On the lattice gas description of hydrogen in palladium: a molecular dynamics study

# On the lattice gas description of hydrogen in palladium: a molecular dynamics study

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**Abstract.** The occupations by hydrogen of octahedral and tetrahedral sites in palladium are determined with the simulation model of Gillan. They are in agreement with the predictions of a lattice gas model. The effect of lattice relaxation on the octahedral site energies of hydrogen in palladium alloys is investigated with the damped molecular dynamics technique. The diffusion coefficients of hydrogen in palladium, as determined from the simulations, are used to construct a useful random-walk model for the calculation of diffusion coefficients.

## 1. Introduction

The equilibrium behaviour of hydrogen in metals is often described by a lattice gas model (Lacher 1937, Hill 1956, 1960, Manchester 1976). In this model the hydrogen atoms are assumed to occupy the interstitial sites in a rigid inert metal lattice. Deviations from the ideal lattice gas model owing to elastic and electronic effects of the interstitial hydrogen atoms on the metal lattice can be accounted for by an effective mean-field hydrogen–hydrogen interaction (Feenstra *et al* 1986). Lattice gas models are also used for the diffusion of hydrogen in metals. The simplest way to calculate the (tracer) diffusion coefficient of a lattice gas is by assuming that the particles make random walks. Fujita and Neugebauer (1988) have proposed a more sophisticated correlated walk model for interstitial diffusion in crystals.

  The objective of this paper is to investigate the validity of the lattice gas description for hydrogen in metals by comparison with computer simulations, which take into account the full interatomic potentials.

  Recently Gillan (1986) proposed a simulation model for hydrogen in palladium and solved it by the molecular dynamics technique. In the temperature range $500 \text{ K} < T < 1000 \text{ K}$, where quantum tunnelling is expected to be of minor importance, Gillan could reproduce experimental diffusion coefficients well but could not reproduce the van Hove correlation function as determined by quasi-elastic neutron scattering. This discrepancy was attributed by Culvahouse and Richards (1988) to the form of the palladium–hydrogen potential.

  Instead of attempting to improve on the potentials, this paper is concerned with the comparison of the molecular dynamics solution of Gillan's simulation model with the lattice gas approximation of this model.

  In § 2 of this paper the details of the molecular dynamics simulations are given. In § 3 the equilibrium site occupations of hydrogen in palladium, as determined by the

**Table 1.** Parameters of the palladium–palladium potential (1).

| | | | |
|---|---|---|---|
| $A_0$ (eV) | 345.5856 | $A_4$ (eV) | −129.0614 |
| $A_1$ (eV) | −247.5615 | $A_5$ (eV) | 25.393 65 |
| $A_2$ (eV) | −204.0164 | $A_6$ (eV) | −1.907 044 |
| $A_3$ (eV) | 292.8391 | $r_0$ (Å) | 3.305 |

simulations, are compared with the values according to the lattice gas model. This section includes a discussion of hydrogen in palladium alloys, in terms of the simulation model. In § 4 the validity of the correlated walk lattice gas model mentioned above is investigated for hydrogen in palladium.

## 2. Molecular dynamics method

For completeness the inter-atomic potentials of the simulation model of Gillan (1986) are repeated here. It will be shown also that the simulations performed in this work yield diffusion coefficients of hydrogen in palladium in agreement with the values reported by Gillan.

### 2.1. Potentials

The potential between the palladium atoms is given by a polynomial which reproduces the phonon dispersion relations of palladium:

$$
V_{PdPd}(r) = \begin{cases} \sum_{s=0}^{6} A_s r^s & r < r_0 \\ 0 & r > r_0. \end{cases} \tag{1}
$$

