Long Jumps in Surface Diffusion: One-Dimensional Migration of Isolated Adatoms

Donna Cowell Senft and Gert Ehrlich

Coordinated Science Laboratory and Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 22 September 1994)

Diffusion of individual metal atoms on a metal is usually viewed as a random walk between adjacent sites. We have now examined the actual jump processes participating in atomic migration by measuring the distribution of displacements for a single atom of tungsten as well as of palladium on W(211), on which diffusion is one dimensional. In the self-diffusion of a tungsten adatom, only jumps between nearest-neighbor sites contribute. For relatively weakly bound Pd atoms, however, significant contributions from jumps spanning two as well as three nearest-neighbor distances have been identified.

PACS numbers: 68.35.Fx, 61.50.Cj, 68.35.Ja, 68.55.Ce

In the usual view of the diffusion of an atom jumping from one binding site to another on a crystal surface, the atom is assumed to make random transitions between nearest-neighbor sites [1]. There has, however, been considerable speculation about the possibility that migrating atoms may occasionally jump over longer distances, spanning several lattice spacings, rather than always moving between nearest neighbors. Information about such events would be important for understanding basic mechanisms in diffusion on surfaces, but also because these jumps could play a significant role in the transport of material in the growth of crystals. In molecular dynamics simulations, possible deviations from the standard description of diffusion were recognized some time ago. Tully *et al.* [2], as well as DeLorenzi *et al.* [3,4] and Mruzik and Pound [5], demonstrated that in self-diffusion on Lennard-Jones crystals jumps to distant lattice sites become increasingly important at higher temperatures. More recent simulations, some relying on realistic potentials, have again shown such effects [6–10]. Long jumps have actually been identified in scanning tunneling microscopy studies of Pb adatoms on Ge(111) [11]. But these are observations of Pb atoms embedded in a concentrated germanium layer with which they are involved in highly correlated motions, rather than of a single Pb adatom interacting only with the substrate lattice [12]. Still lacking is a clear indication from experiments that long jumps play a significant role in the migration of isolated atoms on a crystal. We wish to report here observations which show that jumps spanning more than a nearest-neighbor distance do in fact participate in an important way in the one-dimensional diffusion of isolated metal atoms on a metal surface.

How can the contributions of long jumps be detected? They should affect the magnitude of the diffusivity D describing the surface transport of atoms. If, as usual, the diffusivity is represented by an Arrhenius relation,

$$D = D_0 \exp(-E_D/kT); \tag{1}$$

then in the transition-state approximation, the prefactor D_0 is given by

$$D_0 = \nu l^2 \exp[S_D/k]; \tag{2}$$

here ν is an effective vibrational frequency, l is the root-mean-square jump length, and S_D is the entropy of activation. For diffusion by jumps over several nearest-neighbor distances, the term l^2 should bring about an abnormally large value of the prefactor D_0. This, however, does not lead to a reasonable method for ascertaining the effective jump length. Quite apart from the difficulty of deducing reliable values of D_0 from experiments [13], or uncertainties about the magnitude of the entropy term S_D, there is an additional problem. In systems for which long jumps are expected, the jump rate may be smaller than the value predicted from transition state theory, upon which Eq. (2) is based [14]. The two effects, long jump lengths but a smaller jump rate, may balance each other; even if long jumps were significant, the prefactor in the diffusivity may not provide a clear sign of this.

More insight into jump processes can be obtained by studying the distribution of the individual displacements made by a diffusing adatom, rather than just the mean-square displacement, or equivalently the diffusivity [15]. Suppose that a single atom migrating along an infinite line of sites makes single jumps to nearest-neighbor sites at a rate α, double jumps spanning two nearest-neighbor distances at a rate β, and triple jumps at the rate γ. In such a stochastic process, the probability $p_x(t)$ of a displacement x after a time t is given by [15]

$$p_x(t) = \exp[-2(\alpha + \beta + \gamma)t] \sum_{k=-\infty}^{\infty} I_k(2\gamma t) \times \sum_{j=-\infty}^{\infty} I_j(2\beta t) I_{x-2j-3k}(2\alpha t), \tag{3}$$

where $I_m(u)$ is the modified Bessel function of the first kind, of order m. Provided the mean-square displacement is not too large, the distribution of displacements $p_x(t)$ is sensitively affected by contributions from the different kinds of jumps. The rate of single, double, and possibly higher jumps can therefore be ascertained by first measuring the distribution of displacements, and then fitting the stochastic relation appropriate for this distribution, such as

