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Explicit particle dynamics (XPD) for multi-scale non-equilibrium chemistry (Berman-Molecular Dynamics and Theoretical Chemistry Program

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Georgia Institute of Technology

April 2013
Final Report

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Explicit particle dynamics (XPD) for multi-scale non-equilibrium chemistry (Berman — Molecular Dynamics and Theoretical Chemistry Program)

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Abstract

This on-going project is aimed at understanding the flows of fluids at high speed past obstacles that are catalytic and which may have feature sizes at lengths in the submicron regime. The effective speeds of the fluid may be as high as Mach 10. The sub-micron heterogeneity may be induced by the confinement in the boundaries of the flow field, or they may be created by non-equilibrium behavior at the molecular scales. Such regimes provide a challenge to existing continuum fluid dynamics for their accurate simulations. They also comprise a challenge to the underlying self-similarity along many length scales that is required for understanding the transition to the onset of turbulence. We have developed a multiscale code, called explicit particle dynamics (XPD) that is capable of including nonequilibrium inhomogeneities at the particle scale while including solution follows at length scales up to three to six orders of magnitude larger.

I. Introduction

Engines, projectiles and vehicles are increasingly being used under extreme operation conditions such as when rarefied chemically-reacting fluids are flowing within or around them at very high speeds (well above Mach 1.) The existing technology inside of continuum fluid mechanics (CFD) codes often fails in these regimes. This project has been aimed at creating a new class of models and theories capable of addressing this regime by combining dynamical scales of molecules and macroscopic fluids. These connections lie between the chemical and engineering communities and have consequently not received much attention up to now. Most, if not all, CFD approaches to simulate the equilibrium and dynamic behavior of fluids are based on phenomenological equations describing the continuum and chemical kinetic behavior of the underlying fluids. In principle, these phenomenological equations could be obtained from simulations of homogeneous states of (possibly reacting) fluids using modern statistical mechanics algorithms and molecular dynamics (MD) tools. However, when the molecular structure is heterogeneous and time-dependent, even this simplifying assumption breaks down. The critical challenge to address these regimes hinges on methods capable of addressing inelastic or reactive collisions within the fluid or with the surface that thereby introduce structural inhomogeneities which would not be captured by purely coarse-grained models. Our ongoing research is aimed at understanding such far-from-equilibrium dynamical processes using models at many scales, ranging from

