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1993 J. Phys.: Condens. Matter 5 5543

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Some tests of basic assumptions in transition state theory for hydrogen diffusion in FCC-metals

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Received 24 March 1993, in final form 14 May 1993

Abstract. Transition state theory is frequently used to describe interstitial diffusion in solids. A basic assumption in this theory is that equilibrium statistical mechanics can be used to characterize the different configurations in the transition state, the region in configuration space which acts as a bottleneck for the motion of the interstitial. We have performed a detailed test of this assumption for hydrogen diffusion in palladium by combining the molecular dynamics and the Monte Carlo techniques. The study clearly confirms that equilibrium statistical mechanics can be used to characterize the different transition state configurations even though the presence of the hydrogen atom in the transition state strongly influences the fluctuations in the system and despite the fact that the time-scales for the motion of the H atom and the Pd atoms differ considerably.

1. Introduction

Many dynamic processes in many-particle systems are governed by events that are infrequent on a microscopic time-scale. A common cause for the rare event nature of these processes is the presence of bottlenecks for the motion of the system in configuration space. In order for such a dynamic event to occur a thermal fluctuation is required that brings the system from a locally stable region to a transient region, the bottleneck. The event is rare if the probability for the thermal fluctuation to occur is small. Interstitial diffusion in solids belongs to this category and here we will consider hydrogen diffusion in metals.

An important class of theories which deal with this kind of processes is based on ideas first clearly formulated by Eyring (Glasstone *et al* 1941) and nowadays referred to as transition state theory (TST). The term 'transition state' is used for the bottleneck in configuration space. The theory was developed in applications to solids by Wert and Zener (1949) and by Vineyard (1957), and it has been extended to include dynamic corrections (Keck 1967, Bennett 1975, Doll and Voter 1987, Voter 1989) as well as quantum effects (Pechukas 1976, Gillan 1987, Voth *et al* 1989). The essence of transition state theory is the counting of the various ways the system can pass through the transition state. For this equilibrium statistical mechanics is used.

The aim with the present paper is to test some of the basic assumptions behind transition state theory for hydrogen diffusion in metals. In particular, we are going to test the assumption that equilibrium statistical mechanics can be used to characterize the different configurations in the transient region, the transition state. We are going to make use of results from molecular dynamics (MD) simulations, where the time-scales in the problem

enter, and Monte Carlo (MC) calculations, which are independent of the time-scales. The purpose is to clearly demonstrate that the distribution of transition state configurations is independent of how difficult or easy that region is to enter, or of how quickly a typical hydrogen atom passes through it. We will restrict ourselves to classical mechanics and consequently only consider high temperatures.

As our test case we have chosen hydrogen in palladium. For this system a potential based on the embedded atom method (EAM) (Daw and Baskes 1984, Foiles *et al* 1986) has been developed that is found to well describe the diffusive motion of hydrogen (Li and Wahnström 1992a, b). At the temperature 600 K the hydrogen atom moves between the octahedral (O) sites in the FCC lattice with a mean residence time of the order of a few picoseconds. This makes it feasible to perform direct numerical molecular dynamics simulation of the diffusion process at 600 K and above.

The reason for making these tests for this particular system is twofold. Firstly, the relaxation caused by the presence of the hydrogen atom in Pd is large. For instance, the barrier height for diffusion is reduced from 659 meV to 172 meV when relaxation is taken into account (cf. section 3). This implies that the presence of the hydrogen atom strongly influences the fluctuations in the system. Secondly, the time-scales for the motion of the hydrogen atom and the Pd atoms differ substantially. Hydrogen is about 100 times lighter compared with Pd and its mean velocity is 10 times larger. A typical hydrogen atom passes through the transition state fast, compared with the motion of the Pd atoms.

2. Transition state theory

When applying (TST) to interstitial diffusion (Flynn 1972) we have to define the locally stable regions in configuration space. The obvious choice for H in Pd is to associate a stable region with configurations where the hydrogen atom is located in the vicinity of an O-site. To be more precise, we can use the Wigner–Seitz cells for the O-sites, and the coordinate for the hydrogen atom determines which stable region the system belongs to.

