Statistical mechanical models for dissociative adsorption of O2 on metal(100) surfaces with blocking, steering, and funneling

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Citation: The Journal of Chemical Physics 140, 194704 (2014); doi: 10.1063/1.4875813
View online: http://dx.doi.org/10.1063/1.4875813
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/140/19?ver=pdfcov
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Statistical mechanical models for dissociative adsorption of O₂ on metal(100) surfaces with blocking, steering, and funneling

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(Received 15 February 2014; accepted 29 April 2014; published online 20 May 2014)

We develop statistical mechanical models amenable to analytic treatment for the dissociative adsorption of O₂ at hollow sites on fcc(100) metal surfaces. The models incorporate exclusion of nearest-neighbor pairs of adsorbed O. However, corresponding simple site-blocking models, where adsorption requires a large ensemble of available sites, exhibit an anomalously fast initial decrease in sticking. Thus, in addition to blocking, our models also incorporate more facile adsorption via orientational steering and funneling dynamics (features supported by ab initio Molecular Dynamics studies). Behavior for equilibrated adlayers is distinct from those with finite adspecies mobility. We focus on the low-temperature limited-mobility regime where analysis of the associated master equations readily produces exact results for both short- and long-time behavior. Kinetic Monte Carlo simulation is also utilized to provide a more complete picture of behavior. These models capture both the initial decrease and the saturation of the experimentally observed sticking versus coverage, as well as features of non-equilibrium adlayer ordering as assessed by surface-sensitive diffraction.

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I. INTRODUCTION

For dissociative adsorption of oxygen on metal surfaces, a key goal is reliable theoretical description of the dependence on oxygen coverage, θ_O, of the sticking coefficient, S(θ_O), or of its normalized form,

\[ \hat{S}(θ_O) = S(θ_O)/S(0) = 1 - c_1 θ_O + c_2(θ_O)^2 + \ldots, \]

with θ_O in monolayers (ML).

This requires development and analysis of a realistic “environment-dependent” adsorption model. Such a model should specify the outcome of adsorption attempts for all possible local environments of the impingement site. For the traditional nearest-neighbor (NN) adsorption model with non-activated adsorption onto NN pairs of unoccupied sites, which occur with probability P_{NN}, the normalized sticking probability becomes \( \hat{S}(θ_O) = P_{NN} \). Neglecting spatial correlations leads to the familiar mean-field Langmuir form, \( \hat{S}(θ_O) = (1 - θ_O)^2 \), and for which \( c_1 = 2 \). For adlayers with exclusion of occupancy of NN sites, one has the exact result, \( \hat{S}(θ_O) = 1 - 2θ_O \), for this model where again \( c_1 = 2 \). In either case, availability of a simple analytic form for \( \hat{S} \) is immensely useful for modeling, e.g., oxidation reaction kinetics, at least after suitable refinement to account for the presence of coadsorbed reactant species. However, it is recognized that these simple forms will not be adequate for systems with strong species repulsions, where larger unoccupied “adsorption-site ensembles” may be required for adsorption. A classic example is the Brundle-Behm-Barker (BBB) 8-site model for dissociative adsorption of oxygen at hollow fourfold hollow (4fh) sites on an unreconstructed metal(100) surface (see Fig. 1), as originally proposed for Ni(100). In this model, highlighted in Zangwill’s surface physics monograph, oxygen adsorbs onto diagonal or second NN (2NN) unoccupied 4fh sites, provided that the six 4fh sites NN to these are also free of oxygen. Thus, adsorption does not populate NN pairs of sites. One has that \( \hat{S}(θ_O) = P_8 \), the probability of the required unoccupied 8-site adsorption ensemble. In this model, \( \hat{S} \) vanishes for a 0.25 ML p(2 × 2) overlayer, as suggested by the BBB experiments. For an equilibrated-quasi-random adlayer at low coverage, it is clear that \( c_1 = 8 \) for this model (far above the \( c_1 \)-value for traditional models). We note that the 8-site model was also applied extensively for oxygen adsorption on Pd(100). Furthermore, after refinement to account for the effect of coadsorbed species, the 8-model has been successfully incorporated into both simplified and realistic statistical mechanical modeling of CO-oxidation on metal(100) surfaces. This higher-level modeling goes beyond a traditional Langmuirian mean-field treatment.

For a broader perspective, we note that a complete prescription of a non-equilibrium statistical mechanical adsorption model requires specification not just of the environment-dependent adsorption rule but also of the diffusive dynamics of the adlayer (which in part reflects the adlayer thermodynamics). We emphasize that adlayer structure, and thus the sticking coefficient, depends not just on the adsorption rule but also on the degree of mobility, and in general on the entire history of adsorption (e.g., for varying oxygen pressure). Thus, \( \hat{S} \) does not have universal dependence of \( θ_O \) and may perhaps be better reflected by the notation \( \hat{S} = \hat{S}(O) \), where \{O\} denotes the entire configuration of the O-adlayer. Behavior of such a stochastic lattice-gas model is described exactly by hierarchical master equations for the evolution of the probabilities various local adsorbate configurations which in turn determine the evolution of \( \hat{S} \). However, such equations are not amenable to exact solution, so typically
behavior is instead precisely determined from Kinetic Monte Carlo (KMC) simulation. This KMC approach simply randomly implements the various processes (adsorption and possibly diffusion) according to the rules prescribed by the model, and with probabilities reflecting their relative physical rates.

One exception to the above non-equilibrium scenario is the case of high-mobility with equilibrated adlayers as is expected for higher surface temperature (T). Here, sticking behavior for a specified adsorption rule is completely determined by T and by the adlayer thermodynamics (i.e., the adspecies interactions). For the special case of NN exclusion, we recall the exact result, $\hat{S}(0) = 1$ for the traditional NN adsorption model as described above, and note that the Kirkwood approximation provides a corresponding but approximate expression for the 8-site model (see Sec. II), both of which are actually independent of T.

Rather than higher-T equilibrated adlayers, we shall emphasize in this study behavior for lower-T with negligible thermally activated surface diffusion. In this regime, the resultant far-from-equilibrium adlayer structure is innately dependent on the details of the adsorption mechanism. This regime can be realized for oxygen adsorption on metal surfaces for higher adsorption rates at low T, as the barrier for diffusion is typically substantial. In this regime, the associated “random sequential adsorption” (RSA) type models display a non-trivial saturation or jamming coverage, $\theta_0^S$, where adsorption ceases, i.e., $\hat{S}(\theta_0^S) = 0$. For example with NN exclusion, clearly $\theta_0^S < 0.5$ ML where $\theta_0 = 0.5$ ML is achieved only for perfect c(2×2)-ordering. These RSA models are more amenable to effective analytic treatment than models with significant adlayer mobility. Short-time (low-coverage) Taylor expansion of the associated exact master equations determines the coefficients $c_n$ in (1). One can also perform an asymptotic long-time analysis which reveals that

$$\hat{S}(\theta_0) \sim s_1(\theta_0^S - \theta_0), \text{ as } \theta_0 \to \theta_0^S, \text{ with } s_1 > 0 \text{ (for RSA).}$$

Despite the utility of the 8-site model, there are various indications of its shortcomings. First, we describe experimental observations. Reanalysis of O$_2$/Ni(100) subsequent to BBB suggested a recalibration of coverage wherein $\hat{S}$ became negligible to around 0.37 ML (versus 0.25 ML). This implies a slower initial decrease of $\hat{S}$ with $c_1$ well below the BBB value $c_1 = 8$ (but still above $c_1 = 2$ for the traditional NN adsorption model), and further analysis suggests that $c_1 = 2.5$–4. For Pd(100), our analysis of the available (but limited) data for $S^{25}$ suggests that $c_1 \approx 3$, also significantly below 8. For Rh(100), more precise data indicates even lower $c_1 < 2$, and the shape of $\hat{S}(\theta_0)$ versus $\theta_0$ differs from either the classic Langmuir form or Kirkwood predictions for the 8-site model. Second, recent Density Functional Theory (DFT) analysis indicates the common feature for (100) surface of Ni, Pd, Rh, and other transition metal surfaces of a preferred dissociation pathway through vicinal NN pairs of bridge (br) sites to a third NN (3NN) pair of 4fh sites. See Fig. 1. Direct adsorption to 2NN 4fh sites is generally not favored. Third, detailed multisite lattice-gas (msLG) modeling incorporating adsorption via NN vicinal br sites, and also via NN pairs of other sites, produces sticking behavior reasonably consistent with experiment, and typically with $c_1 \sim 3$–4. However, for these more complex msLG models, it is difficult to extract a simple analytic expression for $\hat{S}$.