The values of the coefficients $A_s$ and the cut-off radius $r_0$ are given in table 1. In the simulations a Pd lattice of $3 \times 3 \times 3$ unit cells (containing 108 Pd atoms) was used, with periodic boundary conditions and a lattice parameter of $a = 4.077$ Å (which is slightly greater than the experimental value of 3.89 Å) was fixed by the equation $a = \sqrt{2} r_{min}$, where $r_{min}$ is the Pd–Pd distance for which the potential (1) has a minimum (i.e. for which the palladium lattice is in mechanical equilibrium). The palladium–hydrogen interaction, which reproduces the local mode frequency of hydrogen in palladium, is given by

$$
V_{Pd-H}(r) = \begin{cases} A \exp(-r/\rho) & r < r_1 \\ 0 & r > r_1 \end{cases} \tag{2}
$$

with $A = 15.3$ eV, $\rho = 0.5$ Å and $r_1 = 3.8$ Å. Finally the hydrogen–hydrogen potential is arbitrarily set equal to the palladium–hydrogen potential (in order to avoid unphysical clustering effects):

$$
V_{H-H}(r) = V_{Pd-H}(r). \tag{3}
$$

## 2.2. Site energies

There are two types of site where the potential energy of a hydrogen atom in the FCC palladium lattice has a minimum: the octahedral sites and the tetrahedral sites. According to experiment (Nelin 1971) the hydrogen atoms occupy the octahedral sites. One expects that the occupations of octahedral and tetrahedral sites are determined by the site energies. In calculating the site energies, it is important to account for the lattice relaxation. Therefore a site energy is defined as the total energy of the lattice with a single hydrogen atom on the site of interest minus the total energy of the perfect lattice without hydrogen (at temperature $T = 0$). Following Gillan (1986), the site energies are calculated with the technique of damped molecular dynamics (Beeler and Kulcinski 1972), which brings a system to mechanical equilibrium at $T = 0$. We find for the octahedral site energy $\varepsilon_1$ a value of 1.605 eV and for the tetrahedral site energy $\varepsilon_2$ a value of 1.900 eV, in agreement with the values reported by Gillan (the hydrogen potentials in the relaxed lattices are respectively 1.555 eV and 1.811 eV, so that there is a substantial contribution of the Pd–Pd interactions to the site energies).

## 2.3. Diffusion coefficient

Constant-energy molecular dynamics simulations (Heermann 1986) of the model described above have been performed, with 20 H and 108 Pd atoms. 20 H atoms were chosen, instead of a single H atom, in order to increase the statistical accuracy. The Pd lattice of $3 \times 3 \times 3$ unit cells is expected to be large enough to exclude serious size effects on the hydrogen diffusion. The system was started with the Pd atoms on their regular positions and the H atoms randomly distributed over the octahedral sites. An integration time step of $2.61 \times 10^{-15}$ s was used and five simulations of length $1.5 \times 10^4$ steps were performed at temperatures of 535, 648, 791, 911 and 1058 K. The coordinates of the hydrogen atoms, averaged over successive intervals of 10 time steps, were recorded for later determination of various ensemble averages.

The tracer diffusion coefficient $D$ of hydrogen in palladium was determined from the mean square displacement of a hydrogen atom as a function of time. The obtained values are shown in the Arrhenius plot in figure 1, together with the data reported by Gillan (1986) and Culvahouse and Richards (1988) (who also used the model of Gillan). The full straight line is a fit to all the data and the activation energy $E_a$ determined from the slope is 0.30 eV, a value which is close to the difference $\varepsilon_2 - \varepsilon_1$ between the tetrahedral and octahedral site energies of 0.295 eV (see § 2.2). This close agreement seems to be consistent with the fact that most of the hydrogen atoms jump between nearest-neighbour octahedral sites passing through the tetrahedral sites, as was shown clearly by Gillan. It should be noted, however, that the tetrahedral site is not a saddle point but a potential minimum. This means that for a jump a hydrogen atom (or, better, the whole lattice) has to overcome first a high barrier and then a low barrier. From the damped molecular dynamics calculations described in § 2.2 we estimate that the height of the first barrier does not exceed the difference of the tetrahedral and octahedral site energies of 0.295 eV by more than a few hundredths of an electronvolt.

