Structure of Chalcogen Overlayers on Au(111): Density Functional Theory and Lattice-Gas Modeling

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Abstract. Ordering of different chalcogens, S, Se, and Te, on Au(111) exhibit broad similarities, but also some distinct features which must reflect subtle differences in relative values of the long-range pair and many-body lateral interactions between adatoms. We develop lattice-gas (LG) models within a cluster expansion framework which include about 50 interaction parameters. These LG models are developed based on DFT analysis of the energetics of key adlayer configurations in combination with Monte Carlo (MC) simulation of the LG models to identify statistically relevant adlayer motifs, i.e. model development is based entirely on theoretical considerations. The MC simulation guides additional DFT analysis and iterative model refinement. Given their complexity, development of optimal models is also aided by strategies from supervised machine learning. The model for S successfully captures ordering motifs over a broader range of coverage than achieved by previous models, and models for Se and Te capture the features of ordering which are distinct from those for S. More specifically, the modeling for all three chalcogens successfully explains the linear adatom rows (and subtle differences between them) observed at low coverages of ca. 0.1 monolayer. The model for S also leads to a new possible explanation for the experimentally-observed phase with a (5×5)-type LEED pattern at 0.28 ML, and to predictions for LEED patterns that would be observed with Se and Te at this coverage.

1. Introduction. The function of sulfur as an anchoring group on Au surfaces is well-known. It has prompted a large number of investigations, both of sulfur alone and of sulfur-based self-assembled monolayers, adsorbed on the Au surface. Interest has also been extended to the heavier chalcogenides, selenium and tellurium,\textsuperscript{1-3} as anchoring groups though they have not proven as attractive due to a higher proclivity for oxidation.

Recently, we conducted a fundamental investigation of S atoms adsorbed on Au(111) at very low coverage \( \theta_S \) (below 0.1 S monolayers (ML). Using scanning tunneling microscopy (STM), we observed that adsorption of S atoms removes (lifts) the
natural reconstruction of the Au surface within well-defined areas where the S adatoms congregate. S atom arrays within those regions adopted a striking structure: they assembled into rows that had a specific atomic spacing and rotational orientation with respect to substrate Au atoms in the close-packed directions, leading us to designate them as $\sqrt{3}R30^\circ$ rows.\(^4\) (In this paper, we will shorten that nomenclature even further to $\sqrt{3}$ rows.) Shortly thereafter, two other STM studies were published which reported similar structures for Se and Te on Au(111) under similar experimental conditions.\(^2,3\) The experimental STM data for all three systems is presented in Fig. 1.

In the specific case of S, we previously employed lattice-gas (LG) modeling successfully to reproduce the $\sqrt{3}$ structures.\(^4\) LG models were developed using a limited cluster expansion based on energetics from density functional theory (DFT). Subsequently, Monte Carlo (MC) simulations were performed on the LG models to generate characteristic adlayer structures for comparison with experimental images. Models that included long-range pairwise interactions, plus selected trio interactions, successfully reproduced the linear rows of S atoms at reasonable temperatures. The question naturally arises, whether a comparable procedure would result in successful models also for two other chalcogen adsorbates, Se and Te. The main goal of this paper is to explore that possibility.

A secondary goal is to elucidate the origin of another S structure which has been observed on Au(111), traditionally denoted (5$\times$5), with ideal S coverage of 0.28 ML (corresponding to 7 atoms per (5$\times$5) cell, i.e. 7/25 ML).\(^5\) This structure has been observed and characterized using low energy electron diffraction (LEED) and normal incidence X-ray standing wavefield absorption (NIXSW),\(^5\) both of which provide long-range average structural information but not direct local structural information (unlike STM). In addition, a ($\sqrt{3}\times\sqrt{3}$)R30$^\circ$ structure with ideal S coverage of 0.33 ML has also been observed with LEED at 300 K.\(^6,7\) In fact, neither the (5$\times$5) nor the ($\sqrt{3}\times\sqrt{3}$)R30$^\circ$ structure has been observed with STM after sulfur adsorption in ultrahigh vacuum, perhaps because imaging has been attempted only at room temperature, where S adatom mobility is assumed to be high on Au(111).\(^8-10\) The (5$\times$5) was described as consisting of rosette motifs, where each rosette was a centered hexagon of S atoms occupying ($\sqrt{3}\times\sqrt{3}$)R30$^\circ$ lattice sites. The rosettes, in turn, were arranged in a (5$\times$5) unit cell. This structure is illustrated in Fig. 2(Ib). Essentially, if our new LG model is successful in reproducing the $\sqrt{3}$ rows of S atoms at ca. 0.1 ML, we ask whether the same model can be extended to higher coverage and reproduce the (5$\times$5) diffraction pattern. We will show that the LG model can indeed be extended in this way, and it provides an alternative to the rosette structure as an explanation for the (5$\times$5) LEED pattern.

This paper is organized as follows. Sec. 2 provides a brief review of the experimental data for the $\sqrt{3}$ rows. Sec. 3 describes the DFT methodology and results. Sec. 4 describes the LG models, and Sec. 5 discusses the interaction parameters extracted from these models. Sec. 6 presents Monte Carlo (MC) simulations of those models, focusing on the $\sqrt{3}$ rows and comparison with experiment, for all 3 adsorbates. Sec. 7 describes results of our analysis for the structure of S with (5$\times$5) periodicity, and makes predictions for Se and Te. Conclusions are summarized in Sec. 8. Additional details are available in the Supplementary Material (SM).
Figure 1. Experimental STM images of chalcogen $X$ adsorbed on unreconstructed regions of Au(111), where: (a) $X = S$; (b) $X = Se$; and (c) $X = Te$. In (a), the local S coverage is 0.07 ML and $T = 5$ K, with sample bias $V_{\text{sample}} = -0.10$ V and tunneling current $I = 1.2$ nA. Reproduced from Ref. 4 with permission from AIP Publishing. In (b), local Se coverage is 0.14 ML and $T = 4.3$ K, with $V_{\text{sample}} = 1$ V and $I = 0.1$ nA. The inset is 8 nm x 8 nm, with $V_{\text{sample}} = 0.20$ V, $I = 0.05$ nA. Reproduced from Ref. 2 with permission from Elsevier. In (c), local Te coverage is 0.08 ML and $T = 4.5$ K, with $V_{\text{sample}} = -0.10$ V and $I = 1$ nA. Reproduced from Ref. 3 with permission from IOP Publishing.

