Nonadiabatic Effects in Hydrogen Diffusion in Metals

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Molecular dynamic simulations for hydrogen diffusion in Pd are performed, using a potential based on the embedded-atom method. It is found that a single adiabatic Born-Oppenheimer potential energy surface cannot reproduce the wave-vector dependence of the quasielastic peak obtained in neutron scattering studies. By incorporating coupling to low-lying electron-hole-pair excitations among the conduction electrons close agreement with the experimental result is obtained. This shows that in some cases one has to go beyond the Born-Oppenheimer approximation in order to characterize correctly the diffusive motion of hydrogen in metals.

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Molecular dynamic (MD) simulations have turned out to be a powerful tool for understanding the structure and dynamics of condensed matter. During the last decade several new approaches have been suggested for describing the interatomic interactions in metals. The aim is to be able to make quantitative statements and predictions about real materials. *Ab initio* electronic structure methods have been combined with MD simulations [1] and efficient semiempirical potential energy surfaces have been suggested [2]. Common to these approaches is that they are based on the Born-Oppenheimer separation of electronic and nuclear motion. The adiabatic multidimensional potential energy surface determines the motion of the nuclei through the classical Newton equations of motion.

The application to metals may pose additional problems due to the presence of conduction electrons. Electron-hole-pair excitations can be produced with infinitesimal energy and on energetic grounds also a nucleus moving with thermal velocity may excite electron-hole pairs. This implies nonadiabatic changes in the electron structure and in order to incorporate these effects into dynamic simulations one has to go beyond the adiabatic approximation.

Here we consider hydrogen diffusion in palladium at low hydrogen concentration. The aim is to show that in order to characterize the diffusive motion of hydrogen correctly the use of a single Born-Oppenheimer potential energy surface is highly questionable.

The reasons for choosing the H-Pd system are as follows: (i) Compared with Pd, hydrogen is light and its coupling to the lattice vibrations is weak. Electronic excitations among the conduction electrons can then become important in providing an additional mechanism for energy dissipation. (ii) Hydrogen diffusion in Pd has been studied experimentally using quasielastic neutron scattering [3-6]. These measurements give detailed information on the hydrogen diffusion on an atomic scale, which is important in the present context. (iii) Semiempirical potential energy surfaces have been developed for H in Pd [7,8] which describe the interatomic interactions in a realistic way.

In a previous MD study by Gillan [9], discrepancies between neutron scattering and MD results were observed for the width of the quasielastic peak. Gillan used a pair potential description and he clearly stressed the likely importance of nonadiabatic effects in H diffusion in Pd. At low temperature ($T < 100$ K) it is now established that nonadiabatic effects are important for explaining the temperature dependence of the motion of hydrogen in metals [10,11].

We have chosen the embedded-atom method (EAM) for the interatomic interactions [7]. This method has been tested in a large variety of situations and has proven very versatile in describing and predicting structural and dynamical properties as well as phase transitions in metallic systems [2]. The model is no more computationally demanding than simple pair potential descriptions, but incorporates some essential many-atom interactions in metals. The method is empirical in nature because of the assumptions about the electronic charge densities and the fitting of the potential to experimentally observed quantities. The details of the method can be found elsewhere [7,12]. For the Pd-Pd interaction we use the parametrization by Foiles, Baskes, and Daw [12]. The embedding energy for hydrogen is taken from the first-principles calculations of Puska and Nieminen [13] and for the effective charge of a hydrogen atom we choose the form $Z(R)=Z_0\exp(-\alpha R)$ [12]. For α we use the reasonable value $\alpha=2$ Å^{-1} and the value for $Z_0=1.75$ a.u. is determined by fitting to the migration energy for H in Pd [14]. Given a set of nuclear positions $\{\mathbf{R}\}$ the above procedure defines our adiabatic multidimensional potential energy surface $E(\{\mathbf{R}\})$. We have tested the model on the vibrational motion of hydrogen in Pd at room temperature. Reasonable agreement with available experimental results is obtained, similar to the results presented in Ref. [15]. The experimental value for the diffusion coefficient is also reproduced, both for the temperature concerned here ($T\sim600$ K) and for higher temperatures ($T\sim800$ and 1000 K).

