

Rapid Local Diffusion of Hydrogen in Niobium Revealed by a Molecular-Dynamics Study

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Molecular-dynamics simulations for hydrogen diffusion in Nb are performed at high temperatures ($T=450$ K and $T=580$ K). Two key experimental observations are reproduced by our model; the strong deviations from simple jump diffusion behavior and the “anomalous Debye-Waller” factor. The simulation reveals a rapid local-diffusion motion, predominantly confined to the so-called $4T$ configuration. The time scale for this motion is found to be of the order 100–200 fs.

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Diffusion of hydrogen in metals has been a subject of great interest, both experimentally and theoretically [1,2]. One of the main experimental tools for studying the microscopic mechanism behind the diffusive motion is neutron scattering. Despite extensive experimental investigations during the last 25 years many features remain unclear for the details of the migration mechanism operating in real systems. One such example is H in Nb above room temperature [3].

In this Letter we will show that molecular-dynamics (MD) simulations using realistic potentials give additional detailed microscopic information and can deepen our understanding of H diffusion in metals. We will show that our model reproduces some key experimental observations; the strong deviations from simple jump-diffusion behavior [4] and the “anomalous Debye-Waller” factor [3]. Our results strongly support the notion of a rapid local diffusion process, a new feature suggested by Dosch *et al.* [3].

The details of the diffusive motion are revealed in the wave vector dependence of the quasielastic peak measured in neutron scattering experiments. For H in Nb above room temperature distinct deviations from simple jump-diffusion behavior are obtained [4]. A double-jump model and a two-state model have been used to successfully fit the data [4], but the physical implications are not very clear. For instance, in the double-jump model the probability of a direct jump to a topological second nearest neighbor is larger than a jump to a nearest neighboring site at the temperature 581 K [4].

Anomalies in the intensity of the quasielastic peak (the Debye-Waller factor) have also been observed [5]. With a more careful fitting procedure it was later found that the quasielastic intensity follows an isotropic Debye-Waller factor for small wave vectors [6], but over a broader wave vector range the intensity still shows anomalies [3].

In a recent paper by Dosch *et al.* [3] the authors proposed, with considerable hesitation, a local-diffusion mechanism on the time scale 10–100 fs in order to resolve the above issues. They were not able to directly observe the rapid local-diffusion motion in the inelastic

scattering signals due to experimental limitations. Their main argument is that both the local and long-ranged lattice distortions (as measured by coherent scattering) as well as the proton form factor (as obtained from incoherent scattering) can naturally be explained by a rapid local-diffusion motion of the H atom.

We have performed extensive classical molecular-dynamics simulations for H diffusion in Nb. The necessary input in a simulation is the interaction between the constituents. Within the adiabatic assumption (the Born-Oppenheimer approximation) the motion of the nuclei, with coordinates \mathbf{R}_i , is obtained from a potential energy surface $V(\mathbf{R}_1, \dots, \mathbf{R}_N)$. We have shown in a previous study [7] that for light interstitials in metals nonadiabatic effects (excitations of low-lying electron-hole pairs) may become important for the details of the diffusive motion of the interstitial. This effect can be included approximately by adding a friction term and a stochastic force into Newton's equation of motion [7].

In the present study we have used exactly the same potential as used by Gillan and co-workers in their study of quantum diffusion [8] and vibrational motion [9] of H in Nb. The potential is based on the Finnis-Sinclair model [10] for the many-body interaction in a metal and reproduces well the vibrational motion of the H atom [9]. The diffusion coefficient is found to be slightly too large [8]. We view the present potential energy function sufficiently accurate for our purpose. Nonadiabatic effects are included in the same way as in Ref. [7] and for the friction coefficient we use the constant value $\hbar\eta = 2.5$ meV, which corresponds to the appropriate electron density for Nb, $r_s/a_0 = 3.0$ [11].