2. Review of Experimental Data for $\sqrt{3}$ Rows.

Sample preparation protocols. The samples share a common history of preparation at or above room temperature, followed by cooling to 4.3-5 K for STM imaging in ultrahigh vacuum. The cooling rate was unspecified and presumably uncontrolled. For S and Se, the substrate was a single crystal of bulk Au(111), whereas for Te it was Au evaporated to a thickness of 140 nm on freshly-cleaved mica. In all cases, the herringbone reconstruction was observed on the clean Au(111) surface, and adsorption of chalcogen lifted the reconstruction in local areas. For S, the substrate was exposed to $S_{2,g}$ from an electrochemical cell.11,12 For Se, atomic Se$_g$ was generated from bulk Se in a Knudsen cell. For Te, the source was accidental contamination of the chamber with Te from heating Bi$_2$Te$_3$, and consequent fortuitous exposure of the Au sample.

Coverages. Coverages were determined for each individual image in Fig. 1 by counting protrusions and equating each protrusion to a chalcogen atom. Coverages are reported in units of monolayers (ML), where 1 ML corresponds to 1 chalcogen atom per Au atom in a bulk plane of Au(111). Notably, coverages of S and Te are nearly identical (0.07 ML and 0.08 ML, respectively), while that of Se is higher by a factor of 2 (0.14 ML).

Structural characteristics. The structures shown in Fig. 1 correspond to equilibrium structures at some undetermined temperature significantly above 4.3-5 K, where these structures are frozen-in during the quench. From Fig. 1, it can be seen that all three adsorbates exhibit $\sqrt{3}$ row-type structures, although there are some differences. For S, the $\sqrt{3}$ rows are rather short (upper limit ca. 8 atoms). For Se, the most striking feature
is the occurrence of double (paired) rows. For Te, there are longer single-atom rows (upper limit ca. 22 atoms). For each adsorbate, there also exist some 2D clusters with local \((\sqrt{3} \times \sqrt{3})\text{R}30^\circ\) structure.

3. DFT Methods and Results.

Energetics were assessed by methods similar to those employed in earlier work. \(^{13-17}\) Briefly, DFT calculations were performed using the plane-wave based VASP code \(^ {18}\) with standard PAW potentials \(^ {19}\) optimized for the PBE method \(^ {20,21}\) that were distributed with VASP versions 5.2 and higher. The energy cutoff was 280 eV, which is sufficiently high for total energy calculations for atoms such as S, Se, Te, and Au. Gamma centered \(k\)-point grids that correspond approximately to \((24\times24\times1)\) for primitive \((1\times1)\) cells were used. All atoms in a slab were allowed to relax except the bottom layer. The Au substrate was modeled as a slab of thickness \(L\) layers, and energetics were calculated by averaging over \(L = 4\text{-}7\) layers. With sufficiently thick slabs, bulk lattice spacing can be achieved without artificially freezing many layers. Even with dense \(k\)-points grids, a large variation in adsorption energies with varying slab thickness was found, which is partly due to quantum size effects from constraining nearly-free electrons in finite slabs. Resulting energies were averaged over values for slabs in a range of thicknesses to mitigate deviations from those for macroscopic substrates caused by finite slab thickness. \(^ {16,22}\) Generally, slabs with layers \(L\) from 4 to 7 were used to generate a single DFT data point. Total energy optimization was performed until the maximum force was less than 0.2 eV/Å. The fictitious dipole interactions between slabs were not corrected, since their contribution to the total energies is mostly cancelled out when lateral interactions are calculated. \(^ {22}\) Furthermore, the dipole interactions between slabs are rather weak and decrease as the slab thickness increases. We calculated energetics both with and without the compensating dipole field proposed by Neugebauer and Scheffler \(^ {23}\) as implemented by VASP with the LDIPOL flag. The differences are very small, generally less than 1 meV. There are some issues with energy convergence using the dipole correction for thicker slabs. These seem due to calculation of the force with the dipole calculated self-consistently causing a positive feedback. Considering the 5 meV criterion we used for energy convergence, we chose not to use dipole correction, with minimal sacrifice in accuracy in exchange for added numerical stability.

The adsorption energy \(E_a\) per atom for chemisorbed chalcogens \(X (X = S, Se, Te)\) is defined as:

\[
E_a = \frac{[E(nX + \text{slab}) - E(\text{slab})]/n - E(X_{2,g})/2}{2}
\]  

Here \(n\) is the number of \(X\) atoms in the supercell, and \(E(X_{2,g})\) is the energy of the triplet state of the gas-phase dimer, determined with spin-polarized DFT, which serves as the energy reference point. It should be emphasized that for non-negligible coverage, the energy \(E_a\) includes not just binding to the substrate, but also the influence of lateral \(X-X\) interactions. Thus, for instance, repulsive \(X-X\) interactions reduce the magnitude of \(E_a\).

There is some flexibility in the choice of energy reference. Typically, it should correspond to the actual desorption product observed in temperature programmed desorption experiments. For S/Au(111) at submonolayer coverages, the observed
desorption product is S$_{2,g}$.

Additionally, calculation of the self-energy of an atom, $X_g$, is subject to more ambiguity and error. Hence we choose $X_{2,g}$ as the reference. This choice also is consistent with earlier work. With our definition, a positive $E_a$ means adsorbed $X$ is unstable toward recombinative desorption as $X_{2,g}$.

The key step in DFT is to identify a finite set of adsorbate configurations that ultimately produce a high-quality LG model describing adlayer energetics. The set of configurations is adjusted iteratively to optimize the quality of the final result. Specifically, the method of choosing configurations, energies of which are to be evaluated, is as follows:

1. Choose regular (hexagonal) supercells with various sizes including one S atom to capture the energetics of isolated adatoms. For larger supercells, one selects configurations that represent various isolated pairs and trios or other motifs of interest. See Fig/Table S1-S3 in Sec. 1 of the SM for descriptions of all such supercells considered, for all three chalcogens.

2. Include various supercells that can accommodate infinitely long $\sqrt{3}$ rows (accounting for the periodic boundary conditions), as in Fig. 2(I). Double and triple $\sqrt{3}$ rows are also included, as in Fig. 2(Ilf) and Fig. 2(IId), respectively. Again, Fig./Table S1-S3 in Sec. S1 of the SM provides descriptions of all supercells of this type that were considered, for all three chalcogens.

3. Perform MC simulations using LG models obtained by fitting to the DFT results, visually inspecting the adlayer configurations produced by the model, and identifying any distinctive long-range ordering and local motifs. We then introduce these orderings and motifs into a new set of structures for DFT calculations and iterate the procedure.

A more detailed discussion of these steps is provided in the following sections. We emphasize that this iterative process is purely theoretical including no comparison with experimental data (Fig. 1). Generally for each system, after about five to six iterations, we obtain a model with no major discrepancies between structures predicted by the LG model and those corroborated by DFT as being energetically viable. This method results in LG models generated from datasets of energetics for 109, 100, and 93 configurations for S, Se, and Te on Au(111), respectively.

