



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

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

STATUS QUO

Empirical Rate Models

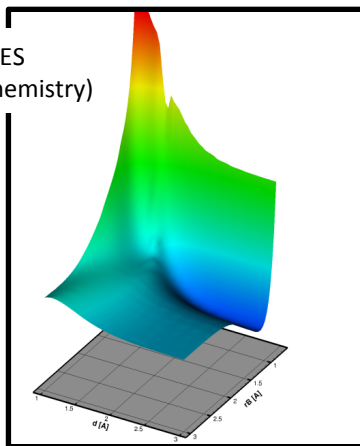
- Empirical models based on few experiments and extrapolated to very high temperatures
- Landau-Teller vibrational excitation, with Millikan and White rates, Park's high-T correction, and Park's T-Tv dissociation model
- Vibration-dissociation model important since gas-phase chemistry and transport through the boundary layer determines boundary conditions for gas-surface interactions

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

N_2+N_2 PES
(Minnesota Chemistry)

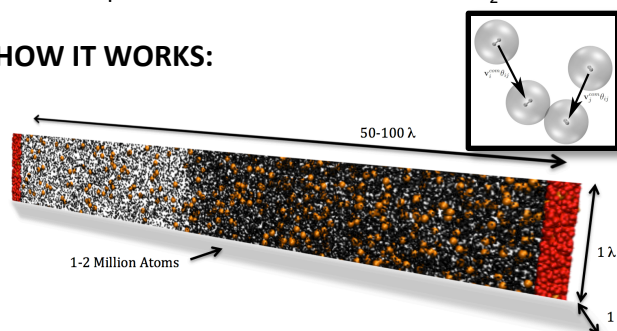
- Collaboration with chemists to model individual collisions and generate new reaction cross-section data.



MAIN ACHIEVEMENTS:

- "Trajectory-based DSMC" method enables direct simulation of 1D, 2D, and even 3D hypersonic flow fields using computational chemistry models only
- New "direction-dependent" rotation model for N_2
- New coupled rotation-vibration model for N_2

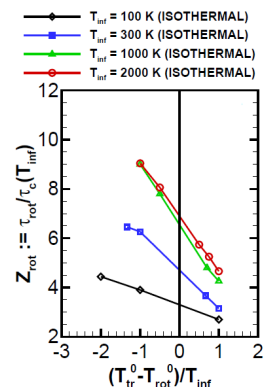
HOW IT WORKS:



- 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 flow simulations where the only model is the inter-atomic potentials between atoms

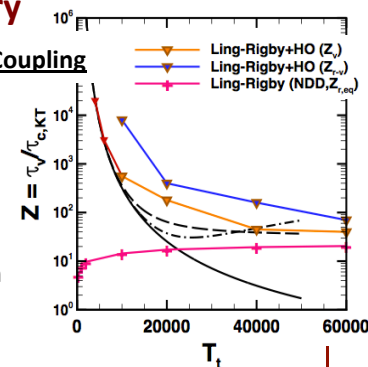
"Direction-Dependent" Rotation Model for DSMC/CFD

- Compressing flows involve fast rotational excitation, expanding flows involve slower rotational relaxation, for the same equilibrium temperature
- New rotation model consistent between Chemistry-DSMC-CFD and agrees with experiment



Rotation-Vibration Coupling

- Rotation and vibration equally important at high temperatures
- A new coupled Rotation-vibration parameter ($\tau_{rot-vib}$) proposed



ASSUMPTIONS AND LIMITATIONS:

- Pure computational chemistry solutions to nonequilibrium fluid problems
- Requires accurate potential energy surface
- ~100 times more expensive than DSMC

Current Impact

- New consistent models for rotation and coupled rotation-vibration energy exchange have been developed

Planned Impact

- Investigate rotation-vibration coupling to dissociation and develop new models
- Incorporate state-of-the-art interatomic potentials from leading chemists

