The objective of our research program is to extend theoretical methods to the study of complex, polyatomic reactions in the gas phase, on surfaces and in condensed media. More specifically, we are interested in the theoretical investigation of N-atom systems where N ≥ 6 and in which there are several reaction channels that are energetically open. Such systems frequently exhibit dynamic behavior strikingly different from that seen in three- and four-body reactions.

The specific methods being utilized in our investigations of molecular dynamics at nanolevel are statistical Monte Carlo methods, classical and quasiclassical trajectories, and some quantum mechanical wavepacket investigations. Each of these computational procedures is being conducted on potential-energy surfaces computed primarily using ab initio electronic structure calculations.

We have also developed several methods of analysis that permit accurate analysis of intramolecular vibrational relaxation rates in polyatomic molecules. In the first of these, the magnitude and pathways for internal energy flow in a molecule are determined from the envelope functions of the temporal variations of the mode kinetic energies computed using projection methods with a coordinate system that diagonalizes the kinetic energy matrix. Since the potential energy is not involved in the analysis, all problems associated with potential coupling between the vibrational modes are eliminated. A second method that is well-suited for analysis of energy flow in small molecules involves the Fourier transform (FT) of the time variation of a local-mode bond energy for an ensemble of trajectories. We have previously demonstrated that this transform is expected to contain a series of spectral bands at frequencies corresponding to the mode-to-mode energy transfer rates. The band assignments to particular mode-to-mode pathways are made using heavy-atom blocking and constrained motion methods. Most recently, we have shown that total IVR rates out of local stretching modes can be obtained from power spectrum line splittings. This line splitting is a consequence of a general interference phenomenon that exists for all systems whose resonant frequencies are a continuously varying function of time.

Previously, almost all theoretical investigations of complex gas-phase reaction dynamics have been conducted on purely empirical potential surfaces. All simulations of cutting, grinding, polishing, indentation, surface tribology, and uniaxial tension have utilized such potentials. The liabilities of this approach to the problem are numerous. Because of this, the accuracy of molecular dynamics simulations on complex systems has, for practical purposes, reached its limit. If we wish to advance beyond this natural limit for empirical potentials, we must develop ways to effectively utilize quantum mechanical methods that have the power to produce more accurate surfaces and force fields that can, in some cases, approach the experimental potential surface. A principal objective of our research program is the development of general methods that permit ab initio molecular dynamics (AIMD) calculations to be executed for complex systems.

The implementation of AIMD calculations faces three major obstacles. (1) Sufficient computational power must be acquired to permit high-level ab initio computation of the energies and force fields for approximately 105 nuclear conformations of the system of interest; (2) A method must be developed that permits accurate sampling of the small subset of the total configuration space for the system that is important in the dynamics being investigated; (3) A method that allows accurate interpolation between the 105 computed energies and force fields must be developed. This method must be robust and relatively easy to implement. Currently, we have developed methods and techniques that we believe will provide solutions to each of the above problems. Exploratory studies on systems containing up to 98 electrons have already been conducted. The results suggest that these methods will work remarkably well.

The accuracy of the AIMD calculations we are conducting are being tested and validated in both gas-phase chemical systems and for a variety of machining processes. For gas-phase reaction dynamics, we are focussing our attention on the unimolecular decomposition of vinyl bromide, vinyl chloride, and ethylene. These systems are selected because there have been several experimental and theoretical investigations reported related to various features of the dissociation dynamics that will provide benchmarks against which we can validate our proposed methods. Our methods will be tested in machining applications by conducting nanometric cutting, indentation, laser ablation, and uniaxial tension simulations on silicon workpieces. There exists a wealth of experimental data at macro level related to this system and our research group has reported both MD and MC simulations at nanolevel using a Tersoff potential. This will provide an excellent data base for comparison and validation of the proposed AIMD calculations when applied to machining processes. In addition, we will execute AIMD calculations related to MEMS applications of carbon nanotubes for gearing assemblies and compare our results to those previously reported using an empirical potential. Investigations of indentation, grinding, polishing, and uniaxial tension experiments are planned. Those involving uniaxial tension are now in progress.

If the proposed studies validate the methods and show them to be general and robust, it is likely that AIMD calculations will become the gold standard for future MD investigations.
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