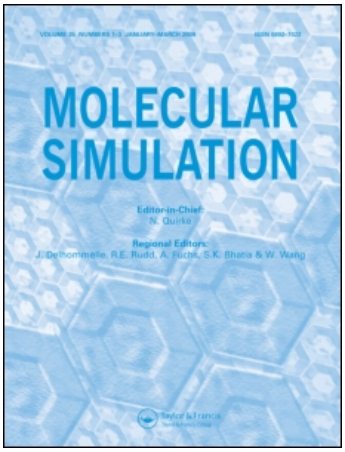

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J. Ludwig[a]; D. G. Vlachos[a]
[a] Department of Chemical Engineering and Center for Catalytic Science and Technology, University of Delaware, Newark, DE, USA

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First Principles Modeling of Dissociative Adsorption at Crystal Surfaces: Hydrogen on Pt(111)

J. LUDWIG and D.G. VLACHOS*

Department of Chemical Engineering and Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716-3 110, USA

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Multiscale simulation has the potential of becoming the new modeling paradigm in chemical sciences. An important class of multiscale models involves the mapping of a finer scale model into an approximate surface that is used by a coarser scale model. As a specific example of this class we present the case of the adsorption dynamics of diatomic molecules on single crystal catalyst surfaces. The prototype system studied is the dissociative adsorption of H_2 on Pt(111). The finer scale model consists of density functional theory (DFT) periodic slab calculations that provide a small dataset for training an atomistic scale potential energy surface. The coarser scale model uses a semi-classical molecular dynamics (MD) algorithm to obtain the sticking coefficient as a function of the incident energy. Comparison to experimental data and published simulation work is presented. Finally, major challenges in multiscale modeling of chemical reactivity in coupled DFT/MD simulations are discussed, specifically the need for a systematic method of assessing the accuracy of the coarse graining process.

Keywords: Multiscale simulation; Density functional theory; Molecular dynamics; Potential energy surfaces; Hydrogen; Platinum

INTRODUCTION

Multiscale simulation emerges as the new modeling paradigm of the new century. A review of multiscale simulation of catalytic reactions and reactors was given in Ref. [1], a classification of various types of multiscale models and examples from various areas of chemical sciences were reported in Ref. [2], and mesoscopic modeling of chemical reactivity was outlined in Ref. [3]. This paper focuses on a specific class of multiscale simulation aiming at integrating quantum with molecular scale models for heterogeneous catalysis.

Over the past decade, molecular simulations, such as molecular dynamics (MD) and Monte Carlo (MC) algorithms, have emerged as preeminent computational tools for science and engineering research. The availability and low cost of cluster computing have recently made quantum mechanical (QM) calculations on systems containing tens or hundreds of catalyst particles tractable. These small-scale electronic structure models provide simulation parameters, such as pre-exponential factors and activation energies, and potential energy surfaces (PES), which allow us to simulate larger atomistic scale processes that are grounded in first-principles physics instead of empirically fitting kinetic parameters or potentials.

While it is desirable to solve the coarser scale model with information from the finer scale model obtained on-the-fly (dynamic or co-current coupling) [2], it is often impractical to do so. In the latter case, a proper mapping of the finer scale model into a reduced form (a surface or map) is the most suitable approach [4]. In this paper, we discuss such parameterizations focusing on first-principles prediction of adsorption dynamics.

Our rationale of studying adsorption is that in many chemical reactions, adsorption and desorption processes are the rate-determining steps. At high temperatures, where most of the surface sites are empty, the rate of the process is usually controlled by adsorption of reactants and mass transfer. At the other extreme of low temperatures, the surface sites are filled, and the competitive adsorption of reactants, as well as the desorption of the most abundant surface species, control the reaction rate.

*Corresponding author. E-mail: vlachos@che.udel.edu

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As a specific example, in previous work on partial oxidation of methane over a platinum catalyst, under many conditions we have found that 6 reactions, namely adsorption and desorption of methane, water, and hydrogen, out of a total of 62 reactions of a microkinetic model control the overall conversion of methane [5]. Furthermore, we have shown numerically [5] and theoretically [6,7] that ignition of fuels depends on the ratio of sticking coefficients of the reactants. In another application, preventing sticking of radicals on the walls of microburners is a key to the successful development of microscale portable power generators [8,9]. These considerations underline the need for a better understanding of adsorption dynamics on crystal surfaces.

