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Vacancy diffusion in the Cu(001) surface II: Random walk theory

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Abstract

We develop a version of the vacancy mediated tracer diffusion model, which follows the properties of the physical system of In atoms diffusing within the top layer of Cu(001) terraces. This model differs from the classical tracer diffusion problem in that (i) the lattice is finite, (ii) the boundary is a trap for the vacancy, and (iii) the diffusion rate of the vacancy is different, in our case strongly enhanced, in the neighborhood of the tracer atom. A simple continuum solution is formulated for this problem, which together with the numerical solution of the discrete model compares well with our experimental results.

Key words: Tracer diffusion, Vacancy mediated diffusion, Surface vacancy, Continuum model

1 Introduction

Diffusion is one of the most commonly observed stochastic processes. Random walks, the paths of diffusing particles, are among the first typical applications in probability theory textbooks. However, the diffusing particles, or their paths, are often invisible, and their effect can be observed only indirectly. This is the case for example in vacancy mediated tracer diffusion, when on a lattice of atoms a diffusing vacancy displaces atoms along its path. The process is

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observed by following a labeled (or *tracer*) atom, whose steps are slaved to the motion of the vacancy.

In this paper we treat theoretically the physical system of diffusing In atoms in a Cu(001) surface layer, described in detail in paper I [1]. In section 2 we review the literature about tracer diffusion. We describe our discrete model in section 3, the classical tracer diffusion problem adapted to better suit our experimental system. Finally section 4 gives a simple continuum formulation whose solution allows one to fit the experiments without adjustable parameters.

We start with summarizing the experimental observations [1–3]. On a Cu(001) surface with up to several hundred atomic spacing wide terraces, a few surface Cu atoms were substituted with In atoms. Then the area was periodically imaged with a scanning tunneling microscope (STM), and the position of the In atoms was followed in time.

To our initial surprise, the In atoms do not move in a typical diffusive way, but instead are stationary for some time, and then suddenly (unresolvable by STM) they jump to a nearby lattice site, often up to 5 or more nearest neighbor spacings away from their original position. These *long jumps* tend to happen at the same instant for different In atoms in the imaged area. To explain this, we found that the only mechanism permissible on physical grounds [1] is vacancy mediated tracer diffusion.

Based on Embedded Atom Model calculations [4,5] we expect [1] that surface vacancies at room temperature have a low concentration, of the order 10^{-9} on Cu(001). They both are created and recombine at steps, and stay in the top layer of a terrace, as it is energetically unfavorable to dive deeper. From the typical jump rate of 10^6 Hz and terrace widths of a few hundred atomic spacings, their lifetime is estimated to be at most of the order of milliseconds. (Vacancies reaching the middle of the terrace have the longest expected lifetime.) As the long jumps of In atoms are the effect of a single vacancy, this short lifetime explains why the dynamics of the jumps can not be resolved with STM (with imaging rate up to 10 Hz), while the long waiting time between jumps, of the order of 10 s, enables one to distinguish independent vacancies.

The measured waiting time between the jump events has an exponential distribution, supporting the explanation of the jumps as independent events. The distribution of the jump vectors, which has been measured, will be compared to the numerical model in this paper.

2 Tracer diffusion

The problem of vacancy mediated tracer diffusion was considered for a long time [6–10]. It has been solved first for the simplest case [7], when the diffusion of the vacancy is unbiased (all diffusion barriers are equal; the tracer atom behaves in the same way as the other atoms), the lattice is two-dimensional and periodic or infinite. There is a single vacancy present, it takes a nearest neighbor step in a random direction at regular time intervals, and has an infinite lifetime, as there are no traps. The solution is constructed by separating the motion of the tracer and the vacancy. The correlation of the steps of the tracer atom is calculated from the probability that the vacancy returns to the tracer from a direction which is equal, perpendicular or opposite to its previous departure. The distribution of the tracer atom spreads with time, and on an infinite lattice for large times it approaches the following functional form:

$$P_t(\mathbf{r}) = \frac{2(\pi - 1)}{\log t} K_0 \left(\frac{r}{[\log t / (4\pi(\pi - 1))]^{1/2}} \right), \quad (1)$$

where K_0 is the modified Bessel function[11], time t measures the number of steps of the vacancy, and at $t = 0$ the vacancy is near the tracer atom. The non-Gaussian shape of the spatial distribution function is typical for vacancy mediated diffusion. The average displacement of the tracer particle diverges with time. This is a direct consequence of the fact that two is the marginal dimension for the return probabilities in the random walk problem. For higher dimensional problems, the probability that the vacancy returns to the tracer particle is less than unity and the average displacement of the tracer particle remains finite. However, for dimensions equal to or smaller than two, the vacancy always returns to the tracer particle and as a consequence its displacement diverges.