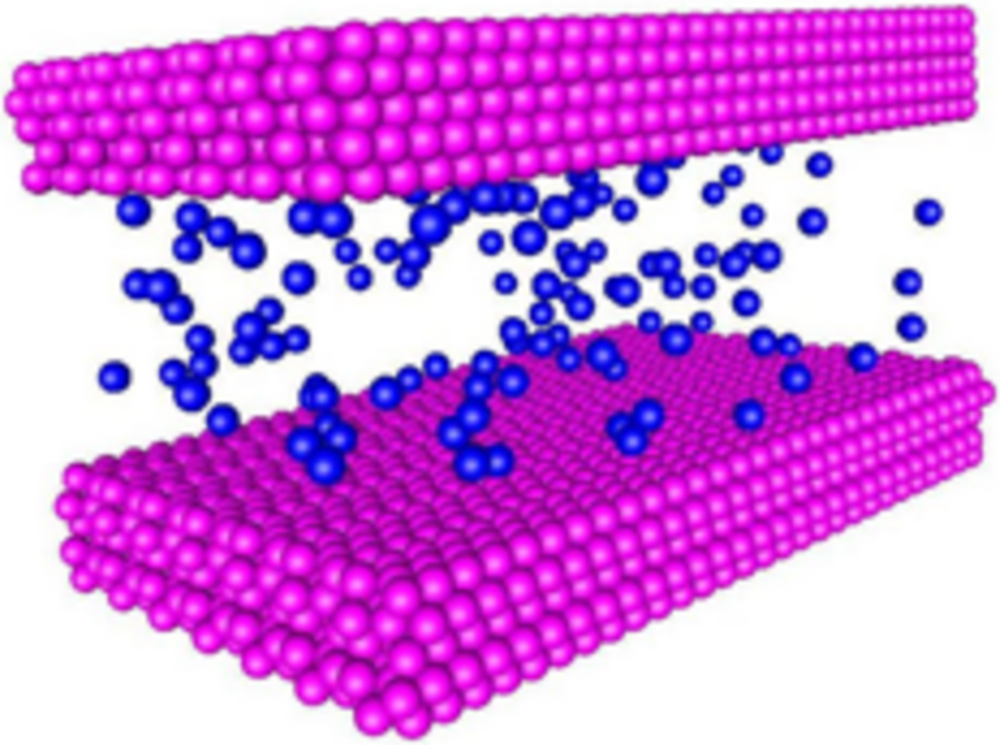

Figure 1: A sketch of a rarefied gas placed between two parallel plates. (The density has been increased for illustration.) When the plates are driven in opposite direction at fast velocities, it induces a shear on the gas.

reduced-dimensional stochastic models to atom-specified molecular dynamics simulations. This report summarizes the success of our first 3-year project funded by the AFOSR in this direction, and sets the stage for our continuing work.

II. Primary Results and Products To Date.

This ambitious project was initiated in August 2009. We have successfully performed simulations of nonreacting and reacting nitrogen atoms sheared by parallel plates at high Reynolds number–cf. the illustration in Fig. 1.[1] We are currently using the method to investigate the connection between the molecular interactions and the corresponding flow properties at high Reynolds number.[2] A connection between molecular scale models and those of coarse-grained models has been developed in the context of many-scales replica dynamics.[3] The results of this work were reported at the AFOSR Molecular Dynamics Contractor's meeting in May 2011. Several articles detailing the success of these models in describing the onset of reactivity with increasing temperature and the heterogeneity of concentration and viscosity are in preparation now.[1-3]

We have used a reduced dimensional theory to better understand the nonequilibrium (and inhomogeneous) temperature in a nanorod sliding across a surface.[4] As we learned during the 2009 AFOSR Molecular Dynamics Contractor's meeting, Hase's group[5] has performed nonequilibrium MD simulations of hydroxilated α-Al_2O_3 nanorods across a surface, and seen temperature oscillations of 1000-3000K. These unexpected oscillations were surprising because despite the steady-state boundary conditions applied to the system, they did not quench to a thermodynamic mean. Our reduced-dimensional nonequilibrium model provides a better understanding of the heat transfer method in the longitudinal and transverse directions as well as between molecules and the various heat baths of the system.[6] In so doing, it is an example of how reduced-dimensional —or coarse-grained— models can on the one hand retain important small-length scale modes, while on the other hand decimate nearly all but a few long scale modes. This is the critical step that underlies the connection between molecular dynamics and hydrodynamics driving our work.

III. Explicit Particle Dynamics (XPD)

In a rarefied gas, the collisions between particles are infrequent and take place between particles that initially may be separated by mesoscocopic to macroscopic distances. In addition, at high speeds reactions can be caused not only by encounters among gas particles, but also by collisions between gas particles and obstacles and walls. The dimensions of this system are potentially so large that it is intractable through the use of standard molecular dynamics engines. On the other hand, as discussed above, CFD and even DSMC does not include either the detailed chemistry or the ensuing long-distance correlations. Our solution is to construct a hybrid of molecular dynamics codes with event-driven dynamics allowing for substantial speed-ups during the non-interacting windows. Collisions with the walls and obstacles are also treated using effective potentials that can give rise to dissociation or even aggregation and recombination. We name the combination of these algorithms implemented within our in-house code as "eXplicit Particle Dynamics" (XPD).

