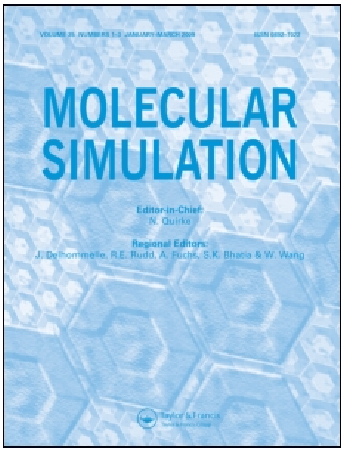

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Muranaka, Tadashi , Uehara, Kentarou , Takasu, Masako and Hiwatari, Yasuaki(1994) 'Molecular Dynamics Study of the Diffusion of Hydrogen in Solid Palladium', Molecular Simulation, 12: 3, 329 — 341

To link to this Article: DOI: 10.1080/08927029408023041

URL: http://dx.doi.org/10.1080/08927029408023041

Molecular Simulation, 1994, Vol. 12(3-6), pp. 329-341
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MOLECULAR DYNAMICS STUDY OF THE DIFFUSION OF HYDROGEN IN SOLID PALLADIUM

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(Received 28 April 1993, accepted 24 May 1993)

The diffusion of hydrogen atoms in solid palladium is studied via a molecular dynamics simulation. In this calculation, the palladium atoms are fixed on the sites of the fcc lattice and the hydrogen atoms are initially put on the O (octahedral) sites. Through the present molecular dynamics simulation, the diffusion constant and activation energy are calculated for several different concentrations of hydrogen atoms. We find that the hydrogen atoms show jump motions between the O sites which lead to super diffusion in the solid palladium. We have also obtained the temperature dependence and concentration dependence of the vacancy factor and jump correlation functions.

1 INTRODUCTION

The diffusion of hydrogen atoms in solid palladium (Pd) attracted much attention [1-7], not only because of interest of the properties of the material such as super diffusion in a solid state, but also because of studying a problem of room-temperature nuclear fusion in recent experimental reports [8]. At a relatively low temperature, the system undergoes a phase transition into a superconductive phase [9, 10]. At a room temperature, the palladium lattice positively effects on bringing a hydrogen-atom pair to a closer distance [8]. In similar reasons, various experimental techniques such as a temperature gradient method [11] have also been used to increase the number of hydrogen atoms per a Pd atom.

In this paper, we study, via a classical molecular dynamics simulation, the nature of super diffusion as well as the static structures of hydrogen atoms in a solid palladium fixed on an face-centered cubic (fcc) lattice. In the present calculation, we have used the effective pair potentials for a couple of hydrogen atoms and for a pair of palladium-hydrogen atoms computed by Ichimaru *et al.* [5, 6], using a perturbation theory. The brief account of this research was previously reported in [12]. The model which we have used in the present simulation is described in Section 2. The results of the molecular dynamics simulation are shown in Section 3. Discussions and future problems are given in Section 4.

Table 1 Parameters used for V_{H-H}.

x	a ($\AA^{-1}$)	p_1	d_1 ($\AA$)	p_2	d_2 ($\AA$)	c_1 (eV)	c_2 ($\AA^{-2}$)	c_3 ($\AA$)
0.1	1.400	−0.277	0.047	—	—	—	—	—
0.2	5.150	−1.060	0.058	—	—	0.14	4.0	1.85
0.3	5.560	−0.926	0.081	3.0	0.2	0.08	4.0	1.80
0.4	6.950	−1.920	0.195	3.0	0.2	0.05	4.0	1.90
0.5	14.10	−6.810	0.257	5.0	0.4	0.03	4.0	1.90

2 MODEL AND MOLECULAR DYNAMICS SIMULATIONS

Our model consists of palladium atoms fixed on an fcc lattice and mobile hydrogen atoms under the following screened Coulombic potential [6].

$$V_{Pd-H}(eV) = \left(\frac{22.2}{r(\AA)}\right)\exp(-r(\AA)/0.42) \tag{1}$$

For the effective pair potential between hydrogen atoms, we have used the following function, which was obtained by Ichimaru *et al.* [6] based on the perturbation theory and taking into consideration the screening effect by conduction electrons:

$$V_{H-H} = \frac{e^2}{\varepsilon_c r}(d_1/r)^{p_1}\exp(-ar)\left[1 + \left(\frac{d_2}{r}\right)^{p_2}\right] + c_1\exp[-c_2(r-c_3)^2] \tag{2}$$

Values of the potential parameters used in the present work are summarized in Table 1. $\varepsilon_c = 1.25$ [c.g.s. esu]. Figure 1 shows the fcc structure for the palladium atoms, in which the octahedral (O-) and tetrahedral (T-) sites are defined.

