Adsorbate surface diffusion: The role of incoherent tunneling in light particle motion

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Abstract

The role of incoherent tunneling in the diffusion of light atoms on surfaces is investigated. With this purpose, a Chudley-Elliot master equation constrained to nearest neighbors is considered within the Grabert-Weiss approach to quantum diffusion in periodic lattices. This model is applied to recent measurements of atomic H and D on Pt(111), rendering friction coefficients that are in the range of those available in the literature for other species of adsorbates. A simple extension of the model has also been considered to evaluate the relationship between coverage and tunneling, and therefore the feasibility of the approach. An increase of the tunneling rate has been observed as the surface coverage decreases.

1. Introduction

Hydrogen diffusion on metal surfaces is being the subject of an intensive applied and fundamental research for many years [1–7]. On the one hand, the involvement of this process in the design of fuel cells or in the storage of H_2 makes it of technological interest. On the other hand, at a fundamental level, a good understanding of this dynamics is essential, for it provides important information on the adiabatic interaction between adsorbate and substrate. Indeed, because atomic hydrogen is the simplest element that may undergo chemisorption, its motion on a weakly corrugated surface constitutes a benchmark to study two possible competing diffusion processes: classical (activated) *over-barrier* hopping *versus* quantum-mechanical *under-barrier* tunneling. These two diffusion mechanisms are intimately related to the role played by phonons and conduction electrons. In the classical regime, the rate decreases with the inverse of the temperature until reaching the quantum/tunneling regime, where the corresponding rate approaches a constant, temperature-independent value. Apart from bulk or surface diffusion problems, this behavior is also typical in many different chemical reactions or processes [8–10].

Motivated by recent measurements of atomic hydrogen on a Pt(111) surface [7], here we tackle this surface diffusion problem assuming that the process is essentially ruled by deep tunneling. The adsorbate quantum motion between neighboring sites will take place mainly through incoherent tunneling for not too low surface temperatures. As shown elsewhere [11, 12], in this regime the Chudley-Elliott model results very convenient to describe the corresponding (surface) dynamics. Now, in order to include properly the effects of deep tunneling and temperature, we have also made use of the approach developed by Grabert and Weiss to account for quantum diffusion in periodic potentials [10, 13, 14]. In particular, the so-called bounce

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technique considered by these authors has allowed us to establish the connection between this approach and the Chudley-Elliott model, and therefore to obtain an analytical expression to account for transition rates in conditions of deep tunneling. The application of this model to the aforementioned experimental data has rendered a good agreement between theory and experiment in a fitting procedure. More specifically, we have been able to extract friction coefficients for the two adsorbed species considered in the experiment, namely H and D. The values obtained are in consonance with the isotopic effect (γ_D is about a factor two smaller than γ_H) as well as with those reported in the literature for other species [15], which are of the order of picoseconds. Furthermore, in order to investigate the effects of the surface coverage on tunneling diffusion, and corroborate the friction coefficients extracted from the fitting procedure, we have also carried out an alternative analysis by means of a temperature-dependent, collisional-friction model [16–18], shown to be valid at low coverages (as it is the case of the experiment, where $\theta = 0.1$ ML, and below). In this model (the so-called two bath model), the adsorbate undergoes a total friction resulting from the sum of two contributions, namely the usual substrate friction plus a collisional friction accounting for the collision among adsorbates. From its application, we have observed that tunneling rates increase as the coverage decreases, which would be consistent with the intuitive fact that tunneling between neighboring sites becomes faster and, therefore, more relevant.