The value of $E_a$ for each configuration is obtained from averaging over DFT calculations with 4, 5, 6, and 7 layers. With this range of slab thickness, and with a sufficiently dense k-point grid, we estimate that the numerical uncertainties are within 0.005 eV. It is useful to distinguish this type of uncertainty (precision) from the intrinsic accuracy of the DFT theory. The numerical uncertainties are mostly limited by finite slab thicknesses and k-points grid density. Some other factors such as energy cutoffs are transferable across supercells and therefore the errors cancel each other to a large extent. Regarding the accuracy of DFT, it may be gauged by the sensitivity of the result to different approximations of exchange-correlation functions. For example, the adsorption energy of S on Au(111) at 1/4 ML is -1.05 eV using PBE, -1.21 eV using optB88-vdW, and -1.28 eV using SCAN, with the energy of triplet $S_{2,g}$ as the reference. Thus, one could argue that the accuracy of DFT at the PBE level is about 0.1 to 0.2 eV, at least regarding the adsorption energy of S on Au(111). However, this large uncertainty is not particularly relevant for the current study, where results depend only on relative energies for different configurations in which the local atomic bonding of S atoms to the substrate is very similar. For example, pair interactions come from: ($E_2 = $ energy of adsorbed atom
pair + substrate) – 2 × (E₁ = energy of adsorbed atom + substrate) + (E₀ = substrate energy). Any error in estimation of adsorption energy should largely cancel out upon taking the difference between E₂ and 2E₁. Thus, numerical precision is more relevant than accuracy.

We use PBE in this work partly because the very large number of calculations would not be tractable with a functional that includes van der Waals interactions. More importantly, in our past work, we have shown that van der Waals interactions have significant impact on relative energies only in chalcogen-adsorbate systems that are more complex than those treated here, i.e. systems with metal adatoms coordinated to the chalcogen atoms, with or without alkane ligands.

Results of DFT calculations are summarized in Fig. 2. Subsets of the configurations included for S/Au(111) have been analyzed earlier by Abufager et al. in Ref. 27 and by our group in Ref. 4. The justification for plotting the adsorption energy versus 1/θ was also provided in Ref. 27. In short, in this representation, points representing minimum-energy phases of the system can be connected by linear segments to form a convex hull. This convex energies hull constitutes a lower boundary to the complete set of data points for configuration energies. This construction corresponds to determining the phase composition (and the corresponding energetics) at any coverage from the well-known lever rule of thermodynamics. Because of the numerical uncertainties in DFT calculations discussed above, structures lying within 0.005 eV of the exact hull should be considered experimentally viable as ground state structures. By ‘experimentally viable’ we mean that experimental observation of these structures should not be deemed contradictory to theoretical prediction.

However, the nature of the hull constructed from DFT can depend on how the search for different phases is conducted. Notably, in the two previous works, 4, 27 the selection of S configurations for DFT calculations, and thus the resulting energy hull, were heavily influenced by experiments. Ref. 27 was motivated by the observation of (5×5) patterns in LEED experiments, and therefore the hull consisted of mostly (5×5) structures. The theoretical work in Ref. 4 was motivated by STM studies of \( \sqrt{3} \) rows reported in the same paper, and therefore the hull reported there consisted mostly of \( \sqrt{3} \) rows. In contrast, in the current work, through interplay between just DFT and MC modeling (without consideration of experimental observations), we have found several structures that are on the S hull that had not been considered previously to our knowledge. One example is the ring-like S structure in Fig. 1(Ig).

The energy hulls for the three chalcogens, shown in Fig. 2, are qualitatively similar. At low coverage (less than 0.1 ML), the hulls for all systems are formed by configurations including \( \sqrt{3} \) rows. Furthermore, the (5×5) rosette structure, which played a crucial role in interpreting the LEED experiments, 5, 6, 27 is present for both S/Au(111) and Te/Au(111), and is labeled (b) for both systems. In fact, the rosette is also quite stable for Se/Au(111), since it lies only 0.005 eV above the hull, i.e., it is effectively on the hull given the numerical precision noted above.

While the hulls are qualitatively similar, they are quantitatively different. At any given \( \theta \), \( E_a \) are negative and the strength of binding \( |E_a| \) follows the sequence S < Se < Te, using \( X_{2g} \) as a reference. This sequence parallels their sequence as Group 6A elements in the periodic table, and agrees with an earlier DFT-based study, which concluded that the adsorption bond on Au(111) is stronger for Se than for S. 24 In the limit of zero coverage,
values of $E_a$ are -1.417 eV for S, -1.620 eV for Se, and -1.899 eV for Te, again with reference to $X_{2,g}$. The sequence is reversed if atomic $X_g$ is the reference state instead of $X_{2,g}$ in Eq. (1), demonstrating the influence of the choice of reference. (See Table S6 of the SM.) Effects of different choices of energy reference states, and the extrapolation method used to obtain the limiting values of $E_a$, are presented more completely in Sec. S3 of the SM.

In closing, we note that our DFT calculations show an apparent unusually slow $1/d$ decay versus separation, $d$, for pairwise interactions between chalcogen adatoms on Au(111), while S/Cu(111) and S/Ag(111) show normal $1/d^3$ decay expected from classic elastic theory.28,29 (See Fig. S4-S5 of the SM.) With a frozen substrate, we find an oscillatory decaying behavior for S/Au(111), consistent with theoretical predictions.29,30,31 It would be interesting to investigate further how the Au(111) surface reconstruction and elastic anisotropy affect the long-range interaction between adsorbates.32
Figure 2. DFT results for X/Au(111), where: (I) X = S; (II) X = Se; (III) X = Te. For each system, the left panel shows the calculated value of adsorption energy $E_a$ of various configurations as a function of $1/\theta$, where $\theta$ is coverage in ML. The solid blue line is the convex hull. Configurations on the hull are labeled by red letters, (a-m), corresponding to schematics shown at right. In the schematics, the horizontal direction is aligned with a close-packed row of Au atoms (gray circles), and the vertical direction is aligned with one possible orientation of $\sqrt{3}$ rows of chalcogen atoms (yellow to orange circles).
4. Lattice Gas (LG) Model Development including Machine Learning Strategies