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

QUANTITATIVE IMPACT END-OF-PHASE GOAL



Dr. Schwartzentruber

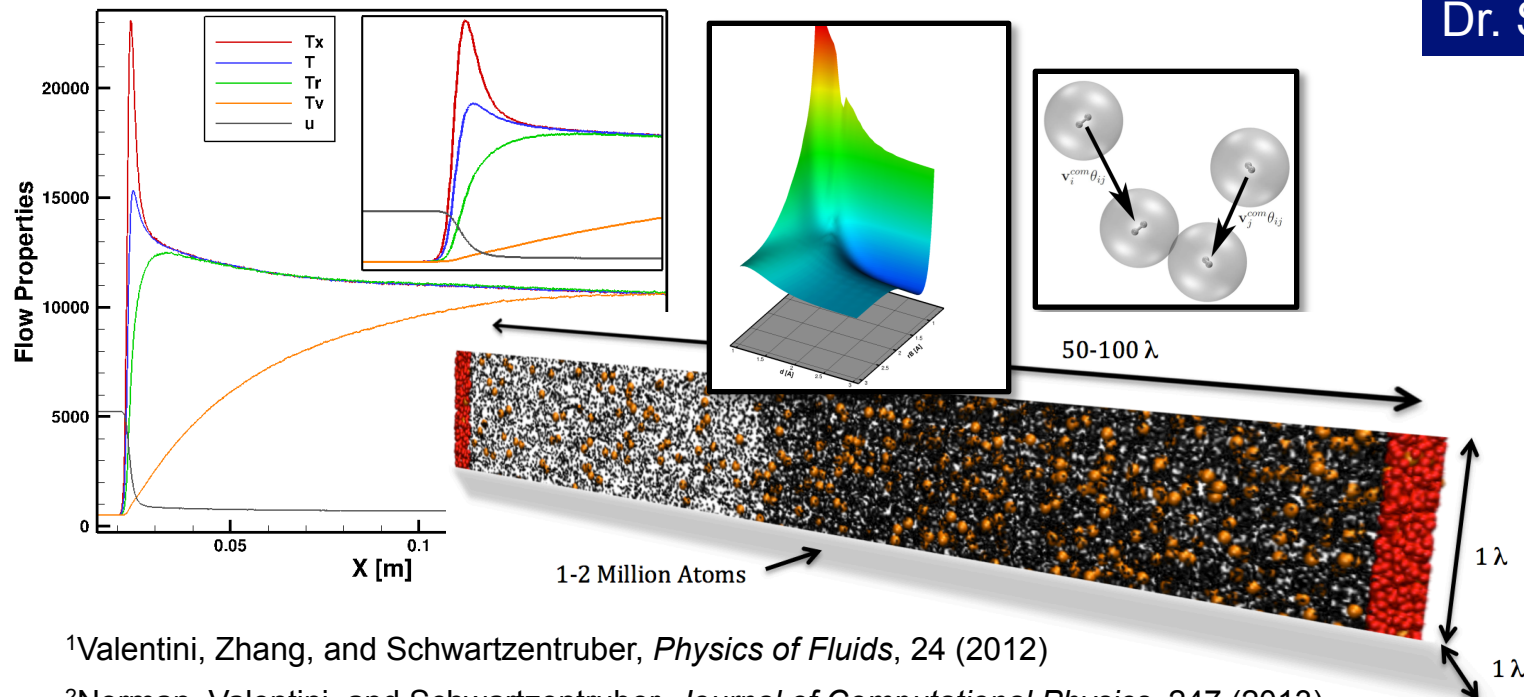
Assistant
Professor

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

Direct Molecular Simulation Links Computational Chemistry to Aerothermodynamics

New tool to study internal energy transfer in hypersonic flows

- No viscosity, diffusion, rotation, vibration, dissociation models required
- Inter-atomic forces provided by computational chemists are the sole model
- Enabled by large-scale computing¹ and a novel numerical method²

