# Direct Molecular Simulation of Nonequilibrium Flows

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**Aerospace Engineering and Mechanics**

**University of Minnesota**

AFOSR Young Investigator Program

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UNIVERSITY OF MINNESOTA
Driven to Discover℠

# Direct Molecular Simulation

- Nearing the point where we can directly simulate high-speed (thermochemical) nonequilibrium flows with quantum mechanics

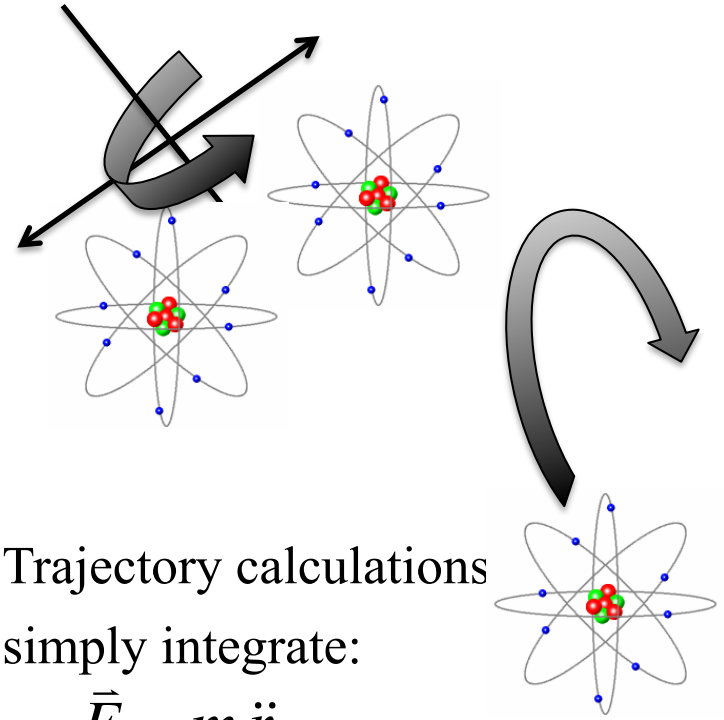
Flows consist of many collisions, each involving 2-6 atoms

Collisions are modeled with quantum mechanics by Physicists and Chemists


- Large-scale computing and the nature of dilute gases will enable the direct simulation of practical flows

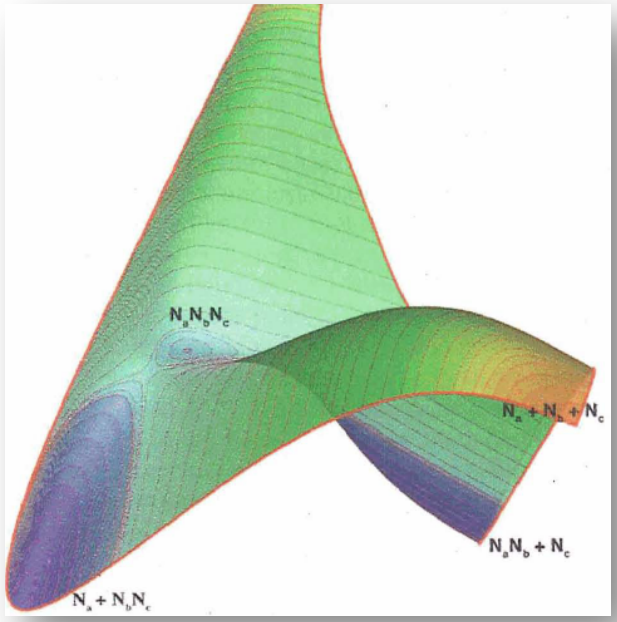
# Current Use of Computational Chemistry

1. Quantum mechanical (QM) energy calculations
2. Fit a potential energy surface (PES)



Trajectory calculations simply integrate:

$$\vec{F}_i = m_i \ddot{\vec{r}}_i$$




Analytical function that inputs atomic positions and returns atomic forces

# Current Use of Computational Chemistry

1. Quantum mechanical (QM) energy calculations
2. Fit a potential energy surface (PES)

Create cross-section-based thermochemical models…

3. Employ DSMC or CFD to obtain shock-layer flow solution

# Current Use of Computational Chemistry

1. Quantum mechanical (QM) energy calculations
2. Fit a potential energy surface (PES)

   - perform millions/billions of trajectories
   - compute state-state cross-sections (thousands)
   - typically bin cross-sections (separate rotation, vibration, electronic, and possibly group states)
   - implement in state-resolved DSMC or in master-equation CFD code (equipartition/detailed balance)
   - thermally average cross-sections to form reduced-order rate models for DSMC and CFD

3. Employ DSMC or CFD to obtain shock-layer flow solution

# Direct Molecular Simulation

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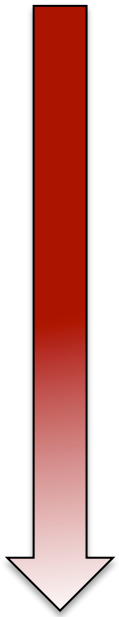
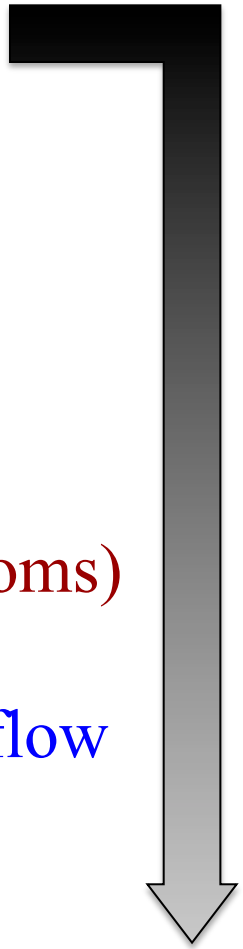


2.1 Pure Molecular Dynamics (all-atom)

2.2 Event-Driven MD (accel. all-atom)

2.3 Trajectory-based DSMC (accel. subset of atoms)

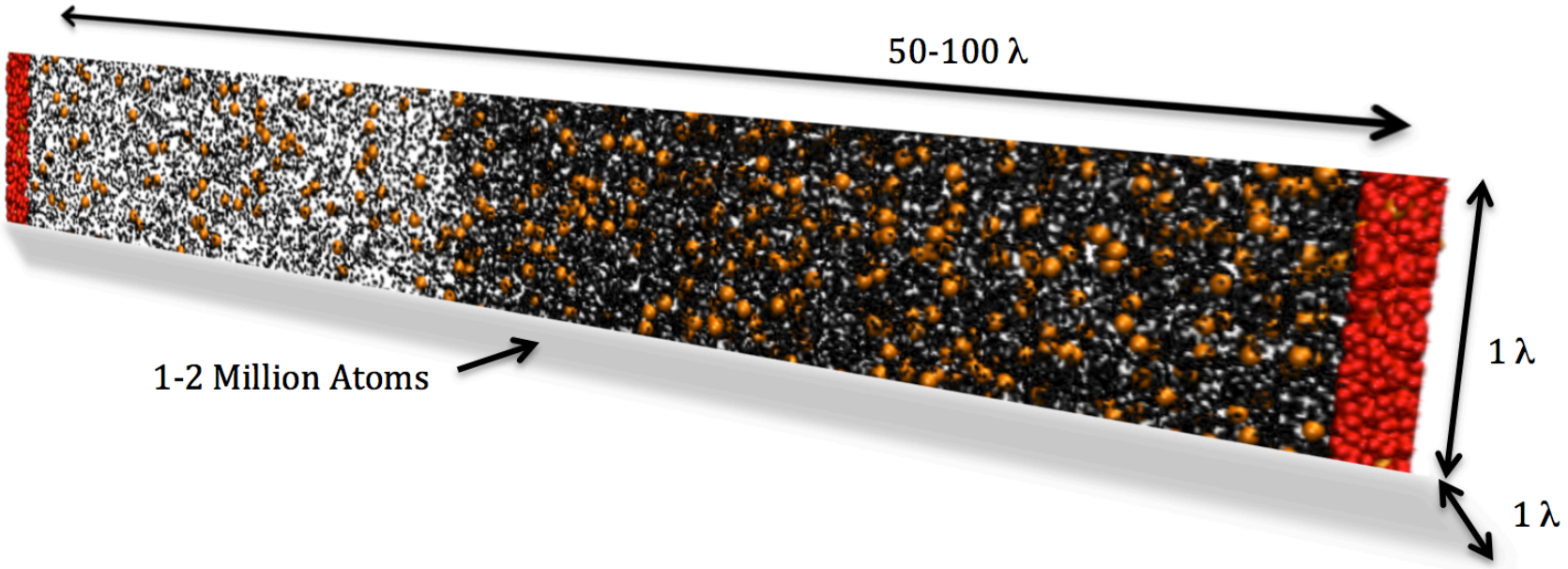
2.4 Direct molecular simulation of shock-layer flow



3. Employ DSMC or CFD to obtain shock-layer flow solution

# All-Atom Molecular Dynamics for Shock Waves

- Pure MD, millions of atoms, millions of timesteps, millions of collisions
- No adjustable parameters, ex. LJ-potential for Argon, Helium, Xenon, and nitrogen (vibrational ground state) are non-negotiable
- Can use freely-available LAMMPS MD code from Sandia



# Pure Argon

Valentini, and Schwartzentruber, "Large-scale Molecular Dynamics Simulations of Normal Shock Waves in Dilute Argon", ***Physics of Fluids***, 21, 066101, pp. 1-9, 2009.