Our perspective on the origin of low $c_1$-values seen in experiment and in msLG model simulation is that the prescription of adsorption is overly restrictive in the simple 8-site blocking model (and also in a similar 9-site model described in Sec. III). For example, steering of the adsorbing diatomic to different orientations, and funneling away from preadsorbed adspecies, can allow greater access to available adsorption-site ensembles. This constitutes an alternative to the traditional view that lower $c_1$-values are associated with the effect of physisorbed precursors, see Appendix A. Indeed, the importance of typically neglected details of the adsorption dynamics on key measurable quantities in surface systems is receiving more attention. For example, a slow nonlinear decrease in $\hat{S}$ versus coverage with $c_1 = 0$ for CO adsorption on Rh(100) was explained by DFT analysis indicating steering of impinging CO to unpopulated top sites. This contrasts the traditional explanation using Gasser-Smith precursor theory. Also, unexpected smooth growth at low-T in metal(100) epitaxial systems has been shown to derive from funneling of depositing atoms off isolated adatoms and off the edges of adatom clusters to nearby 4fh adsorption sites.

With regard to theoretical validation of these ideas, the possible limitations of DFT for describing O$_2$ dissociation on metal surfaces have been a subject of recent debate. Thus, DFT-based ab initio Molecular Dynamics (MD) studies do not provide a definitive picture of dissociation dynamics. For example, we find that changes in the strength of binding to the surface for spin-polarized versus non-spin-polarized calculations can produce quite different behavior. Another issue is the potentially inadequate treatment of energy dissipation into the bulk substrate due to finite lateral unit-cell size and slab thickness. Nonetheless, we have performed selective DFT-MD analyses for Pd(100) which do reveal the occurrence of orientational steering and funneling dynamics during adsorption. See Appendix B for further discussion. However, in this paper, we focus on the development of appropriate statistical mechanical models for O$_2$ dissociation on general fcc(100) metal surfaces.

Our specific goal is to develop models for environment-dependent dissociative adsorption of oxygen on partially
TABLE I. \(c_1\)-values for various models which will be described in Secs. II and III with orientational steering (s) and funneling (f), or both (sf). Row 2 gives values for an equilibrated adlayer subject to NN exclusion. Row 3 gives values for RSA at low-T with no thermal surface mobility. Other models with more extensive funneling give lower \(c_1\)-values (see text).

<table>
<thead>
<tr>
<th>Model</th>
<th>8-site</th>
<th>8s-site</th>
<th>8f-site</th>
<th>8sf-site</th>
<th>9-site</th>
<th>9s-site</th>
<th>9f-site</th>
<th>9sf-site</th>
</tr>
</thead>
<tbody>
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<td>4</td>
<td>2</td>
<td>1</td>
<td>9</td>
<td>5</td>
<td>3</td>
<td>1</td>
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<tr>
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<td>3.5</td>
<td>2</td>
<td>1.25</td>
<td>7.25</td>
<td>4</td>
<td>3.25</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Oxygen-covered metal(100) surfaces. These should incorporate exclusion of population NN pairs of 4fh sites, as well as orientational steering and funneling, but they should also be amenable to analytic treatment. Extension of these models to treat the effects of coadsorbed CO species for application to modeling of CO-oxidation is described in Appendix C. Optimal models should have \(c_1\)-values compatible with experiment as arguably the initial rate of decrease of sticking is its most significant feature. We analyze the 8-site model with 2NN 4fh adsorption sites and refinements in Sec. II. A 9-site alternative with more reasonable 3NN 4fh adsorption sites and refinements is analyzed in Sec. III. A summary of \(c_1\)-values for these models is provided in Table I. These refined models should also produce a reasonable overall shape of \(\hat{S}(\theta_O)\) versus \(\theta_O\), exhibit reasonable values of saturation coverages at which \(\hat{S}\) becomes negligible, and recover features of the short-range order of the adlayer as probed by surface-sensitive diffraction techniques. In Sec. IV, we present Kinetic Monte Carlo (KMC) simulation results for our models and compare with experimental observations. Our conclusions are presented in Sec. V.

II. 8-SITE MODEL AND REFINEMENTS WITH STEERING OR FUNNELING

Given the historical significance and utility of the BBB 8-site model, it is appropriate to first describe its behavior, and then that of various refinements. An analogous treatment will be presented for an alternative 9-site adsorption model in Sec. V. Below, the oxygen diatomic (or dimer) impinges with its center of mass above a target top site with one of two diagonal orientations so that its constituent atoms are aligned with 2NN 4fh sites. Let \(k\) denote the adsorption rate for each orientation, i.e., the adsorption rate per pair of 2NN pair sites.

A. Classic BBB 8-site model

This model has been described in Sec. I. Some insight into its normalized sticking coefficient, \(\hat{S}_8\), comes from application of the Kirkwood approximation for the probability, \(P_8\), of the 8-site ensemble described in Sec. I and Fig. 2(a). Specifically, \(P_8\) is factored as a product of the probabilities of the eight constituent pairs of empty NN sites, compensating for over-counting of the empty site population. Thus, if \(P_1 = 1 - \theta_O\) denotes the probability that a 4fh site is unoccupied, one has that

\[
\hat{S}_8 = P_8 \approx (P_{2NN})^8/(P_1)^8 = (1 - 2\theta_O)^8/(1 - \theta_O)^8.
\]  

(3)

Thus, from a Taylor expansion, one immediately obtains \(c_1 = 8\) and \(c_2 = 20\). One can show that this \(c_1\)-value applies for adsorption via the 8-site rule onto an equilibrated adlayer with any prescription of adspecies interactions. (Note that equilibration is generally assumed due to facile surface diffusion.) The Kirkwood prediction of \(c_2 = 20\) should match exact behavior for the equilibrium hard-square model where particles occupy a square lattice of adsorption sites subject only to strict NN exclusion. Note that while the Kirkwood saturation coverage is strictly 0.5 ML, effective saturation occurs around 0.35 ML where the Kirkwood \(\hat{S}_8 \approx 0.002\). This feature is compatible with experimental observations for Ni(100) and Pd(100).

The low-T RSA regime without significant thermal diffusion is characterized by distinct behavior even for \(\theta_O \ll 1\). If \(P_{2NN}\) denotes the probability of an unoccupied 2NN pair, then it is clear that \(d/dt P_1 \rightarrow -4k\) (four adsorption configurations overlap the empty site), \(d/dt P_{2NN} \rightarrow -7k\) (seven adsorption configurations overlap a 2NN pair), and \(d/dt P_8 \rightarrow -24k\) (24 adsorption configurations overlap the 8-site ensemble), as \(t \rightarrow 0\) or \(\theta_O \rightarrow 0\). Thus, one has that \(c_1 = (dP_8/dt)/(dP_1/dt)|_{\theta_O=0} \approx 6\) (not 8). The shift in \(c_1\) from the Kirkwood value is due to the presence of strong 2NN correlations even for low \(\theta_O (P_{2NN} \approx 1 - 7/4\theta_O \text{ not } P_{2NN} \approx 1 - 2\theta_O)\) due to the nature of the adsorption rule. More detailed analysis of

FIG. 2. Schematics for the BBB 8-site model and refinements. The square grid denotes 4fh adsorption sites, open circles denote unoccupied 4fh sites, \(x\) denotes the top site above which the center of the diatomic impinges, and light blue ovals indicate the target 2NN 4fh adsorption sites. (a) Classic 8-site model: two orthogonal 8-site ensembles. (b) 12-site ensemble which is the union of orthogonal 8-site ensembles. (c) 8s-site model: configuration associated with successful adsorption after rotation where one or more sites denoted by \(\ast\) are occupied. (d) 8f-site model: funneling away from a filled side site (solid circle) to an available 8-site ensemble. (e) 8sf-site model: funneling away from one or more populated end sites (indicated by \(\ast\)) to an available 8-site ensemble.
this RSA model also shows that $c_2 = 135/16$. Also, $\hat{S}_8$ has a concave form (positive curvature) and decreases to zero at a saturation coverage of $\theta_O = 0.362$ ML.\(^{12}\) Interestingly, analysis of a refined model including thermal hopping reveals no change in the $c_1$-value. Thus, the transition from RSA behavior to that for an equilibrated layer is more subtle than a continuous increase of $c_1$ with increasing hop rate, see Sec. IV.