The same problem has been solved in an alternative way for all dimensions [8]. From this solution one can calculate the number of tracer-vacancy exchanges up to time t : in two dimensions its distribution is geometric, with mean $(\log t)/\pi$. The continuum version of this problem has been considered as well in the form of an infinite-order perturbation theory [9]; the solution matches the asymptotic form of the lattice model.

In a very recent study the lattice calculations were generalized to biased diffusion [10]. The difference between the tracer atom and the substrate atoms was taken into account by having different vacancy-tracer and vacancy-substrate exchange probabilities, while the rate of vacancy steps was kept constant. Repulsive interaction reduces, moderately attractive interaction increases the spreading of the tracer distribution.

Although these exact solutions are closely related to our In/Cu(001) system, the differences, e.g. in boundary conditions and vacancy lifetime make a direct comparison with experiments impossible. For this purpose we develop a model of tracer diffusion which includes the essential properties of the experimental system.

3 Discrete model

In this section we describe a discrete model for In/Cu(001) diffusion, solve it numerically, and present the results.

Our model is defined on a two-dimensional simple square lattice of size $l \times l$, centered around the origin. This corresponds to the top layer of a terrace of the Cu surface, with borders representing steps. All sites but two are occupied by substrate atoms. At zero time the two remaining sites are the impurity (or tracer) indium atom, which we release at the origin, and a vacancy at position $(1, 0)$. This corresponds to the situation immediately after the indium atom has changed places with the vacancy, e.g. for the first time.

The only allowed motion is the exchange of the vacancy with one of the neighboring atoms. The exchange rate depends on the local environment, i.e. on the relative position of the vacancy and the impurity atom. This takes into account the effect of the lattice stress induced by the tracer atom on the energy landscape observed by the vacancy. Each rate was assumed to be simply proportional to the Boltzmann factor $e^{-\frac{\Delta E}{k_B T}}$, where ΔE is the activation energy for the considered diffusion step and $k_B T$ is the thermal energy at temperature T . The diffusion barriers of the vacancy were calculated with the EAM method [4]. We used the interatomic potentials proposed by Finnis and Sinclair [5], where the metallic cohesion is taken into account via the second moment approximation to the tight-binding model. The calculation was done on a $15 \times 15 \times 15$ slab of copper. The system with different relative positions of an In atom and a surface vacancy was fully relaxed until a threshold force of $1.875 \cdot 10^{-12}$ N on the atoms. The barriers were taken at the point halfway between the stable sites. See figure 1 for the values for the barriers. Since the barrier differences are large compared to $k_B T$, the difference in jump probabilities are extremely large (see below for typical values).

When the vacancy reaches the perimeter of the lattice, its random walk is terminated, corresponding to the physical process of its recombination at surface steps. During its lifetime, the vacancy displaces atoms along its path, many of them multiple times. Thus also the tracer atom can end up displaced from its original position at the time of recombination of the vacancy. Averaged over the random walks of many independent vacancies, this yields a