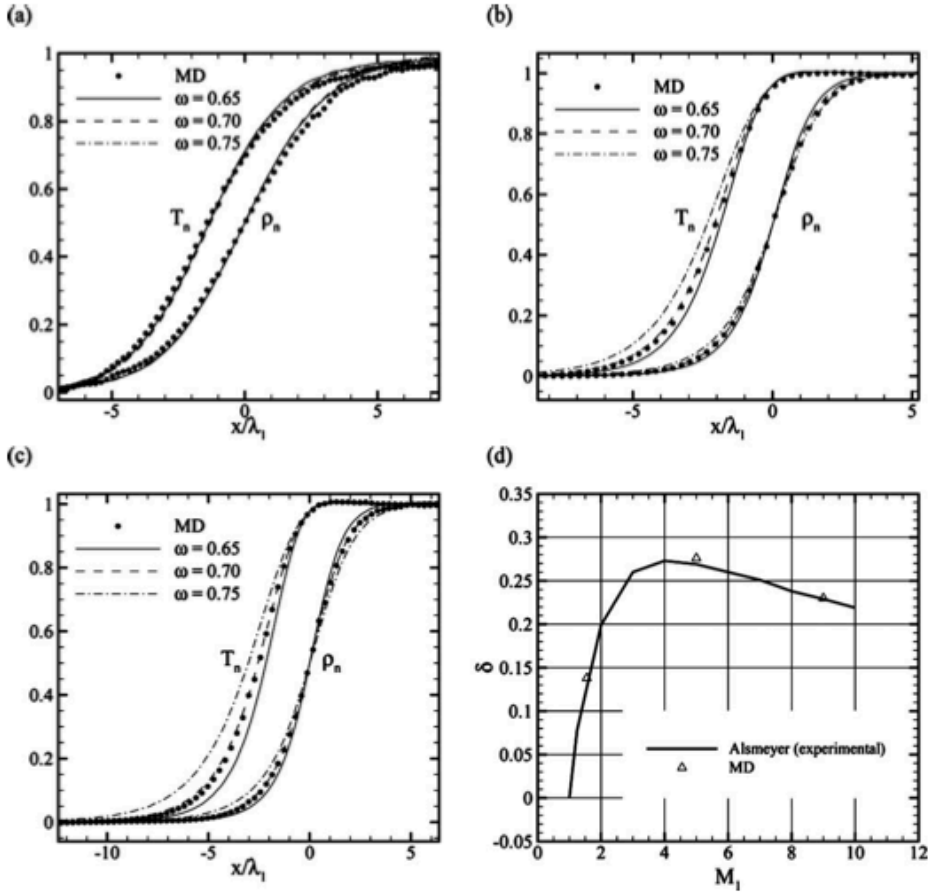



FIG. 3. Comparison between MD and DSMC temperature and density profiles for (a) $M_1$=1.55, (b) $M_1$=5, (c) $M_1$=9; (d) reciprocal shock thickness.

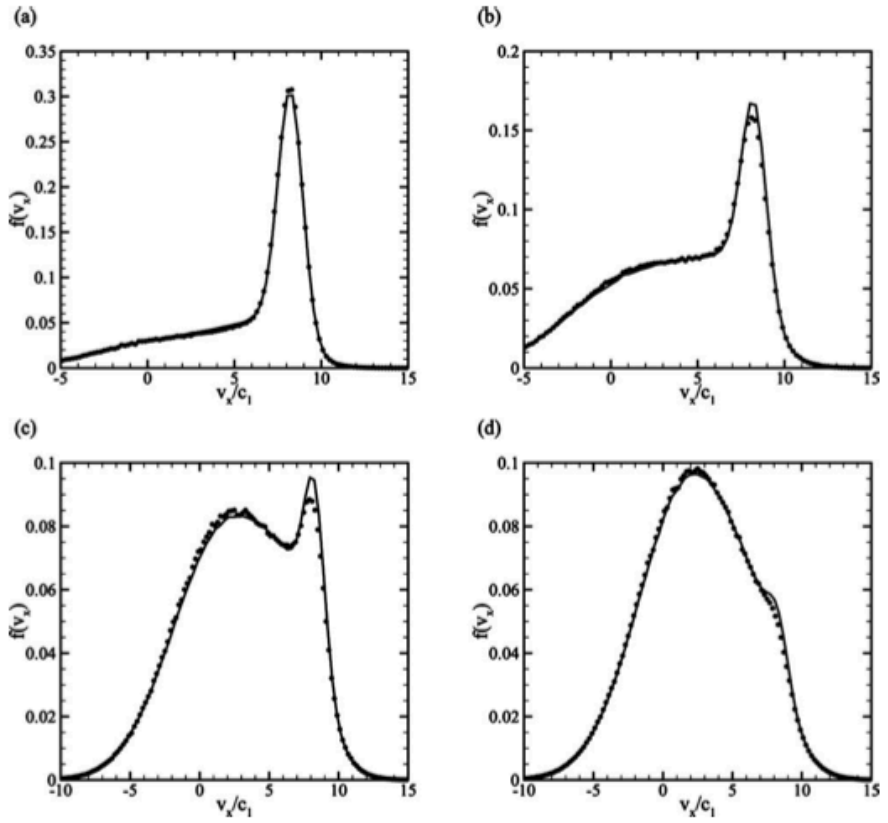



FIG. 6. Perpendicular vdf for $M_1$=9 (DSMC is the solid line, MD are circles). (a) $\rho_n$=0.148 (DSMC) and $\rho_n$=0.144 (MD), (b) $\rho_n$=0.330 (DSMC) and $\rho_n$=0.348 (MD), (c) $\rho_n$=0.540 (DSMC) and $\rho_n$=0.561 (MD), and (d) $\rho_n$=0.743 (DSMC) and $\rho_n$=0.762 (MD).

# Xenon-Helium and Argon-Helium Mixtures

Valentini, Tump, Zhang, and Schwartzentruber, "Molecular dynamics simulations of shock waves in mixtures of noble gases", *under review,* ***Journal of Thermophysics and Heat Transfer***, Feb. 2012.

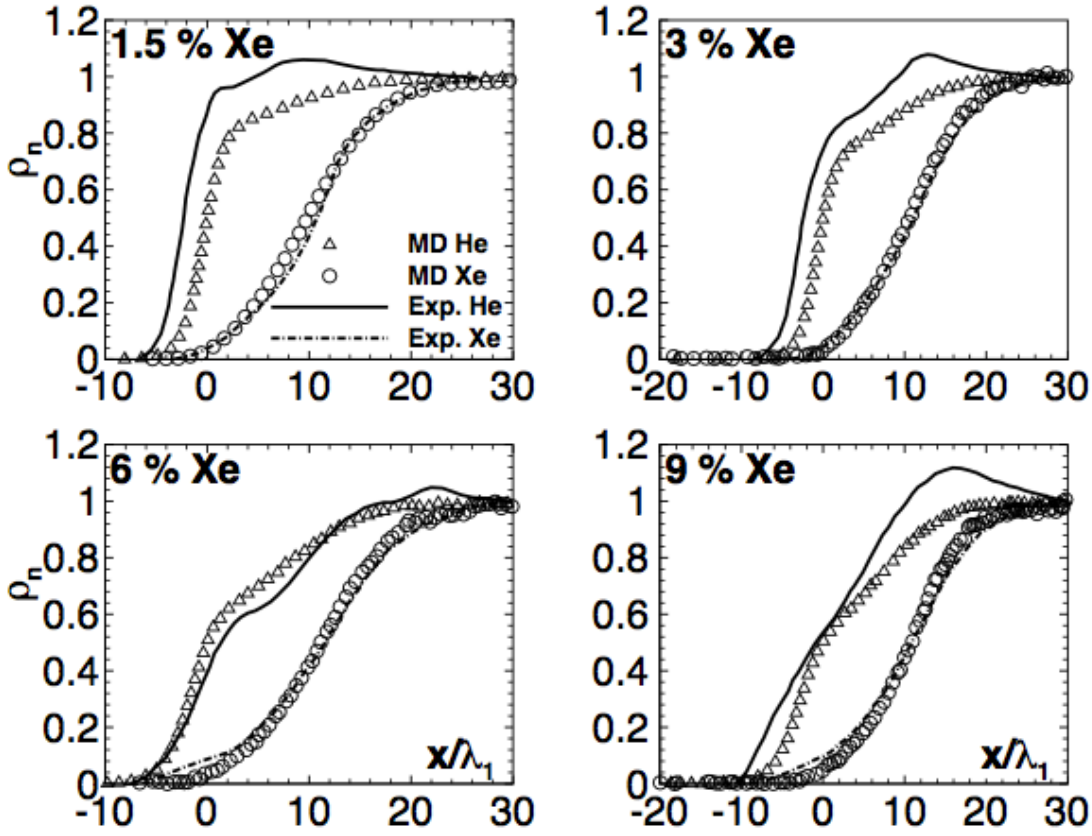



Figure 3: Species normalized density profiles obtained with MD and compared to the experimental measurements of Gmurczyk and co-workers.[19] $\lambda_1$ values are listed in Tab. 2 for each case.