2. Theory

Diffusive surface dynamics is usually described in terms of a series of discrete jumps undergone by the adparticle when it moves on a two-dimensional periodic lattice of binding sites. In the case of activated diffusion, when the thermal energy is higher than the barrier height separating neighboring sites, adparticles are mainly assumed to perform discrete over-barrier jumps between sites. In the specific case of the Chudley-Elliott model, this diffusion dynamics is accounted for by a master equation in terms of the van Hove $G(\mathbf{R}, t)$-function or time-dependent pair correlation function [19]. This function is widely used to describe statistical ensembles of interacting particles, thus generalizing the well-known pair distribution function $g(\mathbf{R})$ from statistical mechanics [20] by providing information about the interacting particle dynamics. In other words, given a particle at the origin at some arbitrary initial time $t = 0$, $G(\mathbf{R}, t)$ gives the averaged probability of finding the same or another particle at the surface position $\mathbf{R}$ at time t.

The same approach can be extended to analyze under-barrier, tunneling transmission. This is the behavior expected for lighter particles, such as atomic hydrogen, and thermal energies lower than the barrier height, where tunneling-mediated diffusion is assumed to be dominant in the dynamics between nearest neighbors [7]. In such a case, incoherent tunneling can be described by means of a general master equation of the form

$$\dot{G}(\mathbf{R}, t) = \sum_{\mathbf{j}} \nu_{\mathbf{j}} \, G(\mathbf{R} + \mathbf{j}, t), \tag{1}$$

where $\nu_{\mathbf{j}}$ accounts for the tunneling rate involved in the transition between the lattice point $\mathbf{R}$ and the nearby one $\mathbf{R} + \mathbf{j}$, with $\mathbf{j}$ being the jump vector among different lattice points running over all lattice vectors (positive, negative, and even zero).

The space Fourier transform of the G-function is the intermediate scattering function,

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K}\cdot\mathbf{R}(t)} e^{i\Delta\mathbf{K}\cdot\mathbf{R}(0)} \rangle, \tag{2}$$

with the brackets denoting an ensemble average. This function measures the time correlation loss for a given parallel (along the surface) momentum transfer of the probe particle, $\Delta\mathbf{K}$. Therefore, it can also provide us with information about friction coefficients at different coverages and (surface) temperatures along with the observed $\Delta\mathbf{K}$ direction. Without loss of generality, we can assume the diffusion process among the different wells formed by the surface corrugation is one-dimensional along this direction. Hence the intermediate scattering function can be expressed as a Fourier series, as

$$I(\Delta K_{\parallel}, t) = \sum_{n} G_n(t) e^{i\Delta K_{\parallel} n}, \tag{3}$$

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where $\Delta K_\parallel$ is a dimensionless momentum transfer resulting from the projection of the lattice vector $\mathbf{j}$ along the direction pointed by $\Delta \mathbf{K}$ multiplied by the lattice constant a, i.e., $\Delta K_\parallel = a\|\Delta \mathbf{K}\|\cos\alpha$, with α being the angle between $\Delta \mathbf{K}$ and $\mathbf{j}$. Only first neighbors are considered. Therefore, in the particular case of the Pt(111) lattice geometry [1], for four of these neighbors $|\Delta K_\parallel| = a\Delta K \cos(\pi/6)$, while for the other two, $\Delta K_\parallel = 0$. Regarding n, it labels the n-th well of the binding site (bearing in mind this tight-binding like model).

Taking this into account, for nearest neighbors, Eq. (1) can be expressed in terms of the $G_n(t)$ coefficients, as

$$\dot{G}_n(t) = \nu_{n-1}^+ G_{n-1}(t) + \nu_{n+1}^- G_{n+1}(t) - (\nu_n^+ + \nu_n^-)G_n(t). \tag{4}$$