The rate k , for moving from one site to an adjacent site is in TST expressed in terms of the probability density for the hydrogen atom to be located at the dividing surface between two different sites, and the flux $f_s(\mathbf{r})$, in one direction, through that surface. By introducing the microscopic density $n(\mathbf{r})$, i.e. the probability of finding the hydrogen atom at position \mathbf{r} , we can write the rate as

$$k^{\text{TST}} = \frac{\int_S f_s(\mathbf{r}) n(\mathbf{r}) dS}{\int_V n(\mathbf{r}) dV} \quad (1)$$

where, in the numerator, the integral is over the dividing surface between two adjacent sites and, in the denominator, it is over a Wigner–Seitz cell. We have also indicated that the flux may depend on the position coordinate \mathbf{r} .

For clarity, we would like to remark that the TST expression for the rate k^{TST} is an approximation for the true rate and that dynamic effects have been neglected. (Keck 1967, Bennett 1975, Doll and Voter 1987, Voter 1989). If the basis for TST is verified it can, however, be combined with short-time dynamical calculations in order to obtain the exact diffusion coefficient at arbitrary temperatures (Voter 1989), assuming classical mechanics to be valid and given a potential energy function. This is a major motivation for the present study. For H in Pd we have found a high probability of direct backward jumps (Li and Wahnström 1992b), which will reduce the value for the diffusion coefficient compared with the TST value. Also quantum effects can be incorporated into TST (Gillan 1987, Voth *et*

al 1989), but in this case dynamic corrections cannot be obtained in the multi-dimensional case at the same level of accuracy as in the classical limit see e.g. Wahnström *et al* (1988).

With these limitations in mind, in the next section we will compare results for the two quantities $f_s(\mathbf{r})$ and $n(\mathbf{r})$ determined in two quite different ways: by using the molecular dynamics technique, where the time-scales enter, and the Monte-Carlo method, which is independent of the time-scales.

3. Results

3.1. The potential

The basic idea behind the (EAM) is that each atom in a metal is viewed as being embedded in the host consisting of all remaining atoms (Nørskov and Lang 1980, Stott and Zaremba 1980). Its embedded energy is related through a function to the local electron density contributed by the surrounding atoms. The cohesive energy for the metal can then be expressed in terms of the embedded energies for the individual atoms plus a pair interaction term which accounts for the electrostatic ion-ion interactions,

$$E(\{\mathbf{R}\}) = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(R_{ij}) \quad (2)$$

where ρ_i is the local electron density at atomic site i , $F_i(\rho)$ is the embedded energy for atom i when immersed into a medium with electron density ρ , and $\phi_{ij}(R_{ij})$ is the two-body interaction energy between atom i and j separated by the distance R_{ij} . A set of atomic coordinates is denoted by $\{\mathbf{R}\}$. In the EAM scheme, the functions F and ϕ are mostly determined phenomenologically by choosing suitably parametrized functions and fitting the parameters to some available experimental data. In this sense it is semi-empirical in nature. We have chosen exactly the same parameterization as in (Li and Wahnström 1992b).

We use 1 H atom and 256 Pd atoms in the MC calculations and 8 H atoms and the same number of Pd atoms in the MD simulations, together with periodic boundary conditions. The larger hydrogen concentration in the MD calculations is used to enhance the statistics. We have found that value to be sufficiently low to accurately represent the low concentration limit (Li and Wahnström 1992b). In all cases the temperature is $T = 800$ K and the lattice spacing $a_0 = 3.957$ Å, which takes the thermal expansion into account in a proper way (Li and Wahnström 1992b).

In figure 1 we show the energy obtained when moving the hydrogen atom along the [111]-direction. This direction corresponds to the minimum energy path when hydrogen is moving in between different octahedral sites. Both the unrelaxed energy, obtained with all Pd atoms fixed at their lattice positions, and the relaxed energy, where for each position of the hydrogen atom the energy is minimized with respect to the positions of the Pd atoms, are shown. The points labelled by O, S, and T in the figure denote the energies when the hydrogen atom is located at the octahedral site, the saddle point along the [111]-direction, and the tetrahedral site, respectively. In the unrelaxed lattice a Pd atom is located at the distance $\sqrt{3}a_0/2 = 3.427$ Å from the O-site, which explains the rapid increase of the potential energy for large distances. It is clearly seen that the relaxed energy differs considerably from the unrelaxed one. At the O-site the energy difference is 48 meV, the so called self-trapping energy (Flynn and Stoneham 1970). At the saddle point it is much larger, 487 meV, clearly indicating the large distortions that are involved in hydrogen diffusion. The barrier height is reduced from 659 meV to 172 meV when relaxation is included.

