

## Energy Dissipation during Diffusion at Metal Surfaces: Disentangling the Role of Phonons versus Electron-Hole Pairs

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Helium spin echo experiments combined with *ab initio* based Langevin molecular dynamics simulations are used to quantify the adsorbate-substrate coupling during the thermal diffusion of Na atoms on Cu(111). An analysis of trajectories within the local density friction approximation allows the contribution from electron-hole pair excitations to be separated from the total energy dissipation. Despite the minimal electronic friction coefficient of Na and the relatively small mass mismatch to Cu promoting efficient phononic dissipation, about  $(20 \pm 5)\%$  of the total energy loss is attributable to electronic friction. The results suggest a significant role of electronic nonadiabaticity in the rapid thermalization generally relied upon in adiabatic diffusion theories.

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Energy dissipation during surface dynamical processes at solid surfaces has been extensively studied, both due to its paramount technological importance and intriguing fundamental richness. Scattering or adsorption of molecules, diffusion, and chemical reactions are all known to be intricately governed by the detailed ways in which chemical and kinetic energy is transferred into and out of substrate degrees of freedom. On insulating or semiconducting surfaces the dynamical coupling to the surface can be attributed to the excitation of and interaction with lattice vibrations with some confidence. In contrast, on metal surfaces the role of competing electronic nonadiabatic effects such as electron-hole (*eh*) pair excitations is a continuing topic of debate. In fact, there is growing experimental evidence that can only be rationalized by breaking with the prevalent Born-Oppenheimer view [1,2]. It may even be argued that due to the continuum of substrate electronic states at the Fermi edge, no dynamical process can strictly be adiabatic at metal surfaces at all [3,4]. On the other hand, many phenomena still seem to be very well described using purely adiabatic theories [5–9].

Recent *ab initio* calculations of dynamical phenomena beyond the Born-Oppenheimer approximation have attempted to resolve some of this ambiguity [10–14]. In particular the numerically appealing concept of electronic friction [10,15–17] within the local density friction approximation (LDFA) [18,19] has become a popular approach in this regard [14,18,20–24]. Scattering processes [8,14,18,25,26] and (dissociative) adsorption events [10,14,23,27] have gained the most attention in this context and with the high incident energies, short contact times, and massive charge rearrangements such processes are likely to be good candidates for a high degree of electronic nonadiabaticity.

In comparison to scattering and adsorption processes, the situation is less clear for surface diffusion. On the one hand, diffusing adsorbates are necessarily close to the surface and in regions of high electronic density, with a concomitant amount of electronic friction. On the other hand, the comparably low velocities that are involved may suppress the nonadiabatic channel and thus favor a coupling to the phononic degrees of freedom to finally render surface diffusion electronically adiabatic. Interestingly, a significant contribution of nonadiabatic energy dissipation in the transient H-atom diffusive motion following H<sub>2</sub> dissociation over Pd(100) has been reported by Blanco-Rey and co-workers only recently [20,21,24]. The results are consistent with a similar prediction by Wahnström made for H diffusion on Ni(100) in the late 1980s [28]. Hydrogen diffusion is, however, a somewhat special case given that competing phononic couplings are small for this very light adsorbate [21,24].

In order to obtain a more comprehensive insight into the relative importance of lattice vibrations and *eh*-pair excitations for the energy dissipation during surface diffusion we therefore address the thermal motion of Na on Cu(111). Alkali metal systems have long been used as prototypical systems due to the relative simplicity of their surface chemistry [29,30] and the Na/Cu combination chosen for the current work benefits from having a much higher adsorbate-substrate mass ratio in comparison to H/Pd. Together with the thermally distributed adsorbate velocities, the coupling to phononic degrees of freedom might be expected to be significantly stronger. Simultaneously, the electronic friction coefficient is a material property that exhibits the well known  $Z_1$  oscillations as a function of the atomic number [17,31,32]. At any embedding density of interest for surface diffusion, the electronic friction is found

to be particularly low for light alkali metals. We might, therefore, expect minimal  $eh$ -pair excitations during the diffusive dynamics of sodium on a free-electron-like metal such as copper. As a consequence one would expect phononic coupling to dominate the overall dynamic interaction with the substrate for Na/Cu(111). Analyzing helium spin echo signatures for surface diffusion with *ab initio* based Langevin molecular dynamics (MD) simulations we nevertheless find that the energy loss due to electronic friction contributes approximately  $(20 \pm 5)\%$  of the total energy dissipation, thus reinforcing the view that diffusion is an important class of dynamical processes in which electronic nonadiabaticity is anything but negligible.