 0031-9007/95/74(2)/294(4)$06.00

Eq. (3) in the present case, to the measurements by adjusting the different jump rates. This, of course, assumes a data set large enough to reduce statistical scatter and adequately define the distribution.

Attempts of this sort, relying on the field ion microscope to locate individual metal adatoms on a surface, have been made in the past, but the statistics have not always been adequate [16]. Here studies of one-dimensional diffusion are advantageous: The analysis is straightforward and requires only a moderate number of observations [17]. On W(211), a channeled plane on which atoms are constrained to move in one dimension only, quantitative measurements of the displacement distribution are available for rhenium, molybdenum, iridium, and rhodium adatoms [16]. No really significant contributions from long jumps were identified, although some double jumps, barely within the limits of detectability, were found for iridium and rhodium atoms.

To provide a guide to the conditions under which long jumps can be expected, surface diffusion has sometimes been modeled as the movement of a Brownian particle, subject to frictional effects, over a periodic potential [14,18–22]. Recent theoretical studies of such models suggest that long jumps occur if the dissipation of energy during the motion of the particle is small [20]. For weakly bonded atoms, the rate of equilibration with the lattice, that is the energy dissipation, should be smaller than for atoms self-adsorbed on their own lattice [23,24], and in searching for diffusion via long jumps we have therefore chosen to examine the diffusion of palladium atoms on W(211). For palladium adatoms, a diffusion barrier $E_D \sim 9.4$ kcal/mol, less than half that for tungsten atoms, is expected on W(211) from the empirical rule that the barrier to diffusion amounts to $\sim\frac{1}{10}$ the heat of sublimation of the atoms in their solid state [13]. As a contrasting example of a strongly interacting adatom, for which long jumps are *not* expected, we have in addition studied the self-diffusion of tungsten. The equipment for observing individual adatoms in the field ion microscope, as well as the techniques for analysis are those standard in our laboratory [25,26].

Diffusivities measured for a single tungsten atom on the (211) plane of tungsten are shown in Fig. 1. They are in excellent agreement with previous determinations [13,27] and lead to an overall activation energy E_D of 19.0 ± 0.85 kcal/mol and a prefactor $D_0 = 3.4(\times 4.2 \pm 1) \times 10^{-3}$ cm^2/s; the latter is of the magnitude expected for jumps between nearest-neighbor sites, with a negligible entropy of activation S_D. The distribution of displacements determined for tungsten atoms after diffusion at 307 K is shown in Fig. 2. In all these experiments, the sample, a single crystal tungsten wire with [111] orientation, is heated for 3.4 s intervals during which migration occurs; no fields are applied during the diffusion step. The displacement of the atom is measured only after cooling the sample to ~20 K, where the field required for imaging has no discernible effect on atom positions. The

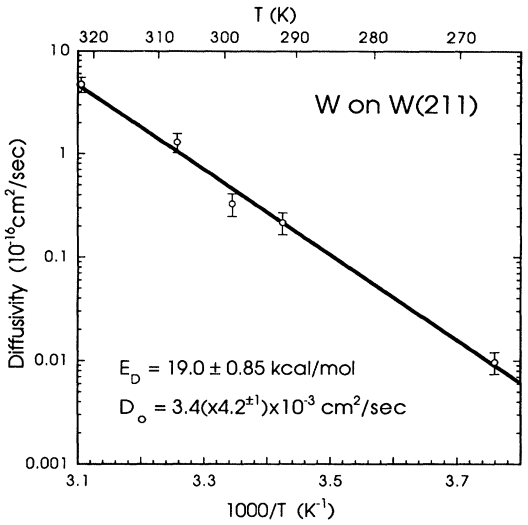

FIG. 1. Temperature dependence of the diffusivity of a single tungsten adatom, self-adsorbed on W(211). Diffusion in this and all subsequent figures occurs in the absence of any applied field.