Here, $\nu_{n\mp1}^\pm$ denotes the tunneling transition rate from the $(n\mp1)$-th well to the n-th one, while $\pm$ account for the tunneling rates to the right or left neighboring well, respectively. Tunneling rates are assumed to be equal for the left or right direction and independent of the well site. The differential equation (4) can be solved analytically for the initial conditions $G_n(0) = \delta_{n,0}$. From this solution, we find that the intermediate scattering function can be recast as

$$I(\Delta K_\parallel, t) = e^{-2\bar{\Gamma}t\sin^2(\Delta K_\parallel/2)} = e^{-\bar{\Gamma}t}e^{\bar{\Gamma}t\cos(\Delta K_\parallel)} = e^{-\bar{\Gamma}t} \sum_{n=-\infty}^{\infty} I_n(\bar{\Gamma}t)e^{i\Delta K_\parallel n}, \tag{5}$$

where I_n is the modified Bessel function of integer order n and $\bar{\Gamma} = \nu/2$ describes the global tunneling rate. This standard form is in agreement with the models found in the literature to describe surface diffusion.

Equation (4) is the same equation already obtained by Grabert and Weiss [10, 13, 14] to describe quantum diffusion in periodic lattices. By means of the so-called bounce technique, they found an analytical expression for the tunneling transition rate between adjacent sites, which reads as

$$\bar{\Gamma} = \frac{\sqrt{\pi}}{2}\frac{\Delta^2}{\omega_0}\left(\frac{\pi k_B T}{\hbar\omega_0}\right)^{2\zeta-1}\frac{\Gamma(\zeta)}{\Gamma(\zeta + 1/2)}, \tag{6}$$

where $\Gamma(\zeta)$ denotes the Gamma function of the dimensionless friction coefficient,

$$\zeta = \frac{ma^2}{2\pi\hbar}\,\gamma, \tag{7}$$

$\omega_0 = V''(r_{\min})/m$ is the well harmonic frequency, m is the adparticle mass, and Δ is the dressed tunnel matrix, which is a function of the so-called bare tunnel matrix [10], Δ_0. Computing the diffusion coefficient through the simple relation

$$D = a^2\bar{\Gamma}, \tag{8}$$

one clearly sees that the usual Einstein relation does not hold anymore in the case of tunneling, since it does not scale with the friction coefficient as γ^{-1}.

The characteristic temperature power law for tunneling rates given by Eq. (6) was first proposed by Grabert and Weiss [13, 14] and Kondo [21] when analyzing the non-adiabatic response of the conduction electrons. This relation is claimed to be valid at any temperature (including zero temperature) provided $\zeta > 1$. This fact is precisely what warranties the applicability of the Grabert-Weiss approach here. As it will be seen in the next Section, the value of ζ obtained for both adsorbates is such that this relation effectively holds, and therefore that this approach is valid to describe the experiment along the whole range of temperatures considered in it.

According to the diffusive model here considered, the loss mechanism may come from the lattice relaxation and/or the electronic contribution. Hence, the spectral densities as well as the corresponding friction coefficients are additive. In principle, the power law (6) is a general result for Ohmic friction regardless of the loss mechanism and for surface temperatures below the crossover temperature. As reported by Sundell and Wahnström [4], this typical power law was first suggested by Kondo [21] and seems to be related to the electronic contribution, i.e., the non-adiabatic response of the conduction electrons to the adparticle (H or D) motion. However, a similar behavior can also be found when the lattice relaxation is replaced by
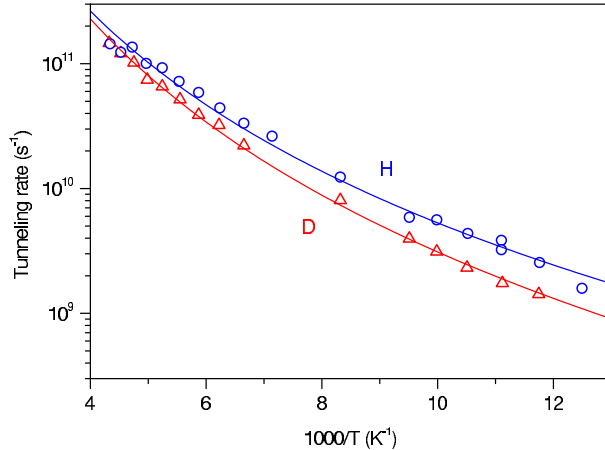
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Figure 1: Tunneling rates for H (experiment: blue open circles; fitting: blue solid line) and D (experiment: red open triangles; fitting values: red solid line) for a coverage of 0.1 ML.