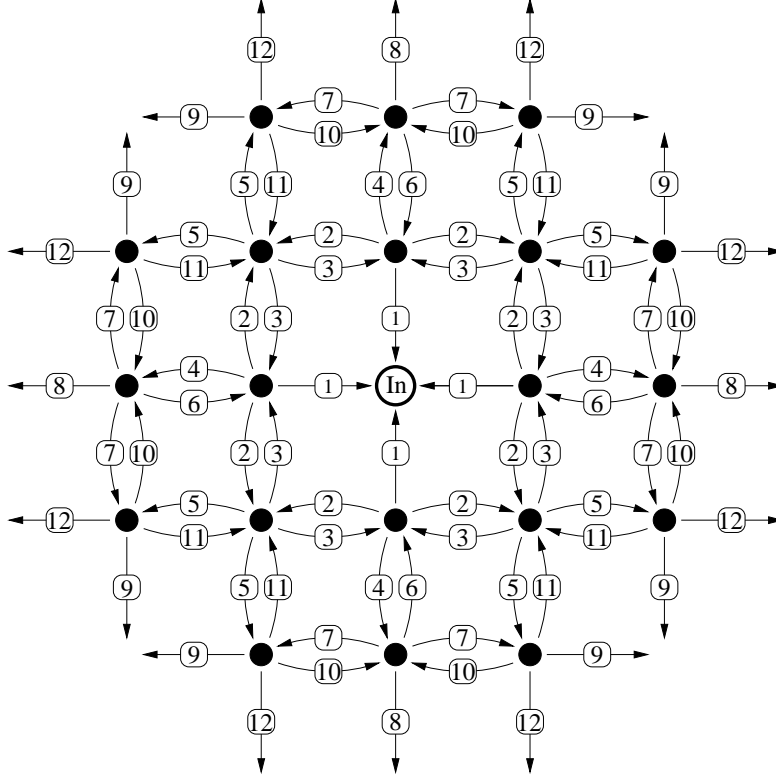


Fig. 1. Special vacancy diffusion barriers near an In atom, calculated with the EAM method. The arrows denote the motion of the vacancy. The following values for the barriers were used in the calculation: $E_1 = 243$ meV, $E_2 = 671$ meV, $E_3 = 503$ meV, $E_4 = 529$ meV, $E_5 = 589$ meV, $E_6 = 382$ meV, $E_7 = 544$ meV, $E_8 = 549$ meV, $E_9 = 577$ meV, $E_{10} = 534$ meV, $E_{11} = 589$ meV, $E_{12} = 576$ meV. For all other barriers $E_{\text{far}} = 588$ meV.

probability distribution of the different displacement vectors that the tracer atom can make as a result of its encounter with a single vacancy. Due to the boundary conditions, introduced by the finite size of the lattice and due to the distribution of exchange rates, an analytic solution to this problem is no longer possible.

When treating the above model numerically, we separate the motion of the vacancy and the tracer atom, as has been performed also in some of the analytical treatments referred to in section 2. In our case of a finite lattice, this separation introduces an approximation, which is valid only if the tracer atom is relatively close to the middle of the lattice. First, we calculate the probabilities that the vacancy, released at one atomic spacing from the tracer, returns the first time to the tracer from equal (p_{eq}), perpendicular (p_{perp}) or opposite (p_{opp}) directions; we also calculate the probability of its recombination (p_{rec}) at the perimeter instead of returning to the tracer. Knowing these return and recombination probabilities, we turn to the motion of the tracer atom, which performs a biased random walk of finite length. The direction of each step with respect to the previous one, and the probability that this was the last

step, are obtained from the return and the recombination probabilities. With this method we lose all temporal information about the random walk of the tracer, but the individual steps of the tracer atom are orders of magnitude too fast to be resolved with the STM, and therefore the STM observations are insensitive to this information anyway.

In practice, both the return probabilities and the motion of the tracer atom are obtained with direct evaluation of probabilities, which has better convergence properties than Monte-Carlo-type methods.

As an illustration of this enumeration method, let us consider the computation of the vacancy return probabilities. We assign a variable to each lattice site, which measures the probability that the vacancy after s atomic steps is at that site, while it has not exchanged with the tracer yet. Initially all probabilities are zero except at $(1,0)$ where it is unity: we release the vacancy from here. The boundary acts as a trap for the vacancy, as well as the site (representing the tracer) at the origin. For each atomic step of the vacancy we update the site variables parallel by distributing their probability to the four neighbors according to the respective exchange probabilities. As the probability flows into the trap at the origin, we record the cumulative flow in each of the four directions leading to that site, which gives the return probabilities at the end. This iteration converges fast, and the convergence can be measured by the sum of the probabilities still on the lattice. The other computation, the motion of the tracer atom, is similar but slightly more complex. In that computation we assign a variable to each incoming edge of each site, which measure the probability that after s steps — each corresponding to a vacancy return — the tracer is at the given site and that it arrived from the given direction. In addition, each site has a variable which accumulates the probability that the tracer become immobile at that site. These probabilities for the tracer arrival and immobilization are updated iteratively according to the previously obtained vacancy return probabilities.