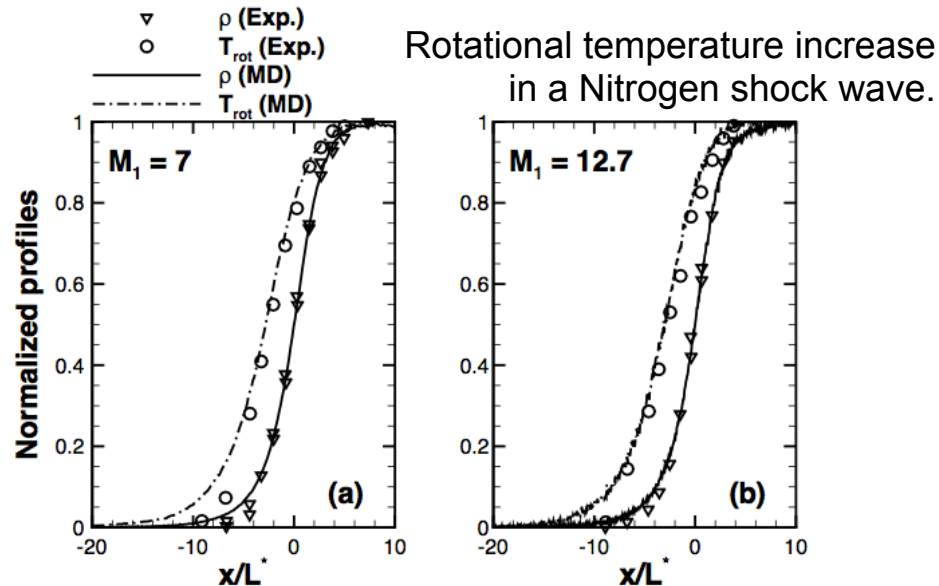


¹Valentini, Zhang, and Schwartzentruber, *Physics of Fluids*, 24 (2012)

²Norman, Valentini, and Schwartzentruber, *Journal of Computational Physics*, 247 (2013)



Validation with experimental shock wave data:
 2011 – Mixtures (Ar-He, Xe-He) - complete
 2012 – Rotation (N_2) - complete
 2013 – Ro-Vibration coupling (N_2) – complete
 2013 – Dissociation (N_2) – in progress

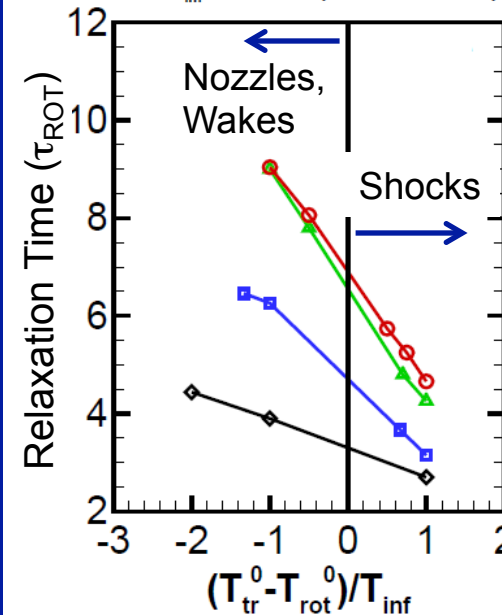


- “All-atom” simulations in excellent agreement with experimental shock wave data (above)
- Results provide a wealth of data used to develop new reduced-order models

A New Model for Rotational Excitation

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

- $T_{inf} = 100$ K (ISOTHERMAL)
- $T_{inf} = 300$ K (ISOTHERMAL)
- $T_{inf} = 1000$ K (ISOTHERMAL)
- $T_{inf} = 2000$ K (ISOTHERMAL)



Old Model:

$$\tau_{ROT} = f(T_{TRA}) \text{ only}$$

New Model:

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

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

We find this trend does not occur for vibrational energy