Modeling adsorption and diffusion of atomic oxygen on the Ag(111) surface using kinetic Monte Carlo simulations

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Abstract

Oxidized silver surfaces are widely used as industrial heterogeneous catalysts to oxidize small organic compounds, such as ethylene. While surface-adsorbed oxygen is known to participate in catalysis, it has been suggested that 'subsurface' oxygen adsorbed in the near-surface region of silver also plays important roles in surface reconstruction and reactivity. However, the formation, motion, and chemical behavior of subsurface oxygen in silver are not well understood. In the present work, a kinetic Monte Carlo (KMC) simulation has been developed using the Python programming language to computationally model the diffusion kinetics of atomic oxygen (AO) at the Ag(111) surface. This simulation allows AO to move between various high-symmetry sites on the surface and in the subsurface of Ag(111). The diffusion rates required for the simulation have been calculated using density functional theory (DFT). The DFT-KMC simulation determines the relative populations of surface oxygen versus subsurface oxygen at various surface temperatures and oxygen coverages, promoting better understanding of the catalyst structure under different reaction conditions. Overall, our kinetic model describes the adsorption and diffusion of oxygen at both the surface and subsurface and helps to elucidate the role of subsurface oxygen in the structural and catalytic properties of silver.
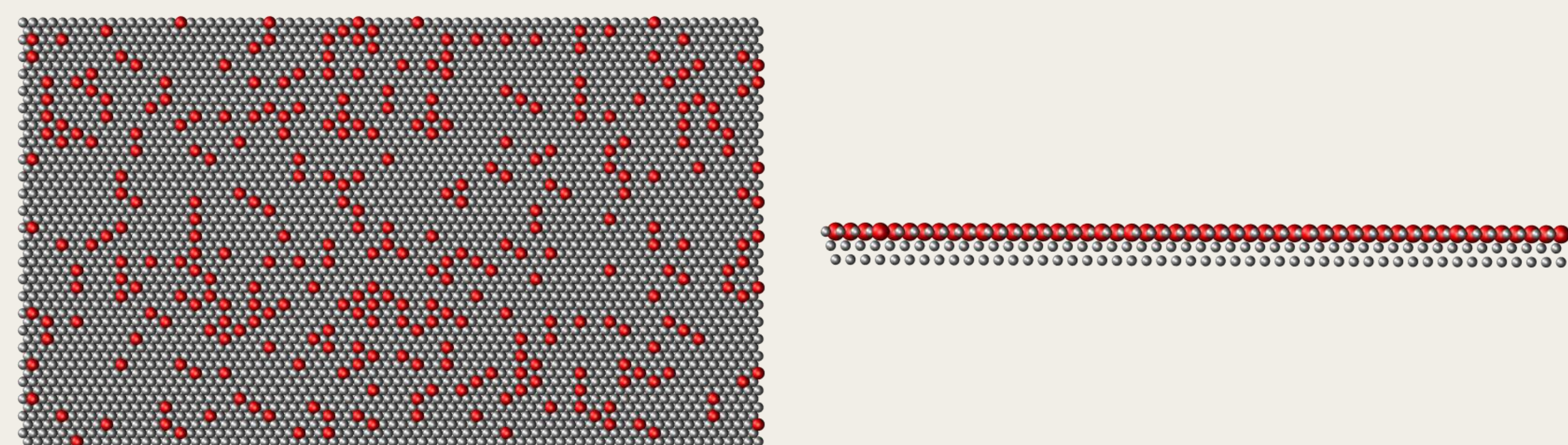
Methods