In the real $PdH_c$ system, phase segregation of the hydrogen occurs at temperatures below the critical temperature $T_c$ of 568 K (Feenstra *et al* 1986). In the simulations no indications of phase segregation were observed. In fact, the tracer diffusion coefficient is not affected by the effect of critical slowing down (Völkl and Alefeld 1978) and furthermore is expected to be only weakly dependent on the hydrogen concentration.
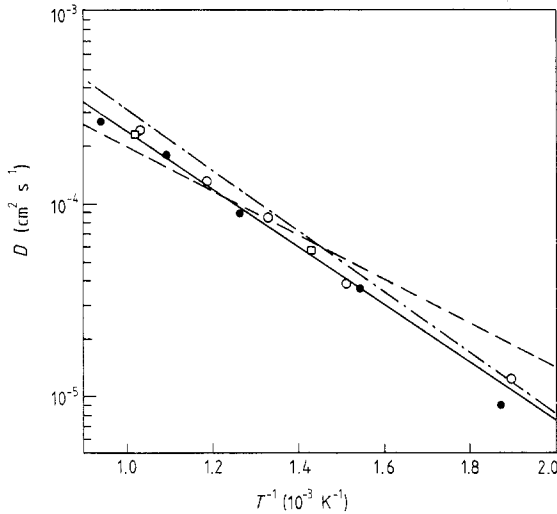
Figure 1. Tracer diffusion coefficient $D$ of hydrogen in palladium from simulations: ●, this work; ○, Gillan (1986); □, Culvahouse and Richards (1988). Also indicated are a fit (——), a model calculation (—·—) (see § 4.3) and a line (— — —) representing the experimental data collected by Völkl and Alefeld (1978).

## 3. Site occupations of hydrogen in palladium

The objective of this section is to determine the validity of the lattice gas approximation for the calculation of the site occupations of hydrogen in palladium.

### 3.1. Lattice gas model for hydrogen in palladium

We construct a lattice gas model for hydrogen in palladium by assuming that a hydrogen atom occupies either an octahedral site or a tetrahedral site and that a site can be occupied by at most one hydrogen atom. Then the total concentration $c$, defined as the number of hydrogen atoms in the lattice divided by the total number of sites, is equal to

$$c = g_1 x_1 + g_2 x_2 \tag{4}$$

where $g_1$ and $g_2$ are the fractions of octahedral and tetrahedral sites, respectively (with $g_1 + g_2 = 1$), and $x_1$ and $x_2$ are the fractional occupations by hydrogen of octahedral and tetrahedral sites, respectively. As an FCC unit cell contains four octahedral sites and eight tetrahedral sites, we have $g_1 = \frac{1}{3}$ and $g_2 = \frac{2}{3}$.

The site occupations $x_1$ and $x_2$ are determined by the minimisation of the free energy $F = U - TS$ of the lattice gas. This leads to

$$\mu_1(x_1, x_2, T) = \mu_2(x_1, x_2, T) \tag{5}$$

where $\mu_1 \equiv (\partial F/\partial N_1)_{T,N_2}$ and $\mu_2 \equiv (\partial F/\partial N_2)_{T,N_1}$ are the chemical potentials of hydrogen atoms at octahedral sites and tetrahedral sites, respectively. In general, lattice gas models with interacting particles are not exactly solvable (note that, in addition to the direct hydrogen–hydrogen repulsion, the lattice relaxation around the hydrogen atoms should be considered as an effective hydrogen–hydrogen interaction, which is the well known elastic interaction of hydrogen in metals). However, if one uses the mean-field
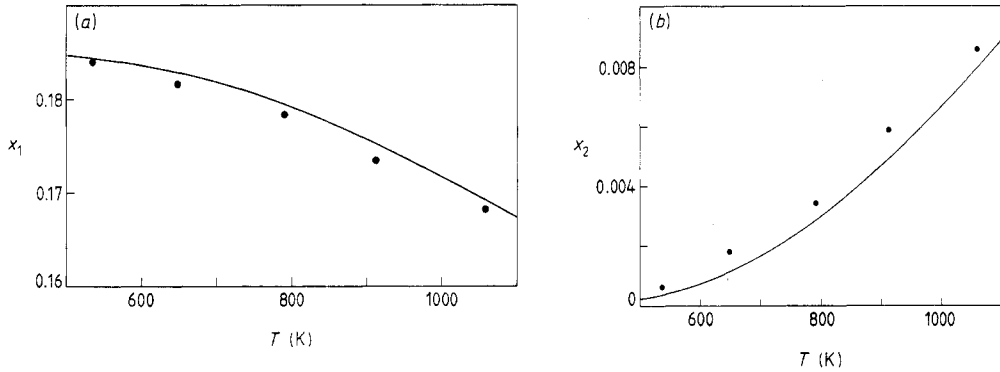
**Figure 2.** Octahedral site occupation $x_1$ and tetrahedral site occupation $x_2$ determined from the simulations (●). The curves correspond to the lattice gas model described in § 3.1.