In the present molecular dynamics simulation, the Verlet algorithm is used, together with Nosé's constant temperature techniques [13]. Initially (at $t = 0$), the hydrogen atoms were randomly distributed on the O-sites with velocities following the Maxwell distribution. The concentration of the hydrogen atoms, x, in the present computation is chosen to be 0.1, 0.3, and 0.5 and the temperature to be $T = 600$, 900 and 1200 K. The time mesh Δt is chosen to be $\Delta t = 2.0 \times 10^{-4}$ psec, which is approximately as small as 1/100 of a typical period of the vibrations of hydrogen at an O-site. The system size which we have used in the present molecular dynamics simulations is $7 \times 7 \times 7$ or $10 \times 10 \times 10$ in the unit of the lattice constant a_0. The periodic boundary condition was used as usual. The total time steps of the molecular dynamics runs are in a range of around 10^6 to 2×10^6.

3 RESULTS

In Figure 2, is shown the density profile of the hydrogen atoms at $T = 600$ K and $T = 1200$ K. At $T = 600$ K, the hydrogen atoms appear to be localized around the O-sites, and slightly around the T-sites. On the other hand, at an elevated temperature $T = 1200$ K, the hydrogen atoms are clearly delocalized. Since the density at the area between two adjacent O-sites is relatively low, one can expect that the hydrogen atoms diffuse from one O-site to another O-site through the T-sites.

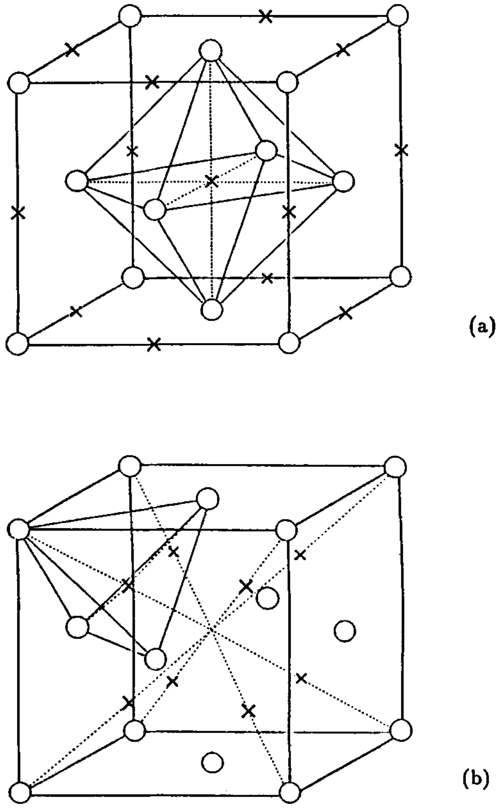

Figure 1 Pd atoms (denoted by O) on the fcc lattice and interstitial sites (denoted by x), (a) octahedral sites and (b) tetrahedral sites.

The Fourier transform of the velocity auto-correlation function, $\tilde{Z}(\omega)$, is shown in Figure 3. The average frequency obtained from the simulation is 16.3 THz, which is consistent with the experimental value of 15.9THz [14]. This is not surprising, since the potential between a palladium atom and a hydrogen atom was determined by the curvature of the potential at the O-site. When the temperature becomes higher, $\tilde{Z}(\omega)$ spreads to a broader frequency range.

Examples of trajectories of the hydrogen atoms in the solid palladium are displayed in Figure 4(a). The hydrogen atom vibrates around one of the O-sites, and occasionally jumps to a near-neighbour O-site. In the trajectories shown in A, B and C, each hydrogen atom clearly shows repeats of 'stay' around one of the O-sites and "jump"; there are twice in A, three times in B, and four times in C. The square displacement $\Delta r^2(t)$ for the trajectory C is shown in Figure 4(b). Clear jumps of the hydrogen atoms are seen in this figure. It turns out that the hydrogen atom makes a zig-zag path going from an O-site to another O-site, occasionally passing through T-sites.

The diffusion constant of hydrogen is plotted in Figure 5. The higher the temperature becomes, the larger the diffusion constant D becomes, as it is expected.