We first tested our model on the case of unbiased vacancy diffusion, which would correspond to infinite temperature. The shape of the tracer distribution was similar to the experimentally observed one, but to achieve quantitative agreement the only remaining parameter of the model — the lattice size l — had to be tuned to astronomical sizes. This clearly shows that taking equal barriers is an unrealistic oversimplification for the In/Cu(001) system.

Using the EAM barriers, for typical parameters $T = 320$ K and $l = 401$ the values for the return probabilities were $p_{\text{eq}} = 1 - 2.4 \times 10^{-7}$, $p_{\text{perp}} = 1.1 \times 10^{-7}$, $p_{\text{opp}} = 4.2 \times 10^{-9}$, and the recombination probability $p_{\text{rec}} = 1.1 \times 10^{-8}$. These values depend weakly on l [e.g. the dependence of the mean square displacement, calculated later in this paper from the return probabilities, is logarithmic: $\langle r^2 \rangle \propto \log(l/l_0)$]. This is a consequence of the fact that two is the marginal

dimension for the return problem of the random walker. In higher-dimensional space the vacancy does not necessarily return, the return probabilities are asymptotically independent of the lattice size, and the final distribution of the tracer — also independent of lattice size for large lattices — takes the following form, e.g. in three dimensions [9]: $p(\mathbf{r}) = C_1\delta(\mathbf{r}) + C_2r^{-1}\exp(-\Lambda r)$.

For the case of an indium impurity in a Cu(001) lattice, the diffusion barrier for a vacancy exchange with the indium atom is considerably lower than all other barriers. Therefore, in most cases the vacancy returns from the direction of its previous departure, and the individual moves of the tracer atom are strongly anti-correlated. Both the numerical and the theoretical treatment are simplified significantly if we do not have to follow the large number of ineffective “back and forth” exchanges of the vacancy and the tracer atom. For this purpose, consider the small probability ϵ that the vacancy does *not* return from the same, equal direction. Thus $p_{\text{eq}} = 1 - \epsilon$. In the case of indium in Cu(001) the EAM calculations yield $\epsilon = 2.4 \cdot 10^{-7}$ (see above). We now define

$$\begin{aligned}\hat{p}_{\text{perp}} &= p_{\text{perp}}/\epsilon \\ \hat{p}_{\text{opp}} &= p_{\text{opp}}/\epsilon \\ \hat{p}_{\text{rec}} &= p_{\text{rec}}/\epsilon\end{aligned}\tag{2}$$

and have

$$2\hat{p}_{\text{perp}} + \hat{p}_{\text{opp}} + \hat{p}_{\text{rec}} = 1.\tag{3}$$

If we represent the quasi-bound state of the rapidly exchanging (on average $1/\epsilon$ times) vacancy and impurity atom with the position of a *bond* of the original lattice, then the vacancy-tracer pair walks on the bonds of the original lattice. The pair steps to each of the four perpendicular bonds with probability $\hat{p}_{\text{perp}}/2$, and to each of the two parallel ones with $\hat{p}_{\text{opp}}/2$, see figure 2. (The factors $1/2$ reflect the probability for the vacancy to escape either at the right or the left side of the quasi-bound position, which is $\frac{1}{2}$ for both sides in the limit of vanishing ϵ . The advantage of this approach is twofold: the path of the tracer is made of fewer steps (beneficial for numerics), and the bond-to-bond steps are now independent (beneficial for theoretical treatment).

Using this, the tracer atom described as if it forms a pair with the vacancy on one of the bonds adjacent to its original site, walks on the bonds lattice, and at the end (which happens with probability \hat{p}_{rec} after each step) it is released at either end of the last visited bond. Results for the probabilities of the different jump lengths (beginning-to-end vectors of these paths) are shown on figure 3. Note, that the model calculations in figure 3 contained no adjustable parameters.