The cluster expansion method is used to convert DFT energetics for selected adlayer configurations into a LG model which can then be used to describe the system energy for any configuration.\(^{33}\) This approach is based upon a classic many-body expansion where the total energy is decomposed as a sum of pair, trio, etc. interactions (where trios correspond to the total lateral interaction energy of an isolated trio minus the interaction energies associated with the constituent pairs, etc.). Below, we refer to the number of configurations (samples), \(N_c\), for which DFT calculations are performed. We also refer to the number of features (distinct interactions), \(N_F\), which are retained in the LG model, where \(N_F \leq N_C\). In the language of supervised Machine Learning (sML),\(^{34}\) the set of \(N_C\) configurations constitutes the input and the associated DFT energies are the output, and together these constitute the training set for identifying a function (i.e., the LG model) connecting the two. The simplest sML approach just corresponds to determination of LG model parameters (interactions) by least-squares-fitting of model predictions to the DFT data. However, refined approaches based upon the formal Bayesian probabilistic basis for sML\(^{34}\) also apply to the cluster expansion method.\(^{35}\) Beyond least-squares-fitting, this leads to various regularization strategies for determining LG model interactions (by assuming non-trivial prior distributions of values, or by adding an additional penalty term in the minimization).\(^{34, 35}\) Some of these strategies are applied here, as described below.

The main criteria for judging the success of our LG models are:

1. Energetics predicted by the LG model based on the cluster expansion are consistent with the DFT results. This can be gauged from the magnitude of the root mean square of the difference in the adsorption energy between LG and DFT for the \(N_C\) configurations. (Refinements such as leave-\(N_V\)-out cross-validation methods are also commonly applied, where just \(N_C - N_V\) configurations are used in developing the LG model, so one leaves out different subsets on \(N_V\) configurations for model validation \((V)\).\(^{36}\)

2. MC simulation of the LG model does not produce any orderings and motifs that cannot be corroborated as energetically viable by DFT calculations.

3. The LG models for the three chalcogens are discernibly different, in order to have overall consistency with experimental data, even though exact characteristics of the experimental data are not applied in constructing the models.

The LG models are constructed with the following constraints. (Below, \(a\) denotes the nearest-neighbor spacing, i.e. distance between adjacent fcc sites on the Au(111) surface. First, the models consider only configurations where the chalcogens are adsorbed on three-fold hollow fcc sites. For S, population of fcc sites at \(\theta_S \lesssim 0.28\) ML is well-established from experiment,\(^{5, 6, 10}\) and is supported by DFT calculations (cf. Table S5 of SM). Second, the models include pair and trio interactions. We include all pairs that are separated by distances \(d\) less than or equal to a certain pair cutoff distance \(d_{\text{pair}}^c\). We include all trios where all the side lengths are less than or equal to a trio cutoff distance \(d_{\text{trio}}^c\), but we exclude those with side length \(d = a\). We classify both pairs and trios by their lengths \(d_c\), i.e., ignoring the overall orientation of the cluster with respect to the substrate. Most of the time this is sufficient for a unique classification, but there are
exceptions with larger distances, such as for \( d=7a \) where there are two nonequivalent pairwise interactions. The choice of cutoff lengths \( d_c \) are subject to constraints, as follows. First, the size of the supercells in DFT calculations determine the upper limit of \( d_c^{\text{pair}} \). Second, the number of DFT samples determine \( d_c^{\text{trio}} \), since the number of trios grows quite rapidly with \( d_c^{\text{trio}} \). Of course, one must stop at a point before more features are introduced than the number of DFT samples.

In our previous work with S/Au(111), we adopted what might be called a minimalist approach. We found that to explain the \( \sqrt{3} \) rows observed in STM, a model with some trio interactions was necessary, and we proposed a model with only three trio interactions. This model could explain the experimental results qualitatively. The model had an attractive interaction for linear trios and repulsive interaction for equilateral triangle trios. One could predict aspects of its behavior intuitively, without Monte Carlo simulations. However, when applied to the three chalcogen systems under consideration here, this previous approach failed to produce any significant qualitative difference between them. Therefore a different approach was developed.

In the present work, in addition to the isolated clusters and \( \sqrt{3} \) rows mentioned in Sec. 3, we choose configurations (samples) by visually inspecting MC results. Any notable orderings and motifs are then introduced into the set of structures for DFT calculations at each iteration of the process, as stated in Sec. 3. To facilitate this analysis, we sometimes plot the difference between LG model prediction and DFT results, and apply a Principle Component Analysis (PCA) to aid identification of features in configurations where the LG model is particularly poor. Then, these are added for DFT analysis. It is also necessary to adopt a sophisticated approach in the spirit of sML, potentially for choosing features (interactions) included in the model, and particularly for determining corresponding interactions. Generally, we include all features corresponding to specific cut-offs \( d_c^{\text{pair}} \) and \( d_c^{\text{trio}} \) without anticipating the end result for each specific \( N_c \). As indicated above, values of interactions in the model can be determined by standard least-squares-fitting, but for large numbers of interactions, ridge or lasso regularization are sometimes helpful to assess which are most important. Then, one increases \( N_c \) “by hand” as discussed above, and repeats the above analysis. In the end, we choose to focus on a model where the number of DFT samples and features grows to \( N_c \approx 100 \) and \( N_F \approx 50 \). The latter corresponds to \( d_c^{\text{pair}} = 8a \) and \( d_c^{\text{trio}} = 4a \). It has 25 pair interactions and 27 trio interactions. Note that the pair interactions at \( d=a \) are not obtained through fitting, but are obtained directly from two different \( (\sqrt{3} \times \sqrt{3}) \) structures at 2/3 ML and 1/3 ML, yielding the values 0.244 eV, 0.264 eV, and 0.394 eV for S, Se, and Te, respectively.

The values of all pair and trio interactions obtained using four different cutoffs are given in Table S4 of the SM, a subset of which are shown for the case of S in Table 1 for pair interactions and Table 2 for trio interactions. As the number of parameters increases, their connection to adlayer ordering gets murkier, as combination of several interactions can be at play. Moreover, with larger cutoffs, symptoms of overfitting start to show up. Thus, it is appropriate at least in part to adopt the sML philosophy that those interaction parameters to some extent serve as a middle layer, and the reader should focus on the initial DFT input, and especially the final MC simulation results. Nonetheless, it is worthwhile to discuss at least trends in the interaction parameters in more detail, and in the following Sec. 5 we focus on behavior for S.
5. Discussion of LG model interaction parameters

For the pair interactions obtained for S, Table 1 shows that results are generally in good agreement with previous studies in Refs.\(^4\),\(^{27}\). All parameter sets include a relatively weak 2\(^{nd}\) nearest neighbor (NN) interaction at \(d = \sqrt{3}a\). Pair interactions increase progressively in strength for 3\(^{rd}\), 4\(^{th}\), and 5\(^{th}\) NN (where 5\(^{th}\) NN interactions for \(d = 3a\) are in all cases the strongest), and then decrease monotonically in strength at least for 6\(^{th}\) - 9\(^{th}\) NN. Pair interactions are generally repulsive. However, here we show that by including many trio interactions, the 2\(^{nd}\) NN interaction can become weakly attractive. In addition, we note that in contrast to Ref.\(^{27}\) where the long-range pair interaction near \(d = 5a\) were suggested to be slightly attractive, pair interactions ranging from 2\(a\) to 7\(a\) are all repulsive in this work. This brings into question an explanation for the experimentally observed (5x5) ordering similar to that in Ref.\(^{27}\). However, we will provide an alternative explanation in Sec. 7.