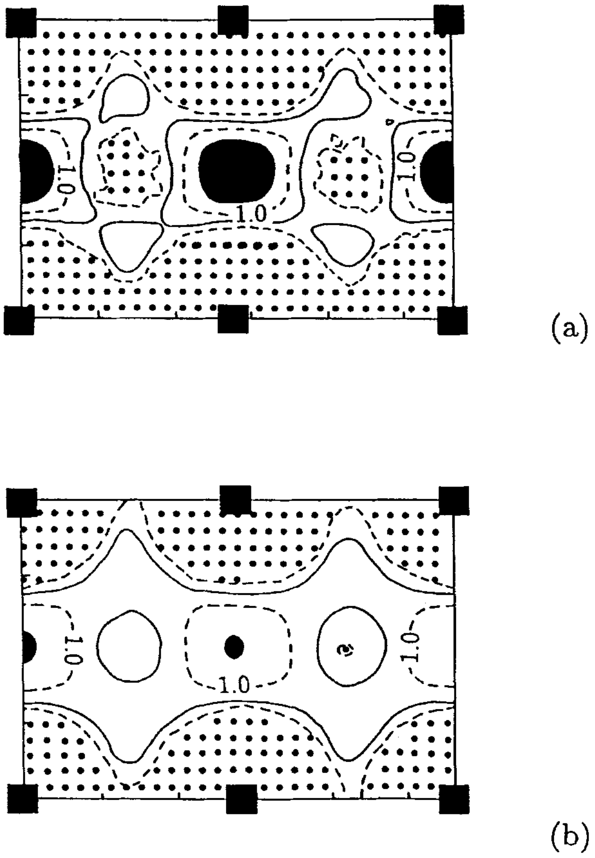

Figure 2 Density profile of H atoms on (110) plane with thickness 0.1333 Å at (a) $T = 600$ K and (b) $T = 1200$ K. The solid squares denote the positions of Pd. The density of the hydrogen atoms is the lowest in the region denoted by small solid circles, and the highest at the black regions.

The dependence on x shows nonmonotonic behaviour: at $x = 0.3$, the diffusion is slower than the cases $x = 0.1$ and $x = 0.5$. At low temperatures, larger x inhibits the diffusion of hydrogen, thus the plot $D(x)$ tends to be a decreasing function of x. At high temperatures, if x is large, the hydrogen atoms collide to each other, which may lead to an increase of diffusion. At intermediate temperatures, these two effects compete, and we obtain $D(x)$ with a minimum at a certain x.

The temperature dependence of D is shown in Figure 6(a). It turns out that the plots follow a well-known Arrhenius behaviour;

$$D = D_0 \exp(-E_a/k_B T). \tag{3}$$

The activation energy E_a calculated from each slope of different x is shown in Figure 6(b) as a function of x. By fitting the data in Figure 6(b) to a straight line, we obtain,

$$E_a(x) = 0.167x + 0.335. \tag{4}$$

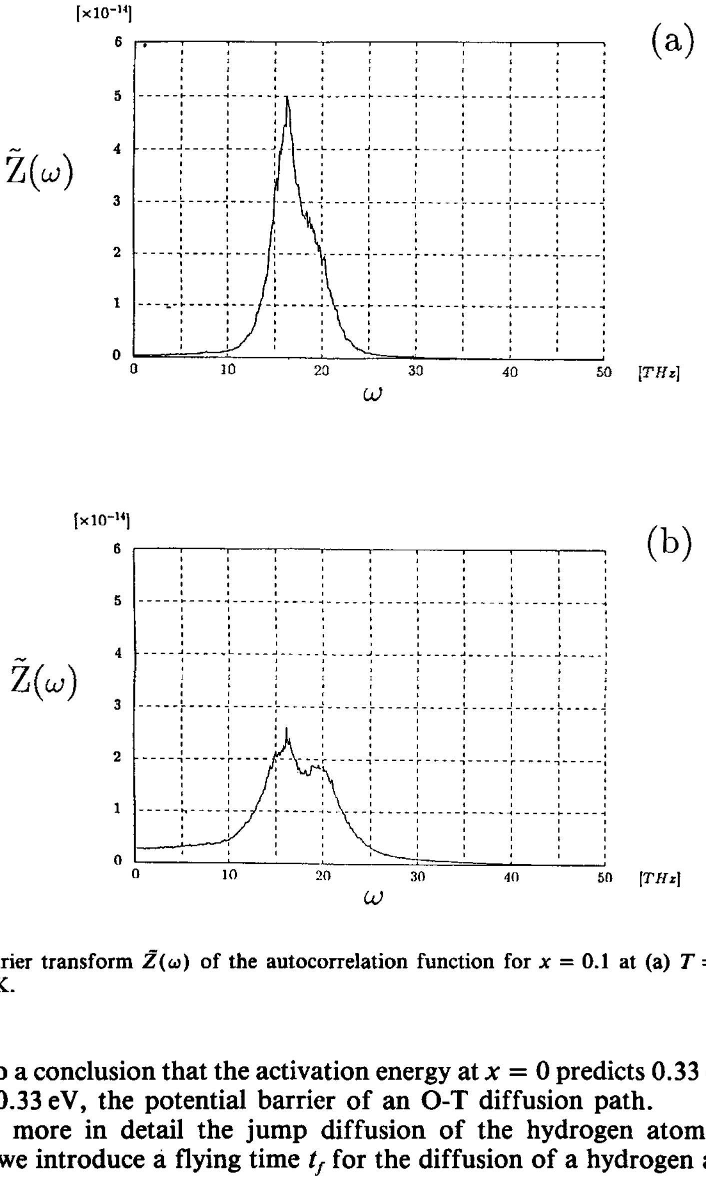

Figure 3 Fourier transform $\tilde{Z}(\omega)$ of the autocorrelation function for $x = 0.1$ at (a) $T = 600\,\mathrm{K}$ and (b) $T = 1200\,\mathrm{K}$.

