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Beyond the static corrugation model: Dynamic surfaces with the embedded atom method

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ABSTRACT
The D$_2$ on Cu(111) system has for many years been one of the major benchmark systems for surface scientists. Generating surface configurations using the embedded atom method (EAM), we investigate the quality of the chemically accurate static corrugation model (SCM) for including surface temperature effects, with a focus on the random displacement approach to its distorted surface generation. With this EAM potential, we also treat the Cu(111) surface of our system fully dynamically and shine a further light on not only the quality of the SCM sudden approach but also the limited effect of energy exchange with the surface. Reaction and (in)elastic scattering probability curves, as well as simulated time-of-flight spectra, show good agreement with both earlier works and experimental results, with surface reactions showing a preference for surface atoms displaced away from the incoming molecule. The good agreement with the non-static surface model also further establishes the limited effect of energy exchange on not only the reaction but also on the elastic and inelastic scattering probabilities, even though some molecular translational energy is deposited into the surface.

I. INTRODUCTION
For many years, theoreticians and experimentalists have been working on describing gas–solid surface reactions. These are especially of interest due to their importance in many (industrial) processes, such as the Haber–Bosch process or H$_2$ dissociation for hydrogen engines. To best describe these processes, the reaction mechanisms are broken up into simple elementary reaction steps. Studying of individual steps would then allow for a very accurate description of the full catalytic process.

Our system of choice for this work is the D$_2$ dissociation on a Cu(111) surface. This system is one of the model systems for surface scientists, with much available experimental and theoretical data. In the past, theoretical work was often performed using the Born–Oppenheimer and the static surface (BOSS) approach, where surface atoms are assumed to be fully static, and the electron and nucleus dynamics are assumed to be separated. Here, the ab initio density functional theory (DFT) results are often fit to a 6D potential energy surface (PES) using an approach such as the corrugation reducing procedure (CRP).

Making use of this method, Díaz et al. developed the specific reaction parameter (SRP) approach. Linearily combining two different DFT functionals, one overestimating and one underestimating the dissociation barrier, this work was able to reproduce experimental molecular beam experiments of H$_2$ on Cu(111) with an error of less than 1.0 kcal/mol.

Although good results were obtained using these methods, the surface slab was kept at its ideal, 0 K configuration, whereas experiments are often performed at higher temperatures. To allow for the PES to take into account surface temperature effects, Wijzenbroek and Somers coined the static corrugation model (SCM). In this model, surface slab atoms are displaced from the ideal lattice but kept static. It was theorized that such an approach would work well for a H$_2$ and D$_2$ on copper system, which is expected to have only limited energy transfer both due to the mass mismatch between hydrogen and copper atoms and the relatively slow speed of the thermally equilibrated copper surface atoms. A two body (H–Cu) coupling potential ($V_{coup}$) was introduced to describe the changes in the PES due to these displacements. This coupling potential was fitted to a dataset of surface configurations obtained using SRP48.
DFT calculations. This initial approach to the SCM showed great agreement with ab initio molecular dynamics (AIMD) calculations using the same DFT functional. Furthermore, it resulted in better agreement with experiment than originally achieved with the SRP-BOSS approach, although the limited size of the dataset also showed a sizable error in the H–Cu coupling potential. To improve upon the SCM, Spiering et al. expanded the SCM to an effective three-body potential by including the H–H distance into the coupling potential. Furthermore, the dataset for fitting was greatly expanded, which reduced the RMSE of the fitted three-body coupling potential to 29.4 meV compared to 66.6 meV for the two-body potential as described in the initial work. To generate these SCM statically distorted surface slabs, each atom is displaced using a normal distribution based on an experimentally determined Debye–Waller factor for a specific modeled temperature, with interlayer distances taken directly from experiment. It is, however, still unclear if such a random displacement generates physically relevant surface slabs.

Several other approaches to (structurally) including surface temperature effects have been shown to be successful for a variety of gas–metal systems, such as the reactive force-field (RFF) approach by Busnengo and co-workers [H2/Pd(111)32, CO/Cu(110), and CH4/Pt(110)33], the reaction path Hamiltonian approach (RPH) by Jackson and co-workers (CH4 on Ni and Pt23–27), as well as high-dimensional AIMD with a moving surface. In general, each of these approaches relies on (a fit of) the DFT results to describe the effect of the distorted surface on the incoming reactant, similar to the SCM. Of particular interest is the RPH work by Jackson et al. as they show the relative accuracy of the sudden approach, of which the SCM is a variant, when dealing with simple systems.

Another approach to include surface temperature effects and even dynamic surfaces that we would like to mention here is the high-dimensional neural network potential (HD-NNP), which has seen a rise in applications within the field of theoretical surface science. The very nature of the high-dimensional neural network approaches, however, also comes with challenges: one needs exactly the right dataset to train such a network for specific uses, which generally requires extensive DFT datasets. In this work, however, we aim to investigate two assumptions made in previous works. Primarily, we will validate the physical relevance of the SCM random displacement approach to surface slab generation by comparing the results of D2 dissociation on such a surface slab to a physically accurate surface slab generated with an EAM potential. Furthermore, we also go beyond the SCM by dynamically treating the metal atoms of the surface slab with this EAM potential. This will allow us to further investigate the quality of the sudden approximation that lies at the base of the SCM as well as investigate the importance of energy exchange with the Cu surface for chemisorption and (in)elastic scattering probabilities.