measured distribution (as well as the diffusivities) therefore provide an indication of diffusion in an entirely ordinary thermal environment. Nevertheless, there are two possible side effects associated with such measurements. Observations are made on planes of finite extent, on which the adatom may at some stage interact with a boundary, rather than on the infinite plane postulated for Eq. (3). To minimize the effects of such encounters, atoms coming within three nearest-neighbor spacings of the plane edge have been excluded from the data set. In addition, some

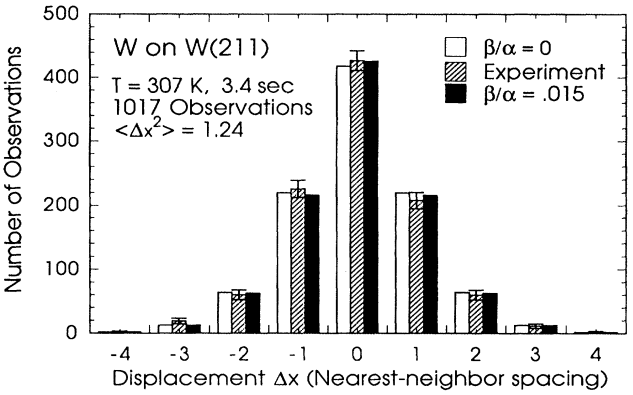

FIG. 2. Distribution of displacements made by W adatom in self-diffusion on W(211) at $T = 293$ K. The best fit of Eq. (3) to the measurements (striped bars) is indicated in black. Distribution expected if only single jumps participate in diffusion is shown in white. For the number of observations made, the contribution of double jumps is negligibly different from zero.

movement of atoms may already occur during temperature transients, while the sample is heating up or cooling down, making for some uncertainty in the effective temperature of the measurements.

For tungsten atoms on W(211), the best fit of the stochastic relation for the distribution of displacements to the distribution actually measured is obtained by varying the ratio β/α of double to single jumps, as well as the ratio γ/α of triple to single jumps, in a minimization routine [28,29] using a log-likelihood estimator [30]. This procedure yields a ratio $\beta/\alpha = 1.5 \times 10^{-2}$, well within the limits of error expected for a system with *no* double jumps at all in a determination based on ~1000 observations. That there really are no contributions from long jumps is in any event clear on comparing the experiments and the distribution of displacements for a particle carrying out a random walk of single jumps, with a mean-square displacement of 1.24, which is also plotted in Fig. 2. The self-diffusion of tungsten is in complete accord with expectations and takes place via single jumps to nearest-neighbor sites.

For palladium atoms on W(211), diffusion occurs as expected at much lower temperatures—that is clear from the Arrhenius plot of the measured diffusivities in Fig. 3. The activation energy for diffusion, $E_D = 7.26 \pm 0.13$ kcal/mol, is in fact significantly less than that predicted empirically from the heat of sublimation [13]. However, there is nothing unusual in the value of the prefactor, $D_0 = 4.1(\times 1.7 \pm 1) \times 10^{-4}$ cm^2/s, considering the low temperature at which diffusion takes place. The distribution of displacements measured for Pd diffusing on W(211) at $T = 133$ K is shown in Fig. 4. It deviates dramatically from expectations for a random walk by nearest-neighbor jumps. To account for the experiments it is necessary to invoke contributions not just from double jumps, but from triple jumps as well. The best fit to the raw distribution data is obtained for $\beta/\alpha = 0.21$, $\gamma/\alpha = 0.14$, but it must be kept in mind that an analysis of the raw data, uncorrected for size or temperature transients, will likely lead to an underestimate of the role of longer jumps.