a non-Ohmic dissipation [22]. In view of the temperature-dependent behavior discussed by Grabert and Weiss [13, 14], and also presented here, the use of this power law seems to be quite more general and valid for any loss mechanism or the addition of several uncorrelated loss mechanisms (which implies the sum of friction coefficients due to electrons, phonons, and adsorbates) than Wolynes' dissipative transition state theory [9, 23].

3. Results

In order to test the feasibility of the above approach and therefore the role of tunneling in adsorbate surface diffusion, we are going to analyze the experimental data obtained [7] for atomic H and D on Pt(111) at a low coverage ($\theta = 0.1$ ML) and a range of temperatures between 80 K and 250 K. The observable in these experiments is the so-called polarization function, which is essentially the intermediate scattering function (5) (or, at least, proportional to it). Thus, by means of a simple fitting of the experimental data to a functional form $I(t) = Ae^{-\alpha t} + B$ for Eq. (5), for a fixed coverage, momentum transfer, and temperature, the dephasing rate, α, is obtained. Combining these results with the Chudley-Elliott model, one obtains the jump statistics, which are used to determine the transition rates, $\bar{\Gamma}$, as the total hopping rate.

In Fig. 1 we show our best fit curves (solid lines) to the experimental data (open symbols) for H (blue) and D (red). To simplify the fitting procedure, but without loss of generality, Eq. (6) is recast as

$$\bar{\Gamma}_{\text{fit}} = C \left(\frac{1000}{T} \right)^{1-2\zeta}, \tag{9}$$

so that eventually only two fitting parameters are needed. Accordingly, we find $C_{\text{H}} = \exp(32.21)$ and $\gamma_{\text{H}} = 13.6$ ps^{-1}, and $C_{\text{D}} = \exp(32.66)$ and $\gamma_{\text{D}} = 7.4$ ps^{-1}, where γ is determined from Eq. (7). As expected, γ_{D} is about twice smaller than γ_{H}, in agreement with the mass scaling factor m^{-1}, i.e., displaying the isotopic effect. Nevertheless, what is more remarkable is the fact these friction coefficients imply dissipation time scales much shorter than those rendered by the theoretical approach followed in Ref. [7], based on Wolynes' dissipative transition state theory [9, 23]. The resulting friction coefficients are $\gamma_{\text{H}} \approx 1.15$ ns^{-1} and $\gamma_{\text{D}} \approx 0.57$ ns^{-1} (which still display the correct factor two between them). It is thus clear that incoherent tunneling seems to be playing an important role (as also acknowledged in Ref. [7]). Nevertheless, our values for the friction coefficients are rather close to those found for other adsorbates considered in the literature, typically lying in the range 0.1–5 ps^{-1} [15]. Moreover, we have also found that $\zeta_{\text{H}} = 2.63$ and $\zeta_{\text{D}} = 2.85$, which ensures the suitability and validity of this approach to describe the range of temperatures considered in the experiment (actually, it should be valid even down to zero surface temperature [13]).
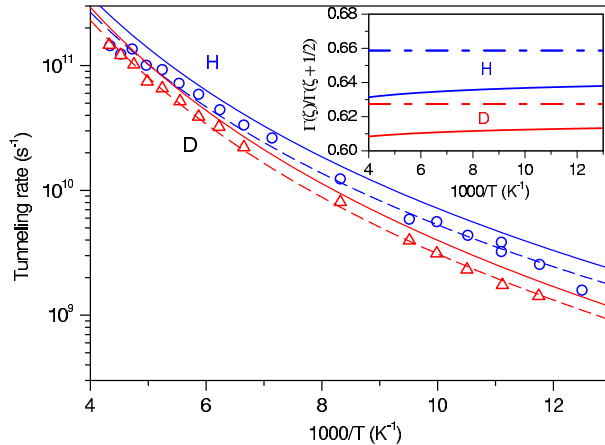
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Figure 2: Tunneling rates for H (blue solid line) and D (red solid line) for a coverage of 0.01 ML; to compare with, the same curves (dashed curves) from Fig. 1 are plotted for $\theta = 0.1$ ML, but fitted according to a two-bath model (see text for details). In the inset, the negligible variation of the prefactor $\Gamma(\zeta)/\Gamma(\zeta + 1/2)$ along the range of temperatures analyzed is also shown for $\theta = 0.1$ ML (solid line) and $\theta \approx 0$ ML (dash-dotted line).