The barrier is higher in other directions. In the [110]-direction it is 292 meV when relaxation is included. Since in diffusion all different paths contribute, one should take a weighted average over all different paths to achieve a proper evaluation of the diffusion coefficient. At high temperatures, where the diffusion is sufficiently large, direct molecular dynamics can be performed. In a previous study (Li and Wahnström 1992b), using exactly the same potential as here, the diffusion coefficient was evaluated at three different temperatures: 626 K, 791 K and 990 K. The corresponding activation energy determined from an Arrhenius-plot was found to be 245 meV, close to the experimental value 230 meV (Völkl and Alefeld 1978). For the two isotopes deuterium and tritium the activation energy is experimentally found to be smaller, 206 meV (Völkl *et al* 1971) and 185 meV (Sicking *et al* 1983), respectively. Assuming TST to be valid the activation energy should be independent of the mass m of the diffusing particle. The diffusion coefficient is simply proportional to $m^{-1/2}$. We believe that the most likely reason for these differences are quantum effects but more work is required to estimate the size of these and those caused by dynamic corrections.

3.2. The mean force

At a finite temperature the positions of the Pd atoms are fluctuating and that effect is included in the potential of mean force (Chandler 1987). If we assume a canonical ensemble, the mean force acting on a hydrogen atom fixed at position r is defined by

$$F(r) = \langle -\nabla_H E(\{R\}) \rangle_r \quad (3)$$

The notation $\langle \dots \rangle_r$ is used for a canonical ensemble average with the hydrogen atom fixed at position r ,

$$\langle \dots \rangle_r \equiv \frac{\int d\{R\} \dots \delta(r - R_H) \exp(-E(\{R\})/k_B T)}{\int d\{R\} \delta(r - R_H) \exp(-E(\{R\})/k_B T)} \quad (4)$$

and $\nabla_H \equiv \partial/\partial R_H$. The notation R_H is used for the coordinate of the hydrogen atom and the ordinary canonical ensemble average will be denoted by $\langle \dots \rangle$. The corresponding potential is defined by

$$W(r) - W(r_0) = - \int_{r_0}^r F(r') \cdot dr' \quad (5)$$

Physically, $W(r)$ is the potential the hydrogen atom would experience if it was moving infinitely slowly. The potential of mean force only depends on the potential energy surface $E = E(\{R\})$ and the temperature, but not on the masses or the time-scales that enter into the problem.

We have determined $F(r)$ along the [111]-direction using the Monte Carlo method, together with the Metropolis algorithm (Allen and Tildesley 1987). This is the most direct way to solve the multi-dimensional integral in equation (3). For each position of the hydrogen atom we have generated of the order 350 statistically independent configurations and the average force is then determined. In figure 2 we show the result and the error bars correspond to the estimate of two standard deviations. In the same figure we also show the forces obtained by differentiating the unrelaxed and relaxed potentials, shown in figure 1. The mean force is close to the force corresponding to the relaxed potential and the thermal fluctuations are seen to be most important where the barrier is steepest.

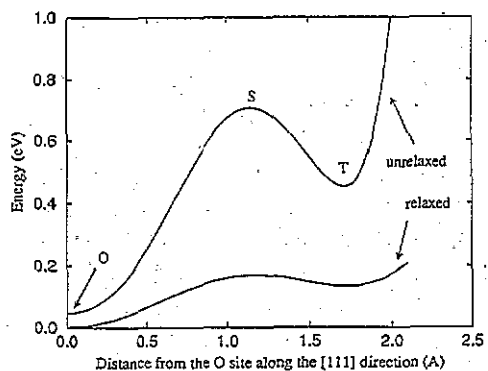


Figure 1. The total potential energy as a function of the H position along the [111] direction. Two cases are shown; unrelaxed (all Pd atoms fixed at their lattice positions), and relaxed (for each position of the H atom the energy is minimized with respect to the Pd positions). System: 1 H and 256 Pd. Lattice spacing: 3.957 Å.