The MD simulations are carried out for a system of 432 Nb atoms and 8 H atoms. The lattice spacing is kept fixed at $a_0 = 3.3008$ Å, the same as in Refs. [8,9]. Other simulation details are the same as in our previous study [7].

We have performed simulations at two different temperatures; $T=580$ K and $T=450$ K, and in both cases we have studied the influence of nonadiabatic effects. At these high temperatures we regard classical mechanics to

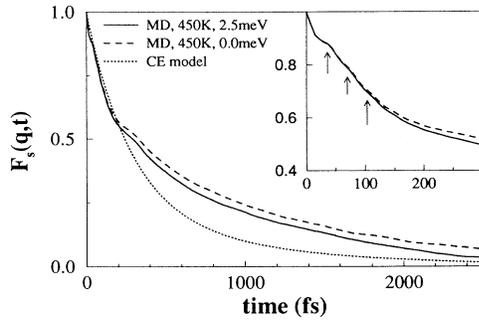


FIG. 1. The incoherent intermediate scattering function $F_s(\mathbf{q}, t)$ for the wave vector $\mathbf{q} = (2.5, 0, 0) \text{ \AA}^{-1}$. Full line: MD result at $T=450$ K with nonadiabatic effects ($\hbar\eta = 2.5$ meV); dashed line: MD result at $T=450$ K without nonadiabatic effects ($\hbar\eta = 0.0$ meV); dotted line: the Chudley-Elliot (CE) model with $\tau_{\text{res}}=324$ fs.

be valid. The diffusion coefficient at $T=580$ K is found to be $D_s = 11.5 \times 10^{-5} \text{ cm}^2/\text{s}$ and $D_s = 10.2 \times 10^{-5} \text{ cm}^2/\text{s}$ with and without nonadiabatic effects included, respectively. The corresponding values at $T=450$ K is $D_s = 7.00 \times 10^{-5} \text{ cm}^2/\text{s}$ and $D_s = 6.58 \times 10^{-5} \text{ cm}^2/\text{s}$. We notice that the nonadiabaticity has a small influence on the magnitude of the diffusion coefficient, consistent with our previous study [7]. The higher temperature corresponds to the temperature used in the experimental studies [3,4] and the lower temperature has been chosen such that the experimental value for D_s at about 600 K is obtained. In all cases the production run is of the order 100 ps.

The incoherent intermediate scattering function $F_s(\mathbf{q}, t)$ contains information on both the vibrational and the diffusive motion of the H atom. Its time Fourier transform, the incoherent dynamical structure factor $S_s(\mathbf{q}, \omega)$, is directly measured in neutron scattering experiments. In Fig. 1 we show $F_s(\mathbf{q}, t)$ for the wave vector $\mathbf{q} = (2.5, 0, 0) \text{ \AA}^{-1}$ at $T = 450$ K, both with and without nonadiabatic effects included. For short times, $t < 200$ fs, the results are essentially identical and for longer times a slight deviation is observed. Similar results are also obtained at $T = 580$ K. The decay is then faster due to the larger value for the diffusion coefficient, but the overall temporal behavior is the same.

The vibrational frequency for H in Nb is 108 meV [9] and the corresponding vibrational period is $\tau_{\text{vib}} = 38$ fs. Oscillations with this period are visible up to about 200 fs and they are indicated by arrows in the inset of Fig. 1. Besides the oscillations $F_s(\mathbf{q}, t)$ also decays substantially in this time interval and a change of the slope occurs around 150–200 fs. This extra decay of $F_s(\mathbf{q}, t)$ is a key finding.