The scenario of several loss mechanisms discussed at the end of the previous section readily arises when considering the fact that diffusion by tunneling is actually affected by surface coverage [1]. In order to analyze this effect as well as to corroborate the previous friction coefficients, an alternative fitting is considered by using a temperature-dependent, collisional-friction model, namely the so-called two-bath model [16–18]. More specifically, this model has been considered to accomplish two purposes: (1) to corroborate the fitting values of the friction parameters obtained with the Grabert-Weiss theory, and (2) to determine the effect of low coverages on tunneling rates. This thus confers much more reliability to the friction values found above, removing any trace of arbitrariness.

Within the two-bath model, one bath describes the effect of surface phonons, while the other one accounts for the collisions among the interacting adsorbates. These two baths are assumed to be uncorrelated and therefore the corresponding frictions are additive. Accordingly, the total friction, now denoted by η, is a sum of two contributions: the usual substrate friction, γ, and a collisional friction, λ, accounting for collisions among adsorbates ($\eta = \gamma + \lambda$). For a convenient and simple analytical estimate of the λ dependence on the coverage and temperature, a simple hard-sphere model (even though we are well aware that the dependence might be much more complex) leads to a collisional friction given by [17]

$$\lambda = \frac{6\rho\theta}{a^2} \sqrt{\frac{k_B T}{m}}, \tag{10}$$

where ρ is the adparticle effective radius. This equation clearly indicates that the collisional friction is proportional to the coverage and to the square root of the surface temperature. Thus, this equation could also be used to extract such a coefficient by considering the proportionality constant a fitting parameter. Accordingly, increasing the coverage leads to an also increase of the collisional friction and therefore of the total friction. This allows us to readily express our relations for tunneling quantum diffusion as a function of coverage (with a range of validity up to $\theta \approx 15 - 20\%$). In order to distinguish in the friction coefficient the contributions coming from the surface thermal effects and the collisions, the fitting is carried out by expressing the exponent in Eq. (6) as $1 - b\gamma - c\sqrt{T/1000}$.

Following the above best fit procedure on the experimental data, we compute again the curves for $\theta = 0.1$ ML, finding $C_H = \exp(32.54)$, $b_H = 0.388$ ps, $\gamma_H = 13.56$ ps^{-1}, and $c_H = 0.462$ K$^{-1/2}$, and $C_D = \exp(32.93)$, $b_D = 0.775$ ps, $\gamma_D = 7.34$ ps^{-1}, and $c_D = 0.382$ K$^{-1/2}$. As seen in Fig. 2, the new fitting curves for $\theta = 0.1$ ML (blue and red dashed lines for H and D, respectively) are also in agreement with both the experiment and the previous fitting curves (see Fig. 1). Furthermore, the values of the substrate friction γ for H and D are nearly equal to those found before assuming that all friction effects were included

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in η, thus making apparent again the isotopic effect and that we are in a moderate collisional regime. Now, according to this new functional dependence of the tunneling rate on the coverage and surface temperature, if we consider $c = c'\theta/0.1$, then the curves for a lower coverage can also be readily determined. For example, in Fig. 2 they are displayed for $\theta = 0.01$ ML (blue and red solid lines for H and D, respectively).