This leads to a conclusion that the activation energy at $x = 0$ predicts 0.33 eV, which is close to 0.33 eV, the potential barrier of an O-T diffusion path.

To study more in detail the jump diffusion of the hydrogen atoms in solid palladium, we introduce a flying time t_f for the diffusion of a hydrogen atom; this means a time interval, in an average sense, for which the hydrogen atom is displaced from any O-site and its neighbour, as defined just below. As a reasonable size (region) of each O-site, here is used a sphere of radius R_0, where R_0 is half the O-T distance: $R_0 = \sqrt{3}/8\,a_0$. As we can see in Figure 7, t_f shows a weak dependence on R, when $R/R_0 = 0.6 \sim 1.2$. Thus, it is reasonable to choose $R = R_0$ in our calculations.

With introduction of R mentioned above, we define a "jump" of the mobile atoms by a movement from one O-site region to another. In Figure 8, is plotted the jump frequency Γ as a function of the inverse temperature. An Arrhenius behaviour is

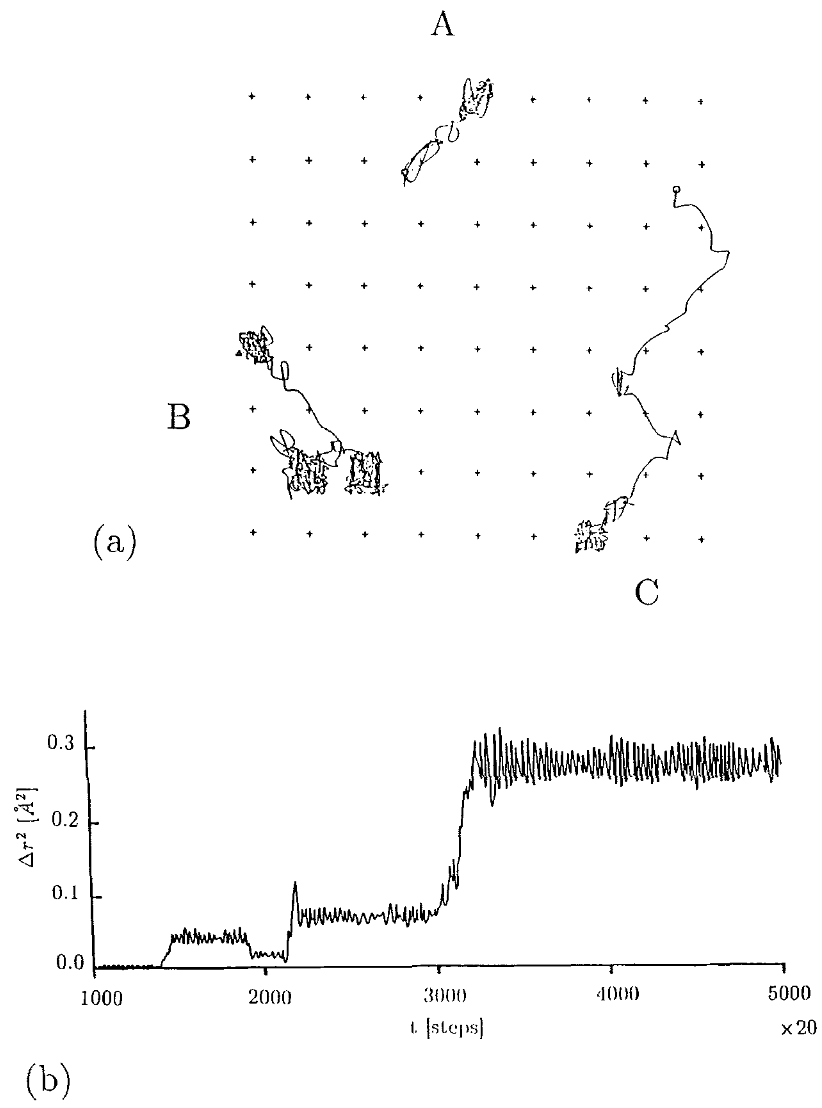

Figure 4 (a) Trajectory of H atoms projected to (110) plane for $x = 0.1$, $T = 1200$ K. + denotes Pd atoms. (b) Time dependence of the square displacement of the trajectory C.

again obtained for the temperature dependence of the jump frequency, similar to the behaviour of the diffusion constant.