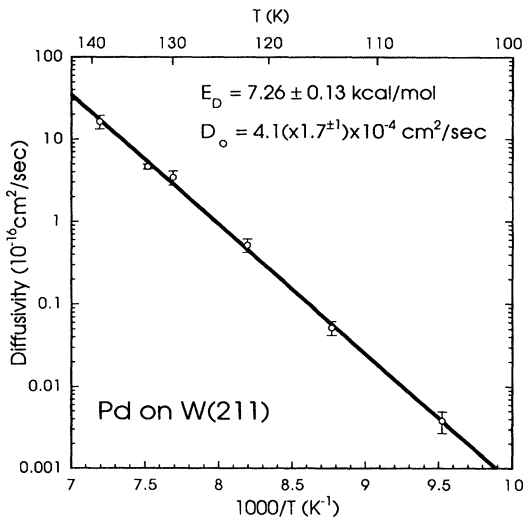

FIG. 3. Arrhenius plot for the diffusion of a Pd adatom on W(211). The prefactor D_0, deduced from the temperature dependence is in agreement with expectations for diffusion by single jumps. The activation energy E_D is significantly lower than expected.

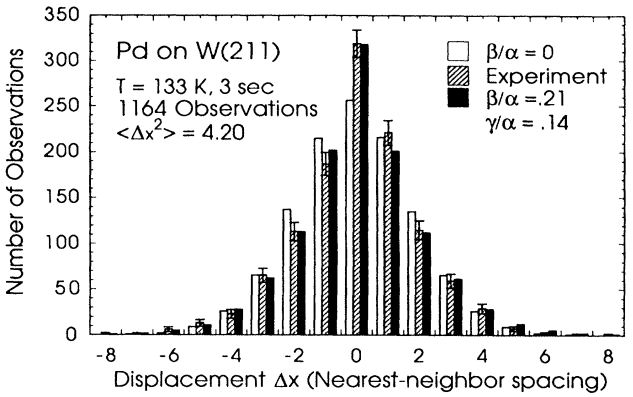

FIG. 4. Distribution of displacements for a single Pd adatom diffusing on W(211) at $T = 133$ K. The best fit (in black) is obtained by invoking significant contributions from double jumps (rate β) and triple jumps (rate γ). Distribution for diffusion by nearest-neighbor jumps only is shown in white.

This is the first time a significant rate of long jumps has been identified in one-dimensional migration. Several effects are surprising. The prefactor D_0 gives no indication of deviations from an ordinary random walk between nearest neighbors, even though the number of triple jumps is comparable to that of double jumps. At least 10% of the total jumps cover three nearest-neighbor spacings and 16% cover two spacings. In fact, triple jumps make a 25% larger contribution to the diffusivity than do single jumps. The other surprise is the great sensitivity of long jumps to temperature. A distribution taken at 122 K, just 11 K lower than for the measurements in Fig. 4, gives *no* indication of anything other than single jumps. This suggests that long jumps arise in an activated process, over an effective barrier roughly twice that for single jumps.

Neither of these results would have been expected from models in which diffusion is represented as the motion of a Brownian particle over a periodic potential. As has been emphasized by Ferrando *et al.* [14], a single quantity, the energy dissipation Δ from the moving atom, serves to determine the distribution of jumps in such Brownian motion, and this parameter varies inversely with the temperature T. At values of Δ which account for the observed ratio of double-to-single jumps β/α, the contribution predicted for triple jumps is less than half of what is observed. More striking is the prediction that

an 11 K lowering of the temperature should have little effect on the contribution of long jumps, lowering it by but 10%, instead of causing it to vanish, as found in the experiments.

Palladium atoms were picked for this study because their low diffusion barrier on W(211) was expected to favor poor energy transfer between adatom and lattice. The fact that for this system we have now established that long jumps do indeed participate significantly in diffusion does not necessarily mean that the factors responsible for long jumps have been properly identified. It is not clear, for instance, if the behavior observed is specific to palladium, or is typical of adatoms diffusing over small barriers. For the distribution of palladium showing significant contributions from long jumps, the effective diffusion temperature kT/E_D is 0.036. This is almost 10% higher than for any of the other distributions measured, and the effect of this high temperature still needs to be explored in order to establish the conditions under which long jumps play an important role in surface diffusion.

