(YIP) Internal Energy Transfer and Dissociation from First Principles Simulations

T. E. Schwartzentruber --- FA9550-10-1-0075 --- U of Minnesota

Studying internal energy transfer and dissociation in shock layers using computational chemistry

STATUS QUO

Empirical Rate Models

•Empirical models based on few experiments and extrapolated to very high temperatures

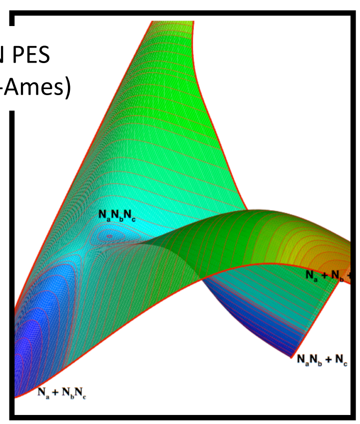
•Landau-Teller vibrational excitation, with Millikan and White rates, Park's high-T correction, and Park's T-Tv dissociation model

•Vibration-dissociation model important since gas-phase chemistry and transport through the boundary layer determines boundary conditions for gas-surface interactions

NEW INSIGHTS

Rate Models based on Computational Chemistry

• Combine advances in high-performance computing with state-of-the-art quantum chemistry calculations to develop new models for use in multi-T hypersonics CFD codes



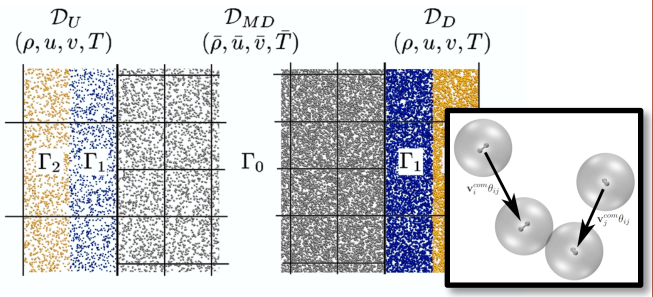
• Collaboration with chemists to model individual collisions and generate new reaction cross-section data.

MAIN ACHIEVEMENTS:

• A novel method for efficient pure computational chemistry simulations of flow features in dilute gases "Event-Driven/Time-Driven Molecular Dynamics"

• Published: *Phys. of Fluids 2009* and *J. Comp. Phys. 2009*

HOW IT WORKS:

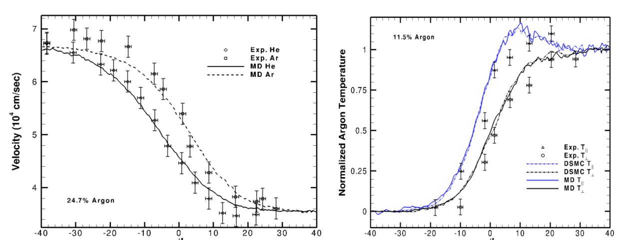


•Molecules are advanced directly to their next collision, then undergo accurate "soft" collisions using arbitrary inter-atomic potential, including multi-body collisions

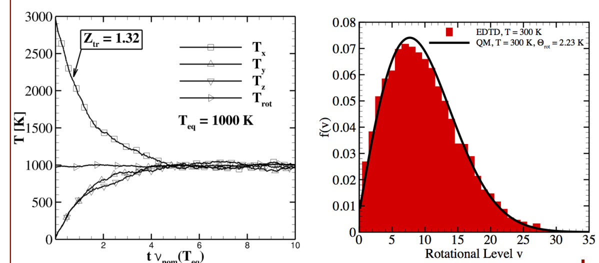
•For first time, enables shock wave simulations where the only model is the inter-atomic potentials between atoms

Shock Wave Simulations Results

•Results for Argon and Argon-Helium mixture shock waves are in excellent agreement with experiment and DSMC



Rotational Relaxation/Excitation Heat Bath Sims



QUANTITATIVE IMPACT

ASSUMPTIONS AND LIMITATIONS:

•Pure computational chemistry solutions to nonequilibrium fluid problems

•Tractable for symmetric (1D) flows only, such as shock waves and stagnation lines

Current Impact

•Results obtained for monatomic simple gases, monatomic gas mixtures, and diatomic gases, for comparison with DSMC

END-OF-PHASE GOAL

Planned Impact

• Investigate translational-rotational-vibrational energy exchange with new PES for nitrogen provided by computational chemists

•Investigate vibration-dissociation coupling

Research Goals

•Develop new models for trans-rot-vib-diss energy transfer (consistent with chemistry theory *and* validated with experiment) for use in DSMC and CFD solvers