The long time behavior of $F_s(\mathbf{q}, t)$ gives information on the diffusive motion. H occupies the tetrahedral (T) sites in Nb and in Fig. 1 we have added the result from

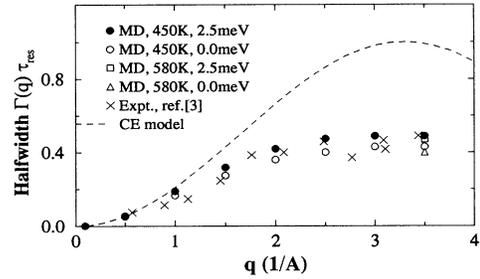


FIG. 2. The quasielastic width $\Gamma(q)$ in units of τ_{res} for \mathbf{q} along the [111] direction. ●: MD result at $T=450$ K with nonadiabatic effects ($\tau_{\text{res}}=324$ fs); ○: MD result at $T=450$ K without nonadiabatic effects ($\tau_{\text{res}}=345$ fs); □: MD result at $T=580$ K with nonadiabatic effects ($\tau_{\text{res}}=198$ fs); △: MD result at $T=580$ K without nonadiabatic effects ($\tau_{\text{res}}=227$ fs); ×: experimental data (Ref. [3]) ($\tau_{\text{res}}=389$ fs); dashed line: the Chudley-Elliot (CE) model [the quantity $\Gamma(q)\tau_{\text{res}}$ is independent of τ_{res} in the CE model].

the Chudley-Elliot (CE) model [12] (which assumes instantaneous jumps to the nearest neighboring sites only). The mean residence time at a T site τ_{res} is determined from the diffusion coefficient of the simulation at 450 K ($D_s = 7.00 \times 10^{-5} \text{ cm}^2/\text{s}$), according to $\tau_{\text{res}} = a_0^2/48D_s = 324$ fs, where a_0 is the lattice spacing. It is clearly seen that the CE model cannot describe the diffusive motion.

The slow decay of $F_s(\mathbf{q}, t)$ gives rise to a quasielastic peak in the spectrum $S_s(\mathbf{q}, \omega)$. A detailed test of the diffusive motion is achieved by determining the q dependence of the width of this peak, which we have done by fitting the decay of $F_s(\mathbf{q}, t)$ to an exponential, $\exp[-\Gamma(\mathbf{q})t]$, in the time interval $1 \text{ ps} < t < 2 \text{ ps}$. In Fig. 2 we show the results for the dimensionless quantity $\Gamma(q)\tau_{\text{res}}$ in the [111] direction, together with the experimental values obtained by Dosch *et al.* [3]. The large deviation from the simple jump-diffusion behavior (the CE model), seen experimentally, is reproduced surprisingly well by our MD data. The effect of adding the nonadiabatic effects is not pronounced; the decay of $F_s(\mathbf{q}, t)$ only becomes slightly faster. Similar results are obtained for the other directions [13].

Dosch *et al.* [3] also determined the intensity of the quasielastic peak $I_{\text{qe}}(q)$, which they denoted by $S_{\text{inc}}^{\text{el}}(Q)$. We have determined the same quantity by integrating the intensity over a fixed energy window $[-\omega_0, +\omega_0]$. The size of this window, $\hbar\omega_0 = 2.5$ meV, is chosen such that the quasielastic peak is inside for all q values considered (2.5 meV corresponds to $\Gamma\tau_{\text{res}}=1.23$ for $\tau_{\text{res}}=324$ fs). The calculations are done directly in time domain.

In Fig. 3 we show our results together with the experimental data [3]. The reduction of $I_{\text{qe}}(q)$ with increasing q is due to rapid motions, which do not show up in the energy window $\pm\hbar\omega_0$. If the H motion can be characterized in terms of only harmonic vibrations and long-range diffusion, $I_{\text{qe}}(q)$ is given by the Debye-Waller

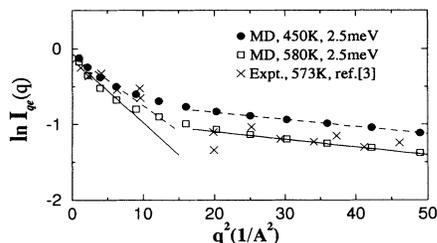


FIG. 3. The logarithm of the integrated intensity of the quasielastic peak, $I_{qe}(q)$, as a function of q^2 (\mathbf{q} along the [100] direction), a “Debye-Waller” plot. ●: MD result at $T=450$ K with nonadiabatic effects; □: MD result at $T=580$ K with nonadiabatic effects; ×: experimental data from Ref. [3]. The lines are only guides for the eye.