II. METHOD

A. Static corrugation model

The static corrugation model (SCM) was designed to improve upon perfect lattice BOSS dynamics by including surface temperature effects due to surface atom displacements. This is achieved by expanding the description of the potential energy surface (PES) into three terms. In addition to the potential for the ideal, static surface, \( V_{\text{DF}}(\mathbf{q}, \mathbf{r}) \), the two additional terms \( V_{\text{strain}} \) and \( V_{\text{coupl}} \) are included to describe the internal strain of the surface due to distortion and the change in surface–adsorbate interaction due to surface atom displacement, respectively. Thus, the total PES can be described as

\[
V_{\text{DF}}(\mathbf{q}, \mathbf{r}) = V_{\text{DF}}(\mathbf{q}^{\text{id}}, \mathbf{r}) + V_{\text{coupl}}(\mathbf{q}^{\text{id}} \rightarrow \mathbf{q}, \mathbf{r}) + V_{\text{strain}}(\mathbf{q}^{\text{id}} \rightarrow \mathbf{q}),
\] (1)
where \( \overrightarrow{q} \) describes the positions of all surface atoms, \( \overrightarrow{q}^i_{id} \) describes the ideal lattice positions of all surface atoms, and \( \overrightarrow{r} \) describes the positions of all adsorbed atoms.

Under the assumption of a static surface, \( V_{strain} \) can be neglected as it will not change during dynamics. Thus, the full dimensional DFT PES of our distorted system can be approximated as

\[
V_{DFT}(\overrightarrow{q}, \overrightarrow{r}) = V_{SCM}(\overrightarrow{q}^i_{id} \to \overrightarrow{q}, \overrightarrow{r}) = V_{DFT}(\overrightarrow{q}^i_{id}, \overrightarrow{r}) + V_{coup}(\overrightarrow{q}^i_{id} \to \overrightarrow{q}, \overrightarrow{r}). (2)
\]

A continuous representation of \( V_{coup} \) is required to do dynamical simulations. For \( V_{DFT}(\overrightarrow{q}^i_{id}, \overrightarrow{r}) \), many approaches to obtaining such a description have been described, with some examples found in Refs. 19, 34, and 40.

The main focus of previous work on the SCM has been obtaining a continuous description of \( V_{coup} \). This was achieved through interpolation of a collection of DFT data using the CRP approach\(^\text{19}\) and fitting this to the functional

\[
V_{coup}(\overrightarrow{r}, \overrightarrow{q}^i_{id} \to \overrightarrow{q}) = \sum_i \sum_j \left[ V_{H-Cu}(|\overrightarrow{r}_i - \overrightarrow{q}_j^i|) - V_{H-Cu}(|\overrightarrow{r}_i - \overrightarrow{q}^id_j|) \right] \quad (3)
\]

with \( \overrightarrow{r}_i \) to describe the positions of adsorbate \( i \) and \( \overrightarrow{q}_j^i \) to describe the surface atom position \( j \). This appears similar to a previous study by Pineau \textit{et al.}, who employed this approach to describe the relaxation of hot atoms on a metal surface.\(^\text{21}\) However, while Pineau \textit{et al.} directly employed the 1D CRP function to approximate the coupling terms of the \( V_{coup} \), Wijzenbroek and Somers instead elected to fit \( V_{coup} \) from raw DFT data using a separate switched Rydberg-like function,\(^\text{44}\)

\[
V_{H-Cu}(R) = (1 - \rho(R)) V(R) + \rho(R) V(P) \quad (4)
\]

with

\[
V(R) = -e^{-P_b(R-P_b)} \left( \sum_{k=1}^{n} P_k (R-P_k)^k \right) \quad (5)
\]

and

\[
\rho(R) = \begin{dcarray}
0 & \text{for } R < P_b \\
\frac{1}{2} \cos \left( \frac{\pi (R-P_b)}{P_7-P_b} \right) + \frac{1}{2} & \text{for } P_b \leq R \leq P_7 \\
1 & \text{for } R > P_7.
\end{dcarray} \quad (6)
\]

The SCM was later expanded by Spiering \textit{et al.} to include an effective three-body potential.\(^\text{22}\) This was achieved by making each fitting parameter \( P_i \) linearly dependent on the distance between the two adsorbates \( r_{H-H} \).

\[
P_i = \begin{dcarray}
P_{a0r_{H-H}^m} + P_{a0} & \text{for } r_{H-H} < r_{H-H}^m \\
P_{a0r_{H-H}} + P_{a0} & \text{for } r_{H-H}^m \leq r_{H-H} \leq r_{H-H}^m \\
P_{a0r_{H-H}} + P_{a0} & \text{for } r_{H-H} > r_{H-H}^m.
\end{dcarray} \quad (7)
\]

Here, the cut-off values \( r_{H-H}^m \) and \( r_{H-H}^m \) are obtained from, respectively, the largest and smallest values of \( r_{H-H} \) used during the fitting procedures.

To account for thermal expansion effects while using the CRP potential of the system for an ideal lattice, the \( H_2 \) CoM vectors are linearly contracted or stretched along the lattice vectors \( u \) and \( v \). By stretching along the lattice vectors instead of the \( x \) - or \( y \)-vectors, accidental introduction of extra artificial vibrational or rotational strain is avoided. Thus, the full effective SCM potential becomes

\[
V_{SCM}(\overrightarrow{r}, \overrightarrow{q}, \overrightarrow{q}^i_{id}) = V_{CRP}(\overrightarrow{q}^i_{id}(\overrightarrow{r}), \overrightarrow{q}^i_{id}) + \sum_i \sum_j \left[ V_{H-Cu}(|\overrightarrow{r}_i - \overrightarrow{q}_j^i|) - V_{H-Cu}(|\overrightarrow{r}_i - \overrightarrow{q}^id_j|) \right] \quad (8)
\]

where \( \overrightarrow{q}^id_j \) scales the \( H_2 \) CoM vectors along the lattice coordinates.\(^\text{23}\)