Regarding the trio interactions for S, Table 2 shows repulsive equilateral trios (labeled as 222), and attractive bent (225) and linear (226) trio interactions using all cutoffs. This is again consistent with the results of Refs.\(^4\),\(^{27}\). The strength of trios with longer side lengths is mostly significantly smaller than the above three dominant cases. Also, values are usually consistent in sign for different cutoffs (with some exceptions), but in some cases vary significantly in magnitude. While the pair interactions decay relatively smoothly with increasing separation, decay of the trio interactions is not so regular. Furthermore, some trios with longer side lengths have relatively large values, e.g., (5 5 5) and (5 7 8), where we note that these interactions are also large for the other chalcogens. We do provide a rationalization for these unexpectedly large repulsions below. However, we would caution attaching strong physical significance to interaction values such as these, as they presumably reflect at least in part slow convergence with increasing cut-off and perhaps overfitting. Thus, in contrast to traditional cluster expansions where each trio interaction value ideally captures well the energy of that isolated trio configuration,\(^{38}\) the emphasis in a sML framework is less on the values of individual interactions and more on their collective values which can reliably predict adlayer structure.

Table 1. Pair interactions for S/Au(111) for models in the current work with various cutoffs, \((d_{\text{pair}}^c/a, d_{\text{pair}}^q/a)\), compared to previous models by Walen et al.\(^4\) and Abufager et al.\(^{27}\). For pair interactions, the first column lists the \(k\): \(d/a\) values of the pair, where \(k\) is an index reflecting its position in the sequence of nearest neighbors, \(d\) is the distance of the pair, and \(a\) is surface lattice constant. For example, \(k=2\) means second-nearest neighbor separation, corresponding to \(d=\sqrt{3}a\). Values in bold are strong NN repulsion and significant 5\(^{th}\) NN repulsion. Values are in meV. Positive interaction energies are repulsive. Data from Walen et al.\(^4\) are reprinted from H. Walen, D.-J. Liu, J. Oh, H. Lim, Y. Kim, J. W. Evans and P. A. Thiel, J. Chem. Phys. \textbf{143}, 014704 (2015), with the permission of AIP Publishing. Data from Abufager et al.\(^{27}\) are adapted with permission from P. N. Abufager, G. Zampieri, K. Reuter, M. L. Martiarena and H. F. Busnengo, J. Phys. Chem. C \textbf{118}, 290 (2014). Copyright 2014 American Chemical Society.
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Table 2. Trio interactions for S/Au(111) for models in the current work with various cut-offs compared to previous models by Walen et al.\textsuperscript{4} and Abufager et al.\textsuperscript{27} For trio interactions, the first column lists the indices \( k \) of the three side lengths of the trio, where \( k \) corresponds to the \( k \)th NN pair interaction. Values in bold indicate dominant short range trios. Values are in meV. Positive interaction energies are repulsive. Data from Walen et al.\textsuperscript{4} are reprinted from H. Walen, D.-J. Liu, J. Oh, H. Lim, Y. Kim, J. W. Evans and P. A. Thiel, J. Chem. Phys. \textbf{143}, 014704 (2015), with the permission of AIP Publishing.
It is instructive to provide additional discussion of several features of the interaction parameter values obtained from our analysis. First, we discuss three such features:

(i) One might anticipate that the formation of $\sqrt{3}$ rows would be driven by 2\textsuperscript{nd} NN ($d = \sqrt{3}a$) attractions. However, this is clearly not the case for S where these interactions were repulsive in a previous model successfully generating such rows,\textsuperscript{4} and for the current study such interactions are only very weakly attractive. Instead, the driving force for formation of $\sqrt{3}$ rows for S is 226 linear trio attractions and 222 equilateral triangular trio repulsions. For Se and Te, the 2\textsuperscript{nd} NN interactions are attractive, and thus contribute to $\sqrt{3}$ row formation.

(ii) As indicated above, interactions for larger trios such as 578 and 555 are perhaps surprisingly strong attractions in our model, although this feature consistently applies for all three chalcogens. This could partly reflect cut-off and overfitting effects. However, another rationalization is possible. For all chalcogens, there is a strong penalty for (3×3) long-range ordering as is evident from the DFT data points in Fig. 2 at 1/9 ML. This feature is captured by the strong 5\textsuperscript{th} NN ($d = 3a$) pair repulsions. However, DFT analysis also reveals that for configurations with many 5\textsuperscript{th} NN pairs, but no long-range (3×3) ordering, there is no particularly strong energy penalty. Thus, to capture this feature, one

\begin{tabular}{|c|c|c|c|}
\hline
2 4 7 & -7.9 & -0.7 & -3.4 \\
2 4 8 & -2.0 & -4.5 \\
2 5 6 & -2.5 & -2.7 & -1.3 \\
2 7 7 & -7.7 & -3.3 & -8.4 \\
3 3 3 & 2.1 & 20.5 & 12.8 \\
3 3 6 & -8.3 & -10.3 & -10.0 \\
3 3 8 & -4.5 & -10.1 \\
3 4 5 & -11.5 & 9.4 & 8.7 \\
3 4 7 & -0.9 & -0.3 & -4.3 \\
3 6 8 & 5.1 & 2.0 \\
3 7 7 & -8.9 & -6.2 & -10.1 \\
4 4 4 & 2.5 & 5.3 & 6.0 \\
4 4 6 & -1.5 & -1.7 & 2.3 \\
4 4 8 & 4.5 & -5.8 \\
4 5 7 & -1.7 & -5.1 & -0.4 \\
4 6 7 & 9.0 & 0.5 & 2.0 \\
5 5 5 & -6.8 & -11.7 & -12.0 \\
5 7 8 & -21.5 & -18.5 \\
6 6 6 & -5.6 & -2.0 & 2.0 \\
7 7 7 & 6.0 & -6.0 & 0.3 \\
8 8 8 & -27.1 & -6.7 \\
\hline
\end{tabular}
requires some significant attractive trios with at least one side of length $3\alpha$ in order to counterbalance the energy contribution of the strong 5th NN pair repulsions.