In this paper, we discuss the multiscale aspects associated with adsorption of species on surfaces and present examples from the dissociative adsorption of H_2 on a Pt(111) surface to elucidate the successes and challenges of multiscale modeling.

OVERVIEW OF ADSORPTION MECHANISMS AND SIMULATION

The dissociation of a molecule at a crystal surface generally follows a precursor-mediated pathway at low energies and a direct pathway at high energies. A review by Weaver *et al.* [10] summarizes experimental and theoretical findings for both of these mechanisms for alkane/single crystal systems. When dissociating via a precursor-mediated pathway, the impinging molecule is temporarily trapped in a weakly bound physisorbed state, from which it can either dissociate or desorb. In this mechanism, the surface plays an active role in the dissociation process by transferring energy to and from the reactive intermediate through lattice vibrations. This necessitates the inclusion of surface degrees of freedom (see Ref. [11] for basic method) in dynamic models and renders rigorous QM treatment impractical at this point in time.

In contrast, reactivity through the direct mechanism depends mostly on the distribution of energy among the various modes of motion of an incident molecule [10]. For a light diatomic molecule, it then becomes necessary to study only the three degrees of freedom of each atom since the role of the crystal is significantly diminished. It is this reduction of dimensionality that renders this problem computationally tractable using an *ab initio* based multiscale approach.

Much effort has been put forth in recent years to develop six dimensional PES based on rigorous density functional theory (DFT) calculations and study the dynamics by performing classical, semi-classical, or fully quantum stochastic trajectory calculations. Comparitive studies [12–15] have detailed the advantages and disadvantages of treating the dynamics quantum mechanically, classically, or semi-classically. The semi-classical method is a hybrid approach where the system is treated classically, except the molecules are given vibrational energy equal to the zero-point energy (ZPE). Overall, QM dynamic calculations are the most rigorous, but as pointed out by Pijper *et al.* [14], it is too computationally demanding to perform these calculations on a wide range of vibrational and rotational states. From an engineering standpoint, the fully QM dynamic models are therefore of limited utility when the ultimate goal of the simulations are the prediction of sticking coefficient over a wide range of temperatures and pressures.

When performing classical trajectory calculations, the inclusion of ZPE (the semi-classical approach) may not always yield a better result than standard classical trajectories. The choice of method is largely dependant on the topology of the PES. For activated surfaces, such as H_2/Cu(100), it has been shown that the classical approach underestimates adsorption rates [13], whereas on non-activated steering-dominated topologies, such as H_2/Pd(100), including the ZPE leads to an over prediction of sticking [15].

The development of a PES and its use in a MD simulation is a typical example of hybrid multiscale simulation based on parameterization of the finer scale model. The inability to perform fully coupled *ab initio* MD for practical heterogeneous catalytic systems of interest renders the parameterization of the lower scale model an essential bridge for addressing the inherent two-way coupling encountered in modeling the reactivity of surface reactions. A major multiscale challenge is how one parameterizes efficiently the PES as a function of gaseous molecules' position using DFT simulations and assesses its accuracy. We would next discuss this problem.

DEVELOPMENT OF PES

The construction of an *accurate* PES is critical to obtaining useful dynamic results. In our opinion, methods that ensure accurate parameterization of a PES with minimal computational cost are at the heart of hybrid quantum/molecular multiscale modeling. The parameterization of high-level theory with a simple, analytic model falls into the general category of surface response or solution mapping methods. These methods have been successful in mapping the response of complex gas phase and surface reaction mechanisms [16,17] with the ultimate goal of parameter optimization against experimental data.

We have recently introduced this methodology of parameterization of the response of molecular (kinetic MC) models [18,19] for extracting molecular model parameters from experimental data in a systematic and efficient way. In the development of approximate response, factorial design [20] ideas have been employed.

