Extending the Tools of Chemical Reaction Engineering to the Molecular Scale

Author: James B. Rawlings
Department of Chemical and Biological Enginering
University of Wisconsin

In classical continuum chemical kinetics, two primary physical situations result in model reduction. The first case is the presence of fast and slow reactions. In this case, the fast reactions are assumed to be in equilibrium and one expresses a slow-time scale evolution of all the species concentrations due to the slow reactions. In the second case, highly reactive intermediates rapidly approach and maintain a low quasi-steady-state concentration. In this case, one can express a simplified evolution equation for the large concentration species (reactants and products). These two cases arise frequently in applications and are a standard part of the classical reaction engineering toolkit. Examples include Michaelis-Menten kinetics and Langmuir-Hinshelwood or Hougen-Watson reaction mechanisms on catalytic surfaces.

But when reactions are considered at small length scales (small catalyst particles, inside living cells, etc.), the concentrations are small enough that the stochastic fluctuations cannot be neglected. In this regime, we often use kinetic Monte Carlo (KMC) methods to simulate the reaction networks of interest. But when confronted with large separations in reaction rates or large separations in species concentrations, the computation time for the standard KMC simulation method becomes excessive, and standard KMC is no longer useful for simulating the reaction network of interest.

This talk presents recent results for extending kinetic model reduction methods to handle this stochastic, molecular regime. The resulting reduced chemical mechanisms can be quite different from what one expects based on knowledge of the results for only the macroscopic, deterministic setting. The model reduction methods will be illustrated by application to a set of illustrative chemical kinetic mechanisms.