approximation for the hydrogen–hydrogen interaction, the following expression for the chemical potentials is easily obtained (Griessen 1983):

$$\mu_i(x_1, x_2, T) = \varepsilon_i + f(c) + kT \ln[x_i/(1 - x_i)] \qquad (i = 1, 2) \qquad (6)$$

where the function $f(c)$ (with $f(0) = 0$) represents the effective hydrogen–hydrogen interaction. From equations (5) and (6) it follows that

$$\varepsilon_1 + kT \ln[x_1/(1 - x_1)] = \varepsilon_2 + kT \ln[x_2/(1 - x_2)]. \qquad (7)$$

The site occupations $x_1$ and $x_2$ as a function of the temperature $T$ and the concentration $c$ are determined by equations (4) and (7).

### 3.2. Comparison with the simulations

To determine the site occupations from the molecular dynamics simulations, an octahedral site was defined to consist of the entire octahedral around it, and a tetrahedral site was defined to consist of the entire tetrahedron around it. The faces limiting the octahedra and tetrahedra were defined in the perfect palladium lattice by the positions of the palladium atoms. In this way a hydrogen atom is always located at a site, and it is straightforward to evaluate the site occupations $x_1$ and $x_2$ from the simulations. Note that the total number of sites in the simulations is $12 \times 27$, so that the concentration $c$, as defined in the previous section, is 0.061 73.

In figure 2 the site occupations $x_1$ and $x_2$ as determined from the simulations are compared with the values according to the lattice gas model (i.e. equations (4) and (7)). The agreement is reasonable. Note that at $T = 1000$ K the number of hydrogen atoms at tetrahedral sites is about 10% of the number of hydrogen atoms at octahedral sites. Below $T \simeq 600$ K the occupation of the tetrahedral sites is almost negligible.

### 3.3. Hydrogen in palladium alloys

For the calculation of the solubility of hydrogen in palladium and palladium alloys, one usually neglects the tetrahedral site occupation and uses a mean-field lattice gas model for the chemical potential of hydrogen at the octahedral sites. For hydrogen in a
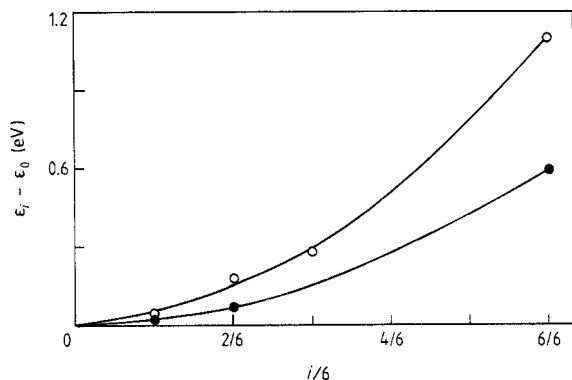
**Figure 3.** Experimentally determined site energies $\varepsilon_i$ of hydrogen in $Pd_{6-i}Ag_i$ and $Pd_{6-i}Cu_i$ octahedra in $Pd_{1-y}Ag_y$ (○) and $Pd_{1-y}Cu_y$ (●) alloys, respectively (Salomons *et al* 1989). The curves are guides to the eye.