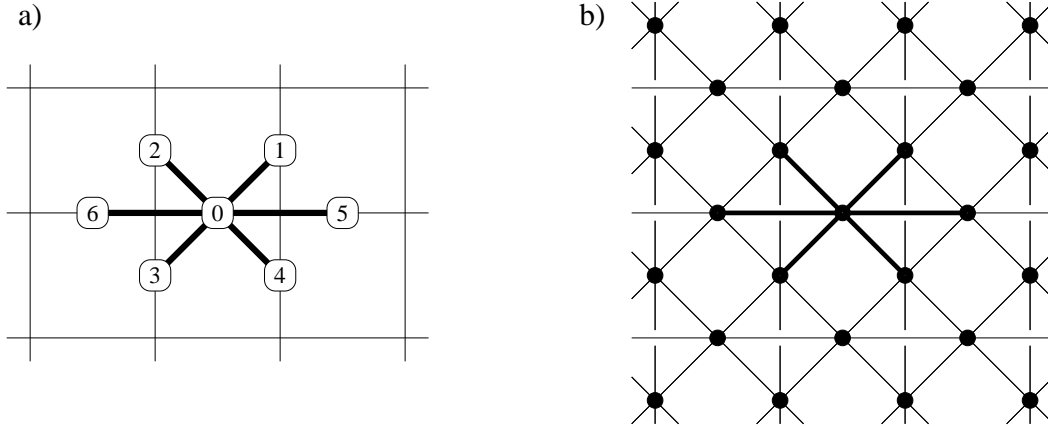


Fig. 2. a) The bond-to-bond steps of the vacancy-tracer pair. If we view the vacancy-tracer pair to live on the center of each bond, indicated by the labels, then the pair hops between these sites. The atomic lattice is drawn with thin lines. b) The lattice (made of bonds of the atomic lattice) on which the vacancy-tracer pair walks. The neighbors that can be reached by a single step from the site at the center are shown with thick lines. This lattice can be considered as a square lattice, rotated by 45° with respect to the atomic lattice, with some extra diagonal bonds. Note that this is not a Bravais lattice.

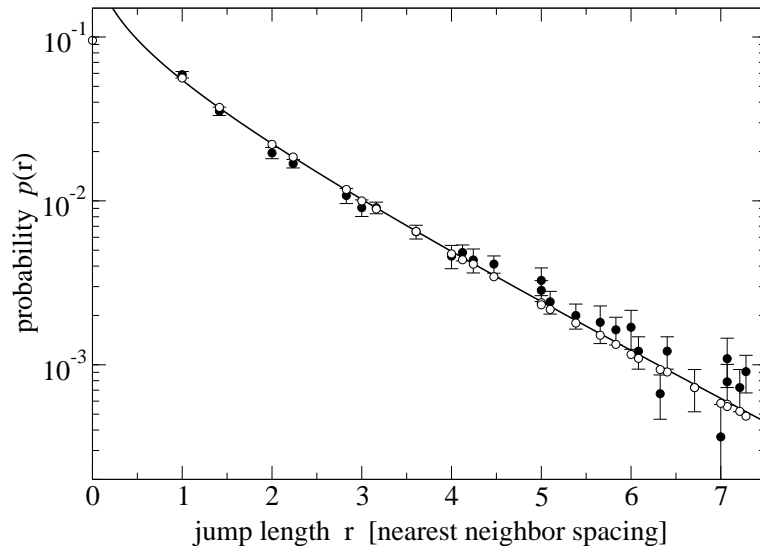


Fig. 3. The probabilities of the jump lengths of the tracer atom for $T = 320$ K and $l = 401$ lattice spacings. Filled circles correspond to experimental values (measured at this temperature and terrace size), open circles are from the model described in the text, and the solid curve is the continuum solution described in section 4. The data shows no significant directional structure: the dependence on the *length* of the jumps is monotonic with good approximation. (Each dataset is normalized separately such that the probabilities corresponding to a subset of the jump vectors, $1 \leq |\mathbf{r}| \leq 6$, add up to unity. These are the probabilities that are determined with good accuracy in the experiment.)