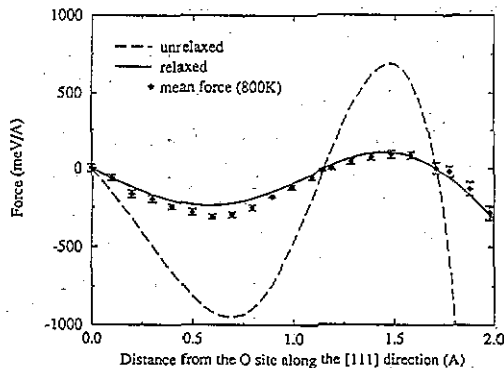


Figure 2. The force on the H atom as a function of its position along the [111] direction. Three cases are shown; the force obtained from the unrelaxed and relaxed potentials (shown in figure 1), and the mean force (defined in equation (3)) at $T = 800$ K. The error bars represent 95% confidence intervals.

3.3. The microscopic density

One of the key quantities in TST is the microscopic density $n(\mathbf{r})$. We can determine $n(\mathbf{r})$ in two different ways. Assuming a canonical ensemble we have

$$n(\mathbf{r}) = \langle \delta(\mathbf{r} - \mathbf{R}_H) \rangle = \frac{\int d\{\mathbf{R}\} \delta(\mathbf{r} - \mathbf{R}_H) \exp(-E(\{\mathbf{R}\})/k_B T)}{\int d\{\mathbf{R}\} \exp(-E(\{\mathbf{R}\})/k_B T)} \quad (6)$$

which is directly related to the potential of mean force $W(\mathbf{r})$, defined in equations (3) and (5), through

$$n(\mathbf{r}) = \frac{\exp(-W(\mathbf{r})/k_B T)}{\int d\mathbf{r} \exp(-W(\mathbf{r})/k_B T)} \quad (7)$$

The density in equation (6) is clearly independent of the time-scales, e.g. how long the hydrogen atom spends in the vicinity of the transition state. This follows rigorously from the use of the canonical ensemble, i.e. the assumption that the system as a whole is in a state of thermal equilibrium.

We can also determine the probability for the hydrogen atom to be located at the transition state in a different way, by using the MD technique. The equations of motion for all atoms are solved simultaneously and a time-dependent trajectory for the hydrogen atom $\mathbf{R}_H(t)$ is obtained. The microscopic density is achieved by making a time-average along the trajectory,

$$n(\mathbf{r}) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \delta(\mathbf{r} - \mathbf{R}_H(t)) \quad (8)$$

where in practice τ has to be finite. Provided the system is ergodic the ensemble average in equation (6) and the time average in equation (8) should give identical results (Chandler 1987). *A priori* we cannot be sure, however, that the two different averaging procedures give the same result. We share the opinion in (Ma 1985) that the time average is more closely related to reality compared with the ensemble average. If they coincide, it then shows that one can use the ensemble method to generate configurations that correctly characterize the behaviour in the transient region.

In the calculation of the time average the proper time-scales for the motion of the light hydrogen atom and the heavy Pd atoms are included. A contribution to $n(\mathbf{r})$ is obtained whenever the hydrogen atom is located in the vicinity of \mathbf{r} . That implies that the density at e.g. the saddle point is obtained from configurations where the hydrogen atom passes a small region around the saddle point in a time which is shorter than the typical lattice vibrational period. On the other hand, the different time-scales do not enter into the evaluation of $n(\mathbf{r})$ using the ensemble average in equation (6). In that calculation the hydrogen atom is placed at the position \mathbf{r} and after that the surrounding has relaxed and equilibrated in the presence of an immobile hydrogen atom, the average force is determined and from that the density is obtained.