### B. Embedded atom method

First described by Daw and Baskes in 1983,\(^\text{42}\) the embedded atom method (EAM) has been a strong tool for theoretical surface scientists. The EAM is based on the quasiatom,\(^\text{43}\) or effective medium,\(^\text{44}\) approach, which was designed to describe impurities in metals.\(^\text{45}\) Here, an impurity, such as a small atom, embedded in the metal is modeled as a particle in a uniform environment of electron density. The EAM, instead, takes it one step further, treating each surface atom as the “impurity” in an electron density obtained from contributions of each of the neighboring atoms. Each atom would thus get an embedding energy, which is defined as the difference in energy between the atom inside the uniform electron density associated with its neighbors and that of the same atom in a vacuum. The total sum of each individual atomic energy is then approximated as the total (potential) energy of the metal,

\[
E_{tot} = \sum_i F_i(n_i), \quad (9)
\]

where \( F_i \) is the so-called embedding energy of atom \( i \) and \( n_i \) is the density this atom experiences at position \( r_i \).

This initial approach to the EAM did not perform as well as was expected, yielding unrealistic properties for solids due to the neglect of core–core repulsion and the “assumption of extreme locality.”\(^\text{44}\) Thus, a second, short-range pair interaction was added to the model to yield a total energy given by

\[
E_{tot} = \sum_i \left[ F_i(n_i) + \frac{1}{2} \sum_{j \neq i} \phi(\rho_j) \right]. \quad (10)
\]

Here, \( \phi(\rho) \) describes the pair interaction potential between atoms \( i \) and \( j \), \( \rho_j \) being the distance pair interaction between the two. In this work, we will use another pair interaction to approximate the density \( n_i \) of atom \( i \) using

\[
n_i = \sum_{j \neq i} \rho_j(\rho_j), \quad (11)
\]

where \( \rho_j \) yields the density contribution of atom \( j \) to the density of atom \( i \).

Thus, the EAM can be used to describe a (metal) system using a total of three functions: the pair function \( \phi \), the embedding function \( F \), and the density function \( \rho \).
We can combine this EAM potential with the SCM-modified DFT potential as described in Eq. (1) to obtain the full potential for a dynamic H₂ on Cu system. Here, we use the EAM potential to describe the strain in the surface (\(V_{\text{strain}}\)), the H₂ + Cu(111) CRP BOSS PES to describe the ideal static surface at 0 K, and the SCM coupling potential to describe the interaction between the two. This yields us the total potential of a fully dynamic H₂ on Cu(111) system,

\[
V_{\text{Dyn}}(\mathbf{r}, \mathbf{q}, \mathbf{q}^\text{id}) = V_{\text{CRP}}(\mathbf{r}, \mathbf{q}^\text{id}) + \sum_{i} \sum_{r} \left[V_{\text{H-Cu}}(\mathbf{r}_i - \mathbf{q}_r)\right] - \sum_{i} \sum_{k} \left[F_{\text{K}}(\mathbf{q}_k)\right] + \frac{1}{2} \sum_{i,k} \phi_{\text{q}}(\mathbf{q}_k - \mathbf{q}_i)\]

(12)

In this work, we will be using the cubic spline fits to \(F\), \(\rho\), and \(\phi\) of the EAM potential as described by Sheng et al. This highly accurate potential has been shown to reproduce a variety of experimental data and has been extensively used in other works.

C. Quasi-classical dynamics of D₂ on Cu(111)

The CRP PES (\(V_{\text{CRP}}\)), its SCM variant (\(V_{\text{SCM}}\)), or its dynamic surface variant (\(V_{\text{Dyn}}\)) can be used to describe the interaction of an H₂ or D₂ molecule on an ideal, non-ideal, or dynamic Cu(111) surface, respectively. This CRP PES was fitted by Mondal et al. and based on the SRP48 functional designed by Nattino et al., while the three-body SCM potential was fitted by Spiering et al. with a dataset obtained from DFT using the same functional. As the name suggests, the exchange–correlation energy of the SRP48 functional is obtained from a weighted combination of the Revised Perdew–Burke–Ernzerhof (RPBE) and Perdew–Burke–Ernzerhof (PBE) functional, with 0.48:0.52 ratio. Although no van der Waals (vdW) correction is included in this approach, a previous comparison of SRP48 with a vdW corrected functional (optPBE-vdW) has not shown any significant improvements for the H₂/D₂ on Cu(111) system.

As we cannot investigate the quality of a PES directly, we will instead focus on the dissociative chemisorption and the (in)elastic scattering of these particles on our model surface using quasi-classical (QC) dynamics. In contrast to classical dynamics, quasi-classical dynamics also takes into account the presence of the zero-point energy of the initial rovibrational states, which has been shown to be important for properly describing the system.

The initial conditions of the adsorbate are generated by first calculating the initial rovibrational energy levels for our chosen PES using the Fourier grid Hamiltonian method. The diatomic molecule is then propagated with a constant time step in the vacuum for one full vibrational phase while recording both the positions and momenta of each atom. This allows us to obtain the QC distribution of \(r_{\text{H-H}}\) and the corresponding classical momenta.

Both the molecular angles with the surface, \(\theta\) and \(\phi\), are chosen from a uniformly random distribution between \([0, \pi]\) and \([0, 2\pi]\), respectively. Internal angular velocities are chosen according to the quantized angular momentum \(L^2 = J(J + 1)h^2\). The normal incidence momentum is chosen according to the initial incidence energy. The angle \(\theta_i\) between the angular momentum vector and the surface normal is chosen randomly but constrained by \(\theta_i = \pi\) for \(J = 0\) and \(\cos(\theta_i) = m_j/\sqrt{J(J + 1)}\) if \(J \neq 0\).