It is instructive to develop a refined Kirkwood approximation accounting for the eight constituent 2NN pairs (in addition to the eight NN pairs) within the 8-site ensemble. This yields a modified expression,

$$\hat{S}_8 = P_8 = (P_{NN})^8 (P_{2NN})^8 / (P_1)^{24}.$$  (4)

Using the equilibrated form $P_{2NN} \sim 1 - 2\theta_O$, (4) recovers $c_1 = 8$ as in the standard Kirkwood approximation. However, using the RSA form for $P_{2NN} \sim 1 - 7/4\theta_O$, (4) recovers the RSA value of $c_1 = 6$ for $\hat{S}_8$. The value of $\hat{S}_8$ from (4) is sensitive to the details of $c(2 \times 2)$ short-range order in the adlayer in contrast to (3). This follows noting that a measure of $c(2 \times 2)$ domain size is the diagonal chord length,\(^{12, 35}\) $L_d = \sqrt{2} \theta_O/(P_1 - P_{2NN})$, in units of surface lattice constant. A related point is that the 8-site RSA model does recover a key feature of experimental diffraction studies of low-T adsorption for $O_2/Pd(100)$: a strong $(1/2, 1/2)$ diffraction spot intensity reflecting non-equilibrium c(2 × 2) ordering, together with a weak $(1/2, 0)$ spot intensity associated with equilibrium p(2 × 2) ordering.\(^{4, 12, 25}\)

Finally, we provide an exact analysis of the nearsaturation behavior of sticking for the RSA model. In this regime, one might expect that each adsorbing diatomic (which adds two O adatoms to the surface) destroys exactly one 8-site ensemble (of which there are two per adsorption site). These considerations imply that $dS_8/d\theta_O \rightarrow -1/4$ at saturation, i.e., $s_1 = 1/4$. A rigorous analysis producing the same result exploits the upper-triangular structure of the matrix form of the hierarchical master equations, see Appendix D. This analysis provides significant additional information on the behavior of $\hat{S}_8$ (beyond the above low-coverage results) which facilitates Padé resummation or other rearrangements of the truncated Taylor expansion (1) for $\hat{S}_8$ to achieve a more uniformly accurate approximation, see Appendix E.

These equilibrated and RSA forms of the 8-site model produce $c_1$-values above well above experimental and msLG simulation values of $c_1 \sim 2-4$. To obtain lower $c_1$-values, we next construct analytically tractable variants of the 8-site model incorporating orientational steering and funneling, see Secs. II B–II D.

### B. Refinement with orientational steering (8s-site model)

In our 8s-site model, an adsorbing diatomic with center impinging above a top site can probe 8-site ensembles with two orthogonal orientations centered on this top site. If both are available, one is selected at random. If just one is available, it is selected. If neither is available, then the adsorption attempt fails. The configuration with both 8-site ensembles available has all sites in a 12-site ensemble unoccupied and occurs with probability $P_{12}(8s)$. See Fig. 2(b). Thus, for this 8s-site model, one has that $\hat{S}_8 = 2P_8 - P_{12}(8s)$. For another perspective, regard the impinging diatomic as randomly selecting one of the two diagonal orientations. Then, there is one contribution, $P_8$, to $\hat{S}_8$ if the 8-site ensemble is not available. The configuration, $P(rot)$, comes from the scenario where one or more of the four end sites of the selected 8-site ensemble are occupied (see Fig. 2(c)), but where rotated adsorption is successful, i.e.,

$$\hat{S}_8 = P_8 + P(rot), \text{ where } P(rot) = P_r - P_{12}(8s).$$  (5)

Using the Kirkwood approximation $P_{12}(8s) \approx (P_{NN})^{16/(P_1)^{20}}$, and (3) for $P_8$, one obtains $c_1 = 4$ for $\hat{S}_8$ for equilibrated adlayers with NN exclusion (cf. $c_1 = 8$ for $\hat{S}_8$).

Next, applying a master equation analysis for the RSA version of this model without thermal mobility, one finds that $d/dt P_8 \rightarrow -24k$ (as for the 8-site model) and $d/dt P_{12}(8s) \rightarrow -34k$ (34 adsorption configurations overlap the 12-site ensemble, as $\theta_O \rightarrow 0$. Consequently, one has that $c_1 = (2 \times 24 - 34)/4 = 3.5$ for the RSA version of the 8s-site model (cf. $c_1 = 6$ for the RSA 8-site model). We also note that a refined Kirkwood approximation also accounting for 2NN pairs, where $P_{12}(8s) \approx (P_{NN})^{16/(P_{2NN})^{4/(P_1)^{48}}}$, recovers this RSA value of $c_1$ for $\hat{S}_{8s}$ if one inputs the RSA form for $P_{2NN} \sim 1 - 7/4\theta_O$.

Finally, considering near-saturation behavior of the RSA model, analysis is more complicated than for the classic BBB 8-site model in Sec. II A. However, one can still consider nearsaturation adsorption onto isolated defects (which can accommodate just one diatomic) in order to assess the decrease in population of 8-site and 12-site ensembles, and thus the decrease in $\hat{S}_{8s}$. Such an analysis suggests that $dS_{8s}/d\theta_O \rightarrow -1/2$ at saturation, i.e., $s_1 = 1/2$ (distinct behavior from the BBB 8-site model). A rigorous analysis producing the same result follows from a detailed examination of the more complex structure of the hierarchical master equations in Appendix D. This result can facilitate development of more accurate approximations for $\hat{S}_{8s}$, see Appendix E. In summary, perhaps the most significant observation is that $\hat{S}_{8s}$ has $c_1$-values are reduced from those for the 8-site model to the desired range for both equilibrated and RSA cases.

### C. Refinement with funneling (8f-site model)

There are many possible prescriptions of funneling, so here we just discuss one choice which facilitates derivation of a simple expression for the sticking coefficient. In our 8f-site model with “restricted” funneling of the impinging diatomic away from preadsorbed adspecies, the original pair of target 2NN sites must be empty in order for subsequent funneling to be successful. Specifically, the diatomic attempts to adsorb with center above a top site, randomly selecting just one of two diagonal orientations. Direct adsorption is successful if the associated 8-site ensemble is available. This gives a contribution of $P_8$ to $\hat{S}_8$. If the 8-site ensemble is not available as a “side-site” is occupied, the diatomic funnels sideways away from this side-site and adsorbs provided the shifted 8-site ensemble is available. This produces an additional contribution, $P'(side) = P_{0f}(side) - P_{0f}(side)$, to $\hat{S}_8$ for each side site, for
the 10- and 11-site configurations are shown in Fig. 2(d). If both side-sites are unoccupied, but one of the two “end sites pairs” is occupied by at least one O, then the diatomic funnels in the opposite direction, and adsors if the associated shifted 8-site ensemble is available. This produces an additional contribution, \( P(\text{end}) = P_0(\text{end}) - P_{11}(\text{end}) \), to \( \tilde{S}_8 \) for each end, for the 9- and 11-site configurations in Fig. 2(e). Thus, one has that
\[
\tilde{S}_8 = P_8 + 2P(\text{side}) + 2P(\text{end}).
\] Implementing a Kirkwood approximation, \( P_8 \sim 1 - 8\theta_0 \), and using \( P(\text{side}) \sim \theta_0 \) and \( P(\text{end}) \sim 2\theta_0 \), one obtains \( c_1 = 2 \) for \( \tilde{S}_8 \) for equilibrated adlayers.

A low-T RSA analysis yields \( d/dt P_{10}(\text{side}) \rightarrow -29k \), \( d/dt P_{11}(\text{side}) \rightarrow -32k \), \( d/dt P_6(\text{end}) \rightarrow -27k \), \( d/dt P_{11}(\text{end}) \rightarrow -32k \), and again \( P_8 \rightarrow -24k \), as \( \theta_0 \rightarrow 0 \). Thus, one obtains \( c_1 = 2 \), a result which is also recovered in a refined Kirkwood approximation. We offer some comments on near-saturation behavior in Sec. II D.