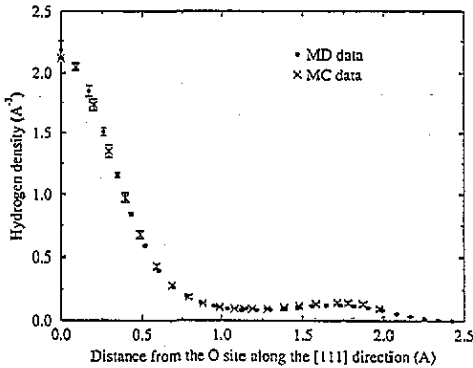


Figure 3. Comparison of the microscopic density for the H atom along the [111]-direction, determined using the (MD) and (MC) techniques at 800 K. The area under the curve is normalized to unity and the error bars represent 95% confidence intervals.

In figure 3 we show the result from the calculations. The ensemble average in equation (6) is obtained directly from the previously calculated values of the mean force $\mathbf{F}(\mathbf{r})$, and is shown as crosses. We have then determined the potential of mean force $W(\mathbf{r})$ by fitting the data points for $\mathbf{F}(\mathbf{r})$ to a spline and integrated. The area under the curve is normalized to unity.

To determine the time average we have done 20 separate MD simulations, starting from different initial configurations. The velocity version of the Verlet algorithm (Allen and Tildesley 1987) is used for solving Newton's equation of motion. The timestep is 0.5 fs which produces very numerically stable trajectories. In recent years many suggestions for algorithms for constant temperature simulations have been proposed (Allen and Tildesley 1987), but in the present study we do not want to add any extra terms into Newton's equation of motion. To be more precise the corresponding ensemble is then the microcanonical, not canonical, but for sufficiently large systems average quantities are independent of the particular choice of ensemble (Chandler 1987). All coordinates are determined with respect to the centre of mass of all Pd atoms and the result is therefore unaffected by an overall translation. We have found this way to define the reaction coordinate (Bennett 1975) most convenient, in particular in a MD simulation. The system is equilibrated for 20 ps and the extension of each production run is 20 ps. The average temperature in the 20 simulations is 800 ± 1 K. In determining the microscopic density along the [111]-direction we have introduced small cubic volumes ΔV . Each time a hydrogen atom is located in one of these volumes a contribution to the density is obtained. We make use of the symmetry in the system and all different [111]-directions are taken into account. The density at position \mathbf{r} is approximated by the average

$$n_{\Delta V}(\mathbf{r}) = \frac{1}{\Delta V} \int_{\Delta V} d\mathbf{r}' n(\mathbf{r}'). \quad (9)$$

If the volume ΔV chosen is too small the statistical fluctuations become too large. On the other hand, a too large ΔV makes the above approximation inaccurate. We have found 0.2 Å to be an appropriate linear size for the cubic volume, around which the fluctuations in $n_{\Delta V}(r)$ are relatively small and the result for the density is not sensitive to the size.

In figure 3 we show the result from the MD simulation. Again, we have normalized the density in such a way that the area under the curve is unity. We see that the results obtained from MD and MC for the density agree with each other within the error bars with a small deviation around the tetrahedral position.

We have also estimated the error due to the finite value of ΔV . We write the true density $n(r)$ as

$$n(r) = A \exp(-\beta\Phi(r)) \quad (10)$$

which implies that it is related to the average density $n_{\Delta V}(r)$, defined in equation (9), through

$$n(r) = C_{\Delta V}(r)n_{\Delta V}(r) \quad (11)$$

where the correction is given by

$$C_{\Delta V}(r) = \left[\frac{1}{\Delta V} \int_{\Delta V} dr' \exp(-\beta[\Phi(r') - \Phi(r)]) \right]^{-1} \quad (12)$$

We have determined $C_{\Delta V}$ by approximating $\Phi(r)$ with the relaxed energy at $T = 0$ K. We find that the density should be increased by 3% ($C_{\Delta V} = 1.03$) at the O-site and about 8% at the S- and T-sites. The increase at the S-site is because the curvature of the potential in the directions perpendicular to the [111]-direction is positive and large. By taking this correction into account the agreement around the tetrahedral site would become slightly better.

3.4. The pair-distribution function

We can make the fact that the time-scales for the motion of the different atoms are irrelevant more explicit. By using the MD technique we can record the positions of all Pd atoms each time the hydrogen atom passes close to e.g. the saddle point along the [111]-direction. After sufficiently many such events the distribution of the surrounding Pd atoms can be obtained. We introduce the notation $g(r)$ for the probability of finding a Pd atom at the distance r from the hydrogen atom when the latter is located at the saddle point.