Figure 9 shows the jump correlation function $g(t)$ [3], where $g(t)dt$ is a probability for a mobile atom to make a jump at the time interval between t and $t + dt$ after it made a jump and enters the O-site region at $t = 0$. In Figure 9(a), we see that as the temperature becomes higher, the peak of $g(t)$ slightly shifts to a shorter time. At $T = 600$ K, $g(t)$ has two peaks. This indicates a significantly different behaviour from the behaviours at higher temperatures. $g(t)$ is also plotted in Figure

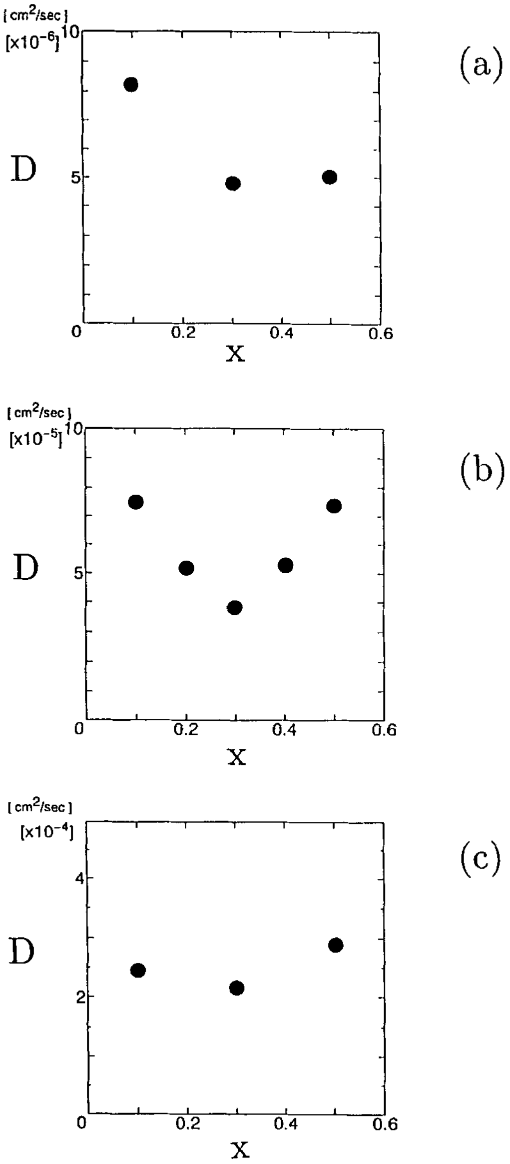

Figure 5 Diffusion constant of hydrogen as a function of concentration x for (a) $T = 600$ K, (b) $T = 900$ K and (c) $T = 1200$ K.