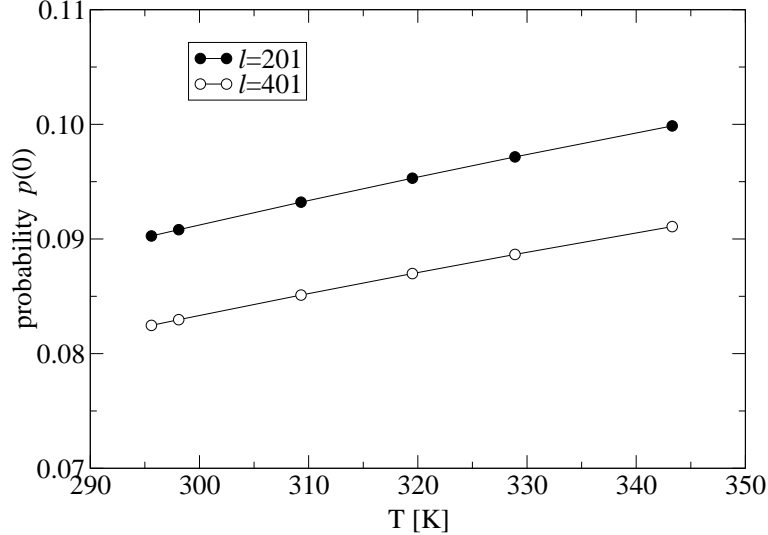


Fig. 4. The temperature dependence of the probability that a tracer atom had an encounter with a vacancy but its net displacement was zero, plotted for two different lattice sizes. The dependence is weak.

A general advantage of numerical modeling is that we have access to quantities which are difficult or impossible to measure experimentally. One example in our simulation is the probability that a tracer atom had an encounter with a vacancy, but its net displacement was zero. The temperature dependence of this quantity is plotted on figure 4. Since the dependence is weak, the assumption in the experimental measurements to associate In-vacancy encounters with visible (non-zero) jumps of the In atom is justified.

For a given set of diffusion barriers, our model has two parameters: the temperature and the lattice size. When we compare results with experiments, both can be independently obtained, and in principle there are no adjustable parameters. For example the case of $T = 320$ K (figure 3) — using the distance to the nearest step in the experiment as lattice size in the numerical model — gave a good match with the experiment, but for the measurements at other temperatures we had to adjust the lattice size to obtain good agreement. Although the best fit lattice size in some cases was a factor of 2-3 smaller than the measured distance to the nearest step, the change in the return probabilities was much smaller, as they depend logarithmically on the lattice size. Undetected defects — acting as trap for the vacancies — closer to the In atom than the nearest step could also be accounted for this difference.

4 Continuum model

In the previous section we solved numerically the version of the tracer diffusion problem which was relevant for the In/Cu(001) experiments. Although this

already enables full comparison, the numerical solution has the disadvantage that it cannot be described with a few parameters. In this section we develop a simple continuum description, where the overall shape of the jump length distribution is described with a single parameter.

We use our previous results for the return and recombination probabilities of the vacancy, and consider the random walk of the tracer-vacancy pair on the bond lattice. Let $\varrho(\mathbf{r}, n)$ denote the probability that the tracer-vacancy pair is at position \mathbf{r} and at instance n , where n counts the number of steps the tracer-vacancy pair takes. Since the subsequent steps of the pair are independent, we can write an effective diffusion equation for the evolution of $\varrho(\mathbf{r}, n)$:

$$\frac{\partial \varrho(\mathbf{r}, n)}{\partial n} = D_{\text{eff}} \nabla^2 \varrho - c \varrho. \quad (4)$$

The first term on the right hand side corresponds to the steps the pair takes on the bond lattice, here D_{eff} denotes the mean square displacement per step of the pair. The second term corresponds to the recombination of the vacancy²; at this point the pair breaks up. In the continuum approximation for space and n , the solution for a Dirac-delta initial condition at the origin is

$$\varrho(\mathbf{r}, n) = \frac{1}{4\pi D_{\text{eff}} n} \exp\left(-\frac{r^2}{4D_{\text{eff}} n} - cn\right). \quad (5)$$

The final distribution of the tracer atom after the vacancy recombined is obtained by the integration of the loss term in Eq. (4):

$$p(\mathbf{r}) = \int_0^\infty c \varrho(\mathbf{r}, n) dn = \frac{1}{2\pi} \frac{c}{D_{\text{eff}}} K_0\left(\frac{r}{\sqrt{D_{\text{eff}}/c}}\right), \quad (6)$$

where K_0 is the modified Bessel function of order 0. The functional form of this solution is similar to that of the infinite lattice system in section 2, in spite of the differences introduced by the finite vacancy lifetime and the different boundary conditions.

