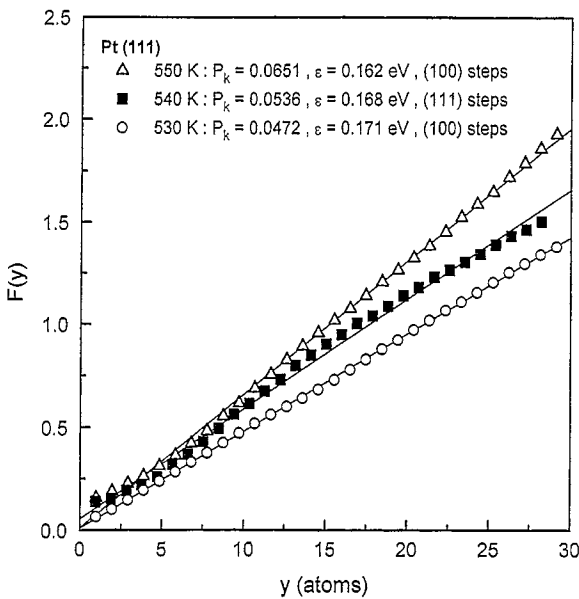


Fig. 2. Plot of the spatial part of the correlation function $F(y, t)$. The kink concentration P_k is determined from the slope. Within the (small) statistical error the kink energies calculated from the concentrations are the same.

using Eq. (3), and values of 0.171, 0.168 and 0.162 eV are obtained for the temperatures of 530, 540 and 550 K, respectively.

The statistical error in the determination of the diffusivity can be calculated from the total length of the steps which have been investigated. If L denotes the total length (in atomic diameters) then the total number of kinks which have contributed to the measurement is

$$N = b^2 L, \quad (5)$$

and $N^{-1/2}$ is the relative error in the determination of the kink concentration. Converted into the error for the kink energies, one obtains statistical errors of about ± 0.005 eV. Within the statistical error, all three measurement result in the same kink energy of

$$\epsilon = 0.167 \text{ eV}. \quad (6)$$

We note that the diffusivity for 540 K is measured on a step with (111) orientation, whereas the two other values refer to steps with (100) orientation. We therefore have the remarkable result that the kink energies for the two differently oriented steps are the same.

3.2. Time fluctuations

We now turn to the time dependence of the fluctuations. Data on the time dependence of the step fluctuation have been acquired using time images as described above. These time images were taken at several locations on the surface in order to ensure an averaging over steps with possibly different local kink concentrations. In Fig. 3 the time dependence is plotted in a double logarithmic plot for a few temperatures. The data sets refer to (100) steps save for one set at $T = 800$ K which is for (111) steps. In all cases the mean square deviation obeys a power law in the time t to a good approximation. Save for the two lower temperatures, one is in the macroscopic limit where $F(t)$ is larger than one. It is only there where the exponent should be compared with the macroscopic models. The exponent of about 1/4 therefore instructs us that the fluctuations are caused by a mass transport along the step edge. In principle, an exponent of 1/4 is also obtained when the atoms are exchanged between the step and the terrace and the atoms are reflected from the Schoebel–Ehrlich barrier of a neighboring step [8]. In that case, however, the fluctuations should depend on the distance between the steps for which we have found no evidence. For the lower temperatures where $F(t)$ is smaller than one, the exponents are higher than 1/4. This is consistent with earlier results on steps of the Cu(100) surface [14]. As shown in Ref. [14] using Monte Carlo simulations, the exponents depend only on the magnitude of $F(t)$, and not on the activation energies and temperatures separately. It was also shown in Ref. [9] that the data of $F(t)$ fall on a common linear line in an Arrhenius plot, despite the slightly different exponents at high and low temperatures. In Fig. 4 a number of data points for $F(t = 10 \text{ s})$ are plotted as a function of temperature in an Arrhenius plot. Due to residual step pinning the local kink concentration is occasionally higher than the equilibrium concentration. Thus, the fluctuations also become larger. In Fig. 4 we have omitted two data points for which the value of $F(t)$ was larger than three times the average value at the particular temperature. The fluctuations for the (111) steps appears to be systematically smaller by about a factor of

