

Coverage dependence and isotope effect in quantum surface diffusion

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We consider tunneling of an adatom through a substrate potential barrier in the presence of phonons. The phonon-adatom interaction leads to a concentration-dependent diffusion constant; the effective tunneling potential is significantly changed by the presence of nearby adatoms. We explain the coverage dependence of the low-temperature diffusion coefficient observed for hydrogen on the (110) plane of tungsten and the isotope effect as tritium is substituted for hydrogen.

The adsorption of hydrogen on metals has attracted considerable attention in surface science in recent years. DiFoggio and Gomer¹ have recently reported some interesting results on diffusion of hydrogen and deuterium on the (110) surface of tungsten, obtained by the field-emission fluctuation method. Among other things, they found a striking dependence of the diffusion coefficients on coverage. In the low-temperature region, where mobility occurs via tunneling, the diffusion coefficient D for hydrogen increases by more than an order of magnitude as the relative coverage Θ changes from 0.1 to ~ 0.3 ; D then starts decreasing as the coverage is increased further. Similar behavior has been observed for tritium by Wang and Gomer,² who also found that the magnitudes of D for the two isotopes deuterium and tritium are close to that of hydrogen. This is unexpected. For example, replacing the mass of ^1H by the mass of ^3H in the usual WKB formula for tunneling predicts a value of D four orders of magnitude smaller than observed.

While hydrogen and tritium behave similarly, the experimental coverage dependence for deuterium is very different. We do not understand this: It may be a consequence of the difference in statistics between bosons and fermions. We shall study hydrogen and tritium only. It has recently been reported³ that a surface reconstruction occurs near half coverage for hydrogen on the tungsten (110) surface. On the one hand this is a strong indication that adatom-phonon coupling is large in such systems and should affect surface diffusion. On the other hand, some of the features we explain using the phonon coupling could be affected by this reconstruction.

We visualize the system as follows. The surface potential is a periodic set of potential wells. At a given coverage, adatoms sit in these wells randomly. Diffusion at low temperature occurs when an adatom tunnels from one well to an adjoining one through the intermediate barrier.⁴ When an adatom sits in one of these wells, the system can gain energy by allowing the nearby substrate atoms to relax. The relaxation of the substrate atoms will contribute to the effective mass of the adatom. The effective mass of the isotopes will not be as different as their bare masses,

so the diffusion constants will vary less. If other adatoms are placed in nearby wells, the adatoms may compete for some of the intermediate substrate atoms, thereby frustrating their attempts to relax. This raises the potential of the tunneling adatom and consequently decreases its effective barrier. We will show in a model calculation, using a simple quadratic barrier potential, that a phonon coupling which changes the barrier width by $< 10\%$ is sufficient to increase the diffusion coefficient by the observed amount, and to explain the isotope effect.

For larger coverage, D is dominated by vacancy diffusion. Subsequent decrease in D at higher coverage Θ is then explained as an approximate particle-hole symmetry [$D(\Theta) \simeq D(1-\Theta)$]. Just as for an adatom, the system can gain energy by allowing the substrate atoms to relax around a vacancy; nearby vacancies will compete, lowering the barrier for their diffusion.

For simplicity we shall replace the substrate by a set of harmonic oscillators or phonons and use an adatom-phonon coupling linear in the phonon coordinate.⁵ Thus, if Q_j is the position coordinate of the j th adatom and q_k is the normal coordinate of the k th phonon mode, then our Lagrangian is

$$\mathcal{L} = \sum_j \frac{1}{2} M \dot{Q}_j^2 - V(Q_j) + \sum_k \left[\frac{1}{2} m \dot{q}_k^2 - \frac{1}{2} m \omega_k^2 q_k^2 - \sum_j \Lambda_k(Q_j) q_k \right]. \quad (1)$$

We use Feynman's path-integral methods⁶ to integrate out the phonon coordinates and obtain an effective Lagrangian consisting of an adiabatic piece⁷ and a time-retarded piece. These, in turn, each separate into a self-interaction and an adatom-adatom interaction mediated by phonons.