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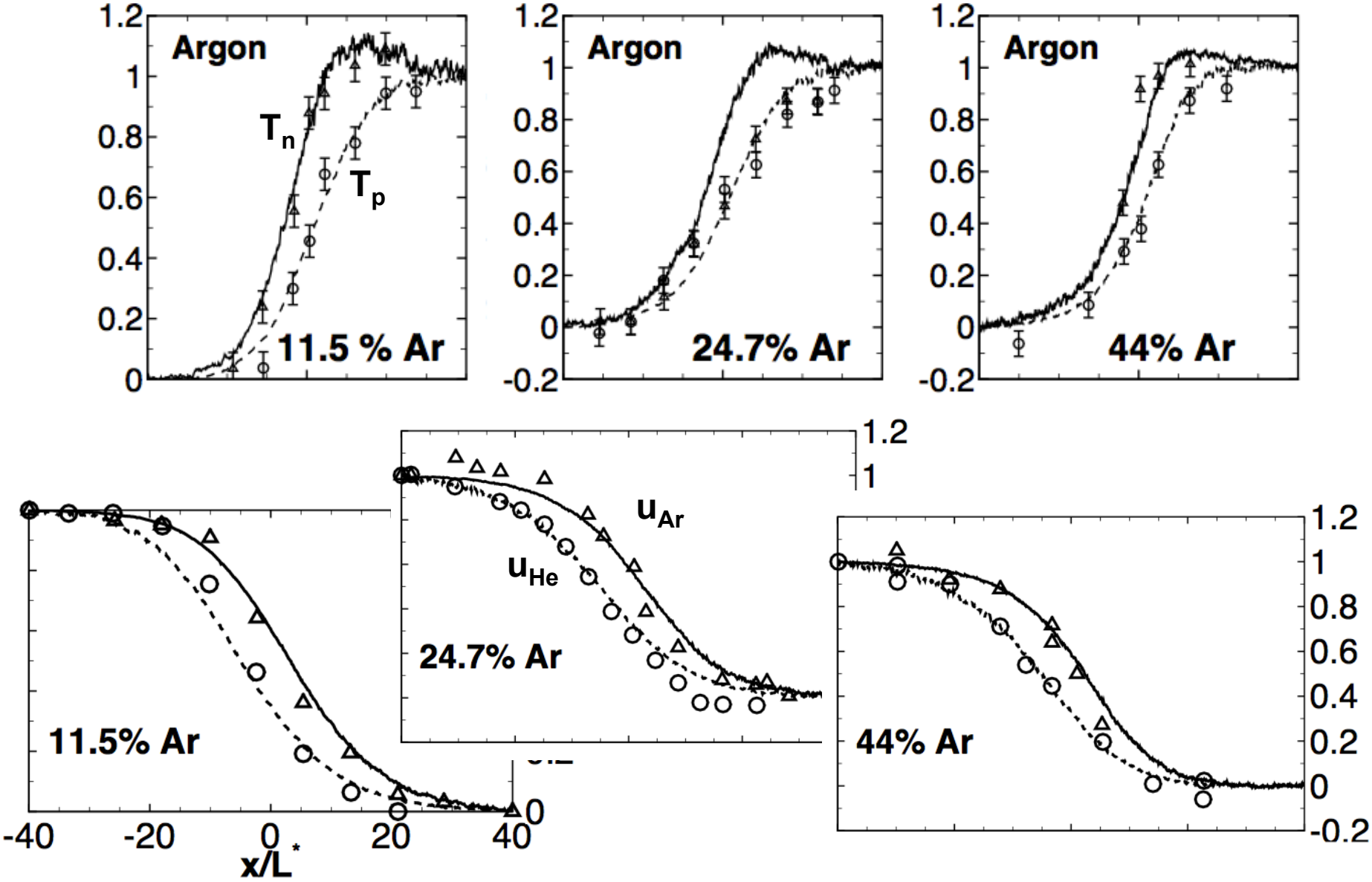
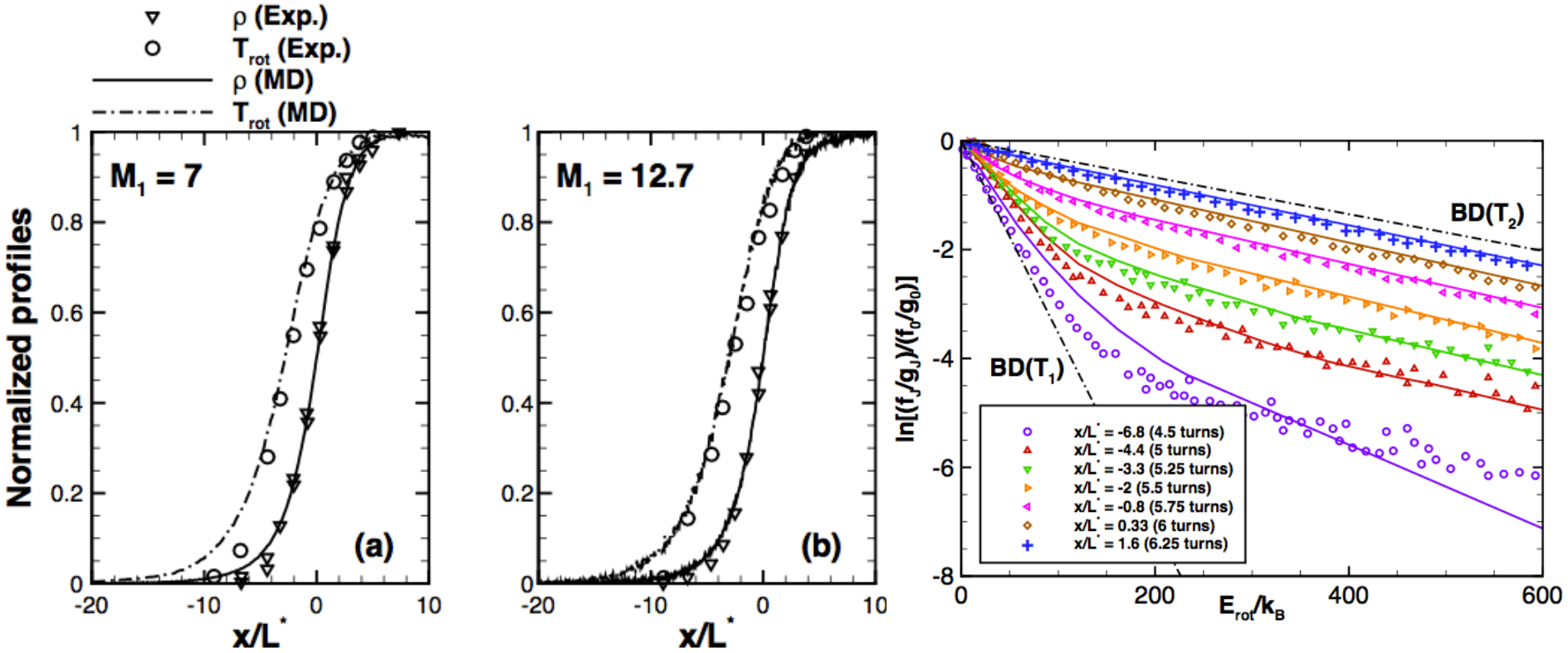


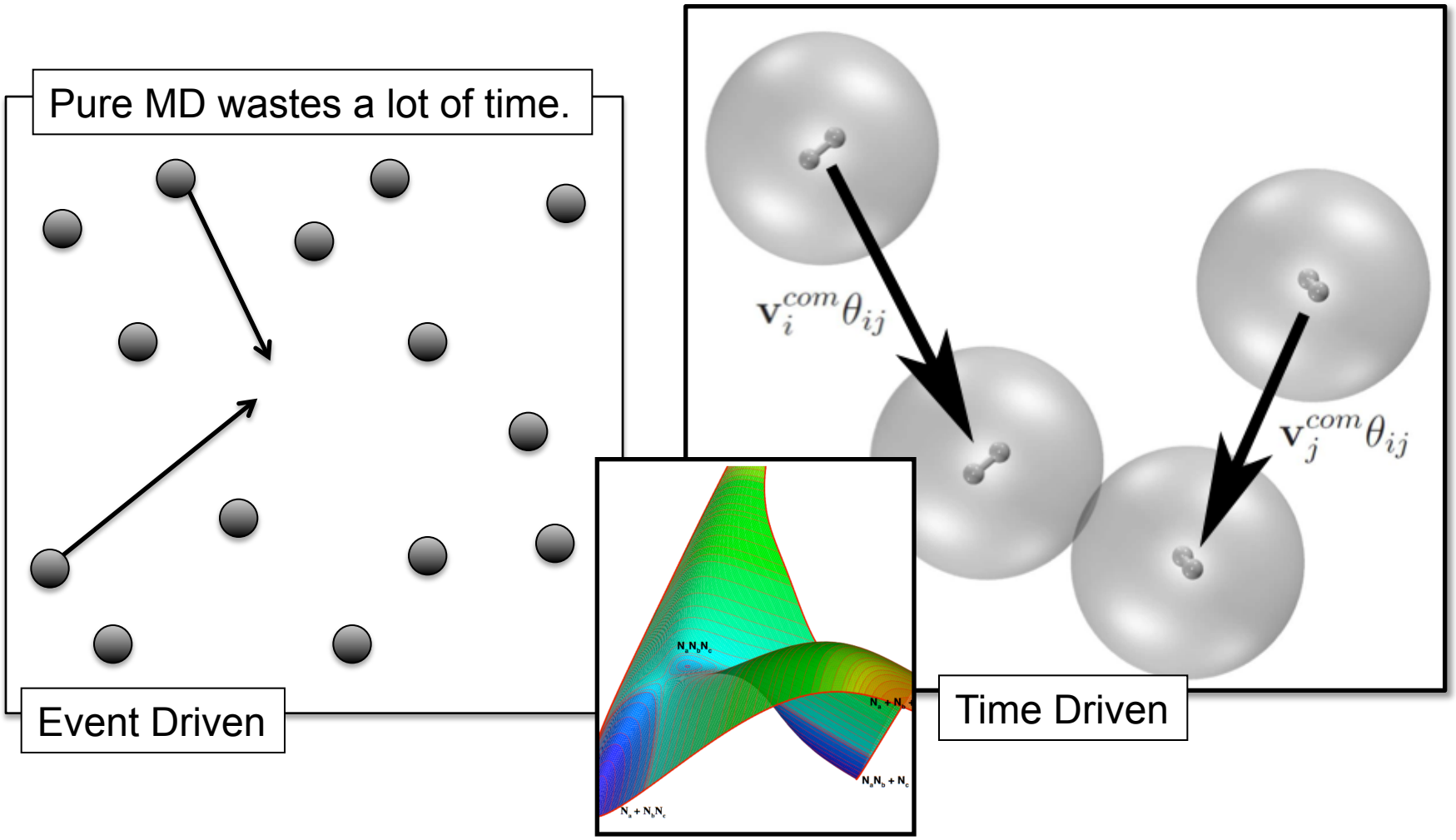
# Diatomic Nitrogen

Valentini, Zhang, and Schwartzentruber, "Molecular dynamics simulation of rotational relaxation in nitrogen: implications for rotational collision number models", *under review,* ***Physics of Fluids***, May, 2012.