The helium spin echo technique utilizes the  $^3\text{He}$  nuclear spin as an internal timer, providing direct access to the intermediate scattering function (ISF)  $I(\Delta\mathbf{K}, t)$  at a momentum transfer  $\Delta\mathbf{K}$  specified by the scattering geometry [33]. As a result of surface adsorbate motion the (auto) correlation determined through the ISF decays in time, and for processes where the adsorbate couples to the degrees of freedom of the substrate would typically exhibit an exponential decay. The decay rate  $\alpha(\Delta\mathbf{K})$  is highly sensitive to the frictional adsorbate-substrate coupling, with a functional dependence on  $\Delta\mathbf{K}$  characteristic of the detailed diffusion mechanism [34,35]. In the present study experiments were conducted at a surface temperature of 155 K with measurements along the  $[11\bar{2}]$  azimuth of a Cu(111) crystal dosed to a coverage of  $\Theta = 0.025$  monolayer (ML) of sodium [36].

The form of  $\alpha(\Delta\mathbf{K})$  extracted from the data is shown in Fig. 1. At large values of  $|\Delta\mathbf{K}|$  the behavior is indicative of single-jump diffusion, consistent with the Chudley-Elliott model [37], while at smaller values below about  $0.6 \text{ \AA}^{-1}$  there is an obvious deviation from the ideal sinusoidal signature that is consistent with “de Gennes narrowing” [38] and observed for previous works on repulsive interacting adsorbates [35], notably sodium diffusing on the Cu(100) surface [39].

A quantification of the adsorbate-substrate frictional coupling can be achieved within the kinematic scattering approximation [35]. As further detailed in the Supplemental Material [40], the ISF is directly related to the real-space motion  $\mathbf{R}_j(t)$  of an ensemble of  $N_{\text{atoms}}$  adsorbates  $j$  through the autocorrelation function of the coherent intermediate amplitudes

$$A(\Delta\mathbf{K}, t) = \sum_j^{N_{\text{atoms}}} \exp[-i\Delta\mathbf{K} \cdot \mathbf{R}_j(t)]. \quad (1)$$

The corresponding trajectories  $\mathbf{R}_j(t)$  are conveniently obtained from Langevin MD simulations, in which the overall friction coefficient  $\eta$  is varied until optimum agreement with the experimental decay rates is obtained [34,35,58]. Specifically, in the current work we employed a system of  $N_{\text{atoms}} = 200$  adatoms in a supercell consisting of

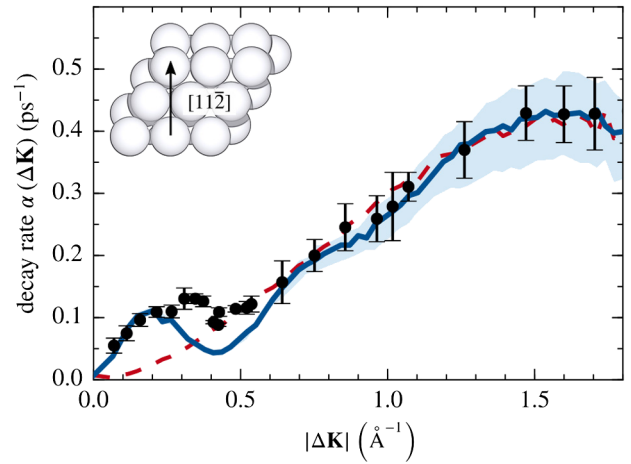


FIG. 1. Experimentally measured decay rates  $\alpha(\Delta\mathbf{K})$  along the  $[11\bar{2}]$  surface direction as opposed to those extracted from simulations with a best-fit friction coefficient of  $\eta = 10 \text{ amu ps}^{-1}$  (solid blue line). The blue-shaded region indicates the sensitivity when varying the free parameter  $\eta$  by  $\pm 30\%$ . Simulations using an optimum value for  $\eta$ , but without adsorbate-adsorbate interaction potentials, yield the dashed sinusoidal red line. This line lacks the de Gennes narrowing peak at small  $|\Delta\mathbf{K}|$ , but is unaffected in the region sensitive to the frictional coupling.

a  $(49 \times 82)$  array of rectangular Cu(111) unit cells and used  $T = 155 \text{ K}$  to match the experimental Na coverage and temperature. Appropriate averaging over 100 MD runs accumulated over 1.6 ns ( $2^{14}$  steps) each ensured converged decay rates  $\alpha(\Delta\mathbf{K})$ .