D. Other refinements

It is natural to consider an 8sf-site model including both orientational steering and funneling, and which should produce even lower \( c_1 \)-values. As in the 8f-site model, the diatomic impingements on 2NN 4fh sites. However, now subsequent dynamics depends on the state of these two “target” 2NN 4fh sites. If these are both available, then one implements a 8f-site funneling model as above. This results in a contribution \( \tilde{S}_8 \) to \( \tilde{S}_{8sf} \). If both of those 2NN target sites are occupied, then the diatomic is steered to the orthogonal orientation, and implements an 8f-funneling model for that orientation. This is only possible if just one of those 2NN target sites is occupied and involves funneling sideways away from that site with probability \( P^\text{rot} \). Thus, one has that \( \tilde{S}_{8sf} = \tilde{S}_8 + P^\text{rot} \). We do not provide a detailed analysis here, but it can be shown that \( P^\text{rot} \sim \theta (3/4\theta) \), and thus that \( c_1 = (1.25) \) for equilibrated adlayers (in the RSA regime).

Rather than incorporate additional orientational steering into funneling models, one could extend the degree of funneling also reducing \( c_1 \). For example, an \( (8f^+) \)-model allowing funneling if one or both of the target 2NN sites are occupied (in contrast to the 8f-site model) yields \( c_1 = 0 \) (0.25) for equilibrated adlayers (in the RSA regime). The RSA value is non-zero as adsorption is blocked by a single preadsorbed diatomic with adatoms on 2NN sites orthogonal to the selected target 2NN sites. Finally, we comment briefly on near-saturation behavior for these RSA models. In general, increasing the range of funneling (or increasing the ease of adsorption) not only decreases \( c_1 \) but also increases the rate of decrease of sticking, \( s_1 = -d\tilde{S}_8/d\theta_0 \), at saturation.

III. 9-SITE MODEL AND REFINEMENTS WITH STEERING AND FUNNELING

As noted in Sec. I, DFT analysis does not support the 8-site model picture of adsorption onto 2NN 4fh sites, but rather shows the preferred pathway is adsorption onto 3NN 4fh sites via a NN pair of vicinal br sites. Thus, we craft a simple 9-site model which captures these essential features, and then discuss refinements of this model. Below the diatomic impinges with its center of mass above a target 4fh site with one of two orientations aligned with a principle lattice direction. Let \( k \) denote the impingement rate per period.

A. Basic 9-site model

In this model, the constituent atoms in the adsorbing diatomic separate to 3NN 4fh sites on opposite sides of a target site 4fh site above which the center of the diatomic impinges. Adsorption is successful if the target impingement site and 3NN adsorption sites are available, as well as the six additional neighbors of the final adsorption sites. Thus, adsorption does not populate NN pairs of 4fh sites, and an ensemble of 9-sites must be available for adsorption to be successful. This occurs with probability \( \tilde{S}_9 = P_9 \). See Fig. 3(a). Applying the Kirkwood approximation, one has that
\[
\tilde{S}_9 = P_9 \approx (P_{NN})^8/(P_1)^7 = (1 - 2\theta_0)^8/(1 - \theta_0)^7.
\]
Thus, from Taylor expansion, one obtains \( c_1 = 9 \) which applies for adsorption via the 9-site rule into an equilibrated adlayer for any prescription of adspecies interactions, and \( c_2 = 28 \) which should match exact behavior for the equilibrium hard-square model.

Next, we consider the regime of low-T RSA in the absence of thermal diffusion. Let \( P_{3NN} \) denote the probability on an unoccupied 3NN pair of 4fh sites. Then, one has that \( d/dt P_1 \rightarrow -4k \) (four adsorption configurations occupy the

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**Fig. 3.** Schematics for the 9-site model and refinements with notation as in Fig. 2. (a) Standard 9-site model: two orthogonal 9-site ensembles. (b) 13-site ensemble which is the union of orthogonal 9-site ensembles. (c) 9s-site model: configuration associated with successful adsorption after rotation where one or more sites denoted by * are occupied. (d) 9f-site model: funneling away from a populated end site (solid circle) to an available 9-site ensemble; (d) 9f-site model: funneling away from one or more populated upper side sites (denoted by *) to an available 9-site ensemble.
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empty site), $d/dt P_{3NN} \to -7k$ (seven adsorption configurations overlap a 3NN pair), and $d/dt P_9 \to -29k$ (29 adsorption configurations overlap the 9-site ensemble), as $\theta_O \to 0$. Thus, one obtains $c_1 \approx \left(\frac{dP_9}{dt}/(dP_1/dt)\right)_{\theta=0} = 7.25$ (not 9). This reflects the presence of strong correlations in occupancy of 3NN sites $P_{3NN} \approx 1-7/4 \theta_O$ not 1-2$\theta_O$ for low $\theta_O$. (As an aside, we note that analysis of a refined model including thermal hopping reveals no change in the $c_1$-value.) More detailed analysis of this RSA model also shows that $c_2 = 125/8$, and $\tilde{S}_9$ has a concave form decreasing to zero at a saturation coverage of $\theta_O^* = 0.358$ ML. Here, a natural refined Kirkwood approximation accounting for the seven constituent 3NN pairs within the 9-site ensemble gives

$$\tilde{S}_9 = P_9 \approx \left(\frac{P_{3NN}^3(P_{3NN})^7}{(P_1)^{21}}\right). \tag{8}$$

Using the RSA form for $P_{2NN} \sim 1-7/4 \theta_O$ recovers the RSA value of $c_1 = 7.25$ for $\tilde{S}_9$. The form (8) reflects adlayer order as $L_p \sim 2\theta_O/(P_1-P_{3NN})$ gives the c(2 x 2) domain size chord length in a principal lattice direction. Finally, we provide an exact analysis of near-saturation behavior for the RSA model. Analogous to the 8-site model, each adsorbing diatomic destroys exactly one 9-site ensemble so that $d\tilde{S}_9/d\theta_O \to -1/4$ at saturation, i.e., $s_1 = 1/2$. See Appendix D for a rigorous analysis based on the hierarchical master equations and Appendix E for discussion of related series rearrangement for $\tilde{S}_9$. Either the equilibrated or RSA forms of the 9-site model produce large $c_1$-values, so model refinement is needed to achieve desired smaller values.

**B. Refinement with orientational steering (9s-site model)**

In our 9s-site model with orientational steering, an adsorbing diatomic impinging with center above a 4th site can probe 9-site ensembles with two orthogonal orientations aligned in the principal surface directions centered on this 4th site. If both are available, one is selected at random. If just one is available, it is selected. If neither is available, then adsorption fails. Let $P_{13}(9s)$ denote the probability that all sites are unoccupied in the 13-site ensemble which is the union of the two 9-site ensembles, see Fig. 3(b). Then, regarding the impinging diatomic as randomly selecting one of the two orientations, there is one contribution, $P_9$, to $\tilde{S}_9$, if the 9-site ensemble associated with that orientation is available. Another contribution, $P$(rot), applies where one or more of the four axial sites of the selected 9-site ensemble are occupied (see Fig. 3(c)), but where adsorption in the rotated orthogonal orientation is successful, i.e.,

$$\tilde{S}_9 = P_9 + P$(rot), \quad \text{where} \quad P$(rot) = P_9 - P_{13}(9s). \tag{9}$$

In the Kirkwood approximation where $P_{13}(9s) \approx \left(P_{3NN}^{16}/(P_1)^{18}\right)$, one has that $c_1 = 5$ for $\tilde{S}_9$ for equilibrated adlayers with NN exclusion (cf. $c_1 = 9$ for $\tilde{S}_9$).

For the RSA version of this model, one finds that $d/dt P_9 \to -29k$ (as above) and $d/dt P_{13}(9s) \to -42k$ (42 adsorption configurations overlap the 12-site ensemble), as $\theta_O \to 0$. Consequently, one has that $c_1 = (2\times29 - 42)/4 = 4$ for the RSA version of the 8s-site model (cf. $c_1 = 7.25$ for $\tilde{S}_9$). A refined Kirkwood approximation accounting for 3NN pairs, where $P_{13}(9s) \approx (P_{3NN})^{16}(P_{2NN})^{10}/(P_1)^{39}$, recovers this RSA value of $c_1$ for $\tilde{S}_9$ if one inputs the RSA $P_{3NN} \sim 1-7/4 \theta_O$. Thus, $\tilde{S}_9$ has $c_1$-values well below those for $\tilde{S}_9$. Finally, considering near-saturation behavior, either an analysis of adsorption onto isolated defects or analysis of the hierarchical master equations in Appendix D shows that $d\tilde{S}_9/d\theta_O \to -1/2$ at saturation, i.e., $s_1 = 1/2$. See Appendix E for discussion of related series rearrangement for $\tilde{S}_9$.

