Chapter 1

Introduction

Modern multi-scale modeling approaches reflect the realization that for the understanding of a large number of materials science applications a treatment over a wide range of length and time scales is required. At the lowest scale are electronic interactions that lead to the formation and breaking of chemical bonds between atoms over length and time scales of the order of Angstroms and picoseconds. At the largest scale one has arrived at macroscopic dimensions where then a resolution of the atomic structure may no longer play a role. Somewhere in between one has what one could call a mesoscopic regime, where as a most important factor the statistics between the manifold of atomic scale processes sets in. While nowadays there are typically well established theories at each individual length and time scale, the links between the different methodologies are only just emerging. What is most prominently still lacking are robust links that enable a control of the error propagation from one scale to the other. Within this context first-principles statistical mechanics approaches try to establish such links between electronic structure theories and concepts that come from thermodynamics and statistical mechanics. The prior are the methods of choice when it comes to a reliable quantum mechanical description of the fundamental binding interactions between the atomic constituents, while the latter are obviously designed to handle the statistical interplay that emerges among the manifold of molecular processes at mesoscopic scales [67].

The description of a solid surface exposed to a realistic gaseous environment is a typical example where such first-principles statistical mechanics approaches are indispensably required. On the one hand side, the complex bonding in particular at transition metal surfaces requires the use of first-principles electronic structure theories if a theoretical description with predictive character is aspired. Such theories, in particular modern density-functional theory [2], have provided tremendous insight into the energetics and electronic structure of solid surfaces and of adsorbates at them. On the other hand, the interplay with the gaseous environment is not that easily grasped. An explicit modeling of even just a very finite chunk of surrounding gas phase over the solid surface would already yield system sizes that are beyond the scope of present-day computing resources. Furthermore, the statistics (or entropy in

a thermodynamic language) is playing a key role. At atmospheric pressures and room temperature on the order of 10^8 gas phase molecules hit every single surface atom per surface. Evaluating this bombardment and its effect on the surface structure and composition can only be handled by resorting to methods from statistical mechanics. This in particular, if the effect of temperature on the structure, composition and order at the surface is to be tackled.

Correspondingly, first-principles statistical mechanics approaches have been increasingly employed to address such issues. Assuming the surface to be in equilibrium with the surrounding gas phase, so-called first-principles atomistic thermodynamics approaches couple the solid surface to a gas phase reservoir. In their prevalent form the effect of configurational entropy at the surface is neglected and the approach is employed to compare the stability of a variety of surface structural models under given environmental conditions. The evaluation of the partition function required to explicitly account for the effect of configurational entropy at finite temperatures necessitates unfortunately an amount of first-principles total energy calculations that still far exceeds present-day supercomputing resources. As one remedy first-principles lattice-gas Hamiltonian approaches first parameterize a coarse-grained lattice model of the surface with the first-principles data and then base the partition function evaluation entirely on the resulting computationally much less demanding model Hamiltonian. Issues in the aforementioned robustness of the link between the theories are then obviously the reliability range of the employed lattice model, as well as its parameterization details.

Despite the achievement in being able to study solid surfaces in contact with technologically relevant environments with pressures of the order atmospheres and elevated temperatures at all, one still has to recognize that such first-principles statistical mechanics studies are at the edge of what is feasible with current computing resources. Correspondingly, existing studies almost exclusively focused on simple model surfaces in the sense of low Miller index surfaces of single crystals. While one can argue that these surfaces represent the dominant facets of real solid surfaces, there are still essential features missing: defects and facet edges. One prominent group of defects are atomic steps, and there in particular close-packed steps due to their low formation energies. Due to the undercoordinated atoms exposed at the step edge, these defects are frequently perceived to play some special, if not decisive role for the surface properties or function in materials science applications. Theoretical studies that quantitatively pinpoint this special role while also accounting for the effect of a realistic (reactive) environment are, however, virtually not existent, not least due to the just described challenges for a first-principles based modeling.

The aim of this thesis is thus precisely to establish a methodological framework that is able to describe with predictive character what happens at an atomic step at a surface, when the latter is exposed (say in a catalytic application) to a gaseous environment. More precisely (and cautiously) the focus is on an important first step in this direction, namely on identifying the structure and composition at the atomic step when the surface is in equilibrium with the surrounding gas phase. As will

become clear in the course of this thesis, already this is a daunting task, in particular when aiming to establish a theory based on robust links between the scales and with predictive character. The modeling will be developed using a Pd(100) surface in contact with an oxygen gas phase as example. Pd is a frequently employed material in a wide range of applications, oxygen is an ubiquitous gas dominating our earths atmosphere and the (100) facet is one of the most stable and thus dominating facets of fcc structured palladium. After introducing the different methodologies underlying the employed first-principles statistical mechanics part in Part I, the robustness of the link between the electronic structure calculations and the statistical techniques in form of the lattice-gas Hamiltonian parameterization will first be critically assessed in Part II by still focusing on the ideal Pd(100) facet. Part III then addresses the step itself, by first discussing the energetic data collected from various Pd vicinal surfaces exposing (111) steps and (100) terraces, and then explaining how this data is considered in the first-principles lattice-gas Hamiltonian that is finally used to address the decoration of the step in finite environments.