Obviously, this is not the only way of parameterization of complex models. For example, tabulating data is an attractive alternative that has been pursued in adsorption dynamics [14] and in complex reacting flow simulations [21]. While this is a straightforward approach, it may require hundreds of DFT simulations for adequately sampling the configuration space, a daunting computational task for large molecules. A physics-based construction of approximate response surfaces is another alternative that has inherent advantages, such as a reduced number of required data points and ease of implementation. Such a construction of a PES is discussed here.

Our initial efforts have been focused on understanding the adsorption of molecular hydrogen on a clean Pt(l11) surface. The approach we have chosen closely follows the development of the PES used to study the Eley–Rideal reaction of H on Cu(111) [22]. This approach uses a corrugated London–Eyring–Polanyi–Sato (LEPS) potential, which, in this case, is a non-linear mixing function of the attractive and repulsive branches of modified Morse potentials. The modified Morse potential has the following analytic form:

$$V_\sigma(\bar{r}) = d_\sigma\big(\exp[-2\alpha_\sigma(r - r_{\sigma 0})] - 2f_\sigma(\bar{r})\exp[-\alpha_\sigma(r - r_{\sigma 0})]\big)$$

$$f_\sigma(\bar{r}) = \exp\left(\frac{-\tilde{\alpha}_\sigma(r - r_{\sigma 0})}{1 + \exp(-\beta_\sigma\alpha_\sigma(r - r_{\sigma a}))}\right).$$

Most parameters are roughly equivalent to their standard Morse potential analogs: d_σ is the well depth, $r_{\sigma 0}$ is the equilibrium position, α_σ, $\tilde{\alpha}_\sigma$, and β_σ control the strength of the exponential decay, and $f_\sigma(\bar{r})$ is a switching function, which changes the exponential decay from $\exp(-\alpha r)$ to $\exp(-(\alpha + \tilde{\alpha})r)$ around $r_{\sigma a}$. Following the notation of Persson *et al.* [22], the subscript σ will either be a or m, which indicates hydrogen–surface or hydrogen–hydrogen, respectively. The use of a modified Morse potential was necessary to obtain a good fit of the tail region of spin-polarized DFT calculations.

The first step in generating a LEPS potential is a full parameterization of the interaction of a lone hydrogen atom with the crystal surface and with itself (generate potentials for all possible pairwise interactions). Generating a pairwise potential for the H–H interaction is relatively straightforward and is omitted from this discussion. To obtain a pairwise potential function for the hydrogen–platinum interaction (the H–Pt PES), we first chose three sites on the crystal surface (bridge, top, hollow), and perform a series of DFT calculations at various z positions above the surface at a fixed x and y. These sites and coordinate system are shown in Fig. 1a.

All DFT calculations were performed using the DACAPO [23] code in a periodic 2×2 unit cell, consisting of 3 layers frozen in their bulk position, with approximately 18 Å of vacuum between layers in the z direction. Within the root mean square error of the potential fit, the effect of relaxing the first layer did not significantly impact the construction of the potential and was omitted from this study. The Kohn–Sham wavefunction was expanded in a planewave basis with a 350 eV cutoff energy. Vanderbilt ultrasoft pseudopotentials [24] were used to model the core electrons and

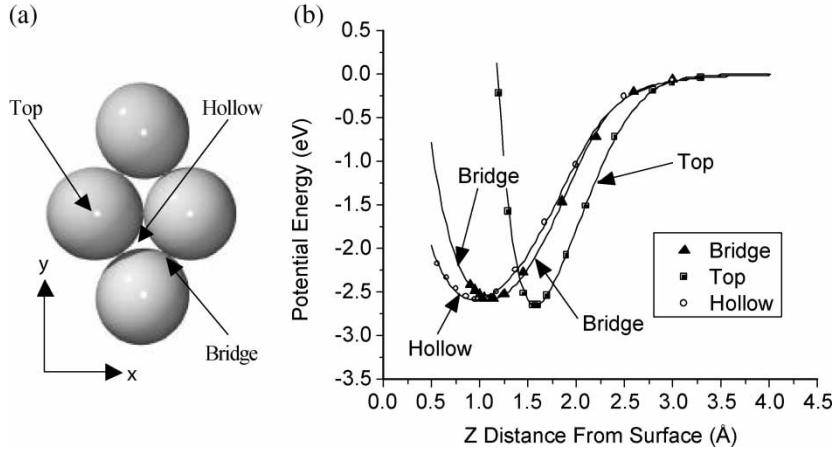

FIGURE 1 (a) Unit cell and coordinate system on which periodic DFT calculations have been performed. (b) Results of DFT calculations. Marks are energies taken from spin-polarized DFT calculations, lines are modified Morse potential fits. Parameters extracted from fits are shown in Table I.