# Combined Event-Driven / Time-Driven MD

Valentini and Schwartzentruber "A Combined Event-Driven/Time-Driven Molecular Dynamics Algorithm for the Simulation of Shock Waves in Rarefied Gases", ***Journal of Computational Physics***, 228 (2009) 8766-8778.



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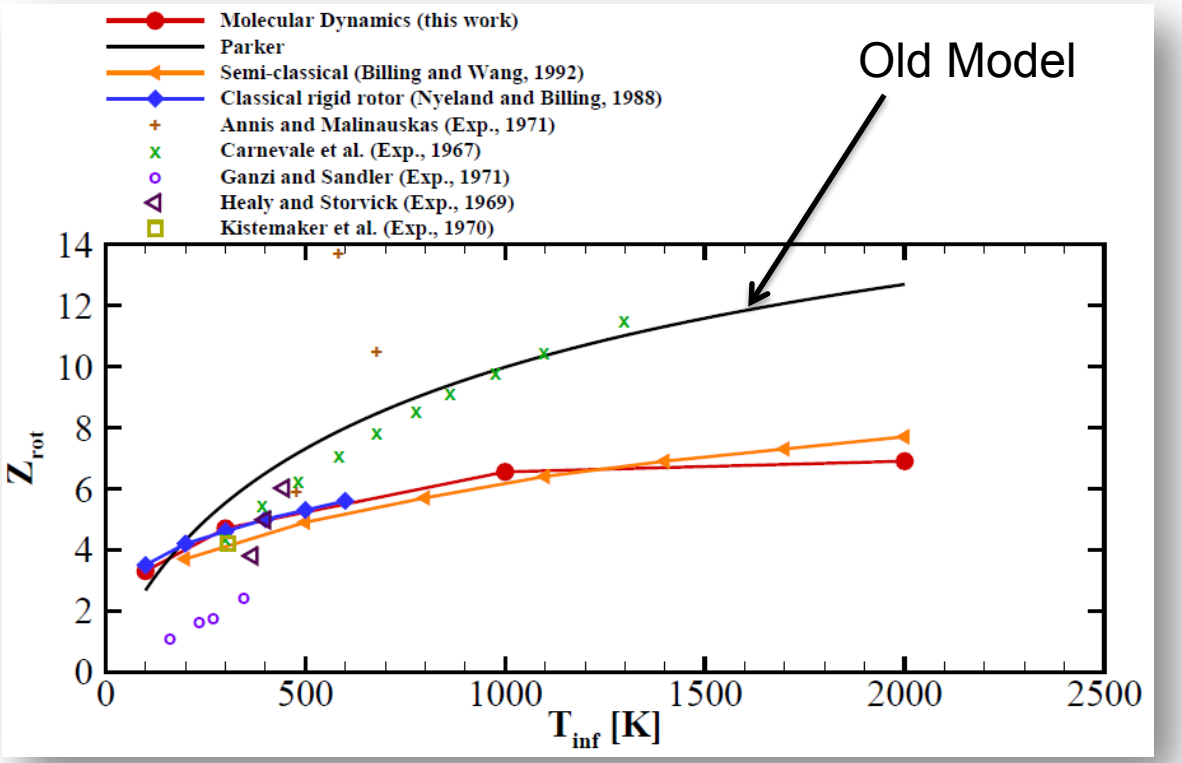
- ED/TD MD algorithm detects and advances simulation to impending interactions, while accurately integrating each interaction using conventional Time-Driven (TD) MD.
- Multi-body interactions are also detected and simulated.
- Recently extended to polyatomic molecules including chemical reactions
- For example, the time of an impending collision is:

$$\theta_{ij} = \frac{(-\mathbf{v}_{ij} \cdot \mathbf{r}_{ij}) \pm \sqrt{(\mathbf{v}_{ij} \cdot \mathbf{r}_{ij})^2 - \mathbf{v}_{ij} \cdot \mathbf{v}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{r}_{ij} - r_c^2)}}{(\mathbf{v}_{ij} \cdot \mathbf{v}_{ij})}$$

- Pure MD shocks: ~128 cores for 4 days
- ED/TD MD shocks: 1 core for 10 days (~50x faster - **exactly** the same result)

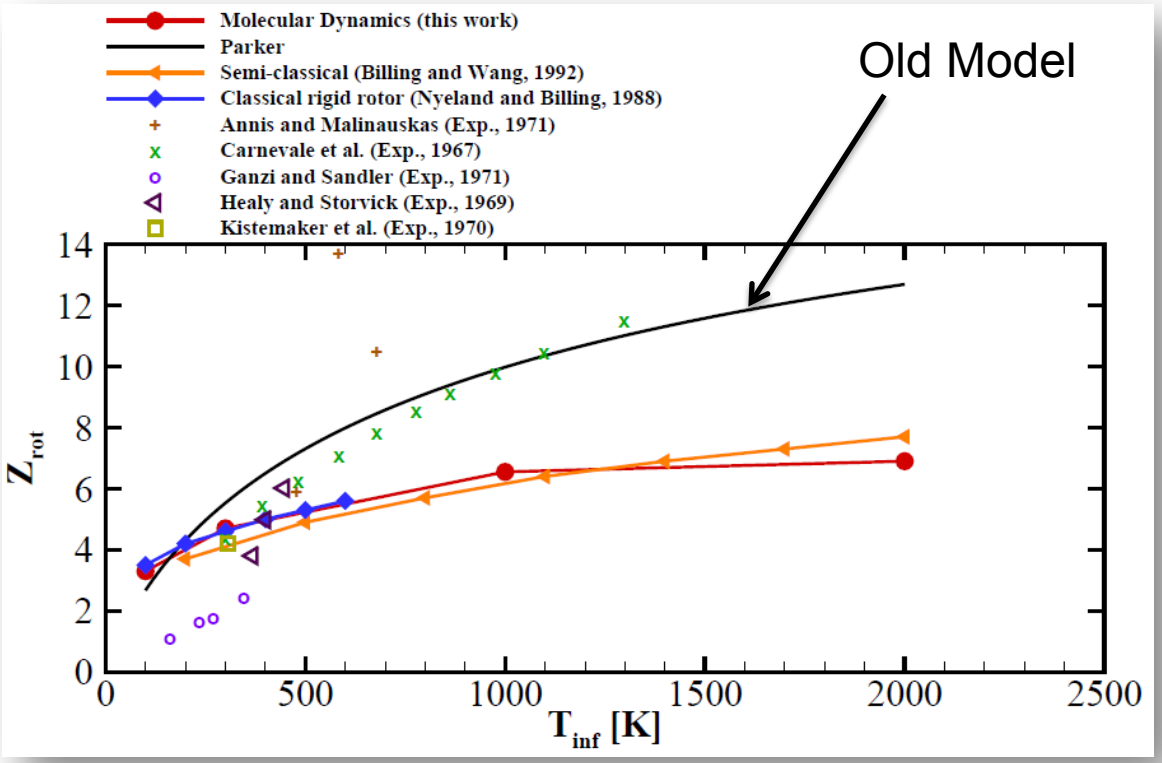
# A *New* Rotational Nonequilbrium Model

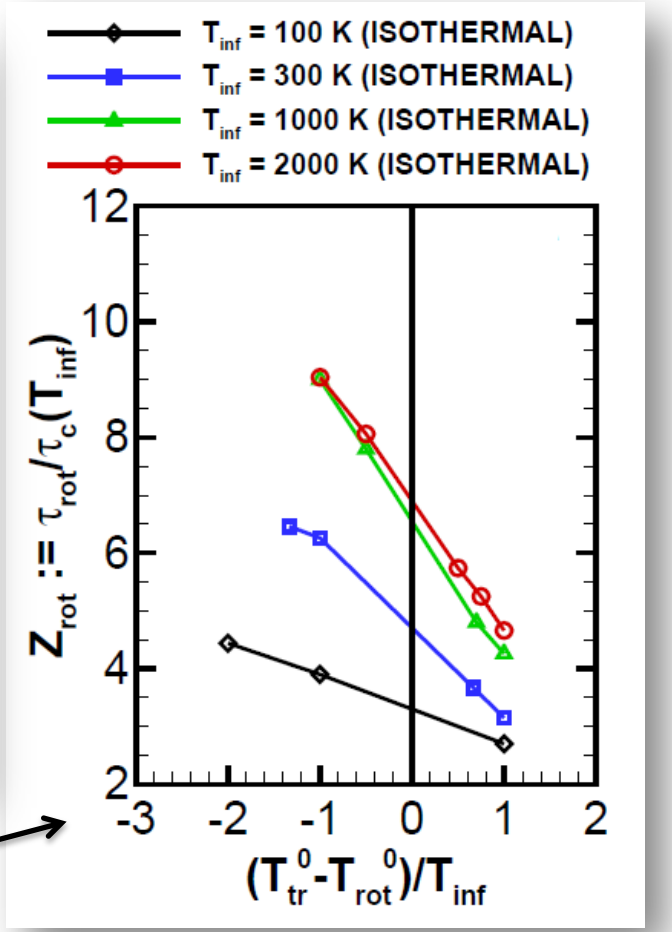
- Current DSMC codes use either $Z_{rot}$=5=constant or $Z_{rot}(T)$ – Parker
- Parker model fit to single experimental data set (experiments vary widely)



# A *New* Rotational Nonequilbrium Model

- Our results clearly show that the rotational relaxation rate strongly depends on the *degree* of nonequilibrium and the *direction* to nonequilibrium