To minimize the number of free parameters the two-dimensional adsorbate-substrate potential energy surface (PES) employed in the Langevin MD simulations was determined by density-functional theory (DFT) calculations using CASTEP [59] at the generalized gradient level in terms of the Perdew-Burke-Ernzerhof (PBE) functional [60]. As detailed in the Supplemental Material [40] these calculations are used to parametrize an analytical Fourier representation of the PES, which faithfully reproduces the DFT PES with a root-mean-square deviation of  $< 2 \text{ meV}$ . As indicated by the de Gennes narrowing feature at small  $|\Delta\mathbf{K}|$  in Fig. 1, we additionally account for repulsive adsorbate-adsorbate interactions through pairwise repulsive dipole-dipole interaction potentials according to Kohn and Lau [61]. The required (coverage-dependent) dipole moments of the respective adatoms are obtained by fitting experimental work function-change measurements [62] to the Topping model of surface depolarization [63], as had already been done successfully for Na on Cu(100) [64].

The resulting analysis exhibits only one remaining free parameter, the friction coefficient  $\eta$ . As shown in Fig. 1 an optimized value of  $\eta = 10 \text{ amu ps}^{-1}$  achieves an overall excellent agreement with the experimental measurements. All prominent features in the experimental curve, i.e., the modulation corresponding to the de Gennes narrowing at

small values of  $|\Delta\mathbf{K}|$  as well as the sinusoidal line shape for larger values are qualitatively reproduced with the major contributory factors to diffusion quantitatively reproduced to a large extent. To obtain an estimate of the sensitivity of our results, we additionally indicate in Fig. 1 the range of  $\alpha(\Delta\mathbf{K})$  values we obtain when varying the best-fit friction coefficient within  $\pm 30\%$ . It is obviously only the region at  $|\Delta\mathbf{K}| > 0.7 \text{ \AA}^{-1}$  that is increasingly sensitive to this friction coefficient, and the  $\pm 30\%$  uncertainty safely brackets the experimental error bars. The small but apparently systematic deviations in the lower  $|\Delta\mathbf{K}|$  region are instead attributed to a conceivably insufficient treatment of adsorbate-adsorbate interactions. When completely switching off the dipole interactions in our simulations, the changes to the sinusoidal shape predicted by the single jump model [37] are exclusively restricted to this low  $|\Delta\mathbf{K}|$  region, cf. Fig. 1. Thus, the friction value we obtain is completely robust with respect to these aspects of our model. A similar robustness is obtained with respect to the PES topology. As detailed in the Supplemental Material [40], variations of the diffusion barrier over the bridge sites by  $\pm 30\%$ , to account for inaccuracies of the DFT PBE functional we use, also lead to a variation of decay rates that falls almost exactly within the shaded region in Fig. 1.

The friction coefficient has contributions from both phononic and electronically nonadiabatic dissipation [65]. In a two-bath model for diffusion, contributions have been shown to be additive [66] so we can write

$$\eta \approx \eta_{\text{phonons}} + \eta_{\text{eh-pairs}}. \quad (2)$$

To disentangle the two dissipation channels approximately, we calculate the ensemble-averaged electronic friction experienced over the Langevin-MD trajectories within the LDFA [15,17–19]. For this we first determine an analytic Fourier representation of the position-dependent electronic friction coefficient of a diffusing Na atom  $\eta_{\text{eh-pairs}}(\mathbf{R}_j)$  using a procedure analogous to that employed for the PES. At each DFT point  $\mathbf{R}_{\text{DFT}}$  calculated for the PES parametrization, the embedding density required in the LDFA ansatz is extracted from the self-consistent total electronic density through an atoms-in-molecules scheme based on a Hirshfeld decomposition [22]. The resulting grid of  $\eta_{\text{eh-pairs}}(\mathbf{R}_{\text{DFT}})$  is subsequently expanded in a Fourier series as further detailed in the Supplemental Material [40]. Figure 2 illustrates the resulting continuous electronic friction coefficient along two high symmetry lines along the Cu(111) surface. Obviously,  $\eta_{\text{eh-pairs}}(\mathbf{R}_j)$  correlates with the inverse height profile of the Na adsorbate; the closer the adsorbate is to the Cu(111) surface, the higher the embedding density and the larger the friction coefficient becomes.