The adiabatic self-interaction $v(Q_j) = V(Q_j) - \sum_k [\Lambda_k(Q_j)/2m\omega_k^2]$ includes the relaxation energy of the nearby substrate atoms. Because of the competition for substrate atoms, the adiabatic adatom-adatom interaction $\gamma(Q_j, Q_{j'}) = \sum_k [\Lambda_k(Q_j)\Lambda_k(Q_{j'})/2m\omega_k^2]$ will be repulsive. We use a mean-field approximation

$\sum_j \gamma(Q_j, Q_j) \approx \gamma(Q_j) \Theta(1 - \Theta)$, where the factor $(1 - \Theta)$ has been heuristically added to preserve the particle-hole symmetry.

The time-retarded self interaction has been discussed in detail in Ref. 7; it represents phonon impediments to the adatom motion. If the adatoms move fast compared to the phonons, it leads to a phonon overlap integral; in the opposite limit it gives rise to a larger effective mass of the adatoms. In most atomic tunneling, the tunneling is slow; hydrogenic tunneling, however, is sometimes an exception.⁷ We shall use the effective mass

$$M^*(Q_j) = M + \sum_k \dot{\Lambda}'_k(Q_j)^2 / m\omega_k^4$$

as a convenient analytical approximation and examine the importance of the corrections later. The time-retarded adatom-adatom interaction reduces the phonon suppression because the substrate atom is not fully relaxed. This velocity-velocity contribution will be small because to first order only one of the adatoms moves. We will neglect this term, so that there will not be any coverage-dependent contribution from the time-retarded part. Our effective Lagrangian is thus

$$\mathcal{L}_{\text{eff}}(\mathbf{Q}) = \sum_j \frac{1}{2} M^*(Q_j) \dot{Q}_j^2 - v(Q_j) + \Theta(1 - \Theta) \gamma(Q_j). \quad (2)$$

To calculate D , we must choose a potential. Motivated by the effective medium potentials,⁸ we use a quadratic barrier with flat wells: $v(Q) = V_B [1 - (2Q/Q_1)^2]$ for $|Q| < Q_1/2$ and $v(Q) = 0$ for $Q_0/2 < |Q| < Q_1/2$, where $Q_0 = 2.72$ Å is the distance between the well centers (Fig. 1). The barrier height V_B contains the electronic contribution,⁷ the lattice-relaxation contribution, and a contribution from the difference between the transverse vibrational frequencies at the bottom of the well and at the top of the barrier,⁹ $\hbar\delta\omega_T \propto M^{-1/2}$. For hydrogen, $V_B = 0.2$ eV is known from experiment, and we shall use $\hbar\delta\omega_T = 0, 0.01, \text{ and } 0.05$ eV as three examples. While the coverage dependence is insensitive to the value chosen for $\hbar\delta\omega_T$, it changes the values of the parameters M^* and Q_1 . Note, however, that since the thermal-activation energy does not show any significant isotope dependence, $\hbar\delta\omega_T$ cannot be very large.

In the effective-mass approximation, the diffusion constant D is given by

$$D = D_0 \exp \left[-\frac{2}{\hbar} \int_{-Q_0/2}^{Q_0/2} [2M^*(Q)v(Q)]^{1/2} dQ \right] \\ = D_0 \exp \left[-\frac{\pi}{2} (M^* V_B)^{1/2} Q_1 / \hbar \right]. \quad (3)$$

The prefactor $D_0 \sim \omega_0 Q_0^2$, where ω_0 is a characteristic vibrational frequency of the potential well; $D_0 \sim 10^{-2}$ cm²/sec. In Eq. (3) we have assumed M^* is independent of Q . This is so if the coupling $\Lambda(Q)$ is taken to be of the form $\Lambda(Q) = \Lambda_0 (2Q/Q_1)$. This gives $M_H^*/M_H = 1 + b\bar{\gamma}(Q_0/Q_1)$, where $\bar{\gamma} = \Lambda_0 / (2m\omega_D^2)$ and $b = 8(\hbar^2/M_H Q_0^2) / (\hbar\omega_D^2)$ is a constant and we have used Einstein phonons with frequency ω_D . We can use $D_H(\Theta=0) = 6 \times 10^{-13}$ cm²/sec and $D_T(\Theta=0) = 4 \times 10^{-14}$