New Model

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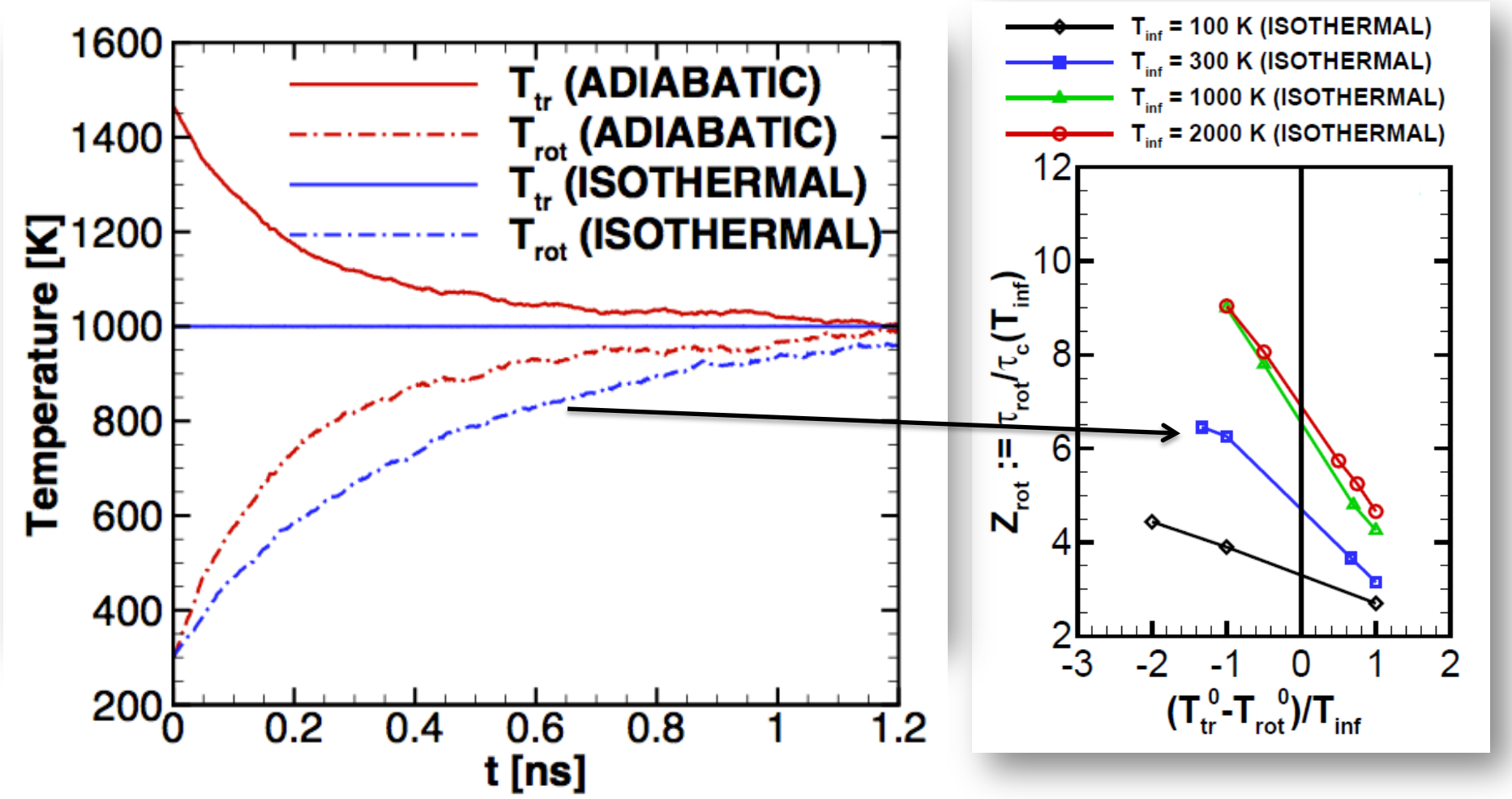
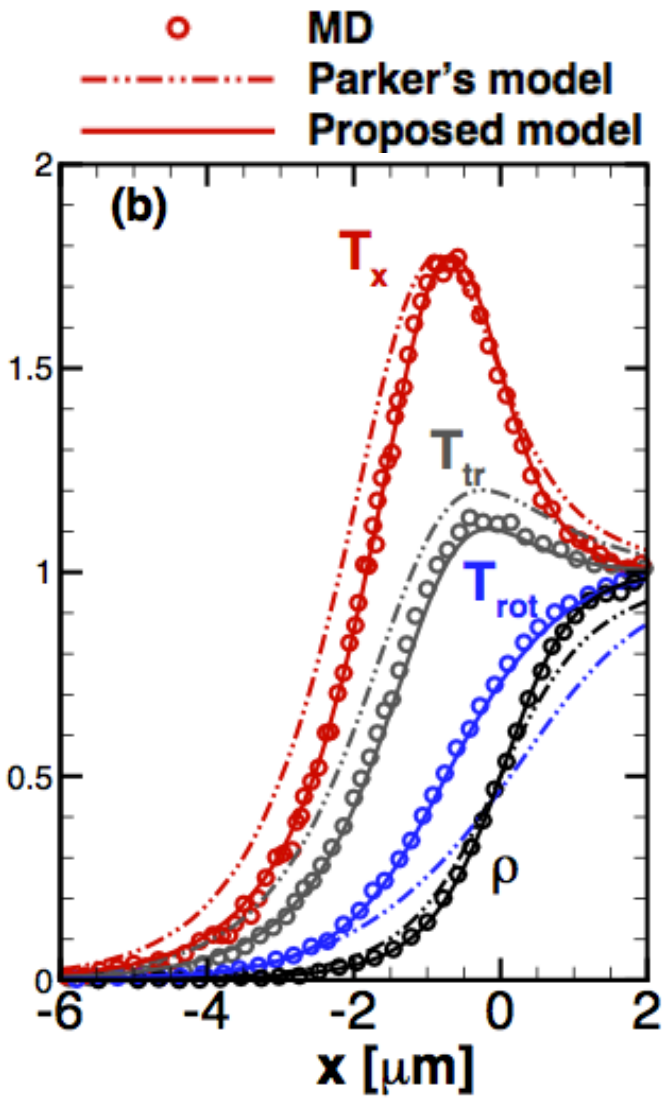


# New Model Results

Shock: $T_1$=300K, $M_1$=7




$$Z_{rot}(T_{tr}, T_{rot}) = Z^0_{rot}\left[1 - b_1\left(1 - \frac{T_{rot}}{T_{tr}}\right)\right]$$

$$Z^0_{rot}(T_{tr}) = a_1\left(\frac{T_{tr}}{1\ \mathrm{K}}\right)^{1/4} + \frac{a_2}{\left(\frac{T_{tr}}{1\ \mathrm{K}}\right)^{1/4}} + a_3\left[\left(\frac{T_{tr}}{1\ \mathrm{K}}\right) - 1000\right]$$

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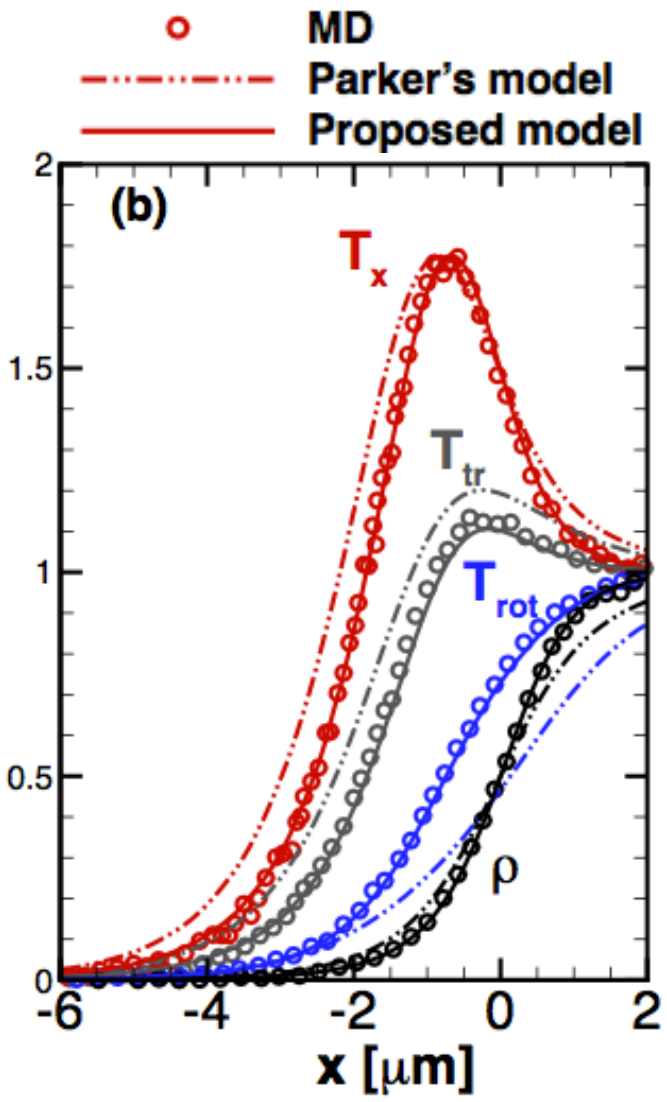
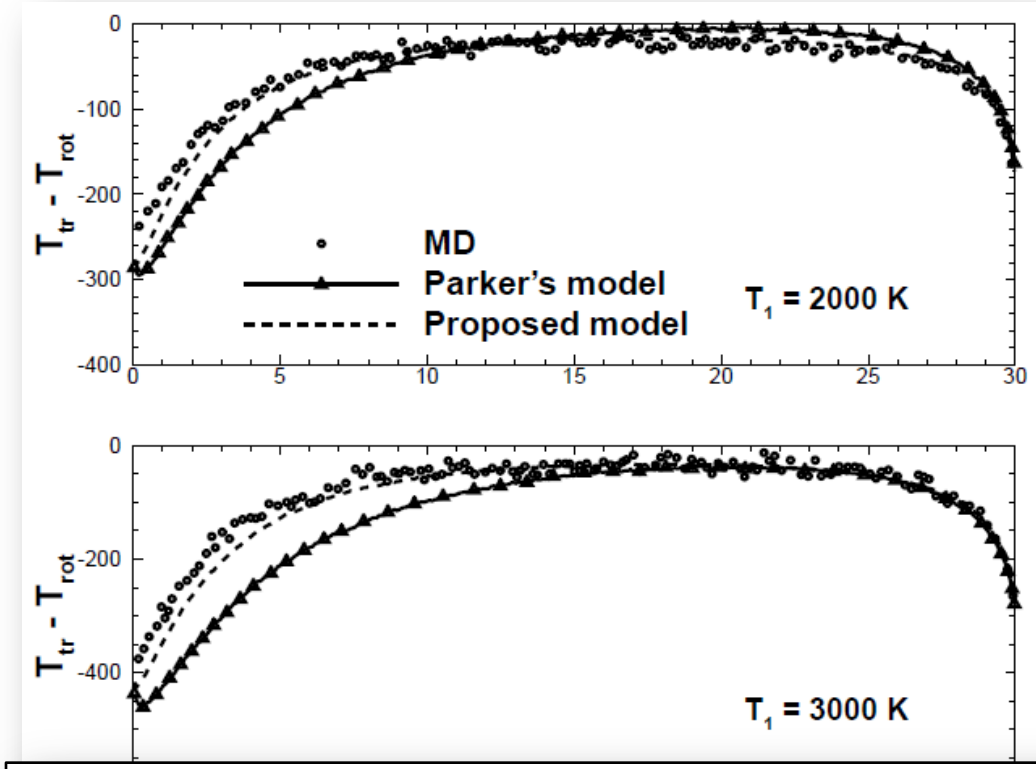



