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Perspective

Perspective on "Statistical mechanics of isomerization dynamics in liquids and the transition state approximation"

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Abstract. This paper provides a perspective on the use of the reactive flux formalism for calculating rate constants in condensed phase systems through molecular dynamics simulations. This approach makes possible the computation of rate constants even for systems with very high energy barriers.

Key words: Reactive flux – Molecular dynamics – Rate constants – Monte Carlo

1 Introduction

This article provides a discussion of the title paper by David Chandler. Here the projection operator formalism of statistical mechanics is used to derive the chemical rate equations for unimolecular reactions in classical systems. What falls out of this formalism is a microscopic expression for the the sum of the forward and backward rate constants that involves an equilibrium ensemble average of the instantaneous flux over the saddle point of the reaction weighted by a function that is unity if the reacting system is in any of its product configurations and zero if it is in any of its reactive configurations at time t. This quantity $\kappa(t)$, called the reactive flux, has several important limits. In the limit $t \rightarrow 0+$ the reactive flux becomes the transition-state rate constant. As t increases from zero $\kappa(t)$ quickly decays to a plateau value from which it very slowly decays as an exponential with the true rate constant for the reaction. If the energy barrier for the reaction is high compared to the thermal energy, the true rate constant can be found from the plateau value of the reactive flux. Since the transition-state rate constant is an approximation based on the assumption that any trajectory that has crossed the saddle point will not recross it, the true rate constant will always be smaller than the transition-state rate constant. The beauty of this reactive flux expression is that it allows one to compute chemical rate constants for reactions in liquids as well as in gases using molecular dynamics simulations.

For reactions involving large activation energy barriers, barrier crossing is an infrequent event. The barrier divides phase space into two regions such that most trajectories starting in one region stay in that region for very long times before making a transition to the other region. Since the crossings are infrequent, it is very difficult to determine the rate constants for barrier crossing from simulation. The reactive flux expression provides a rigorous method for accelerating the calculation of rate constants for activated barrier crossing. According to the reactive flux one can calculate the rate constant by studying trajectories originating at the barrier maximum. This allows one to propagate only initially activated trajectories and thus avoids the need to wait for an initially unactivated trajectory to get activated. This method was anticipated by the pioneering work of Keck [1, 2], Anderson [3] and Bennett [4]. By generalizing and extending the time correlation function approach of Yamamoto [5], Chandler derived the reactive flux in the form in which it is now used in simulations. He then suggested that calculations of the plateau value of the reactive flux from molecular dynamics trajectories provide a rapid method for calculating the true rate constant of the reaction.

There are two parts to a reactive flux calculation. First, one must sample initial states at the barrier maximum and then one must propagate these initial states using molecular dynamics. The sampling of the initial states is done with Monte Carlo methods or with constrained molecular dynamics. The molecular dynamics propagation can usually be carried out for a short time until the plateau value is reached. In practice the efficiency of this method depends on finding a good dividing surface in phase space, for only with a good dividing surface will the reactive flux decay to its plateau value quickly. An additional problem is met when the rate constant is very small. The reactive flux method is equivalent to computing the difference between two large numbers. When this difference is small there is considerable error. In that case various approximation tricks have been devised such as the absorbing boundary method [6].

The reactive flux method is also useful in calculating rate constants in quantum systems. The path integral formulation of the reactive flux together with the use of the centroid distribution function has proved very useful for the calculation of quantum transition-state rate constants [7]. In addition new methods, such as the Meyer–Miller method [8] for semiclassical dynamics, have been used to calculate the flux–flux correlation function and the reactive flux.

The reactive flux method is widely used to compute rate constants. Several reviews [9, 10] illustrate its utility. Because of this utility, the title paper represents an important milestone in theoretical chemical kinetics.

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