

# Method Development and Simulations of Physical Processes and Chemical Reactions in the Various Phases

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The focus of the research at OSU will be simulations and rate calculations of the various physical and chemical processes in the gas, liquid, and solid phases of nitro and nitramine energetic materials. The models will be based on those previously developed in the group with extensions and refinements based on the theoretical developments and results from the work of the MURI team, thus the models will evolve over the grant period along with increasing complexity of the processes being simulated.

**Gas-phase decomposition of cyclic nitramines.** A long-term theme in our research has been the formulation of accurate potential energy surfaces and simulations of decomposition reactions of large energetic molecules. An important aspect of our work within this MURI project will be to continue our efforts to develop methods and apply them for rate calculations and simulations for the complex chemical reactions occurring along parallel, branching sequential pathways for the decomposition of TNAZ, RDX, and HMX. While the focus of the MURI is the chemistry in condensed phases, with potentials to be formulated by Prof. Brenner, it is important that the resulting models accurately describe the gas phase reactions. We will investigate methods of formulating the potentials to take greater advantage of *ab initio* energies and that are consistent with the reaction models for the condensed phase chemistry. This will entail close interactions with the groups at U. Fla. and NCSU.

We will be working closely with Prof. Bartlett to develop better ways of using *ab initio* results in dynamics simulations. A potentially powerful approach, which Prof. Bartlett has already begun to exploit, is “direct dynamics” where the forces are computed by quantum chemistry methods during the course of the trajectory integration. This eliminates the need to fit to analytical functions. However, it suffers from the fact that *ab initio* results are usually not sufficiently accurate since the need for rapid calculations of the points precludes the use of the highest levels of theory. Professor Bartlett is developing some methods to deal with these problems and we will collaborate with him to implement them in simulations. Another potentially practical method is to combine direct dynamics with an “on-the-fly” fitting procedure. Here one proceeds as in a direct dynamics simulation, but fits the points sampled by the trajectories so that a global fit of the surface is generated. The advantage is that the resulting fit is biased by the most important regions of configuration space visited by the system in the simulations and future simulations can be done without the cost of new *ab initio* calculations. We have, as a part of another project, developed an interpolating moving least squares method that is highly accurate and appears feasible for many-dimensional systems, and we will explore its applicability here. Other, more established methods, e.g., empirical valence-bond approaches, will also be investigated for describing the sequential steps in the decomposition of energetic molecules.

The goal is an accurate model that is sufficiently flexible to permit easy variation of critical features as the model is extended to describe the “long-time” chemical decomposition reactions. The model will be formulated such that it is consistent with the

models for the condensed phases that will be developed in the project by the groups at U. of Ill., U. of Md., and NCSU. That is, they will be such that they can be used to study the decomposition of the species that enter the gas phase from a burning surface or in a detonation. Thus, they will provide information about the species contributing to heat feedback from flames relevant to the studies to be performed by Prof. Adams (U. Mo.). They will also provide information that could be useful in refining the continuum flame models developed by Miller and Anderson at ARL.

These PESs will be used to compute rates for the various steps in the decomposition proceeding from reactants (RDX, TNAZ, and HMX) through the various stages and branching to the “final products” (i.e., CO, NO, HCN, H<sub>2</sub>O, N<sub>2</sub>O, and CH<sub>2</sub>O). The studies will be structured around the postulated initial reactions, which we will take to represent the major decomposition channels. For example, we will consider major pathways (with subsequent branching) beginning with the initial reactions: Simple N—N bond fission, NO<sub>2</sub> elimination; ring fission, concerted molecular elimination of CH<sub>2</sub>NNO<sub>2</sub>; nitro-nitrite rearrangement followed by O—N fission; and H-atom migration followed by N—N bond fission to yield HONO. The available experimental data suggest that the decomposition mechanism depends on the specific experimental conditions, thus the models need to have the flexibility necessary to describe the many branching points in the decomposition for various conditions. Our goal is to develop a “universal” model that is applicable to all the cyclic nitramines. Our initial focus will be on TNAZ, RDX, and HMX where we can judge the accuracy of models by predicting experimental data, and then we will explore the predictive capabilities of the model for other nitramines.