Expansion: Similar temperature range

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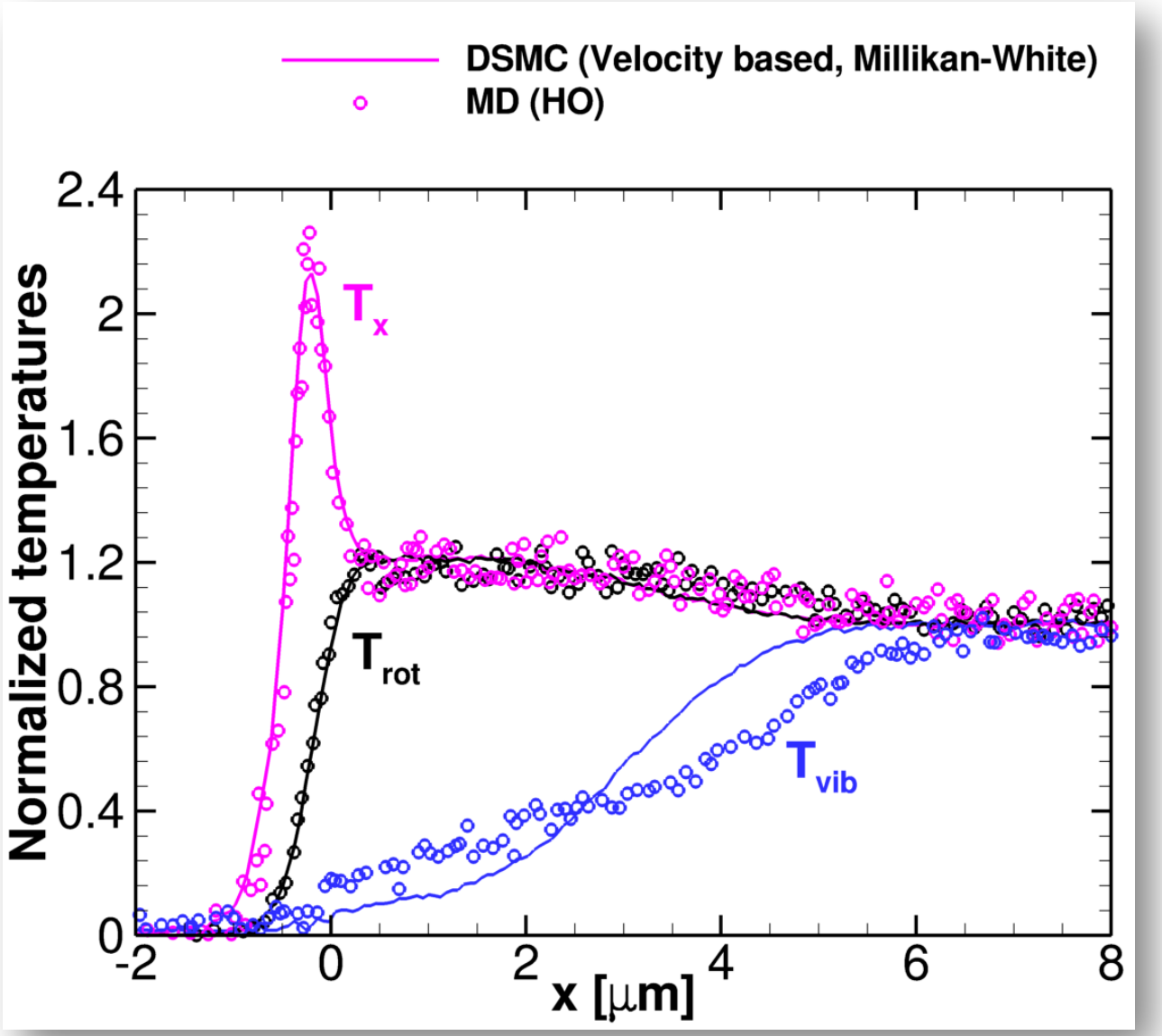
# Vibrational Nonequilibrium (Preliminary)

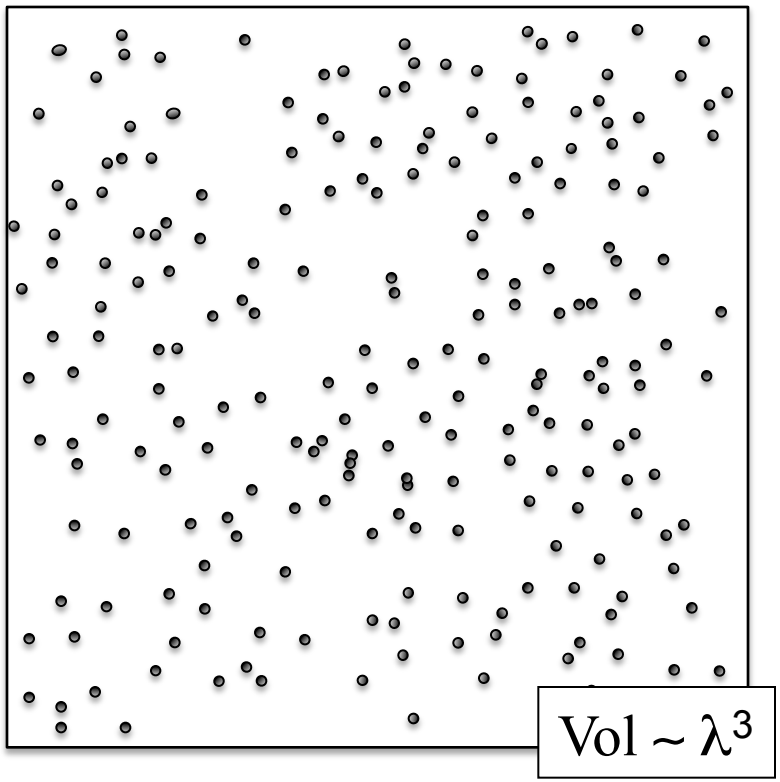
- All-atom simulations
  [trans, rot, vib are post-processed]
- $N_2$ harmonic oscillators
- 5 million atoms
- Vibration will require accurate QM-based PES
- EDTD-MD and Trajectory-DSMC are very promising for arbitrary PES



# Direct Simulation of Practical Flows

Molecular Dynamics

- Simulate every atom in real system
  - Thousands – Millions per $\lambda^3$
- Femtosecond ($10^{-15}$ s) timesteps