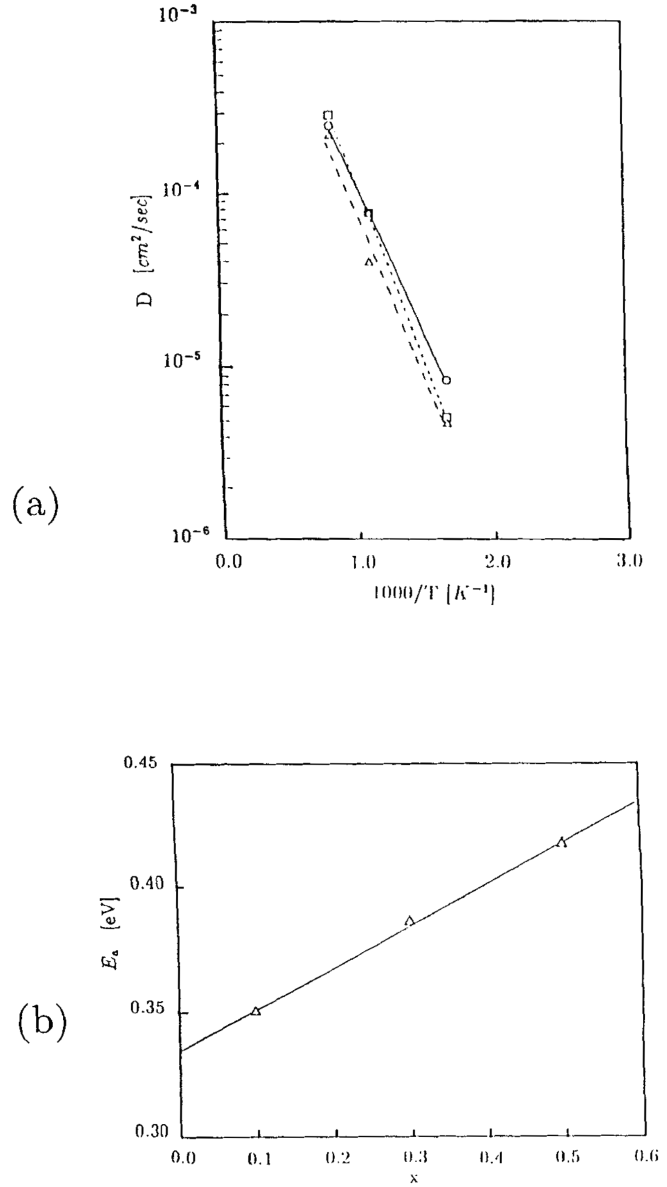

Figure 6 (a) Diffusion constant as a function of the inverse temperature for $x = 0.1$ (○), 0.3 (△), and 0.5 (□). (b) Activation energy obtained from (a).

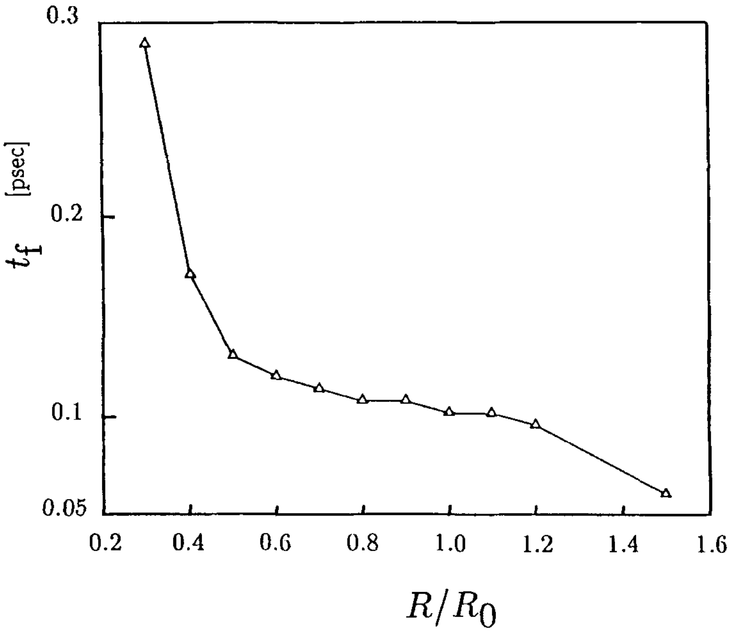

Figure 7 Flying time t_f as a function of a site radius R for $x = 0.1$ and $T = 900$ K.

9(b) for different concentrations at $T = 1200$ K. The position of the peak is about the same for $x = 0.1$ and $x = 0.3$. However, the peak shifts to a shorter time and a long-time tail appears more clearly for $x = 0.5$. The result may slightly be changed in such calculation by taking into consideration the probability that some hydrogen atoms stay all the time at O-sites, which was neglected in the present simulation. The peak is highest for $x = 0.1$ and lowest for $x = 0.5$, whereas, in the plot of diffusion constant in Figure 5 (c), the case of $x = 0.5$ gave the fastest diffusion. This suggests that, for $x = 0.5$, although an individual hydrogen atom stays longer at an O-site, it makes another hydrogen atom to jump. To investigate the hydrogen-atom coexistence in an O-site, we calculated the radial distribution function and the vacancy factor.

The radial distribution function $R(r)$ is plotted in Figure 10 for $T = 1200$ K with two different concentrations $x = 0.1$ and $x = 0.5$. For $= 0.5$, there is a peak around 1 Å. This suggests that two hydrogen atoms are in the same O-site region, when the concentration is as high as $x = 0.5$ and more.

Let us define the vacancy factor V [15] by the average ratio of the number of hydrogen atoms found in the O-site region in a snapshot of configurations. Results obtained are shown in Figure 11. If the interactions between atoms are negligibly small, V follows a straight line, namely $V = 1 - x$. For repulsive interactions, V lies above this line, while for attractive interactions V lies below it. The present results, as shown in Figure 11, suggest repulsive interactions. This also predicts that the effective repulsion becomes larger for lower temperatures and for higher concentrations.