The initial adsorbate CoM position in \(Z\) is shifted 7 Å away from the surface, while the \(U(=X - Y/\sqrt{3})\) and \(V(=2Y/\sqrt{3})\) coordinates are chosen randomly from a uniform distribution between 0 and \(a\), with \(a\) being the lattice constant of the surface slab (Fig. 1). The surface slab atom positions of both the ideal and distorted lattices are required to obtain the SCM potential. The ideal lattice is constructed similar to that of the DFT slab used when constructing the CRP PES. Only those atoms within 16 bohrs of the CoM projection on the xy-plane are included.

The distorted lattice is instead constructed in two steps. First, the ideal lattice positions are expanded along the lattice axes \(u\) and \(v\) using the experimental lattice expansion factor. The interlayer distances are similarly set to experimental results. Then, each surface atom is distorted using a Monte Carlo approach, where the magnitude of the distortion is obtained from a Gaussian distribution with a width based on the temperature dependent Debye–Waller factor, as we will discuss in Sec. II D.

For distorted lattices generated with the EAM, the SCM expansion coefficient is instead calculated as the ratio between the ideal CRP lattice constant and the calculated EAM lattice constant. For these slabs, we similarly only take those slab atoms within 16 bohrs of the center of the surface slab, where \((x, y, z) = (0, 0, 0)\).

By applying the EAM potential to our, in regular SCM, static surface, we can also perform surface dynamics with a dynamic surface. Here, the CRP and SCM approach describe the dynamics of

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Coordinate system of our incoming H₂ (light-blue) with lattice vectors for the Cu(111) surface slab (dark red). The 6 DoFs of the incoming H₂ molecule are described both in atomic coordinates \((x_H, y_H, z_H)\) and molecular, center-of-mass (CoM) coordinates \((X, Y, Z)\), with the H–H distance \(r_{\text{H-H}}\), the polar angle \(\theta\), and the azimuthal angle \(\phi\) relative to the \(x\) axis. The surface atoms are described using only atomic coordinates \((x, y, z)\).}
\end{figure}
our incoming D$_2$ and its interaction with the surface, while the forces between the copper atoms are described by the EAM. Newton’s third law can be applied then to also find the effect of the incoming D$_2$ of the surface Cu atoms. We will refer to this method as the dynamic corrugation model (DCM) using the EAM potential (EAM-DCM).

With these initial conditions defined, we propagate our molecule (and surface) according to Hamilton’s equations of motion using the simple Hamiltonian

$$H = \sum_{i=1}^{n} \left( \frac{\mathbf{p}_i^2}{2m_i} \right) + V(R(t)), \quad (13)$$

where $p_i$ and $m_i$ are, respectively, the momentum and mass of the $i$th atom. $V(R(t))$ describes the total potential energy of all $n$ atoms at positions $R$ and time $t$. The Bulirsch–Stoer predictor-corrector algorithm is used for propagation because of its accuracy and relative speed. For reactive trajectories, propagation ends when the two deuterium atoms are separated more than 2.25 Å from each other within the maximum propagation time frame of 20 ps. These molecules that are reflected and move away further than the initial starting distance of 7 Å from the surface in the Z-coordinate are considered scattered. These molecules are binned to a final rovibrational state and separated into elastically scattered atoms, for those in the same state as the initial rovibrational state, or in-elastically, for those that return in a different rovibrational state. Binning is performed by first finding the closest allowed ($\Delta J = \pm 2$) rotational state using the classical angular energy and then finding the closest vibrational state in energy to this rotational state.

Finally, those molecules that neither scatter nor react within the maximum time interval of 20 ps are considered trapped on the surface. Only for very low incidence energies were these found in significant quantities, primarily due to the very low velocity of the D$_2$ toward the surface, and thus, they did not significantly contribute to the final reaction and scattering probabilities found in this work. Results were obtained for $\sim$100,000 trajectories when using a static surface, compared to at least 4,000 trajectories of EAM-DCM, at a modeled surface temperature of 925 K.

Reaction probabilities and rovibrational (in)elastic scattering probabilities are obtained by dividing the number of reacted or scattered trajectories by the total amount of trajectories computed at each normal incidence energy.

D. SCM slab generation

To model thermally distorted copper surfaces, slabs of Cu(111) surfaces are generated. Previous work with the SCM achieved this using random displacements of each individual atom from its ideal lattice position. Here, the displacement was assumed to be both bulk-like and uniform in the three Cartesian directions. The magnitude of this displacement is randomly selected from a Gaussian distribution with a standard deviation of

$$\sigma = \sqrt{\frac{3B}{8\pi^2}}. \quad (14)$$

Here, $B$ is the temperature dependent Debye–Waller factor obtained from fits to experimental inelastic neutron scattering data. With this random displacement in place, the surface slab positions are next expanded along the $u$ and $v$ lattice coordinates based on an experimental thermal expansion coefficient. Furthermore, the interlayer distances, found in the $z$-direction of the slab, are taken directly from experimental results. This approach to surface slab generation we will refer to as random displacement SCM (RD-SCM) and is what has been used in all previous works of the SCM.