As an aside, regarding the physical origin of the instability of $(3\times3)$ ordering, our analysis suggests that both electronic and elastic mechanism are operating. Without surface relaxation (i.e., in an analysis freezing the Au(111) substrate), both $(3\times3)$ and $(\sqrt{7}\times\sqrt{7})$ long-range ordering are quite unstable. However, allowing surface relaxation, the $(3\times3)$ stands apart in terms of its degree of instability.

(iii) As regards the formation of double $\sqrt{3}$ rows for Se, one might naturally anticipate that this requires equilateral triangular 222 trios to be attractive. However, such trios are repulsive for Se (and also for the other chalcogens). The reason that the 222 trios are not attractive is that such an assignment tends to have the undesired effect of making compact two-dimensional structures more stable. Thus, an appropriate treatment of the subtle observed experimental ordering requires a significant expansion of the trio parameter set relative to previous modeling.

Finally, we discuss two additional aspects of interactions which in both cases highlight differences between Au(111) as a substrate, and the other coinage metal(111) surfaces. Firstly, our modeling includes a large set of trio interactions but no quartets, quintets, etc. One might anticipate a more effective model with fewer trios, and at least some short-range quartets, etc. We have explored such models, but they do not significantly improve the fitting to DFT energetics. This situation appears specific to Au(111) where the interactions are truly long-range, and would not apply at least to the same degree to Ag(111) or Cu(111). (We also note that introducing quartets with cut-off distances similar to trios produces more interaction parameters than the DFT data can support.) Secondly, it is natural to consider a contribution to long-range interactions as being associated with Shockley surface-state mediated interactions. Indeed, we have confirmed that with a frozen Au(111) substrate, the pair interaction energy has the expected long-range inverse square oscillatory decay. However, for the relaxed substrate other effects dominate the interactions. On the other hand, for Ag(111) and Cu(111), these oscillatory electronic interactions are more pronounced relative to elastic interactions. Finally, we note that the instability of both long-range $(3\times3)$ and $(\sqrt{7}\times\sqrt{7})$ ordering on frozen Au(111) correlates well with local repulsive maxima in the long-range oscillatory interactions for the relevant separations.


Methodology. LG model simulation uses the Monte Carlo (MC) method. The code is adapted from the one used in Ref. 4. The main difference is the approach for evaluating the total contribution to the energy from the trios, which is adapted from the algorithm in Ref. 33. The model dynamics mixes adsorption/desorption and hopping to efficiently achieve equilibration. The control parameters are the temperature $T$ and the over-saturation chemical potential $\Delta \mu$. When $\Delta \mu = 0$, there is equal probability for an isolated chalcogen atom to adsorb and desorb. Thus, the simulations are in the spirit of grand canonical (GC) MC simulation since adsorption/desorption allows changes in the number of adsorbed particles in contact with a gas-phase reservoir. However, these are not conventional GCMS simulations since as discussed below, they are used to mimic the experimental quench performed on the system.
To compare with low temperature STM experiments (where chalcogen adsorbs at room temperature or above, followed by a sample quench to 4-5 K for STM imaging), we perform MC simulation of the LG models with the temperature decreasing at a constant rate, while keeping the over-saturation chemical potential $\Delta \mu$ constant. Note that we have not attempted to implement the dynamics of the quench as realistically as possible. The main difference is that in simulations, the sample is equilibrated with gaseous chalcogen constantly during the quenching process, whereas in experiment the sample is exposed to vacuum during the quench. In other words, adsorption/desorption as well as hopping are operative in simulation, versus just hopping in experiment. Quench rate is also an important parameter, but the experimental quench rates are unknown. Thus, differences in both the simulation dynamics and the quench rate from experiment could potentially lead to discrepancies between simulated and experimental adlayer ordering. We do find that the shapes and sizes of small 2D clusters at low coverage are particularly sensitive to different quench rates in simulations (cf. Sec. S4 in the SM). Consequently, we focus on the $\sqrt{3}$ rows at low coverage, and larger $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains at higher coverage, in analyzing the simulated structures and comparing them with experiment.

Fig. 3-5 show configurations at the end of the quenching process simulated at a quench rate of 1 K per Monte Carlo Sweep (MCS, the time during which each site is visited once on average) from 300 K to 10 K. There are some common features among the three chalcogen species: $\sqrt{3}$ rows of various lengths emerge above 0.05 ML, and the surface coverage reaches a local plateau with respect to increasing $\Delta \mu$ at 0.27-0.28 ML (which can be regarded as a local saturation coverage). There are also differences among the three adsorbates. Below, we will first review the coverage-dependence of the LG results for each adsorbate, in the range $0.02 \text{ ML} \lesssim \theta_X \lesssim 0.27 \text{ ML}$.

**LG simulations with variable $\theta_X$.** For S, linear $\sqrt{3}$ rows dominate below 0.10 ML. At 0.10 ML and above, compact clusters form and eventually join to form a network. As coverage increases further to about 0.18 ML, the system can be characterized as interlacing strips of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with many defects inside the strips, and voids between strips. As coverage approaches 0.27-0.28 ML, the voids shrink. Overall, the progression with coverage can be described as linear $\sqrt{3}$ rows initially, followed by evolution toward 2D, defect-rich $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Although not obvious from these real space images, results here are not inconsistent with $(5 \times 5)$ ordering observed in diffraction experiment. We will address this point in more detail in Sec. 7.

For Se, at $\theta_{Se}$ up to 0.11 ML, the system is also dominated by single rows, but they are somewhat longer than for S. As coverage increases, a new feature appears: Long, straight double and triple rows at 0.16-0.19 ML. As $\theta_{Se}$ increases further, these bunched rows meet and grow into 2D $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains. At 0.27-0.28 ML, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ order is longer-range and more obvious than for S.

For Te, single rows again dominate up to 0.11 ML, with lengths similar to Se. As coverage increases, however, the straight double and triple rows do not emerge; instead, the system proceeds directly to 2D domains with local $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, a progression which resembles S more than Se. Also, at 0.27-0.28 ML, the degree of order in the extended structure resembles S more than Se, i.e. the density of defects at this coverage appears higher for Te than for Se.