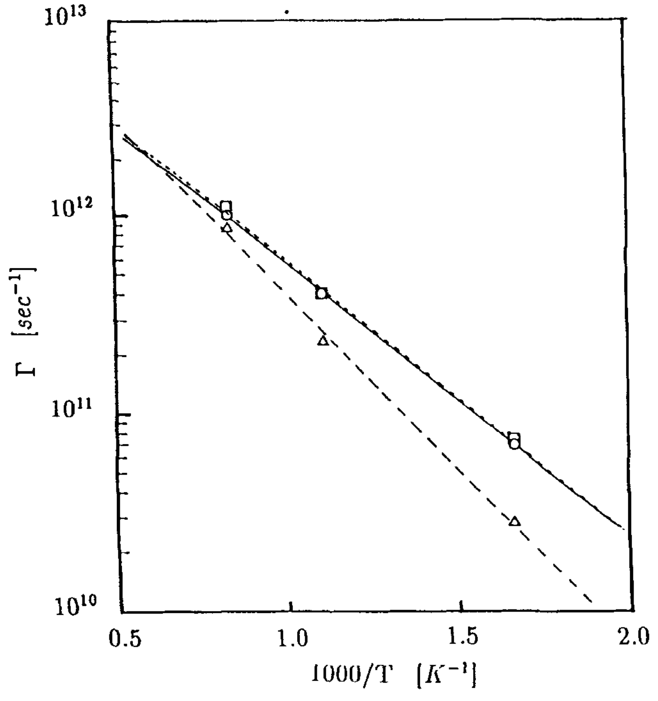

Figure 8 Jump frequency Γ of the hydrogen atoms as a function of the inverse temperature for $x = 0.1$ (○), 0.3 (△), and 0.5 (□).

4 DISCUSSION

We have investigated the diffusion of hydrogen, which is known as superdiffusion, with the fixed palladium lattice model. The hydrogen atoms stay around the O-sites and occasionally make them jump to other near-neighbour O-sites. Such jump diffusion is not specific to the present model, but has recently been found rather popular in various amorphous systems such as a supercooled liquid of the binary soft-sphere mixtures [16] or a solid superionic conductor of the $\alpha - Ag_2Te$ [17].

Both the concentration- and temperature- dependence of the diffusion constant are very much of interest. The present molecular dynamics simulation suggests that, at low temperatures, the diffusion becomes larger for lower concentrations, while at high temperature, it becomes contrary, that is, the diffusion becomes larger for higher concentrations.

The hydrogen-hydrogen potential that we have used in the present calculation becomes unreliable at high x because of the perturbation theory on which the calculation of the interactions are based. Thus, our result for high concentrations may not be reliable.

The present calculation is essentially based on a classical model. Classical treatment is valid when $T \gg \hbar\omega_D$ and $T \gg \hbar\nu$, where ω_D is the Debye temperature and ν is the localization frequency of the hydrogen atoms. According to the

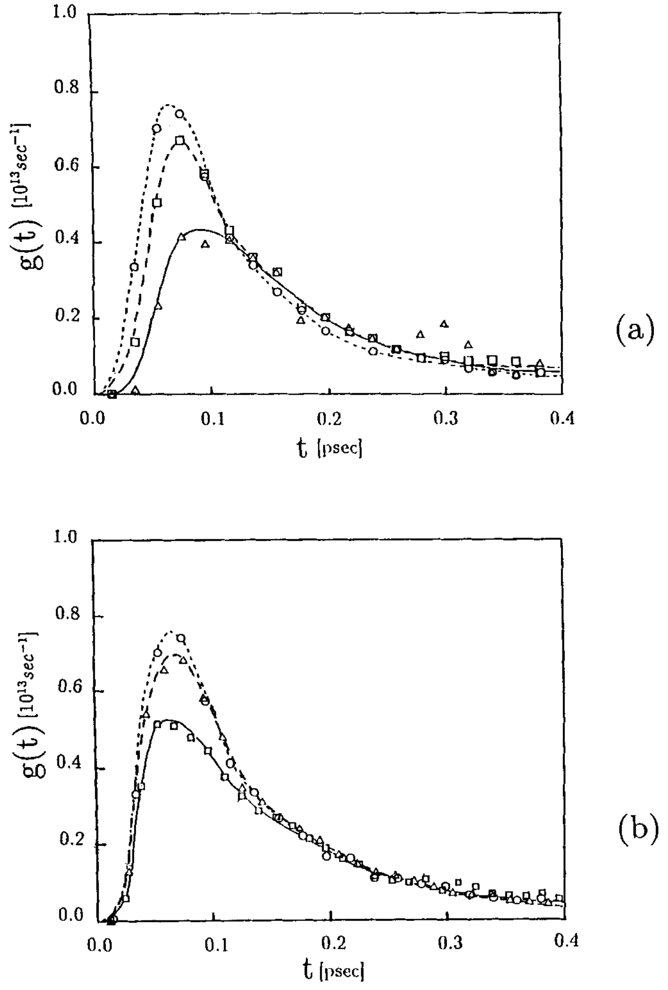

Figure 9 Jump correlation function $g(t)$ for (a) $x = 0.1$ ($T = 600$ K: △, 900 K: □, 1200 K: ○.) (b) T = 1200 K ($x = 0.1$: ○, $x = 0.3$: △, $x = 0.5$: □.)

experiments, $\hbar\omega_D \sim 274\,K$, and $\hbar\nu \sim 768\,K$. Therefore, the calculations of the present simulation both for 900 K and 1200 K are reasonable, but that for the lowest temperature ($T = 600\,K$) of the present simulations may not be appropriate based on the classical model.