We can also determine the same function for a hydrogen atom moving infinitely slowly. In that case, we put the hydrogen atom at the saddle point $R_H = r_s$, let the surrounding Pd-atoms relax and equilibrate at the chosen temperature, and then we determine the pair distribution function $g(r)$ by making a time average where the Pd atoms are moving according to Newton's equation of motion but with the hydrogen atom kept fixed at r_s .

In figure 4 we show the results for $g(r)$, determined in these two different ways. The results coincide, which clearly show that the time-scale for the motion of the hydrogen atom is irrelevant. The configurations of the surrounding Pd atoms, when the hydrogen atom passes close to the saddle point, are independent of the velocity of the hydrogen atom.

For comparison we have also determined $g(r)$ using the MC technique. The hydrogen atom is kept fixed at the saddle point and then we sample the different Pd configurations using their proper weight. After sufficiently many Pd configurations $g(r)$ can be determined. The result is shown in figure 4 and it coincides with the two previous calculations.

We have also determined the distribution in the absence of the hydrogen atom, $g_0(r)$. The result is shown in the same figure as a chain curve. The first peak in $g_0(r)$ is located

at $r = 1.62 \text{ \AA}$, which agrees with the distance between the saddle point and the nearest Pd atom in a rigid lattice, $a_0/\sqrt{6} = 1.62 \text{ \AA}$. The broadening of the peak is due to the thermal fluctuations. In $g(r)$ the location of the peak is shifted to the value 1.81 \AA due to the presence of the H atom and again, the broadening is caused by thermal fluctuations. We notice that in this case the peak is more narrow and asymmetric.

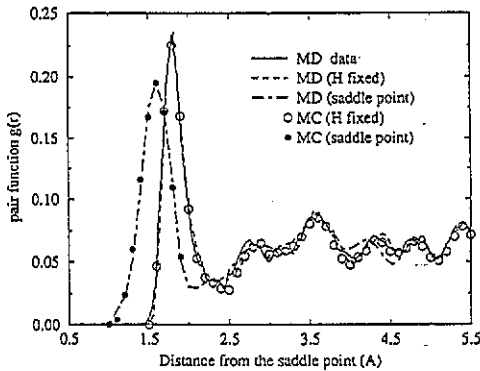


Figure 4. The pair distribution function $g(r)$, which shows the location of the Pd atoms. The distance r is measured from the saddle point. The MD data are shown as lines. The Pd positions are recorded (a) only when the H atom passes close to the saddle point (full curve), (b) continuously but with one H atom fixed at the saddle point (broken curve), and (c) continuously but with no H atom fixed (chain curve). The MC data are shown as circles where (a) a H atom is fixed at the saddle point (open circles), and (b) there is no H atom present (filled circles). All curves are determined at 800 K.

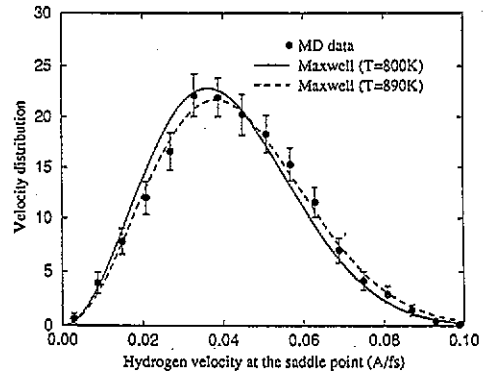


Figure 5. Comparison of the MD data for the velocity distribution of the H atom at the saddle point with the Maxwell distribution. The MD data are determined at 800 K and the broken curve (890 K) corresponds to the best fit to the data. The error bars represent 95% confidence intervals.