Additional details of the event-driven XPD are:

1. Between collisions, unbound atoms are propagated freely, that is, at constant velocities;
2. Between collisions, the vibrational motion of atoms in molecules is governed by cor- responding attractive adiabatic potentials (pairwise potentials in the case of diatomic molecules);
3. During a collision the attractive potentials are retained for atoms in molecules (bound atoms) or for free atoms;
4. During a collision all atoms within proximity contribute to the total interaction (and reactive) potential.

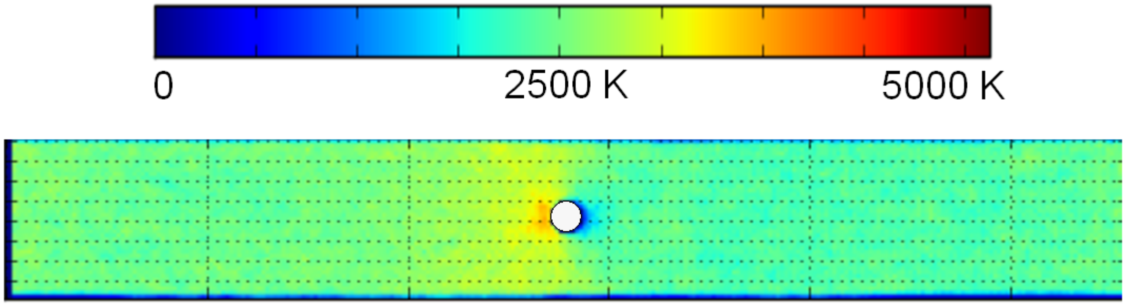

Figure 2: Instantaneous temperature of nitrogen at 5,000 K flowing from left to right through a cuvette with a cylinder obstacle. The flow velocity is V_{fl}=3,000 m/s. The cuvette dimensions are 30nm × 210nm × 8nm.

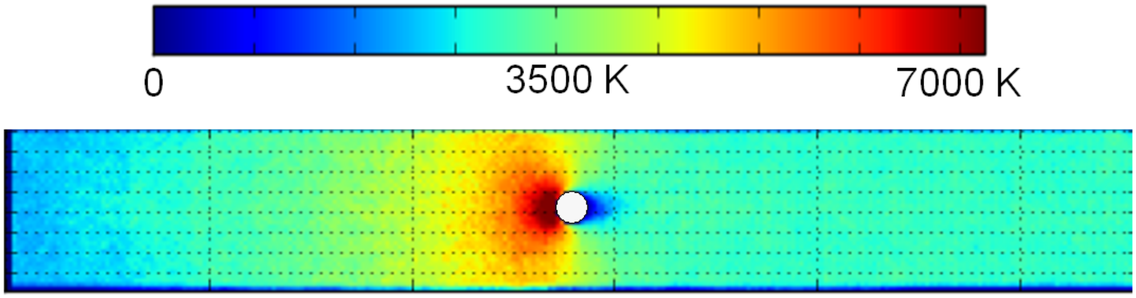

Figure 3: The same as in Fig. 3 except that T = 7, 000 K and V_{fl}=10,000 m/s.

The dimensions of the mixed nitrogen flowing system that is accessible through XPD are presently in the submicron regime though we expect to push them beyond this barrier in the near future. The temperature inhomogeneity typical of these systems is illustrated in Figs. 2 and 3 under different boundary conditions. Several important features of the XPD are notable: First, it is truly a particle model in which all the atoms and molecules are fully specified, and their dynamics is fully obtained (albeit for an approximate potential). The potentials of the approximate model of the previous subsection lead to correct thermodynamic properties within the XPD. It also accounts for the resulting energy exchanges from chemical reactions.