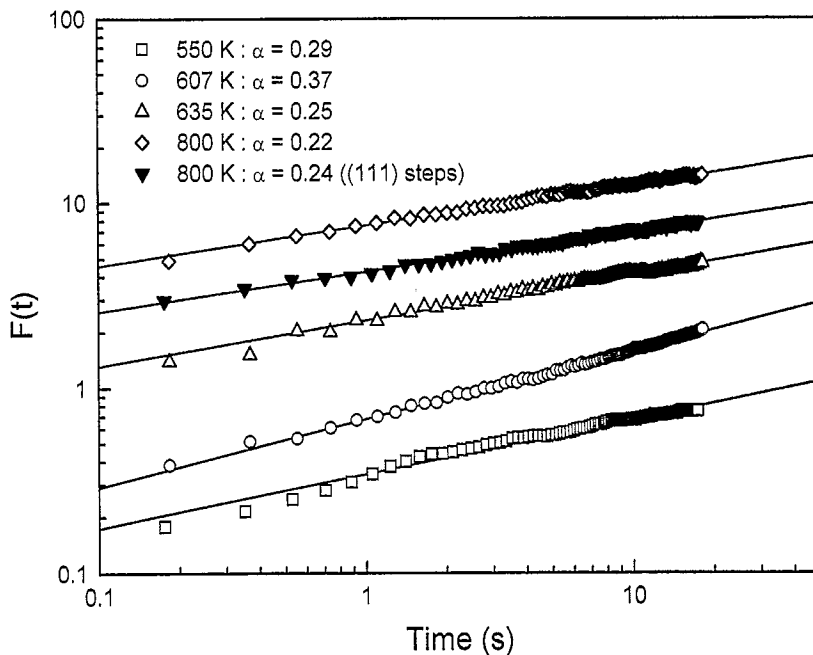


Fig. 3. Time dependence of the correlation function $F(y,t)$. See text for discussion.

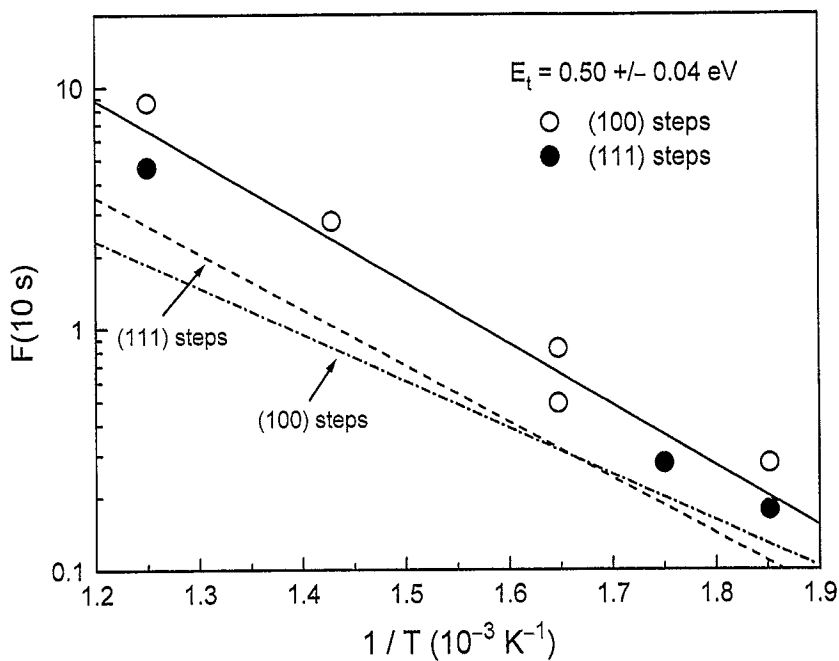


Fig. 4. Arrhenius plot of $F(t=10 \text{ s})$. Within the error margin, the result is the same for both types of steps. The dashed and dashed/dotted line are calculated using low-temperature data on the tracer diffusion coefficients.

two which is, however, within the error bars on each individual measurement. Within the limits of error, the data can therefore be fitted to a common line which is

$$F(t) = 9.4 \times 10^3 \pm 0.32 \text{ s}^{-1/4} e^{-\frac{0.50 \pm 0.04 \text{ eV}}{k_B T}} t^{1/4}. \quad (7)$$

The statistical error in the activation energy is $\pm 0.04 \text{ eV}$, and the error in the prefactor is about a factor of two.