3.5. The flux

The other key quantity in TST is the flux $f_s(\mathbf{r})$. Assuming a canonical ensemble it can be determined directly from the Maxwell distribution according to

$$f_s(\mathbf{r}) = \frac{1}{2} \langle |v_s| \rangle = \frac{\int_0^\infty dv v \exp(-mv^2/2k_B T)}{\int_{-\infty}^\infty dv \exp(-mv^2/2k_B T)} = \sqrt{\frac{k_B T}{2\pi m}} \quad (13)$$

where the factor $\frac{1}{2}$ takes into account the fact that only atoms that exit (or equally well enter) the site should be counted, and where v_s denotes the velocity in the direction perpendicular to the dividing surface. We notice that the flux does not depend on the location of the hydrogen atom which follows rigorously from the use of the canonical ensemble, i.e. the assumption that the system as a whole is in a state of thermal equilibrium. We can compare the result in equation (13) with the flux obtained from the MD simulation. In particular, we are interested in the velocity distribution for the hydrogen atom when it passes close to a saddle point and compare that to the Maxwell distribution.

In figure 5 we show the velocity distribution as a function of v for hydrogen atoms that are close to a saddle point, within a cube of linear size 0.2 \AA . The result is based on 12 independent runs, each 20 ps long and the error bars represent two standard deviations. In the

same figure we also show the Maxwell distribution, $4\pi(m/2\pi k_B T)^{3/2} v^2 \exp(-mv^2/2k_B T)$, with the proper temperature $T = 800$ K.

We notice that the result from the MD simulation shows a systematic shift towards higher temperatures. The best fit to the MD data is shown as a broken curve and it corresponds to the temperature $T = 890$ K. We have also tested the distribution independent of the location of the hydrogen atom. We find a Maxwell distribution with the temperature $T = 825$ K.

It is very difficult to judge if the deviation shown in figure 5 is a real effect or only due to insufficient sampling of the rare configurations when the hydrogen atom is close to the saddle point. More extensive investigations are necessary in order to clarify this point. An indication of insufficient sampling is that the average temperature for hydrogen (825 K) is slightly too high. At the present stage we conclude that the velocity distribution for hydrogen atoms close to the saddle point is Maxwellian distributed but with a higher temperature (890 K) compared to the temperature for the total system (800 ± 1 K).

4. Discussion

In the present paper we have tested some basic assumptions used in the transition state theory for hydrogen diffusion in palladium. The reason for making these tests for this particular system is that the presence of the hydrogen atom strongly influences the fluctuations in the system and that the time-scales for the motion of the hydrogen atom and the Pd atoms differ a lot.

All tests are performed at the temperature 800 K for which sufficiently many events in the MD simulation can be recorded in regions with low probability. Both configurational properties, like the microscopic density $n(r)$ (cf. figure 3) and the pair distribution function $g(r)$ (cf. figure 4), as well as the velocity distribution for the hydrogen atom (cf. figure 5) are determined.

The results obtained clearly show that the distribution of transition state configurations does not depend on how easy or difficult the region is to enter, or on how quickly a typical hydrogen atom passes through. The statement, that the hydrogen atom in making a diffusive jump approaches the saddle point so quickly that the neighbouring Pd atoms do not have time to relax outward fully, is not correct. Bennett (1977) emphasizes very clearly that one cannot regard the outward relaxation of the Pd atoms as solely caused by the approaching hydrogen atom, when it may equally well be that the approach of the hydrogen atom is a result of an outward relaxation of the surrounding Pd atoms. The jump event should be treated as a fluctuation in a many-body system at thermal equilibrium: the presence of the hydrogen atom at the saddle point neither causes, nor results from, but rather is instantaneously correlated with, a relaxation of the mean positions of all surrounding Pd atoms (Bennett 1977). We also show that the velocity distribution for the hydrogen atom when it passes close to a saddle point is Maxwell distributed but with a slightly higher temperature (890 K) compared to the temperature for the total system (800 ± 1 K). More extensive investigations are however necessary in order to clarify if this departure is a real effect or only caused by insufficient sampling of relevant configurations.

In conclusion, the assumption that equilibrium statistical mechanics can be used to characterize the different transition state configurations is strongly supported by the present study.

Acknowledgments

Comments from Professor A Sjölander, financial support from the Swedish Research Council of Natural Science and the Swedish National Board for Industries and Technical Development and allocation of computer time by the National Supercomputer Centre in Sweden are gratefully acknowledged.

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