We performed a series of 3D XPD simulations of nitrogen mixtures in sub- and supersonic flows through cuvettes with and without obstacles. The model system is initialized with 5,400 nitrogen molecules. The cuvette dimensions are L_x = 210 nm, L_y = 8 nm, and L_z = 30 nm. The asymmetry accounts for the flow along the x-axis, the presence of boundary walls at the top and bottom of the z window, and the periodic fluid boundary condition along y. These boundary conditions are similar to those used by Ishiwata and coworkers.[7] The right and left boundaries (along x) are connected periodically so as to ensure mass conservation, but it does impose a periodicity along the flowing direction. The parallel boundary walls (separated by a distance L_z) are represented by several aluminum layers with the geometry of an fcc

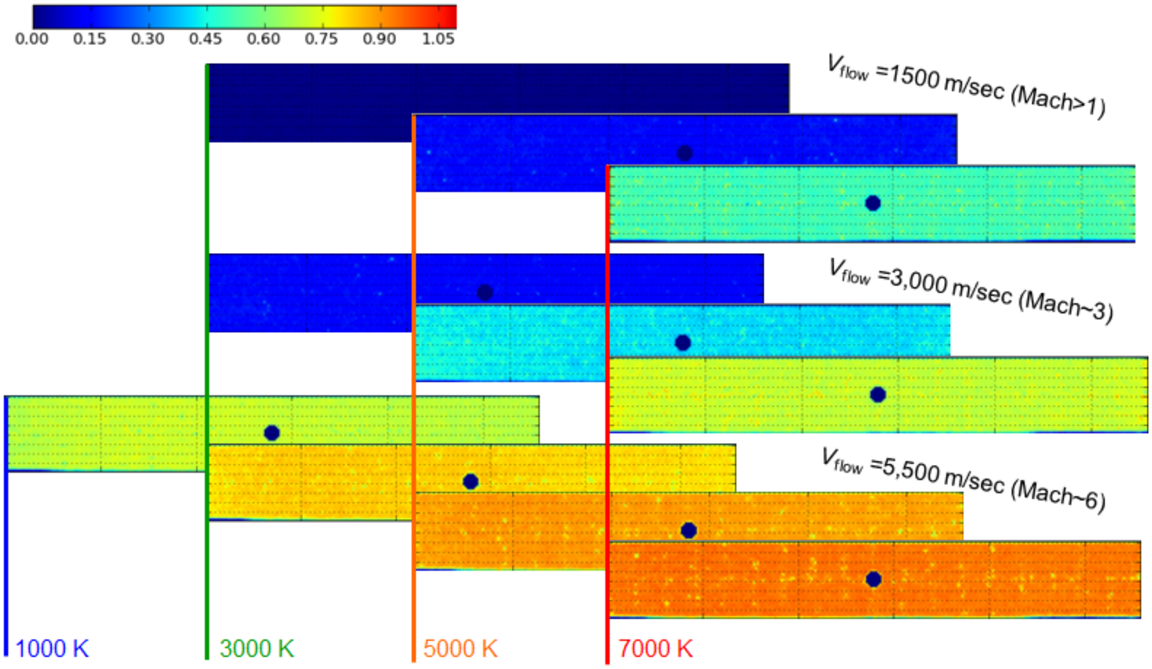

Figure 4: The instantaneous distribution of atomic nitrogen relative to diatomic nitrogen shown through its mole fraction, X_N, at different temperatures and flow velocities.

crystal structure as indicated in the sketch of Fig. 1. The outermost layers are always equilibrated to the imposed thermal temperature T of the environment. In the simulations, we used three and five layers in the substrates with no difference in the results. The flow speed V_{fl} is reestablished for each particle when the latter leaves the box at the right end and enters it from the left side. A new velocity for such particle is sampled from the Maxwell distribution with the x-component shifted at V_{fl}.