**C. Refinement with funneling (9f-site model)**

Here, we just discuss one possible prescription of funneling. In our 9f-site model with “restricted” funneling, the diatomic attempts to adsorb with center above a 4th site randomly selecting one of two orthogonal orientations. In this model, the central 4th site and the 3NN sites must be empty in order for subsequent funneling to be successful. Direct adsorption is successful if the associated 9-site ensemble is available. This gives a contribution of $P_9$ to $\tilde{S}_9$. If the 9-site ensemble is not available, then funneling is implemented as follows. If an end site of the 9-site ensemble is occupied, the diatomic funnels away from this site and adsorbs if the shifted 9-site ensemble is available. The additional contribution to $\tilde{S}_9$ is $P$(end) = $P_9 - P_{10}$(end) for each end site, where relevant configurations are shown in Fig. 3(d). If both end sites in the 9-site ensemble are unoccupied, and one “side-site pair” is occupied by one or two O, then the diatomic funnels sideways away from this pair and adsors if the shifted 9-site ensemble is available. The additional contribution to $\tilde{S}_9$ is $P$(side) = $P_{12}$(side) – $P_{14}$(side) for each side site (see Fig. 3(e)). Thus, one has that

$$\tilde{S}_9 = P_9 + 2P$(side) + 2P$(end). \tag{10}$$

A Kirkwood approximation for $\tilde{S}_9$ shows that $c_1 = 3$ for equilibrated adlayers.

From a low-T RSA analysis, one finds that $d/dt P_{10}$(end) $\to -32k$, $d/dt P_{12}$(side) $\to -39k$, and $d/dt P_{14}$(side) $\to -44k$, and again $P_9 \to -29k$, as $\theta_O \to 0$. Thus, one has $c_1 = 3.25$. This result is also recovered in a refined Kirkwood approximation. We offer some comments on near-saturation behavior in Sec. III D. Finally, we remark that the same $c_1$-values are obtained in a modified implementation with sideways funneling first (either for equilibrated adlayers or RSA).

**D. Other refinements**

Our 9f-site model refinement includes both orientational steering and funneling, producing even lower $c_1$-values. As in the above 9-site models, the diatomic impinges on 3NN 4th sites. Also as above, the 4th site above which the diatomic impinges must be available for adsorption. However, now subsequent dynamics depends on the state of the two 3NN 4th on which the O adatoms attempt to reside. If these are both available, then one implements a 9f-site funneling model as above. This results in a contribution $\tilde{S}_9$ to $\tilde{S}_9$. If one or both of those sites are occupied, then the diatomic is steered to the orthogonal orientation, and implements a 9f-funneling model for that orientation with probability $P$(rot). This implies that
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FIG. 4. Schematic for the 9sf-site model with notation as in Fig. 2. Scenarios where adsorption in the initial orientation fails, but rotation leads to successful adsorption without funneling.

\[ \hat{S}_{9sf} = \hat{S}_{9f} + P^\ast\text{rot}. \]
To assess \( P^\ast\text{rot} \), we note that in all cases with one or both of the 3NN 4fh sites occupied, the rotated diatomic can adsorb without funneling if the appropriate rotated 9-site ensemble is available. This produces a contribution \( \delta P^\ast\text{rot} = P_9 - P_{11}(9sf) \) to \( P^\ast\text{rot} \). See Fig. 4. If both 3NN 4fh sites are occupied, then funneling is not possible, so there is no additional contribution to \( P^\ast\text{rot} \).

Extending the degree of funneling will also reduce \( c_1 \). In a (9f+)-site model, we also allow funneling if the central 4fh site above which the center of the diatomic impinges is occupied in contrast to the 9f-site model. However, adsorption is still blocked if one or both of the target 3NN sites are occupied, as funneling just shifts the adsorbing O adjacent to these sites. This (9f+)-model yields \( c_1 = 2 \) (1.75) for equilibrated adlayers (in the RSA regime). Including extended funneling in the model combining steering and funneling yields \( c_1 = 0 \) for both equilibrated and RSA adlayers. As in Sec. II D, we note that increasing the range of funneling or the ease of adsorption generally both decreases \( c_1 \) and increases the magnitude of the rate of decrease of sticking at saturation.

IV. ADDITIONAL RESULTS FROM THEORY, SIMULATION, AND EXPERIMENT

A. KMC simulation results for RSA models

For the low-T RSA regime, rearrangement of truncated Taylor expansions for \( \hat{S} \) obtained from a master equation analysis can provide a reasonable description of behavior even for higher \( \theta_O \). However, here instead we apply KMC simulation for precise estimates for saturation or jamming coverages, \( \theta_O^S \). We find that

\[
\theta_O^S = 0.362, 0.368, 0.346, 0.353, \ldots \text{ML for 8}, \quad 8s-, \quad \times 8f-, (8f+), \ldots - \text{site models}, \quad (11a)
\]

\[
\theta_O^S = 0.358, 0.353, 0.371, 0.370, \ldots \text{ML for 9}, \quad 9s-, \quad \times 9f-, (9f+), \ldots - \text{site models}, \quad (11b)
\]

respectively. Of particular note is the relatively small variation in these values, a feature which we find persists in other variations our 8- and 9-site models. Of course, for adlayers subject to NN exclusion, the strict upper bound on the coverage is significantly higher at 0.5 ML corresponding to perfect \( c(2 \times 2) \) ordering. Indeed, saturation coverages arbitrarily close to this limit are achieved in cooperative sequential adsorption models which include a propensity for \( c(2 \times 2) \) clustering (e.g., associated with 2NN attractive adspecies interactions). Thus, the above robustness applies only in models without such a clustering propensity.

To further elucidate this robustness, it is instructive to first consider behavior of a related equilibrium model, specifically the hard-square model for adatoms adsorbed a square array of adsorpions sites with NN exclusion. The key feature of this model is a symmetry-breaking phase transition from short-range to long-range \( c(2 \times 2) \)-order as the coverage increases above a critical value of \( \theta_O^c = 0.367743 \) ML. This indicates a natural upper bound at around 0.37 ML for coverages that can be achieved without symmetry-breaking (i.e., while retaining equal populations of the degenerate \( c(2 \times 2) \) subdomains). From this perspective, it should be emphasized that all adsorption models display short-range order.

Second, it is instructive to note that for the extensively studied classic monomer RSA model (adsorption of species onto single 4fh sites subject to NN exclusion), the saturation coverage of \( \theta_O^{\text{8s}} = 0.364133 \) is also in the above range. One issue of consideration for RSA-type problems has been Palasti conjecture that relates saturation coverages for 2D problems can to those of corresponding exactly solvable 1D problems. While not exact, these relations can be remarkably accurate. Here, we extend these ideas to classic monomer RSA to estimate the saturation coverage as

\[
\theta_O^{\text{extended Palasti}} = \frac{1}{2} (1 - e^{-2\theta_O}) = 0.373823 \text{ ML (monomer RSA)}, \quad (12)
\]

a value which should be compared with the precise estimate of Ref. 38. See Appendix F for a derivation which exploits a pictorial representation traditionally used for the equilibrium hard-square model. In summary, for both non-equilibrium models of adsorption monomer and dimers with NN exclusion, and even for equilibrium models with NN exclusion, in the absence of a propensity for \( c(2 \times 2) \) clustering, there is a robustness of the maximum coverage which is achieved without symmetry-breaking (and where this corresponds to the jamming coverage in RSA models).

Of course, KMC simulation can provide complete information on the adsorption process. In Fig. 5, we present results for \( \hat{S}(\theta_O) \) versus \( \theta_O \) for the 9-site model and its variations. Behavior for 9s- and 9f-models reasonably captures
FIG. 6. Peak intensity of the strong (1/2, 1/2) diffraction spot (solid line) and the weak (1/2, 0) spot (dashed line) during adsorption for various RSA models indicated.

FIG. 7. Diffuse (1/2, 1/2) diffraction spot at 2 L for various RSA models as indicated.