**LG simulations with variable cutoffs.** The above models all have $d_{c}^{rai r} = 8a$ and $d_{c}^{t r i o} = 4a$, but behavior can be quite sensitive to the choice of cut-offs for the model.
even using the same sets of DFT data. Hence we compare results of simulated quenching for models that have different choices of cutoffs \( d_{c}^{\text{pair}} / a, d_{c}^{\text{trio}} / a \). Fig. 6 illustrates this comparison, in a narrow coverage range of 0.12-0.16 ML. Results for S are not strongly dependent on cutoffs, but Se and Te are more sensitive, showing long straight \( \sqrt{3} \) rows only for \( (d_{c}^{\text{pair}} / a, d_{c}^{\text{trio}} / a) = (8,4) \) and above. For Se and Te, there is not a strong effect in going from (8,4) to (8,\( \sqrt{19} \)). Considering that the number of features \( N_{F} \) is 52 for (8,4), further increasing \( d_{c}^{\text{trio}} \) will increase \( N_{F} \) to a value close to the number of configurations \( N_{C} \); thus, we consider (8,4) a good compromise between complexity and validity.

LG simulations compared with experiment. Finally, we compare the simulation results using (8,4) cutoffs with the experimental data of Fig. 1. The simulation results in Fig. 3-5, at the appropriate coverages, qualitatively reproduce key features of the experimental data in Fig. 1. For S, comparing simulation (Fig. 3c-d, \( \theta_{S} = 0.06-0.08 \) ML) with experimental data (Fig. 1a, \( \theta_{S} = 0.07 \) ML), we see single \( \sqrt{3} \) rows as dominant features in both cases. For Se, comparing simulation (Fig. 4g-h, \( \theta_{Se} = 0.13-0.16 \) ML) with experiment (Fig. 1b, \( \theta_{Se} = 0.14 \) ML), we see paired \( \sqrt{3} \) rows and 2D patches in both cases (although Fig. 4i, showing simulation results at slightly higher coverage of 0.19 ML, is an even better fit to the experimental data). For Te, comparing simulation (Fig. 5d-e, \( \theta_{Te} = 0.07-0.09 \) ML) with experiment (Fig. 1c, \( \theta_{Te} = 0.08 \) ML), we again see single \( \sqrt{3} \) rows as dominant features, and they are appreciably longer than the single \( \sqrt{3} \) rows for S in both cases. In all these respects, the agreement between theory and experiment is very good. There are discrepancies, however, especially regarding small 2D clusters. For instance, in simulation (Fig. 3c-d) small 2D clusters of S are absent, whereas they are present in experiment (Fig. 1a). As noted earlier, these 2D clusters at low coverage are particularly sensitive to quench rate in the simulations, and we therefore give them less weight in comparisons between simulation and experiment.
Figure 3: (a-l) MC simulations of quenched S/Au(111) with cutoffs $(d_{\text{pair}}^c/a, d_{\text{trio}}^c/a) = (8, 4)$, T = 10 K. In these depictions of MC simulations and all which follow, the horizontal direction aligns with a close-packed direction of Au(111), and the vertical direction aligns with one orientation of $\sqrt{3}$ rows.
Fig. 4: (a-l) MC simulations of quenched Se/Au(111) with cutoffs \(d_{\text{pair}} / a, \ d_{\text{ trio}} / a\) = (8, 4). In each panel, the horizontal direction aligns with a close-packed direction of Au(111), and the vertical direction aligns with one orientation of \(\sqrt{3}\) rows.
Figure 5. (a-l) MC simulations of quenched Te/Au(111) with cutoffs \((d_{c\text{pair}}/a, d_{c\text{trio}}/a) = (8, 4)\). In each panel, the horizontal direction aligns with a close-packed direction of Au(111), and the vertical direction aligns with one orientation of \(\sqrt{3}\) rows.
Figure 6. MC simulations of quenched X/Au(111) at $\Delta \mu = 0.30$ eV and $T = 10$ K, using LG models with different cutoffs, ($d_{cc}^{pair}$/$a$, $d_{cc}^{trio}$/$a$). Quench rate is 1 K/MCS from 300 K to 10 K. (Ia-Id) $X = S$. (IIa-IIId) $X = Se$. (IIIa-IIIId) $X = Te$. In each panel, the horizontal direction aligns with a close-packed direction of Au(111), and the vertical direction aligns with one orientation of $\sqrt{3}$ rows.

7. Structure of S corresponding to the (5x5) LEED pattern. Although the focus of this paper is on comparison with low temperature STM, it is also worthwhile to apply the LG model to interpret LEED experiments, where the (5x5) pattern has been observed for S at temperatures of 83 K and 160 K. Its sharpness deteriorates (reversibly) at 300 K. The (5x5) is so robust that it can be recovered after heating to 670 K. As discussed in Sec. 1, the (5x5) LEED pattern consists of fifth-order...
spots surrounding the ideal locations of the (\(\sqrt{3} \times \sqrt{3}\))R30° spots. The locations of the fifth-order spots are invariant with coverage, i.e. they are always at fifth-order positions.\textsuperscript{5} The accepted model consists of a rosette motif arranged in a (5\(\times\)5) supercell [Fig. 2(Ib)] with an ideal \(\theta_S\) of 0.28 ML.\textsuperscript{5,6} This rosette structure was also assessed by Abufager et al.\textsuperscript{27} using DFT and was found to be more stable than other structures near this coverage. This is consistent with our current calculation, which shows that the (5\(\times\)5) rosette lies on the convex energy hull for S [Fig. 2(I)]. However, this motif is not prominent, and the (5\(\times\)5) ordering is not obvious, from the simulated quenching to 10 K shown in Fig. 3(I\(\ell\)) for \(\theta_S = 0.27\) ML. Thus, a natural question is whether the LG model is consistent with LEED observations.

To answer this question, we perform Monte Carlo simulations at a constant temperature \(T = 160\) K (to match the experiments by Yu et al.\textsuperscript{5}), and then simulate the LEED pattern by assuming each S atom contributes to the diffraction pattern with a Gaussian kernel of width \(\sigma = 0.3a\). The simulated LEED patterns are shown in Fig. 7(a-I) for models with different cutoffs \((d_{\text{pair}}^c/a, d_{\text{ trio}}^c/a)\). All models show split spots around the \((\sqrt{3} \times \sqrt{3})\)R30° spot location, in agreement with experiment, but the locations of the split spots depend slightly on the model. The real space configuration of the (7,4) model (g) is shown in panel (m) of Fig. 7. Neither the rosette motif nor (5\(\times\)5) ordering is apparent.

To identify the location of various diffraction spots, we also calculate 2D pair correlation functions. For model (a), the most prominent spots are associated with strong correlation at a distance \(d = \sqrt{43}a = 6.6a\). For Fig. 7(f) and (g) the most prominent spots are associated with \(d=5a\), which correlates exactly with the observation of fifth-order spots in LEED. For (g), there are additional spots associated with \(d = 3\sqrt{3}a = 5.2a\), and these become the most prominent spots in panel (k). It is possible that a slight deviation from fifth-order spacing, corresponding to \(d=5.2a\), would have gone unnoticed in experiment. Hence, we conclude that models (i) through (k), corresponding to cutoffs (7,\(\sqrt{13}\)) through (8,4), are compatible with experimental data. Model (l), with marked streaking in the split spots, can be ruled out.