Acknowledgements

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. The authors would like to thank Prof. H. Sugimoto for helpful discussions during his visit to Kanazawa University. The numerical

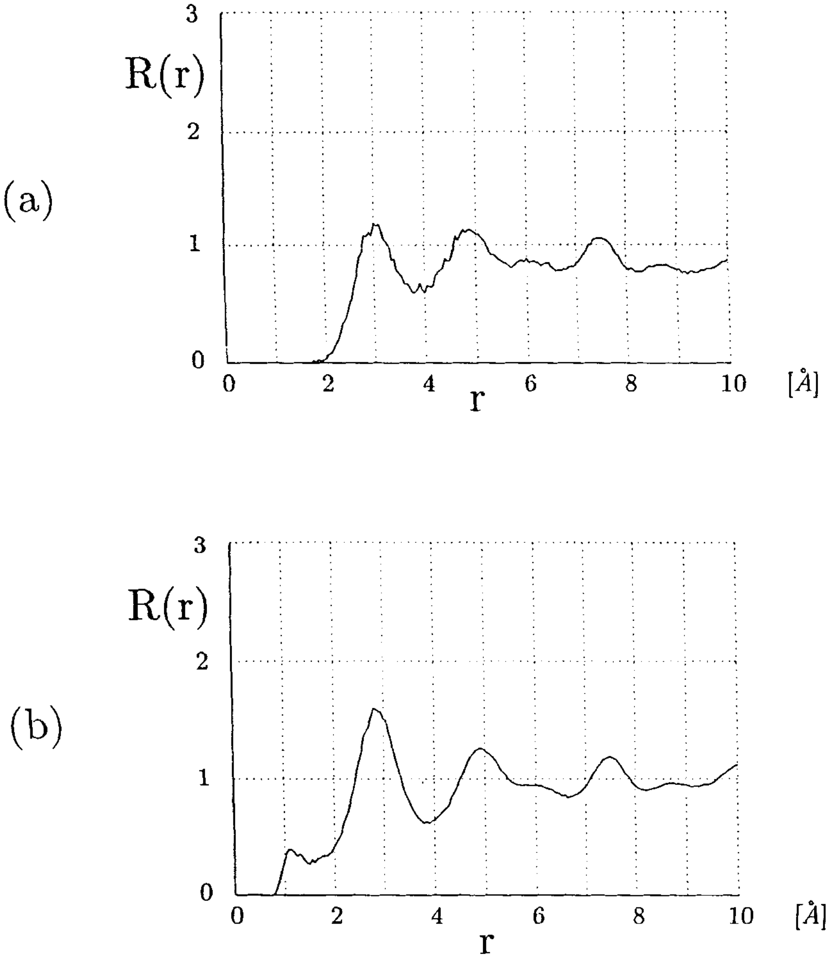

Figure 10 Radial distribution function $R(r)$ at $T = 1200\,\mathrm{K}$ for (a) $x = 0.1$ and (b) $x = 0.5$.

calculations were performed with the computers at the Institute of Molecular Science and Computer Center at Kyoto University.

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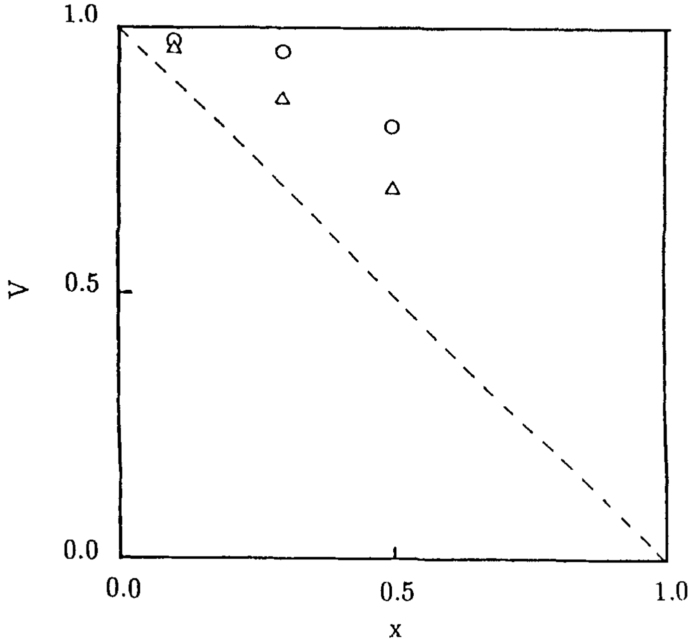

Figure 11 Vacancy factor at $T = 600\,\mathrm{K}$ (○) and $T = 1200\,\mathrm{K}$ (△).

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