FIG. 8. Effect of diffusive hopping at rate h on sticking in the 9-site model. (a) $\hat{S}(\theta_O)$ as a function of $\theta_O$ for various h/k. The inset highlights curve-crossing behavior for higher $\theta_O$. The red curve is the Kirkwood sticking coefficient (7). (b) Data showing invariance of $c_1$. This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.186.176.40 On: Tue, 05 Jan 2016 22:34:06

experimental behavior for O$_2$ on Ni(100) and Pd(100) described below. As noted in Sec. I, diffraction studies of low-T adsorption for O$_2$/Pd(100) reveal a strong (1/2, 1/2) spot intensity reflecting non-equilibrium c(2 x 2) ordering and a weak (1/2, 0) spot intensity associated with p(2 x 2) ordering. This feature is achieved in the 8-site RSA model which naturally generates c(2 x 2)-order given the 2NN 4fh site adsorption rule, and is preserved in variations of this model. For the 9-site RSA model, the (1/2, 0) spot intensity is a slightly higher fraction of the (1/2, 1/2) spot intensity, but is still relatively very weak and thus consistent with experiment. These intensities, which can be obtained by suitable alternating sums over pair correlations, are shown in Fig. 6. One additional observation is that the inclusion of funneling slightly sharpened the diffuse (1/2, 1/2) spot (i.e., reduces its width) for the 9-site model but has an opposite effect for the 8-site model. See Fig. 7. This can be understood since funneling produces O adatoms in a c(2 x 2) domain with the same phase for the 9-site model, but in the opposite phase for the 8-site model. Since the width in the 8-site model exceeds that in experiment for Pd(100), the sharper spot in the 9f-site model improves agreement with experiment. Finally, we mention that addition of orientational steering to the 8-site and 9-site models does not have much effect on the spot width.

B. KMC simulation results for effects of thermal hopping

We have already noted the unintuitive analytic result that inclusion of diffusive hopping which equilibrates the adlayer does not actually shift $c_1$ from its RSA value towards the distinct equilibrium value. For numerical confirmation of this behavior, we add random hopping at rate h to NN 4fh sites provided that this does not create populated NN pairs. Then, the corresponding equilibrium model is the hard-square model. Results are provided in Fig. 8 for the 9-site model with hopping showing that $[1 - \hat{S}_9(\theta_O)]/\theta_O \rightarrow c_1 = 7.25$, as $\theta_O \rightarrow 0$ even for large h = 1000. Corresponding behavior is found for the 8-site model with hopping where $[1 - \hat{S}_8(\theta_O)]/\theta_O \rightarrow c_1 = 6$, as $\theta_O \rightarrow 0$ (not shown). The lack of shift in $c_1$-values can be understood since it takes an infinite amount of time for hopping to erase the 3NN-site correlation associated with the 9-site adsorption rule (or the 2NN-site correlation from the 8-site rule). Thus, the transition of $\hat{S}_9(\theta_O)$ from the RSA-form...
to the hard-square form as $h \rightarrow \infty$ is somewhat subtle only being reflected in the $h$-dependence of $c_{n \geq 2}$.

Another fundamental but subtle feature is effect of hopping on the saturation behavior at higher coverage where $\hat{S}$ becomes negligible. In all the RSA models with no hopping ($h = 0$), there is a well-defined jamming coverage $\theta_{O^5} \approx 0.5$ ML where $\hat{S}$ vanishes. However, even for very small $h > 0$, quite different behavior occurs. Quickly adsorption creates a near-jammed state with negligible population of adsorption ensembles. This state will correspond to small defective ($2 \times 2$) domains separated by domain boundaries free of adsorption ensembles. Vacancy defects within domains consist of empty sites with four occupied NN (3NN) sites for 8-site (9-site) type models, and these are frozen for hopping only to NN sites. Some adatoms along domain boundaries can hop between domains of opposite phase producing a type of curvature-mediated domain boundary dynamics. This leads to Lifshitz-Cahn-Allen type domain coarsening producing an increase in the coverage. This domain boundary motion can also reduce the population of vacancy defects, producing a further increase of the coverage towards a maximal saturation value of 0.5 ML. Fig. 8 also illustrates the feature that for the 9-site model with hopping, $\hat{S}$ retains a significant non-zero value above $\sim 0.01$ at least up to 0.4 ML for $h/k = 1000$.

C. Analysis of experimental data

Next, we review experimental results for sticking or uptake versus $\theta_{O}$ for $O_2$ adsorption on the fcc(100) surfaces of Ni, Pd, and Rh. Fig. 9(a) shows the experimental sticking results for $O_2$/Ni(100) at 300 K$^2$ and the reasonable fit of this data by the standard 8-site model. However, Stuckless et al. argue that the coverage must be recalibrated producing an effective saturation coverage of $\theta_{O^5} \approx 0.37$ ML and $c_1 \approx 3.9$ (reduced from $c_1 \approx 6$). Independent data from Ref. 24 indicates that $c_1 \approx 2.6$. Fig. 9(b) shows oxygen uptake results for $O_2$/Pd(100) at 180 K where $\theta_{O^5} \approx 0.34$ ML. A rough estimate of the decrease in the rate of uptake (red thin lines) indicates that $\hat{S}$ at 180 K drops to $\sim 0.5$ at half-saturation where $\theta_{O} \approx 0.17$ ML, which implies that $c_1 \approx 3$. Overall, behavior for Ni and Pd is quite similar with a convex form (positive curvature) for $S(\theta_O)$ versus $\theta_O$. Fig. 9(c) shows sticking behavior for $O_2$/Rh(100) at 300 K$^2$ which reveals a contrasting concave form (negative curvature) of $S(\theta_O)$ for smaller $\theta_O$.

Comparing behavior for $O_2$ on Pd(100) and Rh(100), it appears that the former is reasonably described by the 9s- or 9f-site models, whereas the latter is better described by the 9s-site model. However, for Rh(100), capturing the higher saturation coverage presumably requires also incorporating significant adatom thermal mobility at 300 K (which is not significant for Pd(100) at the lower temperature of 180 K). More facile adsorption in the latter case might naturally be associated with significantly stronger binding of oxygen to the Rh(100) surface which would naturally enhance steering and funneling to suitable 4fh adsorption sites.$^{10,29}$

V. CONCLUSIONS

The traditional mean-field Langmuir description of dissociative adsorption of oxygen at NN sites, while providing a useful analytic expression for the sticking coefficient, is too simplistic. On the other hand, the classic BBB 8-site model and a modified 9-site model for adsorption at 4fh sites on metal(100) surfaces, incorporating blocking due to NN exclusion and a corresponding large adsorption site ensemble, make adsorption too restrictive. This leads to excessively large $c_1$-values measuring the initial rate of decrease of $\hat{S}$. However, refinements incorporating orientational steering and funneling do capture key features of behavior for various experimental studies, particularly lower $c_1$-values. Significantly, these models are amenable to analytic treatment thereby providing deeper insight into sticking behavior than KMC simulation alone. Finally, we mention that values of $c_1 = 3-4$ can also be obtained in multi-site lattice gas (msLG) models for dissociative adsorption.$^{29}$ Thus, behavior observed in experiment may be due to a combination of msLG-type adsorption, together with blocking, orientational steering, and funneling effects.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (USDOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory Chemical Physics program. We acknowledge use of NERSC computational resources. The work was performed at Ames Laboratory which is operated for the USDOE by Iowa State University under Contract No. DE-AC02-07CH11358.

FIG. 9. Experimental sticking behavior and oxygen uptake versus coverage or exposure. (a) $O_2$/Ni(100) from Ref. 24 gives $c_1 \approx 2.6$ and from Ref. 2 gives $c_1 \approx 3.9$ after recalibration of $\theta_O$. (b) $O_2$/Pd(100) from Ref. 25 indicates that $\hat{S}$ at 180 K drops to $\sim 0.5$ at half saturation from the change in the rate of uptake (red thin lines) implying that $c_1 \approx 3$. (c) $O_2$/Rh(100) from Ref. 26 indicates that $c_1 \approx 1.4$. 