To validate this methodology, surface slabs were also generated using the EAM potential published by Sheng et al. A cell of $7 \times 7 \times 7$ Cu atoms was modeled first in a bulk environment by applying a minimum image convention in all three Cartesian directions. These atoms are then relaxed based on the modeled temperature using a Berendsen thermostat. Then, three of the lowest atom layers, for a total of 147 atoms, were kept frozen, while a vacuum is introduced on the other side of the slab. This slab is then again relaxed, now as a surface. Positions and momenta of each slab atom are then recorded and collected to be used while running surface dynamics calculations. Further computational details can be found in the Appendix. Thus, the slab is generated without any external scaling based on different experimental results, as was done in the RD-SCM approach. It is important to note that an EAM potential is not the only pathway to obtaining such a surface slab, as other potentials could also be implemented.

In this work, we will refer to dynamics on such an EAM surface as EAM-SCM if the surface atoms are not included into the dynamics in contrast to the EAM-DCM approach, where the surface atoms are explicitly included into the dynamics. Both methods, the SCM and the DCM, use the basis of Eq. (1): the $V_{BOSS}$ BOSS PES as $V_{eff}$ (ideal) and the expression of Eq. (3) as $V_{trap}$. The EAM is used to model $V_{strain}$ of Eq. (1) and is only explicitly needed in the dynamics for EAM-DCM. Furthermore, it is used to generate static surface slabs for the EAM-SCM approach.

E. Simulating time-of-flight spectra

To better compare to experimental data, the results from our dissociation simulations were fitted to obtain functional forms matching those of time-of-flight (ToF) spectra.

This was done using a two-step process: first, our theoretical results are fitted to a functional form matching a reaction probability curve to obtain the width parameter, saturation parameter, and effective barrier height. Next, we combine this fit with several parameters, including some geometrical constraints, of the experimental setup of Auerbach et al. to simulate ToF spectra for our different QCT approaches.

This fitting procedure, as well as the functional form used for the reaction probability, and the generalized logistic function (LGS) were obtained from earlier work by Nattino et al.,

$$S(E) = \frac{A}{\left(1 + \nu \exp \left[-\frac{E - E_0}{W}\right]\right)^2}. \quad (15)$$

Here, $A$ is the saturation parameter, which controls the maximum value of the ToF curve, $E_0$ is the effective barrier parameter, and $W$ is the width parameter. With the $\nu$ parameter, the shape of the curve can be further adjusted to a number of related functional forms, such as an ordinary logistic function ($\nu = 1$) and the Gompertz function ($\nu \rightarrow 0$).
III. RESULTS AND DISCUSSION

A. Reaction probability curves

To validate the quality and physical relevance of the random displacement approach to generating SCM surface slabs (RD-SCM), we will compare the dissociative chemisorption reaction probabilities obtained with this approach to those obtained using surface slabs generated with an EAM potential (EAM-SCM). Also included are dissociation curves for the same dynamics on a moving surface using the EAM potential to also describe the interactions between the copper atoms. We will refer to this method as the dynamic corrugation model (DCM) using an EAM potential (EAM-DCM). Comparisons between these different methods will give us insight not only into the quality of the RD-SCM generated surface slabs but also into the effect of energy exchange with our moving surface and the validity of the sudden approach as we use it in the SCM models. Finally, we include the results of an ideal, 0 K static surface, which we obtain using the often used BOSS approach to look at the general effect the different models for including surface temperature effects have on the dissociation curves.

In Fig. 2, we show the reaction probability curves for several different rovibrational states. As expected, the general trend for all the different approaches is relatively similar. At low incidence energy, the D₂ molecule does not have enough energy to pass over the minimum energy barrier for dissociation, and reaction probability will be minimal. As the normal incidence energy increases so does dissociation probability, until it reaches a maximum, or saturation, value.

The first point of note in this figure is the difference in saturation values between the different approaches. Both the RD-SCM and BOSS methods show a similar saturation at around 0.9, while the EAM-SCM and EAM-DCM approaches both have a lower value at around 0.85, with the EAM-DCM approach always being slightly higher. This could indicate that the surface slabs generated with the EAM potential contain somewhat higher maximum barriers compared to those generated through the RD-SCM. These values are, however, very difficult to obtain experimentally and thus is of much less importance for the quality of our model when comparing to experiment.²⁵

All three CM approaches (RD-SCM, EAM-SCM, and EAM-DCM) predict a higher reaction probability than that shown by the BOSS model, yet their curves do not increase as steeply. This broadening of the S-curve is generally attributed to surface temperature effects and has been extensively discussed in earlier work.²²,²³ Both the EAM-SCM and EAM-DCM show a bit more broadening than the RD-SCM approach, although it is harder to quantize due to the lower saturation value. This is especially of note as previous work has shown some indication that the width and the saturation value of the dissociation curves are not completely independent.²⁶

The availability of energy exchange appears to only very limitedly affect our system, as we find great agreement between the static surface approach of the EAM-SCM and the dynamic surface approach of the EAM-DCM. Although earlier work has shown similar results for H₂,²²,²⁶,²⁸,⁵⁹, this is one of the first examples of a direct and extensive comparison between almost identical methods, one with a dynamic surface and one without.

B. (In)elastic scattering probabilities

To further analyze our dissociation simulations, we can also look at the rovibrational elastic and inelastic scattering probabilities. In Fig. 3, we again compare the BOSS (red squares), RD-SCM (green curves), EAM-SCM (blue curves), and EAM-DCM (black circles) methods, now for the elastic [(b), (d), (f), and (h)] and inelastic [(a), (c), (e), and (g)] rovibrational scattering probabilities for the same initial states as discussed before.

In general, we find a preference for elastic scattering at lower incidence energies, where there is no enough energy available within the molecule to reach other rovibrational states. As the kinetic energy of the molecule increases, more and more rovibrational states become available and we find higher and higher probability for inelastic scattering. At very high incidence energies, chemisorption dominates and only limited scattering is observed.