disordered substitutional $Pd_{1-y}M_y$ alloy (M $\equiv$ metal) there are different types of octahedral site. If one assumes that an octahedral site energy is determined only by the numbers of Pd atoms and M atoms in the octahedron, there are seven different types of octahedral site: $Pd_6$, $Pd_5M_1$, . . . , $M_6$. The mean-field lattice gas model for H in Pd can then be generalised for H in $Pd_{1-y}M_y$ with octahedral site energies $\varepsilon_i$ and octahedral site fractions $g_i$ (the index $i$ denotes the number of M atoms in the octahedron). The fractions $g_i$ are determined by the random distribution of the metal atoms (assuming that the effect of short-range order in the alloy is negligible). By fitting this generalised model to solubility data of hydrogen in $Pd_{1-y}Ag_y$ and $Pd_{1-y}Cu_y$ alloys the site energies $\varepsilon_i$ were determined (Salomons *et al* 1989). It was found that the differences $\varepsilon_i - \varepsilon_0$ are approximately independent of the solute content $y$, within experimental accuracy. In figure 3 the differences $\varepsilon_i - \varepsilon_0$ are plotted as a function of $i$, for $Pd_{1-y}Ag_y$ and $Pd_{1-y}Cu_y$. Obviously the site energy $\varepsilon_i$ is not a linear function of the index $i$. In this section we wish to investigate whether this non-linear behaviour can originate from the effect of lattice relaxation.

As the inter-atomic interactions in the pure metals Pd, Ag and Cu are all rather similar functions of the inter-atomic distance (van Heugten 1979), one expects that the variation in the site energies $\varepsilon_i$ shown in figure 3 originates mainly from the metal–hydrogen inter-atomic interactions. Therefore we repeated the damped molecular dynamics calculations with a single hydrogen atom at an octahedral site (see § 2.2), with the following modification: we replaced a number $i$ ($i = 1, 2, . . . , 6$) of the six nearest-neighbour palladium–hydrogen potentials by a different solute–hydrogen potential $V(r) = A \exp(-r/\rho)$ (but with the same cut-off radius). In the cases where two different arrangements of the solute atoms in the octahedron are possible (this is the case for $i = 2, 3$ and 4) the site energy was determined by averaging with weight factors determined by the random distribution of metal atoms.

Instead of trying to determine the parameters $A$ and $\rho$ of the solute–hydrogen potential $V(r)$ by fitting to a vibrational frequency or by calculation, we just investigated two possibilities. First we set $V(r)$ equal to the palladium–hydrogen potential (2) multiplied by a factor of 1.6 (this potential is represented by curve B in figure 4). This resulted in the site energies $\varepsilon_i$ represented by the open circles in figure 5. Next the potential $V(r)$ represented by curve C in figure 4 was used, which resulted in the site energies $\varepsilon_i$ represented by the full circles in figure 5. Only in the latter case does $\varepsilon_i$ as a function of $i$ show a curvature comparable with the experimentally observed curvature (figure 3).
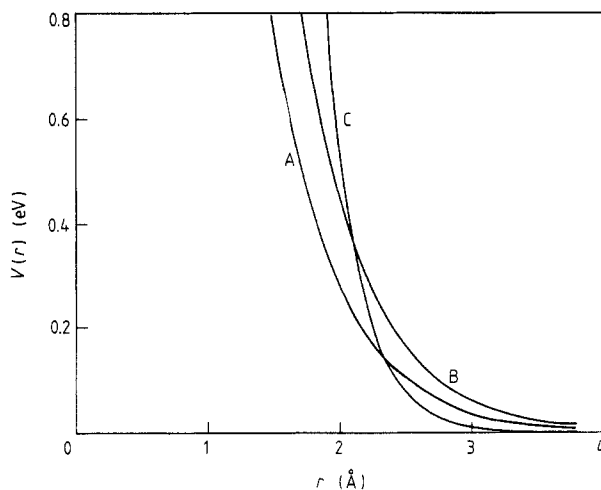
**Figure 4.** Metal–hydrogen potentials $V(r) = A \exp(-r/\rho)$: curve A, $A = 15.3$ eV, $\rho = 0.5$ Å (palladium–hydrogen); curve B, $A = 24.48$ eV, $\rho = 0.5$ Å; curve C, $A = 1606.5$ eV, $\rho = 0.25$ Å.
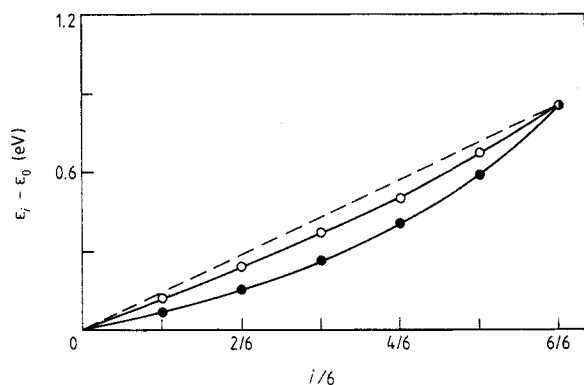