This work was carried out with support from the National Science Foundation under Grant No. DMR-91-01429. We are indebted to M. F. Lovisa for interesting discussions about the experiments and their analysis.

[1] See, for example, R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).
[2] J. C. Tully, G. H. Gilmer, and M. Shugard, J. Chem. Phys. **71**, 1630 (1979).
[3] G. DeLorenzi, G. Jacucci, and V. Pontikis, in Proc. ICSS-4 and ECOSS-3, Cannes, 1980, edited by D. A. Degras and M. Costa, Vol. 1, p. 54.
[4] G. DeLorenzi, G. Jacucci, and V. Pontikis, Surf. Sci. **116**, 391 (1982).
[5] M. R. Mruzik and G. M. Pound, J. Phys. F **11**, 1403 (1981).
[6] G. DeLorenzi and G. Jacucci, Surf. Sci. **164**, 526 (1985).
[7] A. F. Voter and J. D. Doll, J. Chem. Phys. **82**, 80 (1985).
[8] J. D. Doll and A. F. Voter, Annu. Rev. Phys. Chem. **38**, 413 (1987).
[9] K. D. Dobbs and D. J. Doren, J. Chem. Phys. **97**, 3722 (1992).
[10] D. E. Sanders and A. E. DePristo, Surf. Sci. **264**, L169 (1992).
[11] E. Ganz, S. K. Theiss, I.-S. Hwang, and J. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992).
[12] E. Kaxiras and J. Erlebacher, Phys. Rev. Lett. **72**, 1714 (1994).
[13] S. C. Wang and G. Ehrlich, Surf. Sci. **206**, 451 (1988).
[14] R. Ferrando, R. Spadacini, and G. E. Tommei, Phys. Rev. E **48**, 2437 (1993).
[15] J. D. Wrigley, M. E. Twigg, and G. Ehrlich, J. Chem. Phys. **93**, 2885 (1990).
[16] S. C. Wang, J. D. Wrigley, and G. Ehrlich, J. Chem. Phys. **91**, 5087 (1989).
[17] Preliminary investigations suggesting long jumps in the two-dimensional diffusion of metal atoms on W(110) have been reported by M. F. Lovisa and G. Ehrlich, Bull. Am. Phys. Soc. **37**, 190 (1992), Abstract C23 8. These studies are still continuing, however.
[18] An overview of the theory has been given by V. I. Melnikov, Phys. Rep. **209**, 1 (1991).
[19] R. Ferrando, R. Spadacini, and G. E. Tommei, Surf. Sci. **265**, 273 (1992).
[20] R. Ferrando, R. Spadacini, G. E. Tommei, and G. Caratti, Surf. Sci. **311**, 411 (1994).
[21] E. Pollak, J. Bader, B. J. Berne, and P. Talkner, Phys. Rev. Lett. **70**, 3299 (1993).
[22] For a more physical approach, see G. Wahnström, Phys. Rev. B **33**, 1020 (1986).
[23] B. McCarroll and G. Ehrlich, J. Chem. Phys. **38**, 523 (1963).
[24] E. T. Kinzer Jr., Ph.D. thesis, University of Virginia, 1962.
[25] H.-W. Fink and G. Ehrlich, Surf. Sci. **143**, 125 (1984).
[26] D. A. Reed and G. Ehrlich, Surf. Sci. **151**, 143 (1985).
[27] P. G. Flahive and W. R. Graham, Surf. Sci. **91**, 463 (1980).
[28] F. James and M. Roos, Comput. Phys. Commun. **10**, 343 (1975).
[29] S. Dedoussis, M. Chardalas, and S. Charalambous, Comput. Phys. Commun. **31**, 29 (1984).
[30] A. G. Frodesen, I. Skjeggestad, and H. Tøfte, *Probability and Statistics in Particle Physics* (Universitetsforlaget, Bergen, 1979).