TABLE I Parameters used in modified Morse and LEPS potentials. Potential parameters were determined by a least squares fit to total energy calculations

	Modified Morse potential parameters					
Type	d_σ *[eV]*	$r_{\sigma 0}$ *[Å]*	α_σ *[Å^{-1}]*	$\tilde{\alpha}_\sigma$*[Å^{-1}]*	$r_{\sigma a}$ *[Å]*	β_σ
H_2 molecule	4.5450	2.1152	0.7561	0.7291	1.8162	4.0000
Top	2.6525	1.5791	1.7737	0.9994	2.4660	2.5047
Hollow	2.5832	0.9846	0.8218	0.9312	2.0918	4.0000
Bridge	2.5771	1.1328	1.0542	1.1317	2.2832	2.8558

	LEPS potential parametes		
	MEP-LEPS	*2H-LEPS*	*MEPS + 2H LEPS*
Δ_a	0.2172	0.1142	0.0743
Δ_m	−0.1032	−0.2725	−0.1346

the irreducible Brillouin zone was sampled using 18 special *k*-points [25]. Using more *k*-points or increasing the planewave cutoff did not significantly impact results.

Results from spin-polarized total energy calculations are shown in Fig. 1b. Tables I and II detail the parameters used in our pairwise potential functions and the key findings from the lone H/Pt DFT studies. Comparison of our results to those of Olsen *et al.* [26] show that our calculated adsorption energies were within 0.1 eV for the top site and 0.04 eV for the hollow and bridge sites. We have obtained a vibrational frequency of 1134 cm^{-1} for the H/hollow configuration, which is in good agreement with previously reported values [22].

Having a 1D H/Pt PES at three discrete surface sites, we constructed a corrugated pairwise potential function so that the three 1D pairwise potentials collapsed into a single 3D periodic expression that preserves the symmetry of the FCC(111) plane and accurately interpolated intermediate points. This was accomplished by allowing all six of the potential parameters to be periodic functions of x and y. We expanded each parameter in a Fourier series over reciprocal lattice vectors. For example, if we were only to keep the first two terms in this expansion, the parameter d_σ would expand as follows:

$$d_\sigma(x,y) = h_0 + h_1\{\cos(X_b) + \cos(Y_b) + \cos(X_b + Y_b)\}$$

$$X_b = \frac{2\pi}{\Delta}(x\hat{i} + y\hat{j})\cdot\left(\hat{i} - \frac{\hat{j}}{\sqrt{3}}\right)$$

$$Y_b = \frac{4\pi}{\Delta\sqrt{3}}(x\hat{i} + y\hat{j})\cdot(\hat{j}).$$

X_b and Y_b are tile projections of x and y on their respective reciprocal lattice vectors, and Δ is the distance between adjacent atoms on the lattice. Since we have potential parameter values at three different sites, we expanded the series out to a third term. Each of the six parameters is exact at the sample points and the points in between are interpolated by a trigonometric series. This technique is discussed in detail by Busnengo *et al.* [27].

After we obtained suitable expressions for both the H–H and H–Pt potentials, we performed DFT calculations using two hydrogen atoms in the system. In particular, we first studied three, two-hydrogen configurations: adjacent hollow sites, both in the same hollow site, and a hollow-top configuration. We will refer to the potential energy surface developed using these data points as the training set as the 2H-LEPS PES. In these configurations, one H atom was held fixed in a hollow position at its equilibrium distance, and the other H atom was centered over the adjacent hollow site, the same hollow site, or the neighboring top site. The second hydrogen was moved normal to the surface and total energy calculations were performed at various values of z. These types of configurations were used by Ref. [22] to parameterize the H2/Cu(111)[2] LEPS surface and correspond to configurations suggesting an Eley–Rideal pathway.