For the rovibrational ground state [(a) and (b)], as well as the vibrationally excited states [(c), (d), (g), and (h)], the BOSS model predicts much higher elastic scattering for the lower incidence energies. Moving to higher energies, we again see almost perfect agreement with the RD-SCM curves and qualitative agreement with the EAM-SCM and EAM-DCM approaches. Surprisingly, this effect is absent for the v = 0, J = 11 state, where the BOSS model shows good agreement with the all CM results for all incidence energies.

Agreement between the EAM-SCM and EAM-DCM approaches is again very good, with only minor differences that we can partially attribute to the relatively low amount of trajectories run for the EAM-DCM approach. This further validates the quality of the SCM sudden approach. As the main difference between these two approaches is the possibility of energy exchange between the copper surface and the D₂ molecule, this agreement further enforces our observation of the limited effect of energy exchange on not only the final dissociation results but also on these rovibrational (in)elastic scattering results. The latter are expected to be more sensitive to
The energy exchange at very low incidence energies does appear to affect the final rovibrational state of the scattered molecules and appears to be directly related to the z-coordinate as molecules that get closer to the surface obtain a larger amount of energy. It remains however a question on how accurate the QCT method is for these very low incidence energies and to what extent quantum dynamical effects, such as zero point energy conservation, of the molecule and the surface atoms play a role.

C. Simulated time-of-flight spectra

To better compare our theoretical results to experiment, our reaction probability curves were used to simulate time-of-flight (ToF) spectra following the procedure as outlined by Nattino et al. As experimental results are often obtained in the form of ToF spectra and are generally most sensitive for the curve onset of the initial state specific reaction probability curve, we believe that ToF spectra are one of the better ways of comparing theoretical results to experimental data, especially when correct and accurate experimental ToF parameters are known and have been published. Thus, this work is of great interest as it both simulated ToF spectra and fit experimental results using the same expression.

Simulated spectra of a selection of four different rovibrational states for the four theoretical approaches discussed in this work are shown in Fig. 4. The rovibrational states shown were chosen such that they cover a variety of different excited states, as well as the rovibrational ground state. Furthermore, we also included the experimental results from Auerbach et al. as AIMD results, both obtained from the work by Nattino et al. These experimental results were obtained from recombinative desorption experiments of D$_2$ permeating through the bulk metal to a Cu(111) surface at a surface temperature of 925 K and as such rely on the applicability of detailed balance. Surface motion effects were included in these AIMD results, applying a modeled surface temperature of 925 K.

Figures 4(a), 4(e), and 4(i) show our simulated results for the rovibrational ground state. Good agreement between the different CM approaches is found, as was the case for the chemical desorption curves. A slight difference between peak width is observable, with the EAM-SCM approach showing the highest width. The peak location, however, appears to be the same for all three methods. The BOSS model, on the other hand, shows a much more narrow peak with a peak location at a shorter time of flight. The AIMD peak can be found at approximately the same value as the CM peaks, yet its width is significantly lower. In contrast, looking at the experimental curve, we observe a width similar to that of the CM approaches. The curve is, however, shifted compared to the CM curves, showing a peak location at a higher time of flight.

A similar thing can be observed in Figs. 4(b), 4(f), and 4(j) for the vibrationally excited $v = 1$, $J = 0$ state. Unfortunately, however, no AIMD data were available for this state. The width for the three CM approaches is once again similar and close to that of the experimental results. Peak location also shows similar results, with the CM approaches underestimating that of the experiment. The BOSS model shows the worst agreement, with a much narrower peak and a peak height about twice as far from experiment.

Moving to the rotationally excited states in Figs. 4(c)–4(h), we again see that the BOSS model yields both the narrowest peak, as well as the best fit to the experimental data.
as the lower time of flight for the peak. The different CM approaches show peaks at the highest time of flight, each with approximately the same value. The experimental results are found somewhere between these peaks, with a width closer to that of the CM results. AIMD results for these curves are a bit mixed as the agreement for the $v = 0, J = 11$ state appears to be almost perfect, while agreement with the $v = 1, J = 6$ experimental data is much worse.

Overall, we see improved agreement with experiment when including the SCM and DCM approaches, regardless of which variation.

RD-SCM, EAM-SCM, and EAM-DCM all show very similar results, with RD-SCM always showing the narrowest peak of the three. Due to the nature of simulating the time-of-flight spectra, however, small variations are expected. The results when using the BOSS model showed the narrowest peaks as well as the shortest time-of-flight for each rovibrational state we investigated, often well below the value found in experiment. This matches findings from earlier work.\textsuperscript{15}

D. Effect of RD-SCM on atom displacement

In an attempt to directly compare the randomly generated and EAM generated surface slabs, we investigated the displacements of each individual surface slab atom for every Cartesian coordinate. Only those atoms within the SCM cutoff distance of 16 bohrs were included in these results. As was discussed in Sec. II, the RD-SCM approach makes use of the Debye–Waller factor to calculate the standard deviation for the Gaussian displacement of each surface atom. The EAM-SCM approach instead uses surface slabs simulated through another potential, in our case the EAM. Assuming the simulation attains a proper thermodynamic equilibrium, this approach should also result in a Gaussian distribution for our displacements.

In Fig. 5, we outlined the displacements in the x- [(a) and (c)] and y-direction [(b) and (d)] both at the onset of the reaction probability curve [(a) and (b)] and at the saturation value [(c) and (d)]. Only those surface slab atoms at the top layer were included in these results. Separate curves were also included for only those trajectories where the $\text{D}_2$ dissociated.