Next the effect of low-lying electronic excitations are incorporated. The time scale for the electronic motion is very fast compared with the time scale for the nuclear motion. The electrons adjust themselves very rapidly to the motion of the nuclei, but not strictly instantaneously. The single adiabatic potential energy surface has to be replaced by a continuous band of very nearly parallel surfaces, corresponding to different combinations of low-lying electron-hole-pair excitations. In this limit of near adiabaticity the inclusion of electron-hole-pair excitations is straightforward, provided the motion of the nuclei can be treated classically [16,17]. One only needs to add a friction term and a stochastic force with white-noise spectrum to Newton's equation of motion [18,19],

$$m_{\mathrm{H}}\ddot{\mathbf{R}}_{\mathrm{H}}(t)=-\nabla E(\{\mathbf{R}\})-m_{\mathrm{H}}\eta\dot{\mathbf{R}}_{\mathrm{H}}(t)+\mathbf{F}^{\mathrm{st}}(t)\,,$$

where $\mathbf{R}_{\mathrm{H}}$ denotes the position of the hydrogen atom and m_{H} its mass. The friction coefficient η is an electronic property and it can be expressed in terms of the density-density correlation function for the electronic motion [17]. In the general case, it is a tensor and depends on the instantaneous configuration of the nuclear positions [16,17]. Here, we assume a constant value, independent on the location of the hydrogen atom. The stochastic force $\mathbf{F}^{\mathrm{st}}(t)$ is related to the friction coefficient through the fluctuation-dissipation theorem [18]. We only include the friction term and the stochastic force into the equation of motion for the hydrogen atoms. Nonadiabatic effects also influence the damping of the lattice vibrations, but that effect can be neglected here and for the motion of the Pd atoms we only use Newton's equation of motion. More details will be presented elsewhere [14].

An important issue is the magnitude of the friction coefficient, i.e., the strength of the nonadiabatic coupling. We rely on calculations, based on the density functional theory within the local density approximation, for a hydrogen atom immersed in a homogeneous electron gas. Puska and Nieminen [13] obtained the value $\hbar\eta=4.5$ meV for an electron density appropriate for palladium $r_s=1.5a_0$ [20], where a_0 is the Bohr radius. The friction coefficient is directly related to the stopping power of an electron gas for the slow motion of ions and the numbers based on the density functional theory give good agreement with experimental data (for a recent review see [21]). The MD simulations are carried out for a system of 256 Pd atoms and 8 hydrogen atoms. That corresponds to the hydrogen number concentration $x=0.03$, which is the same as in the neutron scattering study by Rowe *et al.* [4]. The "velocity Verlet" algorithm is used [22] and it is extended, following Ref. [22], when the friction term and the stochastic force are included. The time step is equal to 0.5 fs and this comparatively short time step is due to the rapid motion of the hydrogen atoms. Periodic boundary conditions are used.

Initially the hydrogen atoms are put randomly on octahedral sites. The system is evolved in time at a high temperature, of the order 1000 K, to randomize the system, and it is then cooled quasicontinuously by smoothly scaling the velocities. The pressure is adjusted by changing the volume of the simulation cell. Temperature and pressure are monitored and when a stable situation is achieved the subsequent time period, the production run, is used for evaluating static and dynamic quantities. The volume of the simulation cell is then kept fixed.

We have performed two different sets of calculations, one denoted by A, where the motion is determined from the single adiabatic potential energy surface $E(\{\mathbf{R}\})$, and one denoted by B, where the coupling to electron-hole-pair excitations is included with the friction coefficient equal to $\hbar\eta=4.5$ meV. Both sets of calculations are performed at the same temperature as in the neutron scattering study by Rowe *et al.* [4] (see Table I). The pressure is reasonably small, $pV/Nk_BT=0.022\pm0.004$ and $pV/Nk_BT=0.04\pm0.02$ for A and B, respectively, and the lattice spacing is equal to $a=3.94$ Å. To obtain good statistics the production runs are extended to 600 ps (1.2×10^6 time steps) in case A and to 300 ps (0.6×10^6 time steps) in case B.