TABLE I. Parameters Q_1/Q_0 and M_H^*/M_H obtained from zero-coverage data and the corresponding dimensionless phonon frequency Ω and coupling $\bar{\Lambda}$ for hydrogen for different choices of $\hbar\delta\omega_T$.

$\hbar\delta\omega_T$	Q_1/Q_0	M_H^*/M_H	Ω	$\bar{\Lambda}$
0	0.25	10.4	0.22	0.46
0.01	0.26	9.2	0.24	0.46
0.05	0.32	6.0	0.29	0.43

cm²/sec to fix M_H^* (or alternatively $\bar{\gamma}$) and Q_1 . Table I shows Q_1/Q_0 and M_H^* for different choices of $\hbar\delta\omega_T$.

At a finite coverage, the potential $v(Q)$ is replaced by $\tilde{V}(Q) = v(Q) - \gamma(Q)\Theta(1 - \Theta)$, where $\gamma(Q) = \bar{\gamma}(2Q/Q_1)^2$. Note that the coverage dependence is now completely determined since both $\bar{\gamma}$ and Q_1 have already been fixed from zero coverage data. Figure 2 shows the coverage dependence of D for both hydrogen and tritium for $\hbar\delta\omega_T = 0$. Agreement with experiment is quite good for tritium, but not as good for hydrogen. In both cases there is an initial dip, and a small asymmetry, neither of which comes from our model. There are two conceivable mechanisms that might produce the initial dip. It may be a crossover to a bandlike diffusion at very low coverage where D is expected to increase with decreasing Θ . It is also possible that the surface reconstruction mentioned earlier occurs at this coverage. As for the asymmetry, we clearly do not expect the particle-hole symmetry to be exact; on the other hand the deviation from the symmetry is not very large either.

The model also provides an explanation for the discrepancy between the barrier height obtained from the experiment (~ 0.2 eV) and that calculated in the effective medium theories⁸ (~ 0.08 eV). We expect the self-interaction term in Eq. (4) to be of the same order of magnitude as the effective adatom-adatom interaction energy $\bar{\gamma}$ (~ 0.1 eV), the former being essentially the barrier height due to phonons. The effective medium theories consider only the electronic relaxation; our calculations show that phonons are equally important. From the estimate of $\bar{\gamma}$ we can estimate the magnitude of relaxation of a tungsten atom due to the presence of an adatom nearby. If δq is the shift in position of a tungsten atom from its normal equilibrium position, then the elastic energy gain $\frac{1}{2} m\omega_D^2 (\delta q)^2$ must be roughly equal to $\bar{\gamma}$. This gives $\delta q \sim 0.07$ Å.

With our estimate of the adatom-adatom coupling strength we can now consider the validity of the effective-mass approximation. We consider the dimensionless phonon frequency $\Omega \equiv \omega_D / \omega_{DW}$ and the dimen-

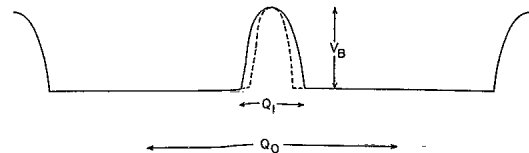


FIG. 1. Quadratic barrier model for the substrate potential. The form for this potential is motivated by the effective medium theories (Ref. 8). Dotted line shows the potential at a finite coverage.