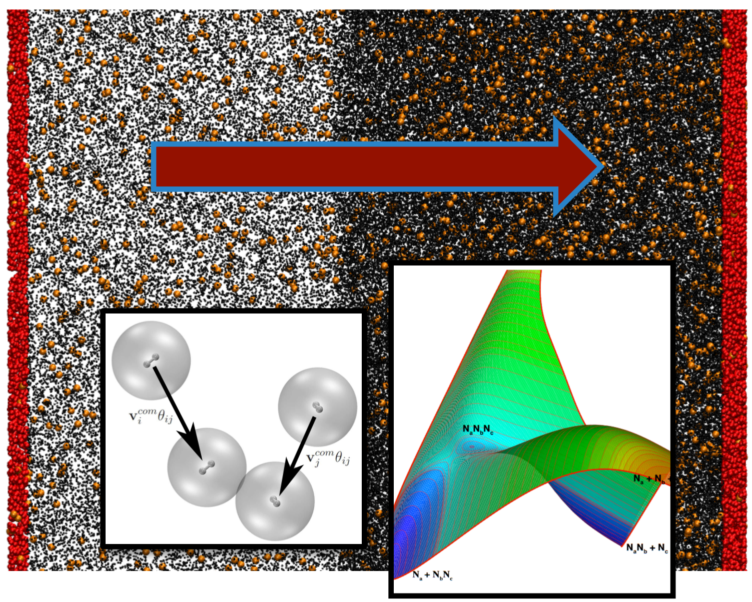
Pure Molecular Dynamics Simulation of Shock Waves Is Now Possible

New tool to study internal energy transfer in hypersonic flows

- No equation of state, transport models, or rate models required
- Inter-atomic forces provided by computational chemists are the sole model, directly linking chemistry and aero communities
- Dominant internal energy transfer mechanisms can be analyzed and reduced models formed
- Enabled by large-scale computing[1] and a novel numerical method[2]

[1]Valentini and Schwartzentruber, *Physics of Fluids*, 21 (2009)

[2]Valentini and Schwartzentruber, *Journal of Computational Physics*, Vol. 228, No. 23 (2009)

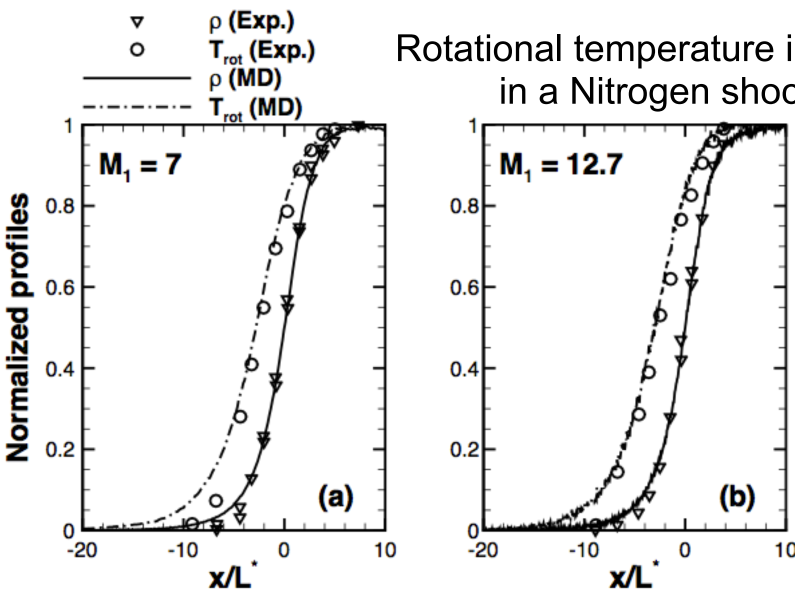


Dr. Schwartzentruber

Assistant Professor

- 2011 Visiting Professor, *von Karman Institute*
- AFOSR *Young Investigator Award* (2009)
- 2007 AIAA *Orville and Wilbur Wright Award*

Validation with experimental shock wave data:
2009 – Monatomic (Ar) - complete
2011 – Mixtures (Ar-He, Xe-He) - complete
2012 – Rotation (N_2) - complete
2012 – Vibration (N_2) … in progress

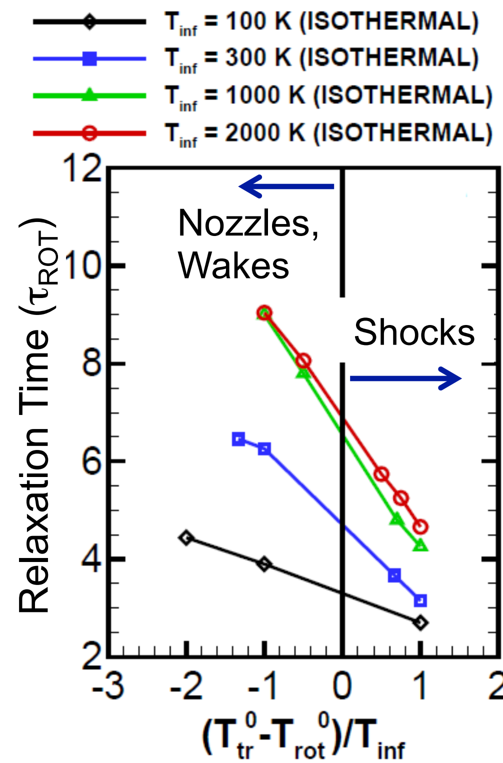


Rotational temperature increase in a Nitrogen shock wave.

- "All-atom" simulations **in excellent agreement with experimental shock wave data (above)**
- Results provide a wealth of data used to develop new **reduced-order models**

A New Model for Rotational Relaxation

- Molecular Dynamics simulations clearly show that rotational excitation (*compressing flows*) is fast while rotational de-excitation (*expanding flows*) is slow



Old Model:
$\tau_{ROT} = f\,(T_{TRA})$ only

New Model:
$\tau_{ROT} = f\,(T_{TRA}\,,\,T_{ROT})$

The new, reduced-order model is now accurate in all (compression *and* expansion) regions

Is this also true for vibrational energy??