One of our long-term interests has been the development of practical methods for performing realistic simulations and accurate rate calculations for chemical reactions involving large polyatomic molecules, and we will continue that work in this project. For the most part we rely upon classical mechanical methods for the simulations and rate calculations. Dr. Rice is developing a suite of simulation codes and ultimately the methods and models developed in the MURI project will be incorporated into it. For much of the developmental work we will be doing in the early stages of the project we will use “general” classical trajectory computer code, GenDyn, that we have developed in the group. It can be directly used in many cases without modifications or easily modified to treat many the problems of interest here. This program includes a number of features that allows it use for a wide range of problems by simply providing basic information about the system of interest. For example, common potential functions are a part of the program, and special potentials can be readily incorporated. Various methods of selecting initial conditions and for analyzing the results are available in the code. The code also includes routines to aid in fitting potentials, locating critical points, performing normal mode analyses, and other functions associated with dynamics calculations. Furthermore, it can be used to carry out various kinds of calculations based on semiclassical approaches, classical diffusion theory, and transition-state theory rate.

**Predictive models for condensed-phase materials.** The central focus of the MURI is the development of general models for predicting the properties of energetic materials. The predictive models will be the practical result of the combined efforts of the MURI team, but the OSU group will be involved in integrating the various contributions to produce the practical models that will be the final product of the project. We will also, working with Dr. Rice at ARL and Dr. Brenner at NCSU, perform

simulations for practical conditions for direct comparisons with experimental data for validation of the models.

The initial focus will be on nitramine (e.g., RDX) and nitro (e.g., nitromethane) compounds. The first step is the formulation of accurate rigid-body potentials that describe the various crystal polymorphs. This step has been essentially completed in a collaborative effort with Drs. Betsy Rice and Dan Sorescu. That work provides the starting point for the more complex models proposed here. Those models have transferable potential parameters that describe entire classes of compounds. They have been successfully applied to rigid-body isothermal-isobaric molecular dynamics (NPT-MD) and molecular packing (MP) predictions of crystal structures for a wide range of compounds, including acyclic, monocyclic, and polycyclic nitramines as well as acyclic and polycyclic nitroalkanes, nitroaromatics, hydroxy-nitro derivatives, nitrobenzonnitriles, nitrate esters and other systems consisting of molecules with functional groups common to energetic materials. The nitromethane model has been used to simulate the liquid phase and is currently being used to study melting.

The goal now is to refine and extend these models for predictions of more complex properties and processes by using the methods and results of the MURI team. We will proceed in a deliberate step-by-step fashion. The initial studies will concentrate primarily on nitromethane, RDX, and HMX, but the models will be applied to other energetic materials after being validated for these systems by comparisons with experimental data. The stages of development can be roughly outlined as follows:

- Develop intermolecular potentials and perform calculations of the physical properties of crystals. This phase of the work is essentially completed as mentioned above. We will, however, work with Drs. Ammon, Ceperley, and Martin to improve the accuracy of these models.
- Predictions of the physical and thermodynamic properties of nitramine crystals. This has been done in our earlier work with Drs. Rice and Sorescu. Comparisons with experimental data will be used to evaluate the accuracy of the models.
- Develop intramolecular potentials for flexible solid and liquid models. This has been done for nitromethane and used in simulations of the solid and liquid phases. We will next develop universal transferable force fields for general classes of energetic materials.
- Investigation of the static and dynamical properties of nitramine crystals under thermal and high pressure conditions of practical interest.
- Dynamics studies of the energy flow in crystals. Including, investigations of processes such as energy transfer in crystals subjected to uniaxial stresses.
- We will next extend the potentials to allow for crystalline phase changes and perform simulations of crystalline phase changes under various conditions, such as thermal heating, static and dynamic pressure.
- Perform simulations of melting and sublimation. In collaboration with Dr. Rice, we have already made significant progress in simulating melting in nitromethane.
- Introduce reactive potentials into the models.
- In the final phase of the work, we will perform a wide range of simulations and calculations for comparisons with experimental data to validate the models. This work will be done in collaboration with Dr. Rice.