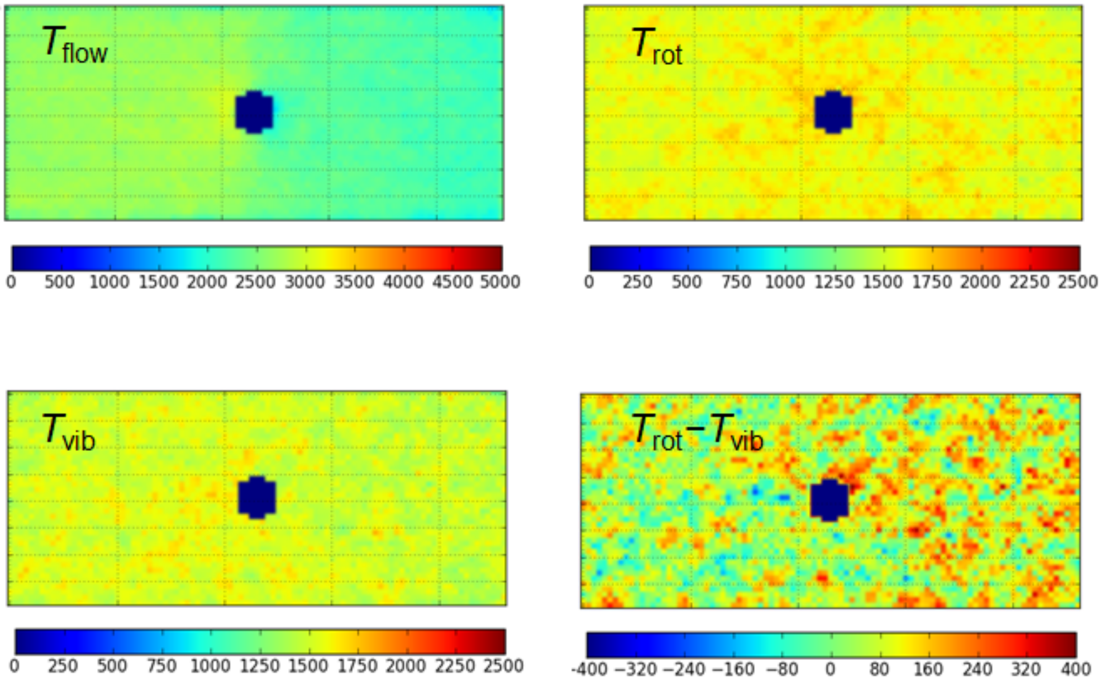

Figure 5: Instantaneous temperatures of nitrogen in the vicinity of the cylindrical obstacle at 3,000 K. The flow velocity (from left to right) is V_{fl}=1,500 m/s. Upper left panel: temperature within the flow; upper right panel: rotational temperature of N_2; lower left panel: vibrational temperature; lower right panel: difference between T_{rot} and T_{vib}.

The resulting temperature distributions in a highly supersonic flow are shown in Figs. 2 and 3 for 5000K and 7000K, respectively. It is notable that there is significant heating of the particles at the higher of these temperatures. Nevertheless, this inhomogeneity gives little warning about the dramatic variation in composition of the gas mixture with varying temperature. The latter is illustrated in Fig. 4. This is particularly notable because it differs dramatically to that seen at the lowest temperatures, and also to the higher-scale distribution seen in a macroscopic cuvette by Briones and coworkers.[8]

We also found that the periodic obstacle can play the role of a catalyst for the nitrogen dissociation causing a quick change in the kinetic energy of the particles. It resembles the shock-induced combustion effect[9] in the sense that a quick change of the conditions of the flow —the speed of molecules in our case— initiates the reaction. On the average, the dissociation is higher at higher temperatures and faster flows. But at very fast flow (V_{fl}= 10,000 m/s) at 7,000 K the atomic nitrogen composition becomes somewhat less. Most probably, this is because the obstacle is not capable to “catch” the same amount of molecules in this regime. This process changes the thermodynamic properties of the flow and may cause other effects if the gas has different composition. Rotational and vibrational temperatures of the nitrogen molecules form almost evenly colored panels (Fig.5), although their difference indicate that the rotational degrees of freedom become more excited after the flow passes the obstacle. This suggests that the geometry of the obstacles as well as the form of the cuvette will lead to new outcomes for the temperature and composition distribution, and the excitation of the rotational motion can be a sign of the onset of turbulence, though this has yet to be confirmed.

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