We also performed a nudged elastic band (NEB) calculation to determine the minimum energy path (MEP) between an H_2 molecule in the gas phase and

TABLE II Summary of DFT results. The binding energy of H–Pt (E_{ad}) is relative to the Pt slab and H atom at infinite separation and includes zero-point vibrational energy normal to the surface. Z_{eq} is the equilibrium bonding distance for H–Pt

	DFT summary	
Site	E_{ad} *[eV/H atom]*	Z_{eq} *[Å]*
Top	−0.380	1.578
Hollow	−0.311	0.976
Bridge	−0.305	1.121

two hydrogen dissociated on the surface in their minimum energy configuration. We created a second potential based on these data points, which we will call the MEP-LEPS. Lastly, we created a third potential which used all two-hydrogen configurations studied as a training set (2H + MEPS-LEPS).

The LEPS potential was used as a functional form to account for third-body effects:

$$V(\bar{r}_1,\bar{r}_2) = U_a(\bar{r}_1) + U_a(\bar{r}_2) + U_m(r) - \sqrt{Q_m(r)^2 + [Q_a(\bar{r}_1) + Q_a(\bar{r}_2)]^2 - Q_m(r)[Q_a(\bar{r}_1) + Q_a(\bar{r}_2)]}.$$

In the above expression, U and Q are functions constructed from the attractive and repulsive branches of the pairwise modified Morse potentials. The subscripts denote the H–H potential (m) and the H–Pt potential (a), as mentioned previously. In the functions representing the branches of the potential, two additional parameters are introduced (see Ref. [22] for the exact analytic forms of these functions). These additional parameters are called Sato parameters, and were fit to the two-hydrogen DFT results described above using simulated annealing (see Table I for Sato parameters for various 2H configurations). To our knowledge, these are the first analytic PES for this system.

The MEP and three potential fits calculated along this reaction coordinate are shown in Fig. 2. The reaction coordinate appears to be only slightly activated, which is in good agreement with the DFT calculations of Olsen *et al.* [26] and molecular beam experiments [28,29]. We see that based on our LEPS parameters on the 2H configurations leads to a drastic over prediction of this activation barrier, less so if we use both configurations (MEP + 2H) as a training set.

Figure 3a shows the MEP-LEPS predictions against the 2H dataset. For the hollow-hollow and hollow-top configuration the fit is very good. The fit is not so good for the co-hollow configuration. Furthermore, this surface systematically under predicts the potential energy. Figure 3b shows the results of the global fit for all four 2H configurations.

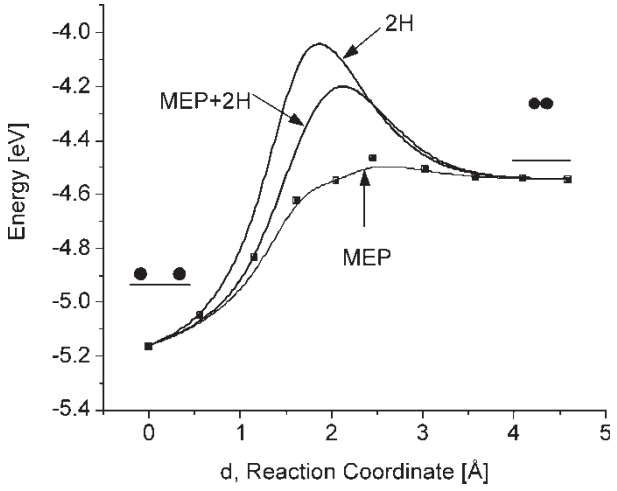

FIGURE 2 The minimum energy path for H_2 dissociation on Pt(111) compared to various LEPS surfaces. Data points are DFT results from a nudged elastic band calculation, MEP line is obtained using the LEPS potential fitted to the 10 two-hydrogen data points of the minimum energy path calculation. The 2H line corresponds to a LEPS surface fit to the sample two-hydrogen configurations shown in Fig. 3 and the MEP + 2H line is a global fit to all two-hydrogen data points presented here. Sato parameters for LEPS surfaces are found in Table I.

