Abstract

This dissertation tackles the problem of limited time and length scale of *ab initio* modeling methods. Methods belonging to this category boast extreme accuracy due to robust treatment of the electrons in molecular and condensed matter systems. This accuracy comes with a large computational cost that, among other restrictions, severely limits statistical sampling power of *ab initio* molecular dynamics (AIMD). Advanced simulation techniques are successfully applied to large, realistic systems.

Density functional theory (DFT), despite being an effective single-body approach, is a tried-and-true method of calculating many properties, discovering new materials, and gaining new physical insight. Recent worldwide trends include high-throughput calculations that take advantage of modern computers and the treatment of increasingly realistic systems, which is one of the themes of research described here.

Here, the DFT framework is applied to the study of dissociative adsorption on gas/solid interfaces. A number of gaseous species is considered, among them methane, carbon dioxide, and related radicals. Their decomposition and adsorption reactions are studied on the surfaces of graphene (ideal and defected), hexagonal boron nitride, and kaolinite. What these surfaces have in common is their morphology – they are all made up of thin layers with weak interlayer bonding.

Two approaches are explored: 1) zero-temperature calculations, where adsorption energies and similar quantities are obtained with predetermined position of nuclei in a computational cell and 2) finite-temperature calculations, where molecular dynamics simulations are performed with quantum-mechanical forces determined from DFT. The second approach is applied to the study of chemical reaction dynamics. Thermodynamic data is gathered and analyzed to produce the Helmholtz free energy landscape of elementary reaction steps. This is a more realistic measure of reaction energetics because at finite temperature, nature minimizes free energy, not the total energy.

Many features appear in the computed free energy landscape, i.e. local minima corresponding to equilibrium states and maxima (or saddle points) that correspond to transition states. The magnitudes of energy barriers that separate the equilibrium states allow to piece together a picture of dissociative adsorption energetics. For example, the presence of graphene drastically lowers decomposition energy barriers of methane. The results points to the preferred mechanism of this multi-step reaction, which is important in understanding graphene mono- and bilayer chemical vapor deposition growth processes.