Comparing the RD-SCM displacements for all trajectories (red) to only those that reacted (green), we see very similar curves both for the x- and y-coordinates. Due to the low reaction probability at the curve onset, the dataset for the reacted trajectories shows a decent amount of noise. This is significantly decreased when looking at the saturation value, although there is still a significant variation in results for very low displacements. There also appears to be a slight preference toward a positive displacement. It is unclear yet why this occurs.

Similar noise is found with the EAM-SCM results for the reacted trajectories at low incidence energy. This, however, disappears when moving toward high energy or also when including the trajectories that did not react. Furthermore, no clear preference can be found toward a positive or negative displacement, as would be expected for in-plane displacements.

Comparing the two methods to each other, we do see a clear difference. While both approaches appear to result in a normal distribution of displacements, they do have a very different width, with the EAM-SCM displacements, obtained from EAM surface slab simulations, showing much broader peaks.
Next, we discuss the most interesting of the three Cartesian directions, the z-coordinate. Displacements toward (+z), or away from (−z), the incoming reactant molecules have in previous works been shown to affect dissociation probabilities.\textsuperscript{27,28,64,65} For example, Bonfanti et al. used a simple 7D model to quantum dynamically show increased reaction probabilities when surface layer atoms are moved away from the incoming H\textsubscript{2} molecule.\textsuperscript{64}

In Figs. 6(a) and 6(b), we compare the EAM-SCM and RD-SCM results at the reaction probability curve onset for the first and second surface layer atoms. Again only those trajectories that reacted were included separately. For EAM-SCM, reacted trajectories appear to show a clear preference toward a negative displacement in z, away from the D\textsubscript{2} molecule, as the peak of the atom displacement distribution is slightly shifted toward negative z. This phenomenon can be observed both for the first layer (a) and the second layer (b) and matches the results found with the simple 7D model.\textsuperscript{64} Interestingly, the opposite effect is found for the CH\textsubscript{4} on Pt(111), Ir(111), and Ni(111) systems, where surface atom displacement away from the reactant increased the barrier height.\textsuperscript{27,28,65} Furthermore, limited surface puckering out of the surface is expected when treating this system dynamically as systems with a large mass mismatch have been shown to be primarily dominated by the recoil effect.\textsuperscript{27,28}

A similar effect cannot be seen with the results for the RD-SCM approach as both the reacted and total slab distributions show a similar width and peak location. This distribution also does not appear to be that of a Gaussian. We attribute this to the way the displacements are generated as it is only ensured that the total displacements in the direction of the displacement, and not x, y, or z individually, follow a Gaussian distribution with the standard deviation calculated with the Debye–Waller factor. Similar distributions are thus found when looking along the u- and v-axes for the (111) surface slab. Furthermore, the second layer shows a static shift of negative z. This is also attributed to the RD surface slab generation, as experimental interlayer distances are applied when generating the surface, instead of the bulk lattice constant, as is used for the x- and y-directions.

At much higher incidence energies [(c) and (d)], we no longer see the EAM-SCM preference toward a negative z-displacement. At such a high energy, almost all trajectories will react, making the lowest barrier path much less visible. For the RD-SCM results, we again see this second layer shift due to the experimental interlayer distance.

IV. CONCLUSION

Using the dissociation of D\textsubscript{2} on Cu(111) as a model system, we investigated the physical relevance of the random displacement approach to SCM surface slab generation.\textsuperscript{22,23} Surface slabs were generated using both this approach and a highly accurate EAM potential, which has been shown to accurately describe copper bulk and surfaces.\textsuperscript{36} Furthermore, we used this EAM potential to dynamically treat our surface, allowing us to both test the validity of the sudden approach and investigate any effect of energy exchange with the surface, which has long been theorized to be of little importance for this system.\textsuperscript{23} Each calculation used the same CRP PES based on the SRP48 functional as had been used in previous works, with the SCM approaches all applying the effective 3-body potential as published by Spiering et al.\textsuperscript{27}

We found good agreement between the dissociation curves of the RD-SCM and the EAM-SCM approaches, as well as with the
EAM-DCM approach. Agreement was especially good for the reaction curve onset, which has been shown to be the most accurate for experimental results, while the saturation value was found to be lower for the two methods based on the EAM surface slabs. All three methods resulted in increased broadening of the dissociation S-curve compared to the BOSS approach, which is generally attributed to surface temperature effects.

Similar agreement was found for rovibrational (in)elastic scattering curves, where only the BOSS model significantly deviated from the results found with the different CM approaches. The good agreement between EAM-SCM and EAM-DCM indicated limited to no effect of energy exchange on the reaction and, more importantly, the (in)elastic scattering probabilities, although we did find a drain of 15% of the translational energy of the scattered molecules for almost the entire incidence energy range, which we have not found to be reported in other works.

A further evaluation of the dissociation curves was performed by simulating a time-of-flight spectrum for each curve fitted to a standard form. Such a simulated spectrum is especially sensitive to the reaction curve onset, as had been seen in earlier work. Again, we found great agreement between the different CM approaches, as well as improved agreement with experiment compared to the BOSS method.

To directly compare the surface slabs generated for the RD-SCM and EAM-SCM approaches, we mapped the displacements for each individual surface atom from its ideal lattice position both for all trajectories and for only those that reacted. As expected, no preference was found for either method when considering the x- and y-coordinate, although the EAM generated slabs did show a much broader distribution of displacements. For the z-coordinate, however, we found a clear preference for reaction when the surface atoms are displaced away from the incoming D$_2$ but only for the EAM-SCM approach. Surface slabs generated using the RD-SCM did not even show Gaussian distributions in their displacement as the displacement method only ensured a normal distribution in the total displacement of the atom.