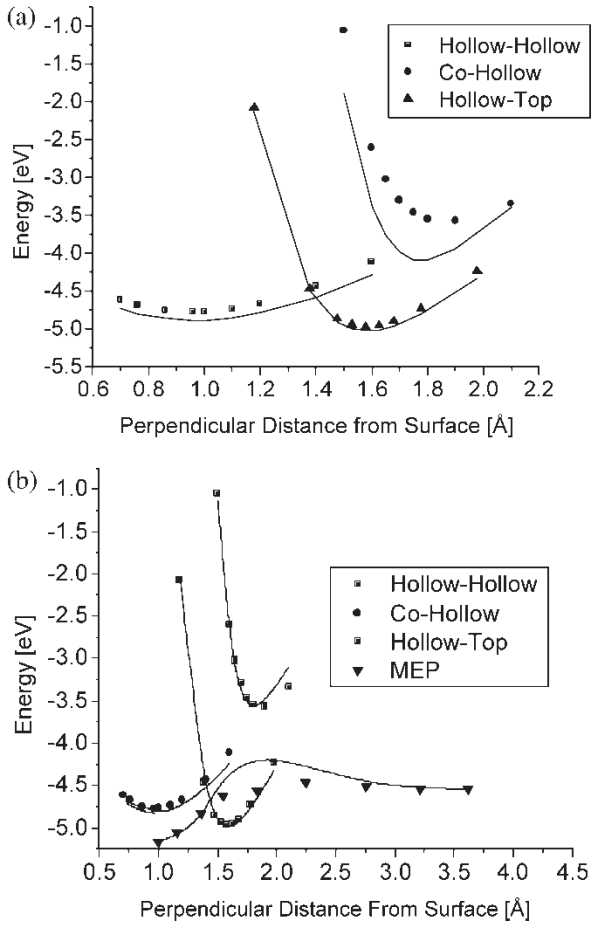

FIGURE 3 Data points are results from DFT calculations and solid lines are various LEPS potential fits. (a) Comparison of MEP-LEPS fit based only on the minimum energy path to the Eley–Rideal type configurations used to train the 2H-LEPS surface. (b) Comparison of a global fit to both the MEP and 2H cuts to all two-hydrogen configurations calculated in this study.

MD SIMULATIONS: PREDICTION OF STICKING COEFFICIENTS FOR MOLECULAR BEAM EXPERIMENTS

We have performed semi-classical trajectory studies to judge the sensitivity of dynamics calculations to our PES. The details of this calculation can be found in Appendix A. The results of this study, in comparison to experimental data [28,29] and a similar dynamics calculation by Pijper *et al.* [14] are shown in Fig. 4.

Our MEP-LEPS potential over-predicts the sticking probability; our 2H-LEPS potential severely under-predicts the sticking probability; and our MEP + 2H-LEPS potential falls in between these two extremes. The dynamics calculation performed by Pijper *et al.* [14] is based on a highly accurate interpolated surface using over 800 data points. Our simulations are based on a total of 50 to 60 data points.

The MEP-LEPS potential underestimates the barriers along reaction pathways and it therefore seems logical that a surface based only on the MEP would over predict reaction rates. Likewise, arbitrary two-hydrogen slices of the PES do not put enough emphasis on the lower energy kinetic pathways. A mixing of the two (based on equal weights) improves the prediction and is closer to the 2H-LEPS surface results because of the larger data set used for this surface. One can easily envision carefully chosen weightings for various cuts of the full 6D surface that would lead to a PES that describes the dynamics more properly.

Despite all three surfaces not yielding results as good as the interpolated surface, we obtain an order of magnitude estimate of sticking probability and the correct experimental trend using far fewer data points than the interpolated surface. But we believe is that these results demonstrate more than anything else the clear need for a systematic method to assess the parameterization, especially in the absence of experimental data.