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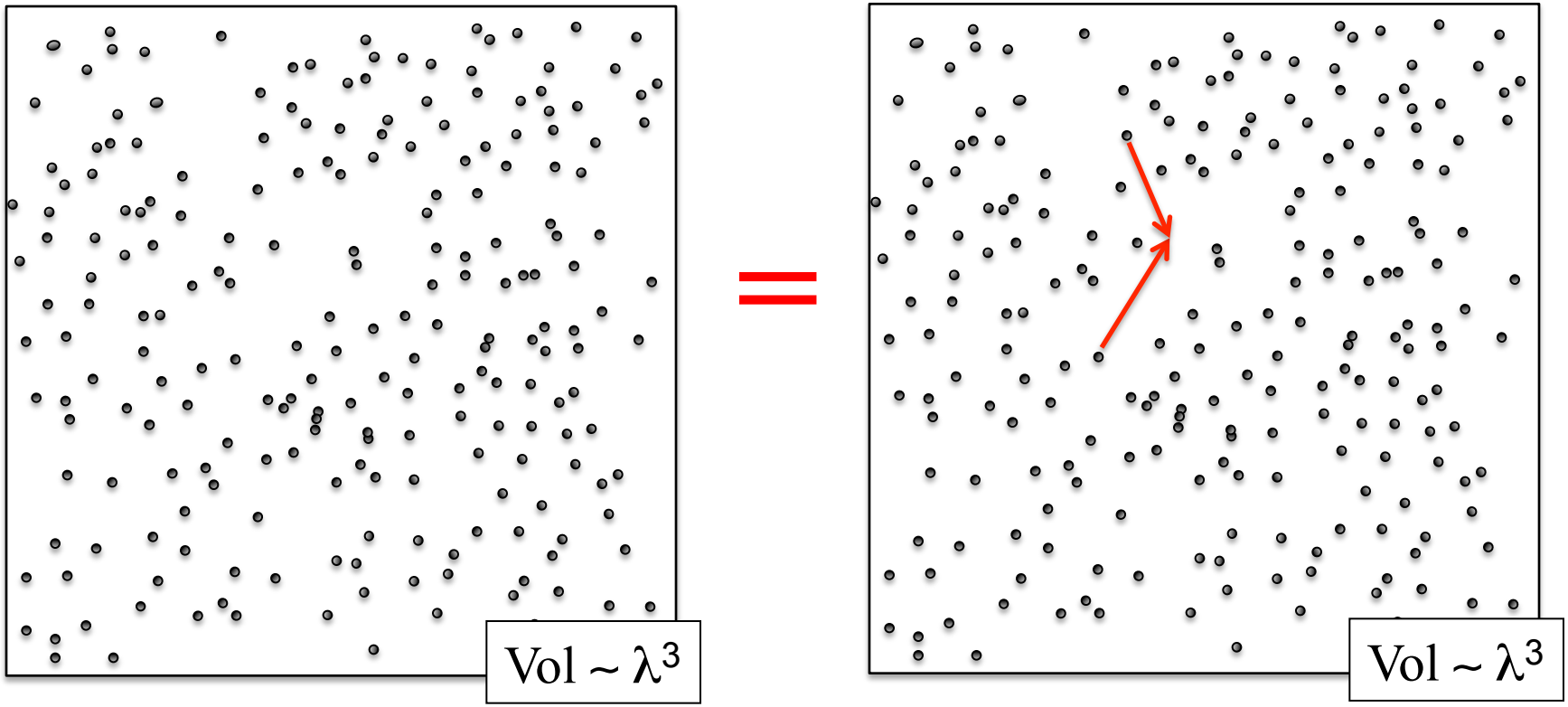
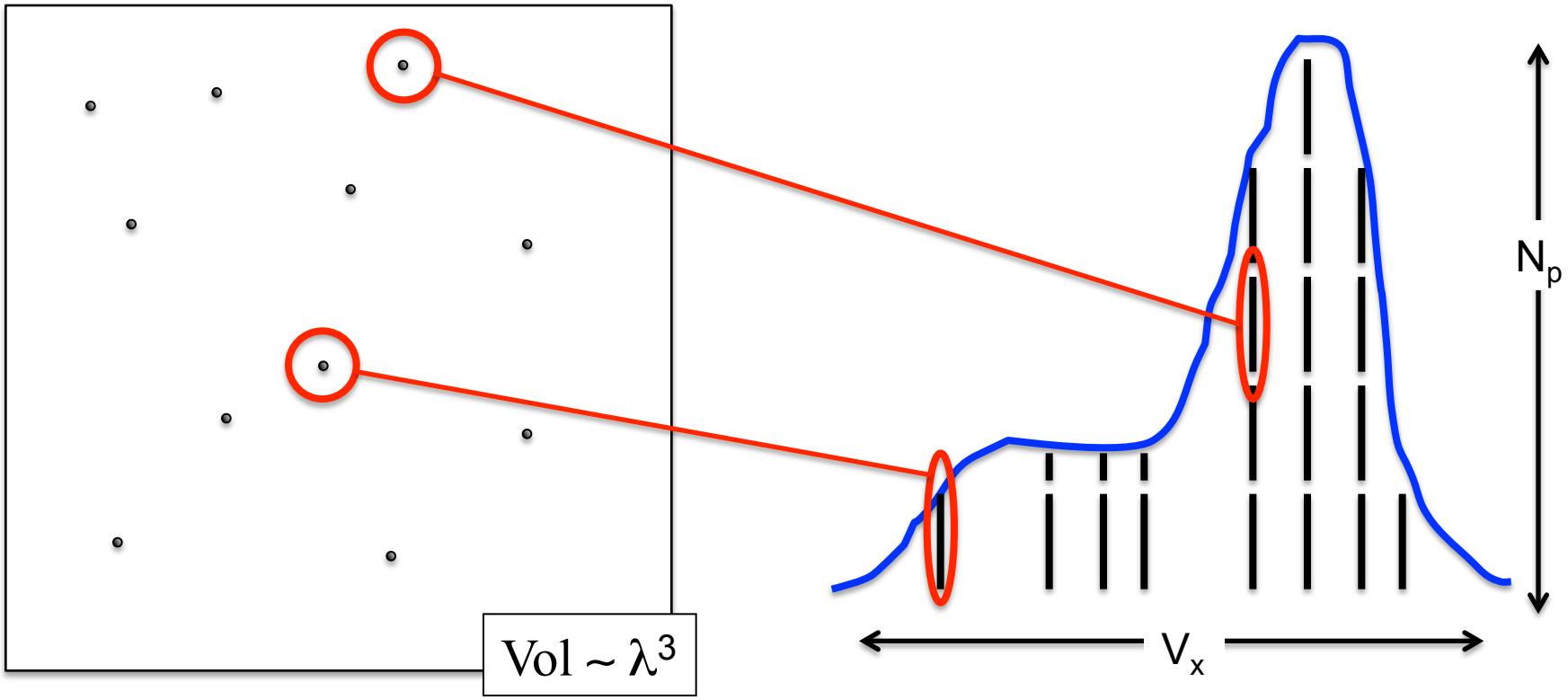
Event-Driven Time-Driven MD

- Simulate every atom in real system
  - Thousands – Millions per $\lambda^3$
- Timesteps ~ $\tau_c$ (mean-coll-time)



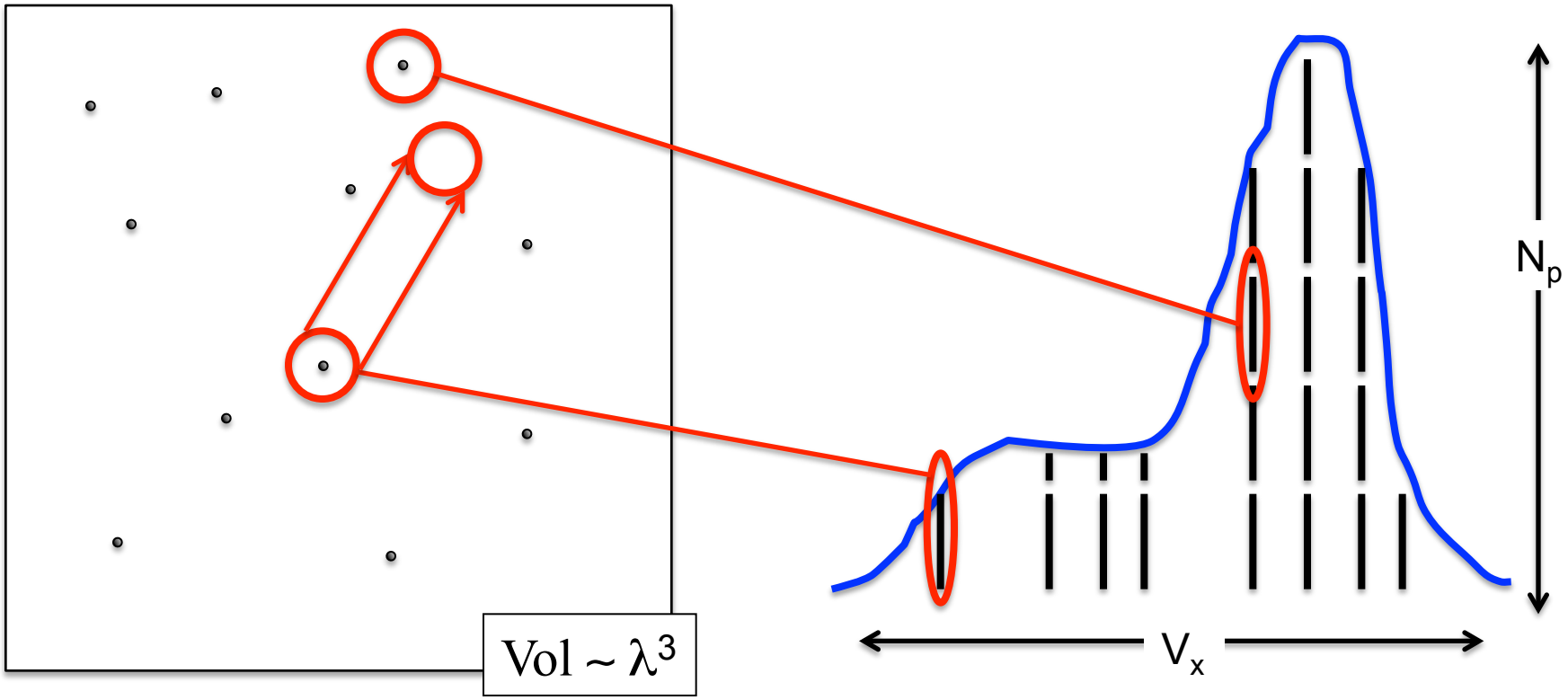
# Direct Simulation of Practical Flows

- One can obtain precisely the same statistics with far fewer molecules. This is what DSMC does.