Focusing on the (7,4) model represented in panels (g) and (m) of Fig. 7, we have checked the sensitivity of the pair correlations and LEED patterns to coverage. The 2D pair correlations and LEED patterns are quite robust, as shown in the SM, Sec. S5. Experiment shows that the (5\(\times\)5) pattern of S is insensitive to coverage in a range approaching the ideal value for the rosette structure,\textsuperscript{5} 0.28 ML, but it disappears at a coverage of 0.33 ML, leaving only the (\(\sqrt{3} \times \sqrt{3}\))R30° pattern. These aspects are consistent with simulation results. It would be very interesting to cool the (5\(\times\)5) phase to low temperatures (where diffusion is inoperative) and image it with STM, to determine whether it corresponds to the rosette structure or the more disordered structure predicted here.

Finally, one can ask whether the (5\(\times\)5) spot splitting would be expected for Se and Te. The simulations in Sec. S6 of the SM show a complex pattern of spot splitting around the (\(\sqrt{3} \times \sqrt{3}\))R30° spot locations for these two adsorbates with the (7,4) model, but no simple (5\(\times\)5). In both cases, spot splitting disappears by \(\theta_X = 0.33\) ML. It would be interesting to test these predictions experimentally.
Figure 7. (a-l) Simulated LEED patterns of S/Au(111) for different cutoffs, \(d_{\text{pair}}^c/a, d_{\text{trio}}^c/a\), at \(\Delta \mu = 0.30\) eV, \(T = 160\) K, and \(\theta_S = 0.24-0.27\) ML. Positions of spots expected in the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern are marked by black circles in panel (k). (m) MC simulation results for the (7,4) model in (g). In (m), the horizontal direction parallels a close-packed row of Au atoms, and the vertical direction aligns with a \(\sqrt{3}\) row.

8. Conclusions.
We have developed lattice-gas (LG) models within a cluster expansion framework that includes about 50 interaction parameters. These LG models have been developed entirely based on DFT analysis of the energetics of key adlayer configurations in combination with Monte Carlo simulation of the LG models to identify statistically relevant adlayer motifs. The latter have guided additional DFT analysis and iterative model refinement. Given their complexity, development of optimal models has also been aided by strategies from supervised machine learning. There has been little input from experimental data, other than requiring that the structures for the three chalcogens should be discernibly different at low coverage of ca. 0.1 ML.

In general the LG modeling is quite successful in reproducing the available experimental data. It predicts, not only the existence of \(\sqrt{3}\) rows for all three adsorbates, but also the subtle differences between them: longer \(\sqrt{3}\) rows for Te than for S at 0.07-0.08 ML, and paired \(\sqrt{3}\) rows for Se at higher coverage of 0.14 ML. It also predicts a \((5 \times 5)\) pattern in LEED at higher coverage of 0.28 ML for S, though this \((5 \times 5)\) is not well-
ordered in real space. With regard to the \((5\times5)\) LEED pattern for S, we do not rule out the rosette structure proposed originally, but we present an alternative based upon predictions of our model which also successfully describes low-coverage behavior, i.e., the formation of \(\sqrt{3}\) rows.

For modeling, the parameter space is rather large, including coverage, temperature, quench rate, and interaction cutoffs. While coverage and temperature can be matched to experiment, the other two parameters cannot. In this paper we have particularly used the interaction cutoffs as fitting parameters. For the \(\sqrt{3}\) rows observed in STM at \(\sim 0.1\) ML, cutoffs in the range \((8,4)-(8,\sqrt{19})\) are quite successful, whereas for the \((5\times5)\) LEED pattern of S at \(0.28\) ML, those in the range \((7,4)-(8,4)\) work best. This small discrepancy may be due to the effect of coverage on the relative importance of various interactions.

This work makes some predictions that can be tested in future experiments. For STM observations of the \(\sqrt{3}\) rows, the prediction is that increasing the cooling rate, all other parameters being fixed, should lead to higher density of small 2D clusters and shorter 1D chains. Regarding LEED observations of the \((5\times5)\), the prediction is that this will be observed only for S; for Se and Te, more complex patterns of spot splitting will be observed. Furthermore, if the \((5\times5)\) of S were to be imaged with STM, with atomic resolution and at a temperature where S diffusion is quenched, it should appear rather disordered, without an apparent rosette motif.

As an aside, we have also presented the adsorption energies of the chalcogens in the limit of zero coverage. The magnitude of adsorption energy follows the sequence S < Se < Te, if the gas-phase dimer is chosen as the energy reference. The sequence is reversed if the gas-phase monomer is chosen as reference, which points to the importance of choosing the energy reference most appropriate for the application at hand, in these systems.

Finally, we note that our strategy of combining DFT and Monte Carlo simulations iteratively should be applicable to a wide range of systems where the lattice-gas framework is appropriate. However, for systems where considerable distortions of the lattice structure are present, both model construction and simulation present a different set of challenges.

**Supplementary Material**

The Supplementary Material provides details about: (1) DFT results for *all* tested configurations, for all three chalcogens, corresponding to the data points in the graphs of Fig. 2; (2) Fitting the lattice gas models; (3) Considerations of \(E_a\); (4) Effect of quench rate; and (5) Sensitivity of predicted chalcogen LEED patterns to coverage.

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DOE under Contract No. DE-AC02-05CH11231. PMS and PAT provided experimental insights and data analysis, and were supported by NSF Grant CHE-1507223.

The data that supports the findings of this study are available within the article and its supplementary material.

References.
(I) $S/Au(111), \Delta \mu = 0.3$ eV

(a) $(6, \sqrt{13}), 0.15$ ML
(b) $(7, 4), 0.15$ ML
(c) $(8, 4), 0.16$ ML
(d) $(8, \sqrt{19}), 0.15$ ML

(II) $Se/Au(111), \Delta \mu = 0.3$ eV

(a) $(6, \sqrt{13}), 0.14$ ML
(b) $(7, 4), 0.15$ ML
(c) $(8, 4), 0.13$ ML
(d) $(8, \sqrt{19}), 0.13$ ML

(III) $Te/Au(111), \Delta \mu = 0.3$ eV

(a) $(6, \sqrt{13}), 0.12$ ML
(b) $(7, 4), 0.13$ ML
(c) $(8, 4), 0.12$ ML
(d) $(8, \sqrt{19}), 0.12$ ML