According to this second fitting model, our preliminary assumption that the multiplying factor $\Gamma(\zeta)/\Gamma(\zeta + 1/2)$ can be considered to be a constant finds a justification. As seen in the inset of Fig. 2, the variation of this function along the range of temperatures considered when ζ is expressed as a function of temperature increases only about 1% for H and 0.8% for D as T decreases in the case of $\theta = 0.1$ ML (for $\theta \approx 0$ this increment is meaningless). It is worth stressing the fact that, as seen in Fig. 2, a decrease in the total friction (by lowering the coverage or equivalently the collisional friction) leads to an enhancement of tunneling ($\bar{\Gamma}$ increases). This behavior is consistent with our model, since the occurrence of tunneling should be favored by decreasing the environmental actions on the adsorbed system. Given the high accuracy that can be reached by ^{3}He spin-echo measurements, this is a result which would be worth checking experimentally. It would help to understand and therefore to uniquely determine whether tunneling play indeed a major role in the surface diffusion of light particles, as claimed here or in Ref. [7] (though approaching the problem from dissipative transition state theory). Notice that this (predicted) behavior of the transition rate with the coverage is opposite to previous experimental results carried out on the same systems with quasielastic He-atom scattering and analyzed in terms of the Arrhenius law [1]. In this case, relatively large coverages were considered (above 15%), out of the range of validity of our model, where collective motion effects could start playing a role and therefore screening any tunneling effect. As observed in these measurements, errors increase largely as one goes to lower temperatures and coverages, this being the reason why possibly ^{3}He spin-echo would be a better experimental method to analyze lower coverages.

4. Conclusion

Summarizing, we have tackled the problem of surface diffusion of light particles from the perspective of the Grabert-Weiss approach to incoherent tunneling in periodic lattices [10, 13, 14]. More specifically, we have focused on a series of recent experimental measurements for H and D on Pt(111). From the feasibility of the fittings obtained to the experimental data, we infer that the process is essentially ruled by incoherent tunneling rather than (over-barrier) hopping. In this regard, even though our approach differs from that considered by Jardine *et al.* [7], equally accurate fittings have also been obtained for the same sets of experimental data. Indeed, by means of this model we have determined friction coefficients, which involve time scales several orders of magnitude smaller and are close to the typical values found for other species [15].

In principle, the theories developed by Grabert and Weiss, and Kondo are more general than Wolynes' one, covering the whole range of surface temperatures involved in the experiment. Moreover, according to Kondo, it takes into account the conduction electrons of the surface, as it is clearly stressed in [4]. In our opinion, these facts could be at the origin of the discrepancies found in the friction coefficients of H and D atoms on Pt(111).

In order to study the dependence of the tunneling rate with the surface coverage and therefore the collisional friction, we have also considered a second two-bath model [16–18], valid for moderate coverages. According to this model, the tunneling rate increases as coverage decreases. Taking into account that $\bar{\Gamma}^{-1}$ provides us with a time scale for the diffusion process, it means that tunneling becomes faster for lower coverages, which would be consistent with the fact that environmental interactions inhibit it. According to previous measurements [1] of this effect for higher coverages than the moderate values considered by us, the process seems to be the opposite. In this case it could happen that collective motions are also contributing to the transition rate, screening the effects purely due to tunneling. Moreover, the order of the errors in these measurements is also relatively large and therefore it is difficult to establish a comparison. New measurements based on the more accurate ^{3}He spin-echo technique could render possibly some light in this regard. Nonetheless, what seems to be clear is that surface diffusion of light particles seems to be still far from a final interpretation and description of the process. The discrepancies in the theoretical descriptions rather suggest that more complete and detailed simulations are needed, perhaps incorporating full ab initio

calculations with the purpose to eventually elucidate the main mechanism involved in these processes as well as to accurately determine the corresponding friction constants.

Acknowledgements

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