**Figure 5.** Octahedral site energies $\varepsilon_i$ of hydrogen in a $Pd_{1-y}M_y$ alloy, with the potentials from curve B ($\bigcirc$) and curve C ($\bullet$) in figure 4 used for the M–H potential: — — —, the situation if no lattice relaxation occurs.

The origin of the curvature in figure 5 can be understood as follows. If one palladium atom in the octahedron is replaced by a solute atom with a more repulsive metal–hydrogen potential, the lattice relaxes in such a way that the hydrogen atom is more distant from the solute atom than from the palladium atoms, thereby minimising the increase in site energy (the off-centre displacement of a hydrogen atom was found to be of the order of 0.1 Å). This relaxation is more difficult if more palladium atoms are replaced by solute atoms.

It should be noted that only the form of the metal–hydrogen potential $V(r)$ for $r > 2.04$ Å (2.04 Å is the unrelaxed metal–hydrogen distance) affects the lattice relaxation. As the curves A and C in figure 4 are not unrealistically different from each other for $r > 2.04$ Å, we conclude that it is possible that the non-linear behaviour of the site energies $\varepsilon_i$ as a function of $i$ for $Pd_{1-y}Ag_y$ and $Pd_{1-y}Cu_y$ alloys originates from lattice relaxation.

## 4. Diffusion of hydrogen in palladium

The objective of this section is to compare the diffusion coefficients determined from the simulations (figure 1) with the predictions of a lattice gas model. Instead of using the conventional random-walk model we decided to use the sophisticated correlated walk model of Fujita and Neugebauer (1988).

### 4.1. Correlated walk model

In the random-walk model a particle jumps between nearest-neighbour sites of a lattice at discrete times $t = n\tau$ ($n = 1, 2, \ldots$). In the model of Fujita and Neugebauer (1988) the particle may also remain stationary at a site instead of making a jump, and furthermore the direction of a jump may depend on the direction of the previous jump. For a walk on an FCC lattice the model prescribes the following rules (Okamura *et al* 1980). If the particle arrives at a site at time $t = n\tau$, it may jump at time $t = (n + 1)\tau$ in the same direction as that of the previous jump with probability $\alpha$, turn at 60° with probability $\delta$ (there are four possibilities to turn at 60°), turn at 90° with probability $\gamma$ (two possibilities), turn at 120° with probability $\varepsilon$ (four possibilities), turn at 180° with probability $\beta$, or it may become trapped (i.e. remain at the site) with probability $\sigma$. The following normalisation condition holds:

$$\alpha + 4\delta + 2\gamma + 4\varepsilon + \beta + \sigma = 1. \tag{8}$$

If the particle is trapped at time $t = n\tau$, it may jump at time $t = (n + 1)\tau$ in any direction with probability $\mu$, or remain trapped with probability $\sigma'$, with the following normalisation condition:

$$12\mu + \sigma' = 1. \tag{9}$$

The tracer diffusion coefficient $D$ for this model is given by (Okamura *et al* 1980)

$$D = \tfrac{1}{6}[(1 + \Delta)/(1 - \Delta)]\{1/[1 + \sigma(1 - \sigma')^{-1}]\}(a_0^2/\tau) \tag{10}$$

