Chapter 3
Ab Initio–Based Stochastic Simulations of Kinetic Processes on Surfaces

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ABSTRACT

We briefly present the theoretical framework of a hierarchical multi-scale approach, which is an ab initio-based stochastic method, and its applications to several chemical/physical kinetic processes on metallic surfaces. We first introduce necessary theoretical basis of ab initio and Monte Carlo (MC) methods, and then illustrate different Monte Carlo algorithms for important ensembles, including canonical and grand canonical ensembles. In the following section, we describe two important protocols which are essential to integrate ab initio data and MC models. Two examples are presented in order to elucidate the power of this multi-scale approach. The first example focuses on the combination of kinetic Monte Carlo and transition state theory. We discuss the detailed processes of performing kinetic Monte Carlo simulation on atomic diffusion on alloyed surface, including some technical aspects. In the second example, we presents a different way to account for the local environment-sensitive metal-catalyzed O_2 dissociation reactions using combinatory techniques including cluster expansion and grand canonical Monte Carlo methods. This approach provides steady-state rates and rate derivatives that are comparable with experiments. Moreover, the connection between the feasible mechanisms and the observed kinetic behaviors can now be built.

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INTRODUCTION

Integrated computational simulations have been experiencing booming developments in the last decade. The concept is originated from the requirements of understanding innovative properties of materials with artificial structures and guiding synthesis of high-performance materials at nano-scale. Contemporary computational materials science demands detailed information of electronic structures with high accuracy and the ability to describe dynamical processes of phenomena covering large spatial and temporal scale, such as material fatigue, heterogeneous catalysis, and crystal growth, etc. Although traditional quantum physics/chemistry methods and phenomenological models have been developed very maturely at both ends of the concept of integrated computational simulations, it is only within the recent ten years that researchers start bridging them together and apply the integrated methods to materials engineering (Reuter2003, Rojal2007). In prevailing studies, stochastic methods (mainly Monte Carlo methods) are employed to mimic the complex nature of kinetics, i.e. multiple evolution options from the current state. Key dynamical parameters are then determined by atomistic simulations, e.g., density functional theory (DFT) or molecular dynamics. Piana *et al.* employed molecular dynamics to obtain 40 key kinetic parameters and performed simulations on urea crystal growth in two different solutes. (Piana2005). Honkala *et al.* used *ab initio* calculations to determine reliable parameters even including local chemical environments to calculate the productivity of ammonia synthesis catalyzed by nanoparticle of Ru (Honkala2005). Their calculated turn over frequencies are in good agreement with measured ones. *Ab initio*-based stochastic simulations also have been applied to study mechanical failure of materials (Fu2004), self organization (Mo2005, Negulyaev2008, Ziegler2008), thin film deposition (Huang1998), and electrochemical processes in solid oxide fuel cells (Pornprasertsuk2007, Wang2010), etc. Computational simulations are able to present detailed insight of phenomena or study effects of various factors which are very difficult or even impossible to be obtained by experiments. For example, Zhu *et al.* performed systematic kinetic Monte Carlo simulations to study effects of external stress on the growth of quantum dots on substrates (Zhu2007).

However, due to the diversity of the properties of materials, processes, and purposes of simulations, corresponding models are very different from one to another. General requirements of models are: (1) the model should be able to describe critical steps of kinetics, i.e., the rate determining steps of chemical reactions or atomic piling ups during quantum dot growths, etc., and (2) the model should contain reasonable number of parameters which can be handled by *ab initio* calculations. Different models and/or algorithms have been developed to meet different simulation goals and interested systems. For instance, Voter developed “hyperdynamics” to expedite the system evolution (Voter1997). Henkelman and Jónsson developed on-the-fly dynamical simulation method so that the simulator is able to automatically determine and update the migration list during simulations (Henkelman2001). Parallel algorithms of kinetic Monte Carlo methods have also been developed by several groups (Shim2005, Martínez2011). These developments essentially strengthen the powers of this hierarchical multi-scale approach. In this chapter, we introduce basic theory and several key algorithms of *ab initio*-based stochastic methods. Two examples are presented in order to illustrate the general processes of these stochastic methods, including generating models, incorporating *ab initio* data into models, analyzing outputs, etc. Both examples describe the morphological evolution and chemical/physical kinetic processes on surfaces since surface has become a very important medium in modern science and technology.