factor, $I_{qe}(q) = \exp(-q^2 \langle u_H^2 \rangle)$. Figure 3 clearly shows two different “Debye-Waller-like” behaviors (the straight lines). For large q vectors ($q > 4 \text{ \AA}^{-1}$) we obtain the values $\langle u_H^2 \rangle = 0.0095 \text{ \AA}^2$ and $\langle u_H^2 \rangle = 0.0102 \text{ \AA}^2$ at $T=450$ K and $T=580$ K, respectively, assuming a Debye-Waller behavior. For smaller q vectors ($q < 3 \text{ \AA}^{-1}$) the corresponding numbers are $\langle u_H^2 \rangle = 0.068 \text{ \AA}^2$ and $\langle u_H^2 \rangle = 0.085 \text{ \AA}^2$, respectively. A local vibration with frequency 108 meV corresponds to $\langle u_H^2 \rangle = 0.0128 \text{ \AA}^2$. (Notice: In the two other directions the frequency is higher, 174 meV [9], and the mean square displacement is reduced.) For large q vectors only the local vibrations are revealed. In contrast, for small q vectors also more delocalized motions influence the Debye-Waller factor, provided that that motion is rapid enough.

The result in Fig. 3 is also consistent with the fact that our model reproduces the vibrational motion very accurately but gives a slightly too large value for the diffusion coefficient. The large q vector behavior in Fig. 3 is determined by the local vibrations and our data at 580 K agree with the experimental values, which are obtained at $T=573$ K. For smaller q vectors also motion in between T sites contributes and here our results at $T=450$ K are more consistent with the experimental observation.

To reveal the microscopic details of the H motion we have determined the Van Hove self-correlation function $G_s(\mathbf{r}, t)$. The quantity $4\pi r^2 G_s(r, t)$ is shown in Fig. 4, which is equal to the probability at time t to find the H atom at the distance r from its location at $t = 0$. Already at $t=170$ fs (about half the mean residence time $\tau_{res} = 324$ fs) a substantial contribution is obtained at other T sites. Defining the occupancy of the initial site by the integral of $G_s(r, t)$ over a sphere with radius 0.6 \AA (half the distance between T sites) we get the occupancy 50% at $t=170$ fs. This should be compared with the CE model where the corresponding number is 85%. The large difference between these two numbers reveals the existence of a rapid diffusive type of motion (the H atom changes site), which is not accounted for in the simple CE model. We also notice that there is a large amplitude in

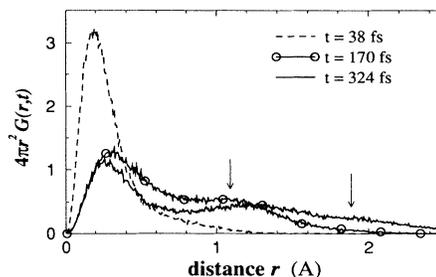


FIG. 4. The Van Hove self-correlation function $G_s(r, t)$ at $T=450$ K with nonadiabatic effects. The spatial dependence of $4\pi r^2 G_s(r, t)$ is shown at three different times: τ_{vib} , $\tau_{res}/2$, and τ_{res} . The two arrows indicate the distances to the nearest and to the second nearest neighboring T sites, respectively, assuming a T site to be located at $r = 0$.

between the sites, which shows that the H atom spends considerable time in these regions.