with $\Delta \equiv \alpha + 2\delta - 2\varepsilon - \beta$ and $a_0$ the jump distance. For the jump distance of hydrogen in palladium we take the geometrical distance between two neighbouring octahedral sites, although the real jump path is slightly longer (about 25%). The factor $(1 + \Delta)/(1 - \Delta)$ is a correlation factor, which is unity for a random walk. The jump time $\tau$ is given by (Fujita and Neugebauer 1988)

$$\tau = a_0/v \tag{11}$$

where $v = g(2kT/\pi m)^{1/2}$ is the average speed of a jumping particle, with $m$ its mass and $g$ a numerical factor which varies between 1 and 3 if the activation energy varies between 0 and 11 $kT$. We take $g = 2$.

### 4.2. Comparison with the simulations

For the comparison of the correlated walk model with the simulation model we define the jump correlation function $g(t')$ as the probability per unit time that a particle (hydrogen atom), which made its last jump at time $t = 0$, makes a jump at time $t = t'$ (in any direction).

It is straightforward to determine the jump correlation function from the simulations. A jump is said to take place at the moment that a hydrogen atom enters a new octahedron.
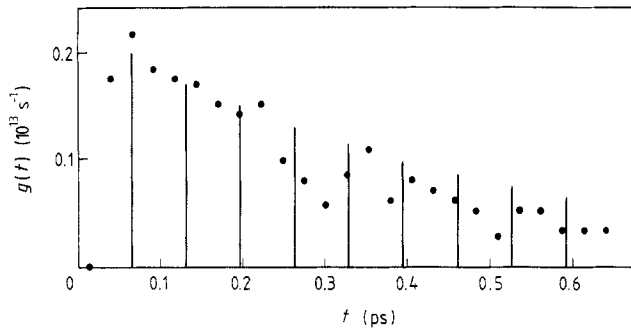
**Figure 6.** The jump correlation function $g(t)$ determined from the simulation at $T = 911$ K (●) and according to the correlated walk model with $\sigma = \sigma' = 0.87$.

In figure 6 the jump correlation function as determined from the simulation at $T = 911$ K is represented by the full circles (in total, 831 nearest-neighbour jumps were registered in this simulation).

According to the correlated walk model the jump correlation function $g(t)$ is not a continuous function of time, as a particle can jump only at discrete times $t = n\tau$ ($n = 1, 2, \ldots$). Hence $g(t)$ is a sum of $\delta$ functions:

$$g(t) = (1 - \sigma)\delta(t - \tau) + \sum_{n=2}^{\infty} \sigma(1 - \sigma')\sigma'^{n-2}\delta(t - n\tau) \tag{12}$$

as follows from the definition of the probabilities $\sigma$ and $\sigma'$. For the comparison with the jump correlation function determined from the simulations, the $\delta$ functions are smeared out over time intervals with width $\tau$ and centred at $t = n\tau$ ($n = 1, 2, \ldots$). This leads to

$$g(t) = \begin{cases} (1 - \sigma)/\tau & \text{for } \frac{1}{2}\tau < t < \frac{3}{2}\tau \\ \sigma(1 - \sigma')\sigma'^{n-2}/\tau & \text{for } (n - \frac{1}{2})\tau < t < (n + \frac{1}{2})\tau \qquad (n = 2, 3, \ldots). \end{cases} \tag{13}$$

The best fit of equation (13) to the jump correlation function determined from the simulations was obtained for $\sigma = \sigma' = 0.87$. For clarity this fit is shown in figure 6 as a set of peaks located at $t = n\tau$ ($n = 1, 2, \ldots$). Note that the conventional random-walk model predicts a single peak located at $t = 0.78$ ps (as follows from the random-walk formula $D = a_0^2/6\tau$ and the value of $D$ at $T = 911$ K).

It is surprising that the best fit is obtained for $\sigma = \sigma'$. One would expect that $\sigma' > \sigma$, since a trapped hydrogen atom is expected to have a larger probability of remaining trapped than a jumping hydrogen atom. A possible explanation of the equality $\sigma = \sigma'$ is that a jumping hydrogen atom does not lose its excess kinetic energy immediately after trapping but rather loses it during several vibrational periods (a vibrational period is of the order of 0.06 ps). This means that the probability of remaining trapped increases slowly with increasing residence time of a hydrogen atom at a site and that the fitted values $\sigma = \sigma' = 0.87$ represent the probability of remaining at a site averaged over the residence time.