The width of the quasielastic peak, obtained in incoherent neutron scattering measurements, gives direct information on the diffusive motion. In particular, the wave-vector dependence of the width reveals the nature of the diffusive motion on an atomic scale. For small wave vectors the half width at half maximum $\omega_{1/2}(q)$ approaches the limiting behavior $\omega_{1/2}(q)\rightarrow D_sq^2$, where D_s is the self-diffusion coefficient.

We have determined the mean square displacement as well as the incoherent scattering function $F^s(q,t)$ for several different wave vectors q. In Table I we give the result for the self-diffusion coefficient obtained from the slope of the mean square displacement. Our results compare well with different experimental results (cf. Table I) and it is partly due to the fact that we have fitted the parameter Z_0 in the EAM potential to the experimental value for the migration energy [14]. Notice also that the value for D_s is hardly affected by including the coupling to the electron-hole-pair excitations. For larger values of η ($\hbar\eta>5$ meV), we expect the value for D_s to be reduced.

We have also determined the half-width $\omega_{1/2}(q)$. To reveal the character of the diffusive motion as clearly as

TABLE I. The friction coefficient η, the simulation temperature T, the hydrogen number concentration x, and the self-diffusion coefficient D_s, for both set A and set B. The error bars represent a 95% confidence interval. Our results compare well with different experimental ones: $D_s=0.45\times10^{-4}$ cm^{2}s^{-1} ($T=623$ K, $x=0.03$) [4], $D_s=0.55\times10^{-4}$ cm^{2}s^{-1} ($T=630$ K, $x=0.03$) [3], and $D_s=0.35\times10^{-4}$ cm^{2}s^{-1} ($T=623$ K, $x=0.04$) [5].

Set	$\hbar\eta$ (meV)	T (K)	x	D_s (10^{-4}cm^{2}s^{-1})
A	0.0	628.0 ± 3.0	0.03	0.51 ± 0.05
B	4.5	621.5 ± 0.2	0.03	0.53 ± 0.05

possible we show the result for the dimensionless half-width $\Delta(aq) \equiv \omega_{1/2}(q)a^2/D_s$ in Fig. 1. For short wave vectors $\Delta(aq) \rightarrow (aq)^2$, and for larger wave vectors the character of the diffusive motion determines the q dependence. If we assume a simple-jump diffusion model [23] with uncorrelated jumps between nearest-neighboring octahedral sites, $\Delta(aq)$ has the form $\Delta(aq) = 8[1 - \cos(aq/2)]$ in the $\langle 100 \rangle$ directions and $\Delta(aq) = 4[3 - 2\cos(aq/\sqrt{8}) - \cos^2(aq/\sqrt{8})]$ in the $\langle 110 \rangle$ directions. These functions are shown in Fig. 1 and we will refer to this as the Chudley-Elliott (CE) model. The experimental results in Refs. [3-5] follow closely the CE model. In Fig. 1 we show the result by Rowe *et al.* [4], which is obtained for a single crystal of Pd and at the same temperature and hydrogen concentration as used here. A contradictory experimental result has been reported [6], but crucial objections have been raised [9,24] against the analysis made in Ref. [6]. First we consider A, the simulation without coupling to electron-hole pairs. The result from A does not agree with the experimental result (see Fig. 1). It shows strong non-CE behavior. This kind of behavior can be explained phenomenologically in terms of more complicated diffusion models than the simple CE model [25]. Similar results have been obtained previously by two other groups [9,25], using MD simulation and simple pair potentials. Gillan [9] considered higher temperature and larger hydrogen concentration. He obtained a strong non-CE behavior and he made a large number of trial simulations in order to investigate the sensitivity of the result on the form of the potential. He concluded that it was unlikely that the disagreement with the experimental fact was due to inadequate interatomic potentials. We have also used the potential proposed by Gillan at the present temperature and hydrogen concentration. Strong non-CE behavior is obtained [14], more pronounced than with the EAM potential. Culvahouse and Richards [25] found that by using a harder-core potential the result can be brought to closer agreement with the CE model, compared with using the Gillan potential. However, they were not able to achieve complete agreement with the CE model, even by going to a very hard-core potential. Our conclusion is that the departure from the CE model is most likely not due to an inaccurate adiabatic potential energy surface.

