

Advances toward Obtaining Kinetics from Reactive Molecular Dynamics

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Valid computer predictions of kinetics have become a reality, but Reactive Molecular Dynamics (RMD) is necessary to advance beyond using foreknown transition states. The ideal way to run such kinetics experiments would be with truly ab-initio molecular dynamics, valid for covalent systems. Two approaches will be described that move toward this goal. First is use of reactive force fields like our RMDff [1], adapting conventional covalent force fields to allow realistic bond-breaking and -making. Second, our BEBOP energy analysis [2] is based on fast electronic-structure calculations, allowing the anharmonic motions of reactions to be captured with greater accuracy.

Background. Part of the challenge is that in stepwise time, reactions normally are rare events relative to internal motions and to intermolecular collisions. Transition-state theory eliminates time by using statistical mechanics, allowing stationary states of isolated molecules to be calculated. For transition states with classical energy barriers, calculation is now fairly routine thanks to high-accuracy, user-friendly ab-initio codes. Solvated molecules and transition states can be analyzed fruitfully with continuum-solvation methods. If a reaction site is known within a complicated molecule, the ONIOM method [3] allows calculation of the transition state by extrapolating from high- and low-level calculations on the central reaction site, coupled with fast, low-level analysis of the entire molecule.

Molecular dynamics allows events to occur in time as atoms and molecules move through space and other molecules. For simple collisions, trajectory analysis allows quantum-chemical calculations at each step. Classical molecular dynamics uses Newton's Second Law $\Sigma F=ma$, evaluations of the forces on each particles with parameterized forcefield expressions, and timewise integration to move the particles as they interact. "Ab initio MD" methods like Car-Parrinello MD [4] use electronic density-functional theory, planewave/pseudopotential basis sets, and periodic boundary conditions to analyze periodic domains like crystals and their surfaces.

Reactive Molecular Dynamics refers to methods that apply reactive force fields in classical molecular dynamics. Example force fields are RMDff [1], REAXff [5], the Brenner potential [6], and AIREBO [7]. Harmonic potentials for bond stretching must be replaced by alternatives such as Morse potentials, and other degrees of freedom are affected by the evolving reaction coordinate. Quantum effects like tunneling are neglected, and as system density decreases, problems can arise from neglecting the quantized nature of rovibrational energy transfer.

Results and Discussion. We will examine how Reactive Molecular Dynamics performs with RMDff in predicting the kinetics of polymer decomposition. Reactions can occur anywhere in the polymer melt and initiated by homolytic dissociation, making transition states difficult to pre-locate and determine. The results show that energetic and entropic effects combine to lower the activation below the bond dissociation energy.

A more general solution is offered by BEBOP, our Bond Energy from Bond Order and Population method [2]. By calculating bond order and populations from low-level, fast electronic-structure methods, the energies and forces are freed from classical forcefield functions that can fail dramatically as structures distort toward transition states.

Advances in computing power occur increasingly by more CPUs rather than faster CPUs, favoring simulations like RMD that can be stochastic and hyperparallel. The promise of this future is fast determination not only of rates but also of the mechanisms by which they occur, from gas kinetics to polymers to biofuels to biochemistry.

References

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