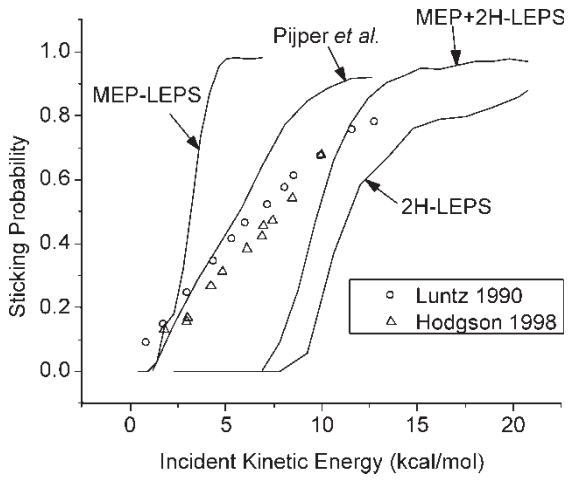

FIGURE 4 Comparison of semi-classical trajectory studies to molecular beam data. Marks are experimental molecular beam data [28,29]. Dynamics results from Pijper *et al.* [14] based on an interpolated PES. The three simulations presented in this study correspond to those using a potential based only on the minimum energy path (MEP-LEPS), 2D Eley–Rideal style cuts taken from the 6D surface (2H-LEPS), and a global fit to all two-hydrogen configurations calculated (MEP + 2H-LEPS).

CONCLUSIONS AND OUTLOOK

We have performed DFT total energy calculations for the H_2/Pt(111) system with good agreement regarding vibrational frequencies and binding energies compared to previous experimental and theoretical studies. An approach used to model the H_2/Cu(111) system [22] was followed, which uses corrugated modified Morse potential functions for pairwise interactions to smoothly interpolate between surface sites where DFT data is unavailable. This functional form preserves the symmetry and periodicity of the H/Pt(111) potential energy surface.

Based on DFT results from three, two-hydrogen Eley–Rideal type configurations and a NEB calculation, we used simulated annealing to fit the Sato parameters of three corrugated LEPS potentials. Based on this limited dataset, we have found that the surface based only on the MEP over-predicts sticking probability, whereas the surface based on "sensible" 2H cuts under estimates the rate. Finally, an intermediate surface based on both of these falls in between these two extremes. All three surfaces yield the correct trend and a reasonable order of magnitude estimate of the sticking behavior of the H_2/Pt(111) system.

The current multiscale modeling paradigm involves creating a candidate potential energy surface, verifying the potential by comparing the sticking coefficient with experimental data, and then deciding which representative configurations should be included in generating the potential energy surface. Our example here indicates that what is currently missing from this multiscale framework are methods that (1) provide some guidance as to what part of configuration space needs to be sampled to obtain the proper potential in an efficient way and (2) assess the accuracy of these surfaces. Unless such methods are developed, the power of multiscale simulation in being able to predict sticking coefficients and adsorption rates without relying on experimental data cannot be fully materialized.

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We thank John Kitchin for useful discussions on the computational details of DFT calculations.

APPENDIX A: DETAILS OF SEMI-CLASSICAL TRAJECTORY CALCULATION

The center of mass of a hydrogen molecule was chosen randomly over the surface unit cell. The center of mass velocity was taken to obtain the correct incident energy normal to the surface. The ZPE of the molecule obtained from DFT data in its first vibration state ($v = 0$) was imparted to the molecule as relative motion (randomly directed towards or away), with the molecule having equilibrium bond length. Rotational motion was not considered ($j = 0$) and the initial angular orientation of the molecule was taken to be completely random. All trajectories started 10 Å above the crystal surface. The Hamiltonian for this system was:

$$H = \frac{1}{2M}P_1^2 + \frac{1}{2\mu}P_2^2 + V(\bar{r}_1, \bar{r}_2)$$

where M is the total-mass of the hydrogen molecule, $\bar{r}_1$ and $\bar{r}_2$ are the positions of hydrogen atoms, μ is the reduced mass, P_1 and P_2 represent the momentum about the center of mass and relative to its center of mass, and $V(\bar{r}_1, \bar{r}_2)$ is the LEPS potential.

Trajectories were integrated using a standard velocity Verlet [30] algorithm and a time step chosen to conserve energy down to 1% of the total system energy. If at any time the molecule's effective bond length became greater than 3 Å, the trajectory was classified as dissociated. If the molecule's center of mass crossed the initial 10 Å starting position, the trajectory was classified as reflected. We did not observe any unclassified trajectories.

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