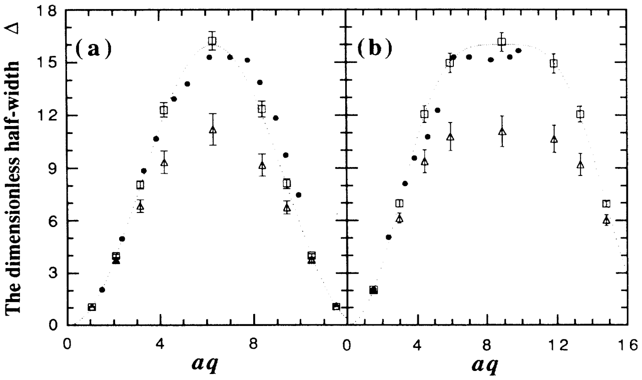

FIG. 1. The dimensionless half-width, $\Delta(aq) \equiv \omega_{1/2}(q)a^2/D_s$, vs aq, where a is the lattice spacing and D_s the self-diffusion coefficient. (a) **q** along $\langle 100 \rangle$ directions and (b) **q** along $\langle 110 \rangle$ directions. ●: experimental results [4]; △: set A, without friction ($\hbar\eta = 0.0$ meV); □: set B, with friction ($\hbar\eta = 4.5$ meV); and ····: the CE model. The error bars represent a 95% confidence interval.

Next we consider B, the simulation where the coupling to the electron-hole-pair excitations are included. With the reasonable value $\hbar\eta = 4.5$ meV for the coupling strength close agreement with the experimental results is obtained (see Fig. 1). We have investigated how sensitive this result is on the value of η [14]. Using $\hbar\eta = 2.0$ meV a similar result as with $\hbar\eta = 4.5$ meV is obtained, but with $\hbar\eta = 0.5$ meV the result is closer to the result from simulation A. From this we conclude that $\hbar\eta = 2.0$ meV is sufficient for explaining the experimental result, but not $\hbar\eta = 0.5$ meV. It follows that the result is not sensitive to the value of the friction coefficient, provided that $\hbar\eta \sim 2\text{-}5$ meV. Using the calculations by Puska and Nieminen [13] for a homogeneous electron gas, this corresponds to r_s values in the range $r_s \sim (1.5\text{-}3.4)a_0$.

We have also investigated what causes the different behavior between A and B and more details will be presented in Ref. [14]. In the CE model the residence time is exponentially distributed. We find a nonexponential dependence for the residence time at the octahedral sites, with a comparatively high probability of a short residence time. This is more pronounced in A compared with B, and it is the main reason for the different result for the half-width. Particularly in case A, a hydrogen atom can move rather freely in between several different octahedral sites. Its coupling to the lattice vibrations is weak [26]. The directions for two consecutive jumps are found to be uncorrelated, besides a tendency for making a jump directly back to the octahedral site from which the hydrogen atom made the previous jump. This effect is rapid in time and uninfluenced by the coupling to the electron-hole pairs.

Even with an accurate adiabatic potential energy surface the result can be in error due to quantum effects. The MD simulation is based on classical mechanics for the motion of the nuclei. It seems, however, very unlikely that quantum effects can make the motion more close to the CE behavior at the present temperature, $T \sim 623$ K. The departure from the CE behavior is due to highly excited hydrogen atoms that move rather freely in between several different octahedral sites. Treating this motion classically at the present temperature is highly justified.

In conclusion, we have applied the EAM potential for hydrogen diffusion in Pd and performed MD simulations at the same temperature and hydrogen concentration as used in the neutron scattering study by Rowe *et al.* [4]. We find that the EAM potential cannot reproduce the details of the diffusive motion and we conclude that the discrepancy with the experimental fact is most likely due to the use of a single adiabatic potential energy surface, and not the particular form of the EAM potential. By incorporating coupling to low-lying electron-hole-pair excitations among the conduction electrons in a reasonable way, close agreement with the experimental result is obtained. This is a strong indication that in some situations one has to go beyond the Born-Oppenheimer approximation in order to characterize correctly the diffusive motion of hydrogen in metals.

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