The KMC simulation algorithm works by first assessing to what sites on the Ag(111) surface an oxygen atom can move based on its current adsorption site. It then weighs the probabilities of those site options according to the rate constants associated with moving to them (calculated with the Arrhenius rate equation) and chooses one at random. If the move that was chosen is impossible (due to occupation of the new site by another oxygen atom), the algorithm repeats the process with the remaining possible moves until the oxygen atom has either successfully moved or until all options are exhausted, in which case the oxygen atom does not move during that iteration. The code performs this procedure for every oxygen atom for each iteration.
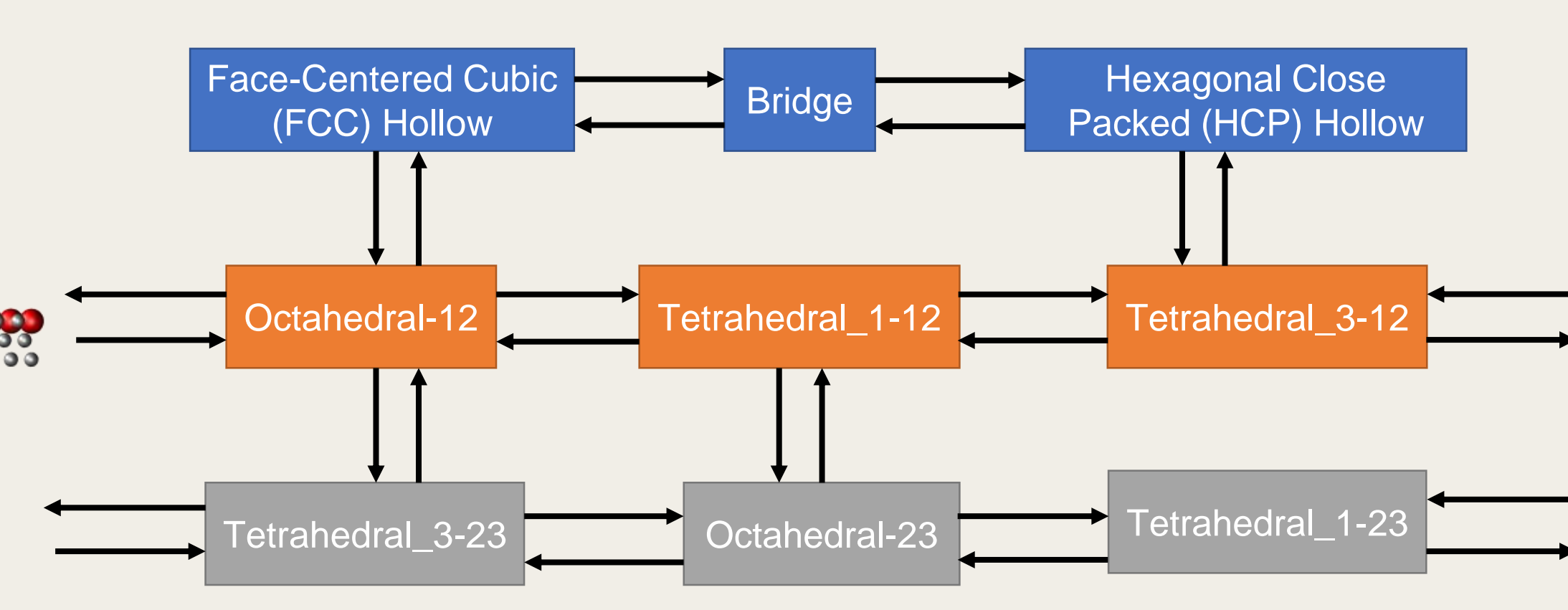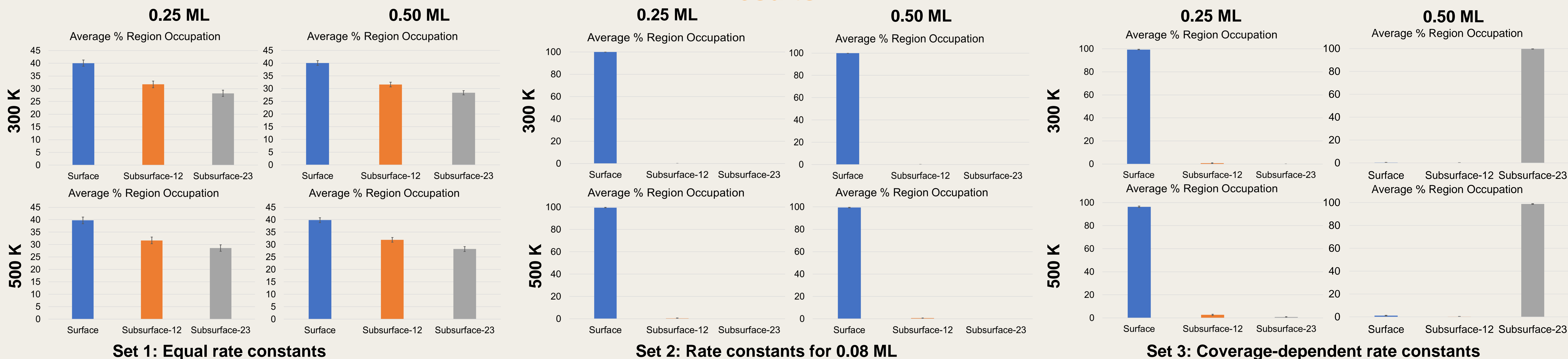
flow-diagram of KMC algorithm
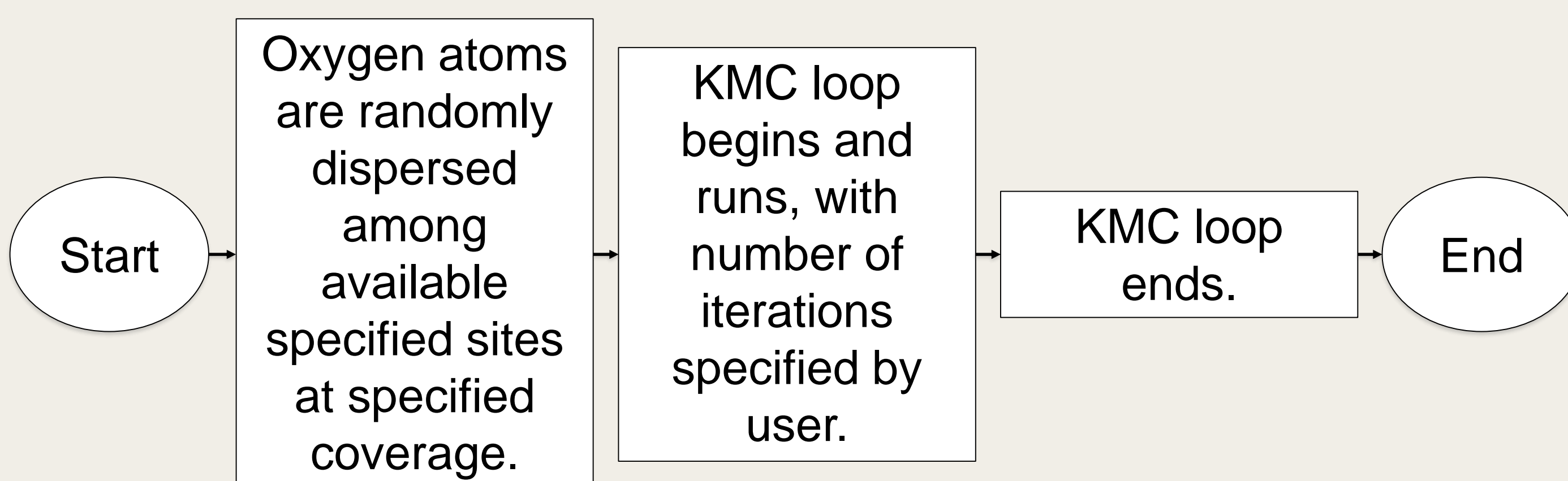
top-down (left) and side view (right) images of Ag(111) supercell

map showing connectivity of possible AO sites

Results

0.25 ML | **0.50 ML**

Set 1: Equal rate constants

0.25 ML | **0.50 ML**

Set 2: Rate constants for 0.08 ML

0.25 ML | **0.50 ML**

Set 3: Coverage-dependent rate constants

Conclusions and Future Work

In Set 1, despite having equal rate constants, the regions are not favored equally; this is likely due to the ways in which the various sites are connected. In Set 2, a large preference for the surface region is observed, which is expected given that the rate constants used were calculated for a 0.08 ML case. Previous DFT calculations have shown surface AO is favored at low coverages. In Set 3, it is seen that depending on which rate constants are used (0.25 ML rates or 0.50 ML rates), the favored region switches from surface to subsurface-23. In future work, we plan to make use of coverage-dependent rate constants at more coverages. We also plan to add more features to the KMC code to model desorption, adsorption, and time-dependence.

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Acknowledgements

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