The fact that the probability $\sigma$ of remaining at a site is close to unity implies that the correlation factor $(1 + \Delta)/(1 - \Delta)$ in equation (10) is close to unity, as can be seen as follows. Equation (8) and $\sigma = 0.87$ imply that $\alpha$, $\beta$, $\gamma$, $\delta$, $\varepsilon \ll 1$. Hence $\Delta \ll 1$ and $(1 + \Delta)/(1 - \Delta) \simeq 1$.

The fitted values $\sigma = \sigma' = 0.87$ imply that the jump probability is $1 - \sigma = 0.13$ at $T = 911$ K. This jump probability is about twice the equilibrium probability $g_2 x_2/c$ that a hydrogen atom is located in a tetrahedron (see § 3). This can be understood by the fact that a jumping hydrogen atom spends about half of the jump time in a tetrahedron and half of the jump time in an octahedron.

It should be noted that Culvahouse and Richards (1988) have made a more accurate fit to the jump correlation function of the simulation model. The reason why we have performed the above-described fit is that we wanted to construct a simple model for the diffusion coefficient, which is described in the next section.

### 4.3. A random-walk model for the diffusion coefficient without fitted parameters

Let us now use the information obtained in the previous section to construct a simple random-walk model for the diffusion coefficient of hydrogen in palladium (or more general, in an FCC metal). We start from equation (10) and use

$$(1 + \Delta)/(1 - \Delta) = 1 \tag{14}$$

and

$$\sigma = \sigma'. \tag{15}$$

It follows that

$$D = \tfrac{1}{6}(1 - \sigma)(a_0^2/\tau) \tag{16}$$

in which the jump probability $1 - \sigma$ is given by

$$1 - \sigma = 2g_2 x_2/c \tag{17}$$

and $\tau$ is given by equation (11). The tetrahedral site occupation $x_2$ is determined by equations (4) and (7).

In figure 1 we show the comparison of the diffusion coefficient according to equation (16) with the values determined from the simulations. The agreement is satisfactory. It should be noted that the objective was to compare the diffusion coefficient according to the lattice gas model with the values determined from the simulations (and not with the experimental data for the real PdH$_c$ system). Finally, for $c \to 0$, equation (16) reduces to the following Arrhenius form:

$$D = \tfrac{2}{3}(a_0^2/\tau) \exp[-(\varepsilon_2 - \varepsilon_1)/kT]. \tag{18}$$

For the concentration $c = 0.061\,73$ used in the simulations this expression yields values which differ less than 20% from the values according to equation (16).

It should be noted that in this form the model cannot explain the reversed isotope effect of hydrogen diffusion in palladium. This would require the introduction of the zero-point energy of a hydrogen atom (Fujita 1989).

### 5. Conclusions

It has been shown that a mean-field lattice gas model predicts the equilibrium octahedral and tetrahedral site occupations of hydrogen in palladium reasonably well. This justifies the lattice gas description of the equilibrium behaviour of hydrogen in palladium, or

more general in FCC metals. It would be interesting to use the simulation model of Gillan for a sensitive test of the mean-field approximation for the effective hydrogen–hydrogen interaction. Such a test would be rather difficult, however, since a mean-field interaction has an infinite range, so that a large lattice should be used for the simulation. Furthermore, the effective hydrogen–hydrogen interaction in palladium contains an electronic band-filling effect (Feenstra *et al* 1986) not accounted for by the simulation model.

The diffusion coefficient of hydrogen in palladium has been compared with the predictions of the correlated walk model of Fujita and Neugebauer (1988). It turned out that this model reduces in good approximation to a simple random-walk model for hydrogen in palladium. For the calculation of diffusion coefficients this random-walk model is rather useful, since it does not contain a vibrational frequency as a fit parameter (as in conventional diffusion models (see, e.g., Murch and Thorn 1977)).

## Acknowledgments

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