In general, we found good agreement between the reaction probabilities and rovibrational (in)elastic scattering probabilities obtained using the EAM-SCM and RD-SCM approaches, although the RD-SCM approach to surface generation showed much narrower atom displacement distributions. Furthermore, the good agreement with the non-static surface approach of EAM-DCM indicated both the very limited effect of energy exchange on the dissociation and (in)elastic scattering probabilities, despite having observed some energy drain into the surface.

With the success of the SCM sudden approach, combined with physically relevant surfaces generated with an EAM potential, we have opened a pathway toward quantum dynamically treating the motion of D$_2$ on a non-ideal Cu(111) surface. Accurate quantum dynamical treatment of such systems would be a major step forward in describing the rovibrational (in)elastic scattering as well as the low incidence energy regime, which are dominated by quantum effects ill-described by QCT dynamics.

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APPENDIX: ADDITIONAL COMPUTATIONAL DETAILS

In this work, we used the highly accurate EAM potential for copper as described by Sheng et al. The 1001 equidistant data points of the pair, density, and embedding functions were fitted using cubic splines, with a cutoff at 0 Å and 6.5 Å for the pair and density function and a cutoff at 0.0 and 1.0 density for the embedding function. Outside these final spline knots, both the value and derivative of the functions yields 0.

NVT dynamics were run using a velocity-Verlet algorithm and the Berendsen thermostat, while NVE propagation was performed using the Bulirsch–Stoer predictor-corrector algorithm.

Stepwise volume scaling was performed to equilibrate the pressure and Cu lattice constant by running 1 ps of NVT dynamics and storing the virial pressure each step using the equation

$$P_{ij} = N k_b T + \frac{1}{2} \sum_{\{i\}} r_{ij} \cdot F_{ij},$$

where $N$ is the number of (mobile) surface atoms, $k_b$ is the Boltzmann constant, $T$ is the instantaneous surface temperature, and $r_{ij}$ and $F_{ij}$ are, respectively, the distance and force between surface atoms $i$ and $j$. Due to double counting, this dot product in halved. The total average pressure is then divided by a scaling factor of 2500 GPa and used to scale the simulation box volume. This scaling factor was chosen arbitrarily to ensure the surface is not scaled too fast or too slow.

To ensure this yields satisfactory results, we also determine the pressure from the diagonal components of the virial stress tensor. Both these methods are grounded in theory and will result in the same values under equilibrated conditions.

1. Bulk lattice constant determination

To determine our relaxed bulk lattice constant, a cell of $7 \times 7 \times 7$ Cu atoms was placed in the optimal FCC lattice structure. Some initial momentum was also included using a normal distribution based on the modeled surface temperature. This is to avoid any rapid changes during the initial surface relaxation steps. The minimum image convention is applied in the x, y, and z Cartesian directions. Next, this slab was propagated in the canonical ensemble (NVT) for 40,000 steps with a step size of 0.005 ps, yielding a total propagation of 200 ps. Volume rescaling was performed between 40 ps and 160 ps of this run, scaling every ps to ensure the thermodynamically favored box volume is attained. To evaluate the quality of this run, the average atom–atom distance, temperature, and kinetic and potential energy of the bulk copper are calculated each step and stored for evaluation. Next, this NVT relaxed bulk is propagated for 250 steps (≈6 ps) in the micro-canonical ensemble (NVE), where total propagation time varies due to the use of a predictor-corrector algorithm. Here, we again evaluate the stability of our copper based on the temperature, average atom–atom distance, kinetic and potential energies, and virial pressure and virial stress. The relaxed bulk lattice constant is finally obtained from the final volume of our box. This is repeated 200 times, each with a unique seed to generate the initial conditions, to obtain the average bulk lattice constant of this potential for our chosen temperature.

2. Surface slab generation

To generate surface slabs, we take our bulk lattice constant to generate the initial $7 \times 7 \times 7$ FCC copper lattice and again apply some...
initial momentum from a normal distribution based on the modeled surface temperature. We further repeat all steps for our bulk lattice, as described above, but without applying any volume rescaling.

Then, three consecutive outer layers of our surface slab, for a total of 147 atoms, are set locked to their current positions, and the minimum image convention is applied only in the x- and y-directions. This new surface slab is then propagated in the canonical ensemble for a total of 250 ps and a step size of 0.0005 ps (50 000 steps). It is important to note that we do not apply any volume rescaling during these steps to ensure our static layers properly model the bulk. This does also mean that our top layers will exhibit some stress due to the change in pressure when moving from bulk to a surface. A short NVE run of 1000 steps (=40 ps) is again used to determine the stability of our surface slab. To ensure the surface slab atoms are always located approximately at the same position, we next attempt to center our slab. We then performed an NVE dynamics run of 25 000 steps (=1100 ps), logging the average position of each atom in the top layer of our surface slab. After this run, we shift our entire slab, including the static, bulk-like, layers, so that the average position of the entire top layer is found at (x, y, z) = (0, 0, 0). With this process completed, we start our final dynamics run to obtain traces of our surface slab positions and momenta. During an NVE dynamics run of 1250 steps, we take a snapshot every 50 steps (=2 ps) of both the surface slab positions and momenta for a total of 25 snapshots each. To obtain a suitable and diverse amount of trajectories, we repeat this entire surface slab generation scheme 1000 times for a total of 25 000 surface slab positions with matching momenta. These can then be loaded into our SCM dynamics as an alternative to the random displacement approach of the earlier works.

DATA AVAILABILITY

The data that support the findings of this study are available from the research group’s public repository at https://pubs.tc.lic.leidenuniv.nl/.

REFERENCES

12. Rotational excitation and vibrational relaxation of H₂ scattered from Cu(111).