The time dependence of the mean square deviation of the step position can be expressed in terms of the diffusivity b^2 and the diffusion coefficient for the mass transport along the step D_s [7,8]. Save for a numerical factor which is of the order of one, the result is

$$F(0,t) \approx (b^2)^{3/4} (D_s)^{1/4} t^{1/4}. \quad (8)$$

By using the measured temperature dependence for the diffusivity (Eqs. (3) and (6)) and Eq. (7), we find for the mass transport diffusion coefficient D_s

$$D_s = 9.8 \times 10^{14 \pm 1.3} e^{-\frac{1.50 \pm 0.16 \text{ eV}}{k_B T}} d^2 \text{ s}^{-1}. \quad (9)$$

Because of the metric we have chosen in the beginning, the diffusion coefficient is in units of $d^2 \text{ s}^{-1}$, where d is the diameter of a Pt atom. Again we have a considerable uncertainty in both the prefactor and the activation energy, which are a factor of 20 and $\pm 0.16 \text{ eV}$, respectively. The pre-exponential factor is larger than the canonical value of $k_B T/h$ ($= 1.5 \times 10^{13} \text{ s}^{-1}$ at 700 K). This suggests that the true value of the pre-exponential factor and the activation energy may be near the lower bound of the error margin. We shall comment on this later.

Mass transport along the steps proceeds via the hopping of adatoms along the steps. In the temperature range considered here, the concentration of adatoms is very small. The mass transport diffusion coefficient is then equal to the equilibrium concentration of adatoms at the steps multiplied by the tracer diffusion coefficient D_t [14].

$$D_s = c_{ad} D_{tr}. \quad (10)$$

To a very good approximation, the energy for an adatom at the step edge is twice the energy of a kink. The equilibrium concentration of adatoms

along steps is therefore

$$c_{ad} = e^{-2\beta\epsilon}, \quad (11)$$

with ϵ the kink energy as in Eq. (3).

The tracer diffusion coefficient D_{tr} can be expressed in terms of microscopic hopping rates following the work of Natori and Goodby [19] (see also Ref. [14]).

$$D = \frac{n^2 \Gamma_d}{(n-1+1/S)(n-1+\Gamma_d/\Gamma_a)}, \quad (12)$$

where

$$\Gamma_d = \Gamma_0 e^{-\beta E_d}, \quad \Gamma_a = \Gamma_d e^{-2\beta\epsilon}, \quad S = e^{-\beta\Delta}, \quad (13)$$

and n is the distance between kinks in units of the diameter of an atom. The prefactor Γ_0 is assumed to be equal for all hopping processes. The energy E_d is the activation energy for the hopping of an adatom along the step edge, and Δ is the Schwoebel barrier. The meaning of the rates Γ_d , Γ_a and S , as well as of the energies, is illustrated in Fig. 5. In the derivation of Eq. (12) the kinks were assumed to be equally spaced along the step. Here, we replace n by the mean distance in equilibrium which is just the inverse of the kink concentration. With these notations, and after making use of the

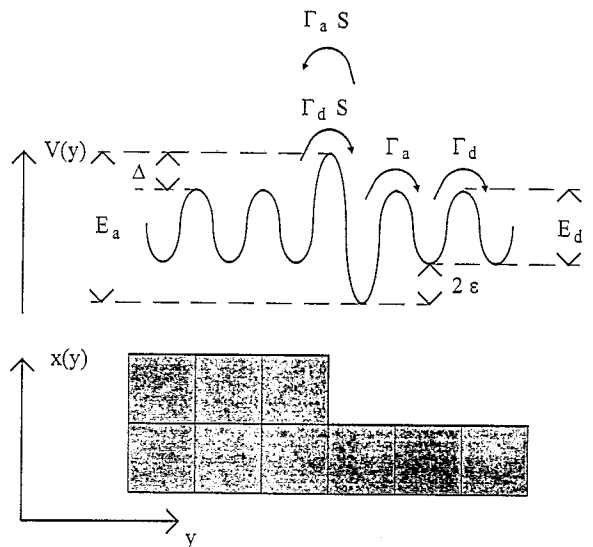


Fig. 5. Illustration of the energy barriers for an adatom hopping along the step.

fact that the kink concentration is small, one has

$$D_{\text{tr}} = \frac{\Gamma_0 e^{-\beta E_d}}{2 e^{\beta \epsilon} + 4 e^{\beta \Delta}}. \quad (14)$$