The average electronic friction experienced by the entire Langevin ensemble of adatoms  $j$  is then approximated non-self-consistently at each MD time step as  $\eta_{\text{eh-pairs,av}}(t) = \sum_j^{N_{\text{atoms}}} \eta_{\text{eh-pairs}}(\mathbf{R}_j(t)) / N_{\text{atoms}}$  for each trajectory generated

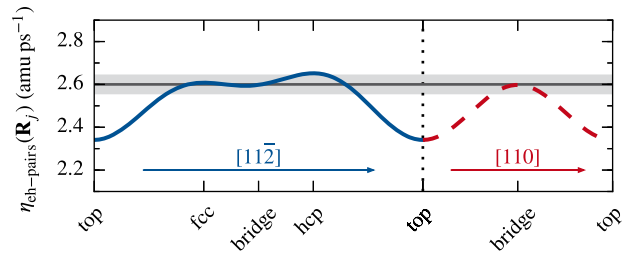


FIG. 2. Interpolated electronic friction coefficient  $\eta_{\text{eh-pairs}}(\mathbf{R}_j)$  experienced by a Na atom along the  $[11\bar{2}]$  (solid blue) and  $[110]$  (dashed red) surface direction. The horizontal dark gray line indicates the determined ensemble- and time-averaged electronic friction  $\eta_{\text{eh-pairs}}$ , with the light-gray corridor indicating the standard deviation over all time steps and trajectories.

in our best-fit simulations. Averaging over all trajectories and time steps we finally arrive at an estimate of the electronically nonadiabatic dissipation contribution to the overall  $\eta$  of  $\eta_{\text{eh-pairs}} = 2.60 \text{ amu ps}^{-1}$ . As apparent from Fig. 2 this average value is somewhere between the friction coefficients experienced at the most stable fcc and hcp adsorption sites and the lowest-energy diffusion barrier over the bridge sites. As also shown in the figure, the standard deviation resulting from this average  $\eta_{\text{eh-pairs}}$  is very small ( $\pm 0.04 \text{ amu ps}^{-1}$ ), consistent with the fact that the thermalized Na atoms spend the predominant time in the corresponding (meta)stable basins of the PES. In terms of the motion through the surface electron density, the situation is thus highly comparable to vibrational dynamics, an area where the LDFA has been shown to perform quantitatively [22]. Correspondingly, we expect this level of theory to provide a reliable assessment of the relative amount of electronic friction, even though it would be conceptually interesting to compare to higher-level theories that for instance account for tensorial aspects of friction [67] or that additionally provide the explicit  $eh$ -pair excitation spectra [12,68]. We further note that similar to the findings for adsorbate vibrations [22], a key element in the use of the simple LDFA scheme is the appropriate determination of the host embedding density experienced by the adsorbate. For the analysis so far, we used the atoms-in-molecules approach based on Hirshfeld's projection scheme [22]. The corresponding integrated Hirshfeld charges indicate a charge transfer of  $0.3e$  from a Na atom adsorbed in the fcc or hcp sites to the Cu substrate, which naturally enhances the embedding density and thus the electronic friction coefficient. Use of the independent-atom-approximation as originally employed within the LDFA context [18] does not account for such a charge transfer in constructing the embedding density but relies on the self-consistent screening of the underlying isotropic model system. This would then predict an  $\eta_{\text{eh-pairs}}$  that is just about 63% of the value determined here. Because of the ambiguous choice of the embedding density, both methods

can be considered to yield an upper and lower limit of the LDFA approach, respectively [22].

Given these considerations and comparing the determined  $\eta_{eh\text{-pairs}}$  with the total friction coefficient, we arrive at the surprising result that electronic nonadiabaticity amounts to about  $(20 \pm 5)\%$  of the total energy dissipation, and this in a system that was selectively chosen to minimize this dissipation channel. Tentatively, we would thus expect even more pronounced influences of  $eh$ -pair excitations in the diffusive motion of adsorbates like potassium atoms, i.e., elements that correspond to a maximum of the  $Z_1$  oscillations of the electronic friction coefficient. As had been shown in the previous work on H diffusion [20,21,24,28], the relative contribution will, of course, also be increased at smaller adsorbate-substrate mass ratios by the concomitant suppression of phononic dissipation. All in all, the picture that emerges is of surface diffusion in which electronic nonadiabaticity plays a much more prominent role than hitherto anticipated. Indeed, one could conjecture that it is in fact electronic nonadiabaticity that ensures rapid thermalization in adsorbate systems with a large frequency mismatch and that explains the long-term success of adiabatic theories to determine diffusion constants and other kinetic parameters for growth and catalysis applications.

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