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APPENDIX A: PRECURSOR-MEDIATED ADSORPTION

Traditionally, a slower than expected decrease in $\hat{S}(\theta_O)$ versus $\theta_O$ might be associated with precursor effects. Kisliuk theory$^{42}$ relates the normalized sticking coefficient with precursor effects, $\hat{S}$ (precursor), to that analyzed above without precursor effects, $\hat{S}$. If the precursor is highly mobile, and $\tau$ denotes its lifetime before desorption in units of the mean time to chemisorb, then one has that$^{10,42}$

$$\hat{S}(\text{Kisliuk}) = (\tau + 1)\hat{S}/(\tau \hat{S} + 1)$$

$$= 1 - (\tau + 1)^{-1}(1 - \hat{S}) + O[(1 - \hat{S})^2]. \quad (A1)$$

Thus, $c_1(\text{precursor}) = c_1/(\tau + 1)$ is strongly reduced for large precursor lifetimes. However, for the systems considered here, DFT analysis of the potential energy surface for the binding energy during dissociative adsorption$^{29}$ does not provide evidence for a physisorbed precursor. Thus, it is reasonable to propose that the low $c_1$-values compared to the standard 8-site and 9-site values are due to effects of steering and funneling.

Another cruder Gasser-Smith precursor theory$^{43}$ assumes that the physisorbed species makes exactly $q$ attempts to chemisorb before desorbing, and that each of these succeeds with probability $\hat{S}$. Then, it follows that $\hat{S}(\text{Gasser-Smith}) = 1 - (1 - \hat{S})^q \approx 1 - (c_1\theta_O)^q$.

APPENDIX B: DFT-MD ANALYSIS

DFT-MD calculations were performed using the plane-wave VASP code$^{44}$ for $O_2$ adsorption on Pd(100) for slab geometries representing the metal surface and with the Perdew-Burke-Ernzerhof exchange-correlation functional.$^{45}$ The projector augmented wave (PAW) method$^{46}$ was used for computation efficiency. Molecules were adsorbed on one side of the slab, and induced artificial dipole interactions are corrected using the method of Neugebauer and Scheffler.$^{47}$ The energy cutoff for the plane-wave basis set was 400 eV, and the k-points grid was $(4 \times 4 \times 1)$ for $(2\sqrt{2} \times 2\sqrt{2} \times 1)$ R 45° lateral supercells and $(6 \times 6 \times 1)$ for $(3 \times 3)$ lateral supercells. Spin-polarized calculations below were performed on 3-layer slabs with the bottom layer fixed. The initial of $O_2$ height was 0.47 nm above the surface with a 70 K thermal velocity and dynamics was run in a microcanonical ensemble.

A general conclusion follows from this DFT-MD analysis of $O_2$ adsorption with various arrangements of preadsorbed $O$: the picture of traditional adsorption models with blocking and large adsorption site ensembles is too simplistic. Specifically, impinging molecules do not simply bounce off the surface if they are not aimed at a suitable available adsorption site ensemble. In fact, the impinging $O_2$ can transiently bond to preadsorbed $O$ before veering off to a nearby 4fh site and subsequently dissociating. Here, we just provide two selected examples to illustrate the features of orientational steering and funneling in the vicinity of an isolated preadsorbed $O$. Fig. 10(a) shows snapshots of rotational steering to an orientation allowing adsorption of an $O_2$ which adsorbs parallel to the surface at a 45° angle to this orientation. Fig. 10(b) shows snapshots of the funneling of an $O_2$ impinging partly above the preadsorbed $O$ to a nearby configuration allowing adsorption.

It is often assumed that kinetic energy transfer from the adsorbing molecule to phonon modes of the substrate is efficient during dissociative adsorption of oxygen on metal surfaces. Potentially, the above microcanonical ensemble simulations may not be compatible with such a picture of efficient energy transfer, as the finite system size in these simulations may artificially inhibit such transfer. However, given the very short fs time scale of the dynamics of interest relative to the natural ps time scale of energy transfer (associated with typical phonon frequencies), we do not expect such artifacts to be significant. A reliable assessment of energy transfer, and confirmation of the above claim, has been recently become possible and has in fact been provided by novel QM/MM simulations.$^{28}$ These provide for the first time a capability to treat such subtleties as non-equilibrium energy transfer into surface phonon modes, and avoid spurious reflections from periodic boundary conditions used in conventional DFT-MD analysis. Such simulations for $O_2$ on Pd(100) confirm minor dissipation of heat to substrate phonon modes over the few hundred fs considered in our simulations.$^{28}$ These QM/MM simulations also reveal hot $O$ adatoms compatible with inhibited energy transfer. Nonetheless, despite the above validation of a microcanonical analysis, we have also performed simulations incorporating a contrasting rapid energy transfer which is achieved by velocity rescaling. Common features in both types of simulations should be robust. We do find steering and funneling in both, supporting the existence of this type of dynamics (but the simulations with velocity rescaling show additional features such as stronger knock-out of pre-adsorbed $O$ atoms).

APPENDIX C: EXTENSION OF ADSORPTION MODELS FOR COADSORBED CO

Here, we augment the prescription of our models for dissociative adsorption of oxygen on partially oxygen-covered metal(100) surface to also account for the effect of coadsorbed CO. In developing realistic models, it should be recognized that typically CO occupies multiple site types on metal(100) surfaces.$^{10}$ For example, on Pd(100), both bridge
sites and hollow sites can have significant CO-population. On Rh(100), both bridge sites and top sites can have significant CO-population.

The simplest case is for the classic 8-site or 9-site models. We modify these models to require that in addition to the 8-site or 9-site ensemble being free of O, it is also necessary that the hollow sites where the constituent O atoms adsorb are free of CO. In addition, we require that no sites a distance shorter than one surface lattice constant, a, from these (i.e., either bridge or top sites) are populated by CO. Together with a prescription of adlayer diffusive dynamics, this model determines the normalized sticking coefficient, ˆS(θ_{CO}, θ_O), for oxygen. Again for simplicity we just indicate a dependence on coverages, but in fact for non-equilibrated adlayers ˆS depends on details of the adlayer configuration.

One instructive formulation for these models writes ˆS(θ_{CO}, θ_O) = ˆS(θ_O) Q(θ_{CO}, θ_O). Here, ˆS(θ_O) is the sticking coefficient in the absence of CO. Also, Q(θ_{CO}, θ_O) is the conditional probability that if the 8- or 9-site ensemble is free of O, then the additional O adsorption sites are free of CO. In addition, we require that no sites a distance a, from these (i.e., either bridge or top sites) are populated by CO. Together with a prescription of adlayer diffusive dynamics, this model determines the normalized sticking coefficient, ˆS(θ_{CO}, θ_O), for oxygen. Again for simplicity we just indicate a dependence on coverages, but in fact for non-equilibrated adlayers ˆS depends on details of the adlayer configuration.

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APPENDIX D: EXACT NEAR-SATURATION RSA ASYMPTOTICS

Our rigorous analysis of near-saturation behavior is based in part on the observation that if ˆS ∼ c exp(−αkt), as t → ∞, then integration of d/dt θ_O = −4k ˆS yields

θ_O^{S} − θ_O ∼ (4/α)c exp(−αkt), so that ˆS ∼ α/(4)(θ_O^{S} − θ_O).

(D1)

approaching saturation. Thus, ˆS vanishes linearly with coverage.

1. 8-site and 9-site models in the RSA regime

Let σ denote a configuration of empty sites which incorporates m distinct adsorption site ensembles. Then, the probability P[σ] of this configuration satisfies

d/dtP[σ] = −mkP[σ] − R[σ].

(D2)

where R[σ] involves a linear combination of P[σ'] with positive coefficients where all configurations σ' include m' > m adsorption site ensembles. It is convenient to incorporate the P[σ] into an infinite dimensional vector P, where the P[σ] are ordered with non-decreasing m. Then, recasting (D2) in matrix form d/dt P = A · P, it is clear that the ∞×∞ matrix A is upper triangular with eigenvalues λ = −mk corresponding to the diagonal entries. Furthermore, contributions to P[σ] comes exclusively from the eigenvectors with eigenvalues λ = −m'k satisfying m' ≥ m. Consequently, one has that P[σ] ∼ c[σ] exp(−mkt), as t → ∞. Another way to rationalize the latter result is to recognize that the evolution of P[σ] is only coupled to that of faster decaying P[σ'] with m' ≥ m. Thus, since m = 1 for 8 = P_8 (P_9), it follows that P_8 ∼ c_8 exp(−kt) [P_9 ∼ c_9 exp(−kt)] for the 8-site [9-site] model, as t→∞, i.e., α = 1. Then (D1) implies that

\[ \hat{S}_8 \sim \frac{1}{4} (\theta^{S}_O - \theta_O) \] and \[ \hat{S}_9 \sim \frac{1}{4} (\theta^{S}_O - \theta_O). \]

(D3)

2. 8s-site and 9s-site models in the RSA regime

Analysis of near-saturation behavior for models with orientational steering is more subtle. Now for configurations, σ, of empty sites incorporating m distinct adsorption site ensembles, we let m_1 (m_2) denote the number of these for which the rotated ensemble is not included (is also included), so that m = m_1 + m_2. Then, it follows that

\[ \frac{d}{dt}P_8 = -(2m_1 + m_2)kP[\sigma] + \ldots, \]

(D4)

where implicit terms are negative and involve configurations with larger m_1 and/or m_2. The factor of 2 multiplying m_1 reflects the feature that if the diatomic adsorbs with an orientation orthogonal to one of the m_1 ensembles, it can adsorb onto that ensemble after rotation.