Hence the activation energy for the tracer diffusion coefficient for adatoms at step edges is either $E_d + \epsilon$ or $E_d + \Delta$, depending on whether the barrier for hopping over a kink site is smaller or larger than the kink energy. Using Eq. (10) and Eq. (11) we obtain from the experimental data an activation energy of 1.17 eV for the activation energy of D_{tr} . Hence, we obtain for E_d an upper bound of

$$E_d \leq 1.0 \pm 0.16 \text{ eV}. \quad (15)$$

The value of 1.0 eV applies when $\Delta < \epsilon$. We now turn to the discussion of the data in the light of the available literature on this subject.

4. Discussion

4.1. Kink energy

To our best knowledge, theoretical calculations of the kink energies and the activation energies pertinent to this data are only available on the basis of semi-empirical models such as the effective medium theory (EMT) [20], the embedded atom model (EAM) and the equivalent crystal theory (ECT) [21]. It seems that EMT, at least in the lower levels of approximation, does a rather poor job on the Pt surface. The kink energy for steps of unspecified orientation on the Pt(111) surface for example was calculated to be 0.104 eV [20], which is significantly smaller than the experimental value $\epsilon = 0.167$ eV. It is noteworthy in this context that EMT also underestimates the step energy [20,22]. In the EAM model, the kink energies are 0.161 and 0.178 eV for the (100) and (111) steps, respectively [21], in good agreement with the experiment. The ECT model [21] finally, provides values of 0.384 and 0.431 eV, which are much too high. In the ECT model the kink energies are also too high for the Ag surface, for which both EMT and EAM produce values in close agreement with the experimental result [20,21,23].

The large scatter of the theoretical values for the

kink energy and the deviation from the experimental value highlights the fact that semi-empirical total-energy calculations are questionable for transition metal surfaces. This is presumably because these models do not properly take into account band-structure effects such as the reduced width of the d-bands at the surface and the different occupation of the d-levels. The situation is quite different for the metals with a completely occupied 3d shell. For the Cu(100) surface for example EMT and EAM [20,24] both converge nicely on the experimental value of the kink energy [14].

As we have reported above, we find no difference in the kink energy for the (111)- and (100)-oriented steps on the (111) surface. On the other hand, the free energies of the steps are different for the two orientations. From the equilibrium shapes of 2D islands, Michely and Comsa [25] calculated a 13% smaller free energy for the (111) step. In the most accurate total-energy calculation to date, Feibelman [22] could not reproduce this difference in the energies of the steps. With the result that the kink energies are (at least very nearly) the same for the two steps, the discrepancy between experiment and theory cannot be attributed to a possibly different contribution of a configurational entropy to the step free-energy. Using our value for the kink energy, one can calculate the contribution of the configurational entropy to the free energy of a step atom

$$\Delta F \approx 2k_B T e^{-\beta \epsilon}, \quad (16)$$

which gives only 7.5 meV per atom at 700 K. The configurational entropy is therefore rather small in the temperature range of interest here.

4.2. Time dependence of the fluctuations

As noted above, the $t^{1/4}$ power law proves that the fluctuations are dominated by the mass transport along the step edge. The same result was found earlier for the Cu(100) surface [14], the Pb(111) surface [15], and also recently for the Cu(111) surface [26]. It appears, therefore, that for steps on the close-packed metal surfaces, the prevailing effect of mass transport along the step is the rule. It is interesting to compare this result with the observations and the analysis of the

Brownian motion of vacancy islands on Ag(111) [27,28]. There, the conclusion was that the Brownian motion is caused by an exchange of atoms between step edges over the flat bottom of the vacancy island, and not by mass transport along the step edge which forms the perimeter of the vacancy island. It would be an interesting issue to investigate whether the step fluctuations on Ag(111) are also dominated by the mass exchange with the terraces, if the mass exchange with the terrace dominates the Brownian motion of a vacancy even when the ordinary step fluctuations are dominated by mass transport along the step. This is not inconceivable, since the Brownian motion of a vacancy is mathematically a different measure to the step fluctuations used in this study.