The Van Hove self-correlation function is only a two-point correlation function and more information can be gained by studying higher order correlations. For that reason we have investigated the correlation character for the H motion. We define the H atom to be located at a particular T site whenever it is within the distance $r_0 = 0.3 \text{ \AA}$ from that site. H can then move between different T sites and for simplicity we call this motion jumps. Two consecutive jumps define an angle θ . In Fig. 5 we show the most common cases, found in the simulation. Cases (a), (b), and (c) correspond to two consecutive nearest neighboring jumps and in case (d) and (e) a nearest neighboring jump is followed by a second nearest neighboring jump (or vice versa). We are interested in the correlation in directions for the different jumps. This is quantified by $g(\theta)$, the jump-angle distribution function, which gives the relative number of jumps with the angle θ [7]. Figure 6 shows the result at $T=450$ K and in all cases we have divided the result with the number of equivalent jump directions which all give the same value for θ . Assuming the CE model we should have $g(\theta = \pi) = g(\theta = \pi/2) = g(\theta = \pi/3)$ and all other

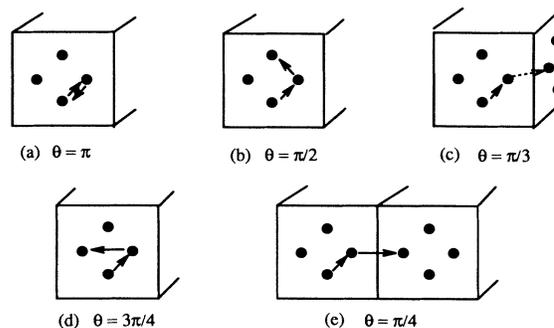


FIG. 5. Illustration of different jump directions.

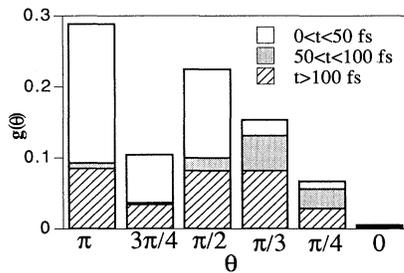


FIG. 6. The jump angle distribution $g(\theta)$ (see Fig. 5 for definition of the different cases). The total number of jumps for a given θ value is divided into three categories, depending on the magnitude of the residence time: $0 < t < 50$ fs, $50 < t < 100$ fs, and $t > 100$ fs.

g equal to zero. Obviously this is not the case and in particular we find a high probability of direct backward jumps.

In order to extract more information we have also determined the residence time at the site between the two consecutive jumps. The residence time is defined as the time difference between the moment when the H atom *first* enters the site and when it enters the next site. In Fig. 6 we show the result and we have then divided the total number of jumps into three different categories, depending on the magnitude of the residence time. We find that for the cases $\theta = \pi$, $\theta = \pi/2$, and $\theta = 3\pi/4$ a large portion of the jumps has a residence time shorter than 50 fs (the white areas). In the two other cases, $\theta = \pi/3$ and $\theta = \pi/4$, this is much less pronounced. We can now directly conclude that the rapid motion is a local motion essentially confined to a so-called $4T$ configuration [3]. The $6T$ or $3T$ configurations, which involve case (c) ($\theta = \pi/3$) only, are considerably less involved in the rapid motion.

In summary, we have shown that our model for H in Nb reproduces surprisingly well two key experimental observations; the strong deviations from simple jump-diffusion behavior [3,4] and the “anomalous Debye-Waller” factor

[3]. The results are found to be similar at both temperatures considered, $T = 450$ K and $T = 580$ K.

Our findings confirm the suggestion by Dosch *et al.* [3] about the existence of a rapid local diffusive type of motion and, in contrast to the neutron scattering data, our results unambiguously reveal the microscopic characters of the motion. The simulation clearly shows that on a time scale of the order 100–200 fs the H atom moves in between different T sites with high probability. This local diffusion is predominantly confined to the so-called $4T$ configuration. The time scale for the motion is found to be independent of temperature, but it is shifted to larger times if the mass of Nb is artificially increased [13].

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