Thus, for the 8-site model, contributions to d/dt P_8 where the center of the adsorbing diatomic aligns with the center of the 8-site ensemble include: direct adsorption aligned with the center of the impinging diatomic is misaligned with the center of the 8-site ensemble [−kP_8], direct adsorption orthogonal to this ensemble [−kP_{12}(8s)], and adsorption aligned with this ensemble after rotation [−kP(rot)]. These sum to −2kP_8, so one has that

\[ \frac{d}{dt}P_8 = -2kP_8 + \ldots (m_1 = 1, m_2 = 0). \]

(D5)

where the implicit negative terms involve adsorption where the center of the impinging diatomic is misaligned with the center of the 8-site ensemble. These involve larger configurations of empty sites. Similarly, one can show that

\[ \frac{d}{dt}P_{12}(8s) = -2kP_{12}(8s) + \ldots (m_1 = 0, m_2 = 2), \]

(D6)

with implicit terms negative. Thus, one has \[ \hat{S}_{8s} = 2P_8 - P_{12}(8s) \sim c_8 \exp(−2kt), \] so that α = 2. An analogous conclusion applies for \[ \hat{S}_{9s}, \] so then (D1) implies that

\[ \hat{S}_{8s} \sim \frac{1}{2} (\theta^{S}_O - \theta_O) \] and \[ \hat{S}_{9s} \sim \frac{1}{2} (\theta^{S}_O - \theta_O). \]

(D7)
3. Other models

For the 8f- (9f-) site model, one has that $\hat{S}_M = P_s + \ldots$ ($\hat{S}_M = P_0 + \ldots$) where the implicit positive terms reflect funneling. This structure is preserved in refined funneling models with more complex implicit terms. The structure of the master equations is also more complex inhibiting simple analysis. However, we reiterate the general observation that increasing the range of funneling can increase the magnitude of the rate of decrease of sticking at saturation.

APPENDIX E: $\hat{S}$ SERIES REARRANGEMENT FOR RSA

The simplest strategy to incorporate both the low-coverage and near-saturation rates of change of $\hat{S}$ (as quantified by $c_1$ and $s_1$) into a functional form for $\hat{S}$ is to adopt a quadratic form constrained to match these features, i.e.,

$$\hat{S}(\theta) = (1 - a\theta O)(1 - b\theta O),$$

where $a = \frac{1}{2}(c_1 + s_1)$ exceeds $b = \frac{1}{2}(c_1 - s_1)$. \text{(E1)}

Then, the saturation coverage corresponds to $\theta_O^S = a^{-1} = 2(c_1 + s_1) = 0.320, 0.267, 0.500, \text{ and } 0.444 \text{ ML for the } 8\text{-site, 9-site, 8s-site, \text{ and } 9s\text{-site models, respectively. More complex forms are required to more accurately capture } \theta_O^S\text{-values.}$

If $c_2$ is also known, then low-coverage quadratic behavior and the near-saturation rate of change of $\hat{S}$ can be matched by a Padé form,\textsuperscript{12,48}

$$\hat{S}(\theta) = (1 - a\theta O)(1 - b\theta O)/(1 + c\theta O),$$

where $a > b$ so $\theta_O^S = a^{-1}, a + b + c = c_1$, etc. \text{(E2)}

With this form, one obtains $\theta_O^S = 0.311 \text{ ML for the } 8\text{-site model and } \theta_O^S = 0.290 \text{ ML for the } 9\text{-site model. A more accurate description requires additional input, e.g., } c_2 \geq 2.$

One strategy is to exploit the robustness of $\theta_O^S \approx 0.36 \ldots 0.37 \text{ ML using a Padé form and choosing } b \text{ and } c \text{ to match } c_1 \text{ and } s_1\text{-values yields}$

$$\hat{S}(\theta) = (1 - \theta_O^S)/(1 - b\theta O)/(1 + c\theta O),$$

where $b < (\theta_O^S)^{-1} b + c = c_1 - 1/\theta_O^S$, etc. \text{(E3)}

One obtains $(b,c) = (2.44, 0.80), (2.35, 2.10), (2.54, -1.76), (2.58, -1.42)$ for the 8-site, 9-site, 8s-site, and 9s-site models using reported values of $\theta_O^S$. These forms almost exactly recover KMC results for $0 \leq \theta_O \leq \theta_O^S$. Even more precise forms replace the denominator in (24) with $1 + c\theta_O + d(\theta_O)^2$ and also match $c_2\text{-values.}^{12}$

APPENDIX F: EXTENDED PALASTI CONJECTURE FOR MONOMER RSA

The continuum Palasti conjecture and its discrete lattice generalization identifies the fractional area or coverage at jamming for 2D RSA problems as the square of that for corresponding 1D RSA problems (the latter generally being exactly solvable). This conjecture provides accurate, but not exact estimates.\textsuperscript{21,39} This approach has not been applied previously to the classic monomer RSA problem on a square lattice. Appropriate application comes from considering the fractional area in a hard-square representation of this 2D problem as shown in Fig. 11. Adsorbed monomers are identified with $\pi/4\text{-rotated hard-squares whose side length, } L$, equals $\sqrt{2}$ times the lattice constant. Then, hard-squares for 2NN monomers in the same $c(2 \times 2)$ domain have touching edges, and those on opposite sides of a domain boundary between $c(2 \times 2)$ domains of opposite phase have edges separated by $1/L$. Also, the fractional area, $A_{2D}$, of hard-squares is given in terms of the monomer coverage, $\theta_{2D}$, by $A_{2D} = 2\theta_{2D}$.

We claim that corresponding 1D problem involves monomer RSA on a 1D lattice where the monomers are identified with hard-rods shown in Fig. 10(a) whose length, $L$, equals twice the lattice constant. Then, adjacent hard-rods in the same double-spaced domain have touching edges, and those on the opposite sides of a domain boundary between domains of opposite phase have ends separated by $1/L$. Also, the fractional area, $A_{1D}$, of hard-rods is given in terms of the monomer coverage, $\theta_{1D}$, by $A_{1D} = 2\theta_{1D}$. In the spirit of Palasti, we further claim that $A_{2D} \approx (A_{1D})^2$, and thus that $\theta_{2D} \approx \theta_{1D}^2$ at saturation or jamming. Since $\theta_{1D}^2 = \frac{1}{2}(1 - e^{-2}) \text{ ML,}\text{ one obtains an extended Palasti-type estimate of } \theta_{2D}^2 \approx \frac{1}{2}(1 - e^{-2})^2 = 0.373823 \text{ ML.}$ It should be noted that the exact 1D result used here follows from a classic 1939 result of Flory.\textsuperscript{49}

One has $L_d = \sqrt{2\theta O / \rho_d}$. Here $\rho_d = P_1 - P_{NN}$ is a measure of the diagonal $(2 \times 2)$ domain boundary density taken as the probability of 2NN occupied-unoccupied pairs.

One has $L_p = 2\theta O / \rho_p$. Here $\rho_p$ is a measure of the $(p(2 \times 2))$ domain boundary density which is taken as the probability of linear triples with one occupied (x) and two unoccupied (o) sites, i.e., $\rho_p = P_{oo} = P_{oo} = P_{NN} - P_{oo}$. Note that $P_{oo} + P_{ox} = P_{oo} = P_{NN}$, and $P_{ox} = P_x = 1 - P_1$, so one has that $P_{oo} = P_1 - P_{NN}$.