In Eq. (15) we have found an upper bound for the activation energy E_d for hopping along the steps of 1.0 eV. The upper bound represents the value of E_d if the extra barrier for hopping over a kink site Δ is smaller than the kink energy ϵ . While no explicit calculation on the additional barrier Δ for hopping over a kink site appears to be available, an estimate is provided from the EMT calculation of Jacobsen et al. [29], who found a value of less than 0.1 eV for the extra barrier for the hopping around the corner of an hexagonal island. In general, the activation energies in this EMT model appear to be lower than the experimental values by about 0.1 eV [29]. But even given this margin, Δ remains comparable to ϵ and hence we obtain $E_d = 1.0 \pm 0.16$ eV, for both orientations of the steps.

In Table 1 we compare the value for E_d and the prefactor $v_0 = 2 \times 10^{15 \pm 1.3} \text{ s}^{-1}$ to the values calcu-

lated in the EMT model [29] and the tracer diffusion coefficient obtained for the hopping of Pt atoms along the (100) steps of a (311) surface, and along the (111) steps on the (331) surface [30]. As noted above, the EMT results on activation barriers for diffusion are systematically low compared to experimental values [29]. In their effort to use EMT results to simulate the growth forms of islands on Pt(111) and bring their results into agreement with the experiment, Jacobsen et al. [29] have scaled up all the activation energies in the simulation, which brought the activation energy for hopping along steps (of either orientation) to 0.64 eV. This value is still low compared to our result. The last column in Table 1 provides activation energies and prefactors from the direct observation of hopping events in a field ion microscope on a Pt(311) surface ((100) steps) and on a Pt(331) surface ((111) steps). As discussed by Kellogg [2], the prefactor for the (100) step is presumably too low. A scaling of this value to the generally observed 10^{12} s^{-1} brings the activation energy up to 0.69 eV. For the hopping along the (111) steps, a value of 0.84 ± 0.1 eV was found for the activation energy, which is consistent with our result, considering the error bars. The pre-exponential factors found in the FIM observations are considerably lower than our result. The difference is outside the statistical error. We note, however, that the FIM observations were made at about four times lower temperatures. Since the pre-exponential factor has a T^α dependence on the temperature, where the exponent α depends on the free energy of the atom in the transition state, a larger prefactor at higher temperatures is rather likely.

One may also use the diffusion coefficients of Bassett and Webber [30] to calculate directly the expected values for the fluctuations. For that purpose, we write for Eq. (14)

$$D_{\text{tr}} = \frac{1}{2} v_0 e^{-\beta(E_d + \epsilon)}. \quad (17)$$

The equation describing the fluctuations (Eq. (8)) then reduces to

$$F(0,t) \approx \sqrt{2} e^{-\beta(1/4 E_d + 3/2 \epsilon)} v_0^{1/4} t^{1/4}.$$

This equation instructs us that the fluctuations

Table 1

Comparison of data on the hopping of atoms along (100)- and (111)-oriented steps; the results from the EMT model are taken from Ref. [29]; the data from field ion microscope observations (FIM) are from Bassett and Webber [30] (see text for discussion)

Quantity	This work	EMT	FIM (exp.)
$E_d(100)$ (eV)	1.0 ± 0.16	0.45	0.53 ± 0.2
$v_0(100)$ (s^{-1})	$2 \times 10^{15 \pm 1.3}$	—	1.3×10^9
$E_d(111)$ (eV)	1.0 ± 0.16	0.4	0.84 ± 0.1
$v_0(111)$ (s^{-1})	$2 \times 10^{15 \pm 1.3}$	—	5.2×10^{11}

depend on the kink concentration to the power $3/2$, and not to the power $5/4$ as stated by Kuipers et al. [15], who apparently did not consider the effect of the kink concentration on the mass transport diffusion coefficient. After inserting the data from the FIM observations the dashed and dashed/dotted lines in Fig. 4 are obtained for the (111) steps and the (100) steps, respectively. Both lines fall significantly below the experimental data. As discussed above, a temperature-dependent pre-factor would bring about a better agreement.

In summary we conclude that the fluctuations of both the (111)- and (100)-oriented steps on the Pt(111) surface are determined by the mass transport along the step. A possible Schwoebel–Ehrlich barrier for the hopping of adatoms along a kink site is small, so that the mass transport finds no restriction by this barrier. The magnitude of the fluctuations is roughly consistent with an earlier determination of the hopping rates using the field ion microscope.

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