The mean square displacement $\langle r^2 \rangle$ is directly proportional to the square of the width of the Bessel solution, apart from lattice corrections. We can determine the width of the Bessel solution from the parameters D_{eff} and c , which are

² Note that since n counts the number of steps of the vacancy-tracer pair on the bond lattice, the term $-c\varrho$ does not imply that the vacancy can recombine at any lattice site — in fact it recombines at terrace steps, between subsequent returns to the In atom.

obtained from the return probabilities in the Appendix:

$$\langle r^2 \rangle \propto \frac{D_{\text{eff}}}{c} = \frac{\hat{p}_{\text{perp}} + \hat{p}_{\text{opp}}}{4\hat{p}_{\text{rec}}}. \quad (7)$$

This continuum solution is shown in figure 3. It closely follows the numerical solution of the model, even for relatively small distances from the origin, where one would expect stronger lattice effects.

5 Summary

In this paper we described a model for vacancy mediated tracer diffusion on a finite lattice with absorbing boundaries for the vacancy. These boundary conditions were appropriate to model the vacancy mediated diffusion of In atoms embedded in the top layer of Cu(001) terraces. In addition to the numerical solution of the discrete model, we set up a simple continuum formulation of the model. The spatial distribution of the tracer atom in the continuum solution has a modified Bessel function profile. This form of non-Gaussian distribution is typical for tracer diffusion assisted by other diffusing particles. In order to enable a quantitative comparison with the STM measurement of the In/Cu(001) system, we introduced modified vacancy diffusion rates near the In atom, calculated with the EAM method. The modified rates affect the width of the Bessel function, without changing the functional form of this characteristic distribution.

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A Obtaining D_{eff} and c from the return probabilities

In this Appendix we calculate the parameters of the continuum model, D_{eff} and c , from the return and recombination probabilities in Eq. (2). The probability $P_0^{(n+1)}$ that the vacancy-tracer pair is at site “0” (not necessarily the origin) after $n+1$ steps of the pair is contributed from sites 1, 2, . . . , 6 (see figure 2a; no upper index refers to probabilities after n steps):

$$P_0^{(n+1)} = \frac{\hat{P}_{\text{perp}}}{2}(P_1 + P_2 + P_3 + P_4) + \frac{\hat{P}_{\text{opp}}}{2}(P_5 + P_6). \quad (\text{A.1})$$

During one step in n , the change in P_0 is (using Eq. 3)

$$\begin{aligned}
P_0^{(n+1)} - P_0 &= \frac{\hat{p}_{\text{perp}}}{2}(P_1 + P_2 + P_3 + P_4 - 4P_0) \\
&\quad + \frac{\hat{p}_{\text{opp}}}{2}(P_5 + P_6 - 2P_0) - \hat{p}_{\text{rec}}P_0.
\end{aligned}
\tag{A.2}$$

The finite difference on the left hand side approximates the derivative, and the terms on the right hand side can be collected to form a lattice approximation to the Laplacian:

$$\nabla^2 P = a_{\text{perp}}^{-2}(P_1 + P_2 + P_3 + P_4 - 4P_0) \tag{A.3}$$

and

$$\partial_x^2 P = a_{\text{opp}}^{-2}(P_5 + P_6 - 2P_0) \approx \frac{1}{2}\nabla^2 P, \tag{A.4}$$

where the distances $a_{\text{perp}} = 1/\sqrt{2}$ and $a_{\text{opp}} = 1$ are in units of nearest neighbor spacing of the atomic lattice. In the approximation of Eq. (A.4) we assumed on average equal second derivatives in all directions. After these substitutions

$$\frac{\partial P_0}{\partial n} = \underbrace{\frac{\hat{p}_{\text{perp}} + \hat{p}_{\text{opp}}}{4}}_{D_{\text{eff}}} \nabla^2 P - \underbrace{\hat{p}_{\text{rec}}}_c P_0, \tag{A.5}$$

and the coefficients D_{eff} and c can be read off.