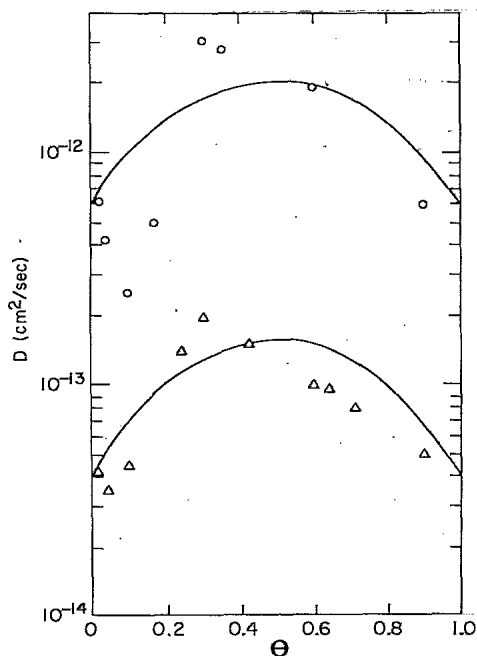


FIG. 2. Coverage (Θ) dependence of diffusion coefficient D for hydrogen and tritium [on the (110) plane of tungsten] in the quadratic barrier model for $\hbar\delta\omega_T=0$. (The curves are quite insensitive to the choice of $\hbar\delta\omega_T$.) Experimental points (\circ for hydrogen, Δ for tritium) are from Wang and Gomer, Ref. 2. We mention two possible mechanisms for the initial dip in the diffusion coefficient. Our theory fails to explain the deuterium data.

sionless coupling $\bar{\Lambda} = \Lambda^2 / [m\omega_{DW}^2(Q_0/2)^2]$, where the double-well (DW) frequency ω_{DW} is the frequency of the top of the barrier (Fig. 1). Table I shows Ω and $\bar{\Lambda}$ for different choices of $\hbar\delta\omega_T$. The values for hydrogen are somewhat out of the slow-flip regime⁷ and the effective-mass approximation will overestimate the effects of phonons by 20 to 50%. A more careful self-consistent instanton calculation will presumably increase the predicted coupling Λ_0 by similar amount. Tritium with $\Omega \sim 0.5$ will be pretty accurately described with an effective mass. We plan to pursue both the correction to the effective-mass

approximation and the assumption of no coherence between hops in future work. (The deuterium data seem to imply some coherence.)

In summary, we have investigated the effects of adsorbate-phonon coupling on the low-temperature surface mobility of hydrogen on the tungsten (110) surface. Using an adsorbate-phonon coupling strength that is compatible with experimental bounds and with small tungsten displacement, we can explain three features of the experimental data. First, we explain the isotope effect. The effective mass contributed by the phonon modes reduces the change in tunneling rate as tritium is substituted for hydrogen. Secondly, we explain the discrepancy between the experimental barrier height and that predicted by effective medium theories. The computer simulations ignore substrate atomic relaxation, whose contribution to the effective barrier in our model is of the same order as the "bare" electronic barrier. Finally, we explain the striking coverage dependence of the surface mobility. In our model the adsorbate atoms compete for the tungsten atoms lying between them. The effective adsorbate-adsorbate interaction is therefore repulsive, and tends to lower the barrier for diffusion. Together with an approximate particle-hole symmetry, this phonon coupling describes the coverage dependence well. Adsorbate-phonon couplings clearly are of large importance in this system.

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⁴We assume that the diffusion constant is proportional to the tunneling matrix element squared, and the coherence is destroyed between tunneling events [T. Holstein, Ann. Phys.

(N.Y.) 8, 343 (1959)]. This is in contrast to band theories proposed recently to describe hydrogen diffusion on nickel [M. J. Puska, R. M. Nieminen, M. Manninen, B. Chakraborty, S. Holloway, and J. K. Nørskov, Phys. Rev. Lett. 51, 1081 (1983)]. Most of our qualitative conclusions would be unchanged with, say, a linear dependence of D on the tunneling matrix element.

⁵Although we shall consider phonons only, the formalism will clearly be valid for plasmons (electronic relaxation) as well. Plasmons will not contribute to the effective-mass suppression of the tunneling rate.

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