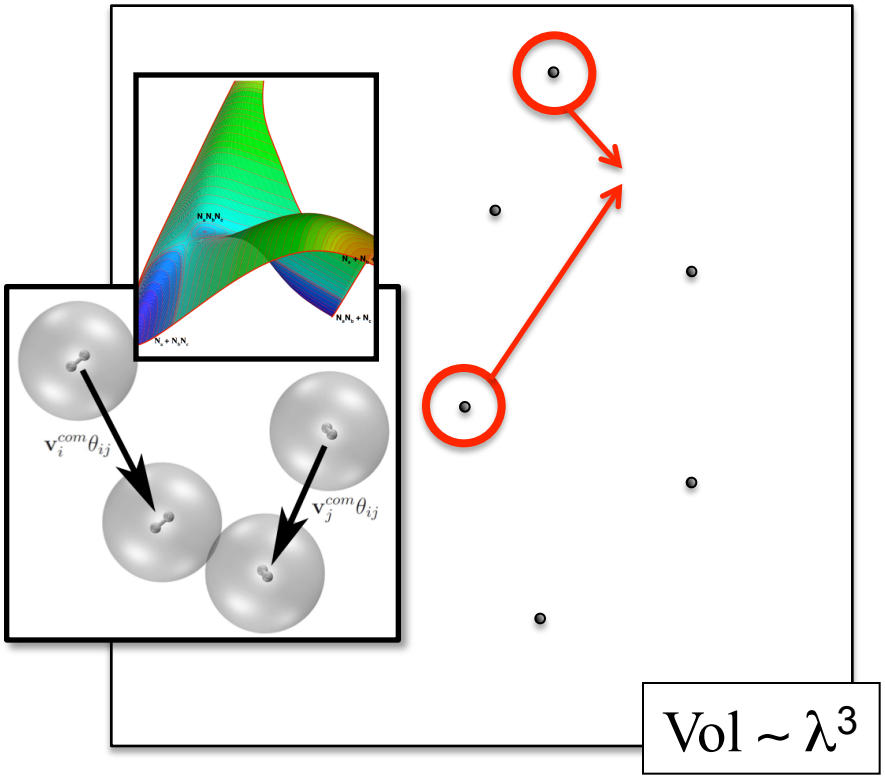
# Direct Simulation of Practical Flows

- One can obtain precisely the same statistics with far fewer molecules. This is what DSMC does.
- But now, what is the collision rate between simulator-molecules?
- For hard-spheres, the precise collision rate is easily determined (MD=DSMC)



# Direct Simulation of Practical Flows

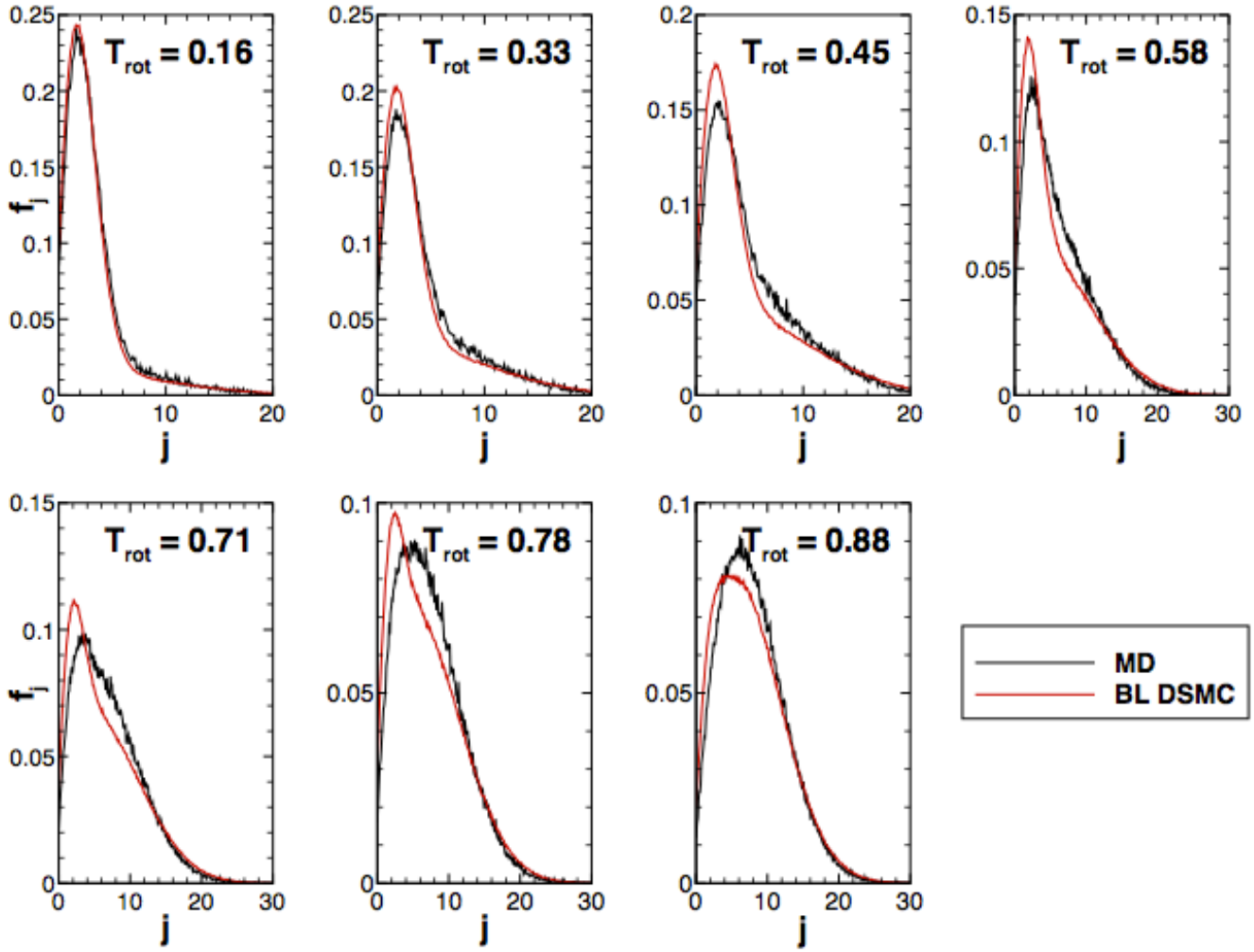
- For real gases, DSMC attempts to model the true cross-section (and also employs probabilistic models for post-collision properties).
- However, an alternative is to integrate collisions directly within DSMC (**"Trajectory-based DSMC"**) [only ~100x slower than DSMC]




- Carefully match the HS cross-section with the impact parameter variation used for the collision calculations
- Simply make the HS cross-section conservatively large, and it will be the PES that determines the collision rate (and also post-collision states)
- We are working on 3-body collision rates for recombination.

# Standard DSMC vs. Pure MD

- Rotational level distribution functions within shock wave.



# Trajectory-DSMC vs. Pure MD

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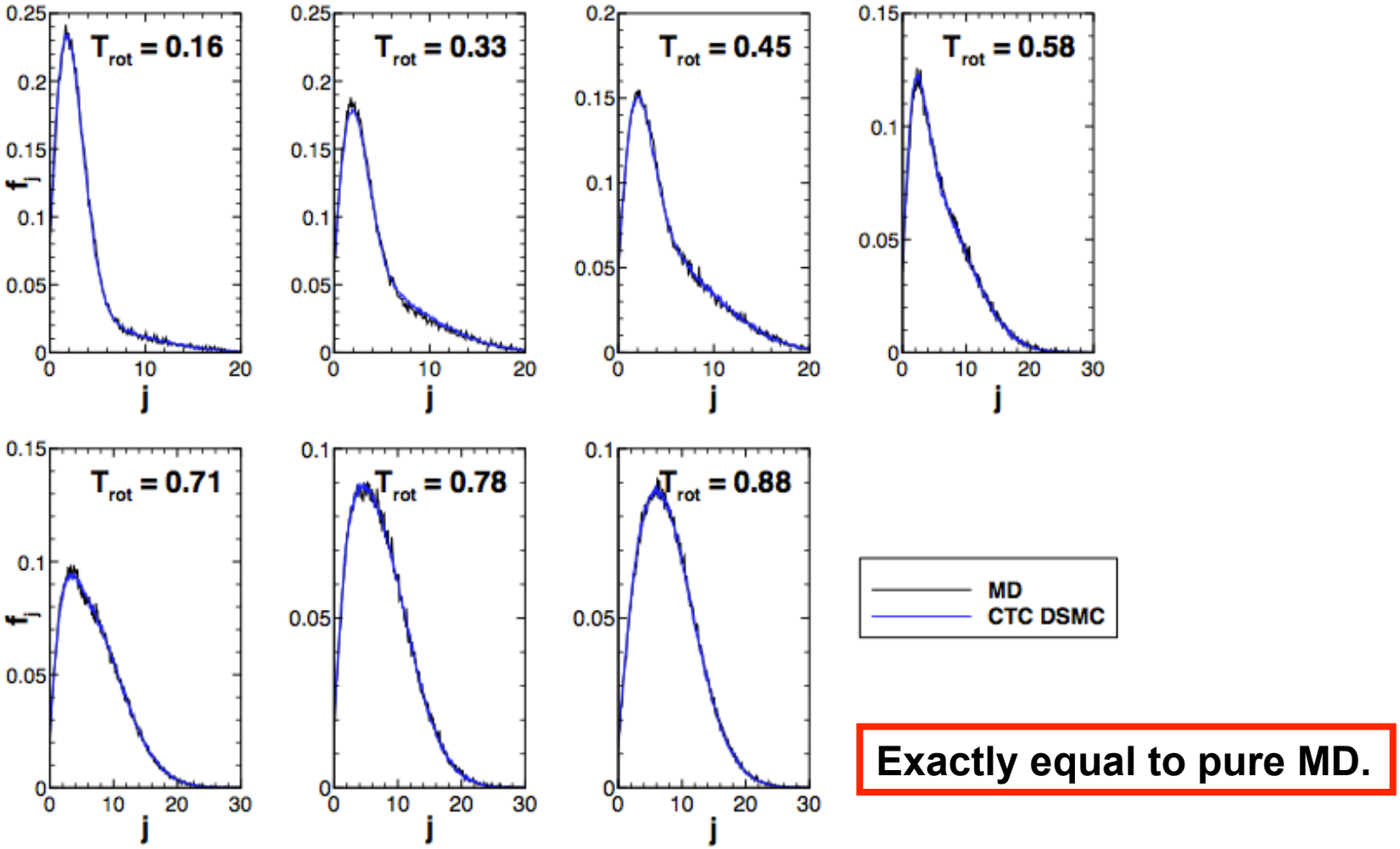


**Exactly equal to pure MD.**

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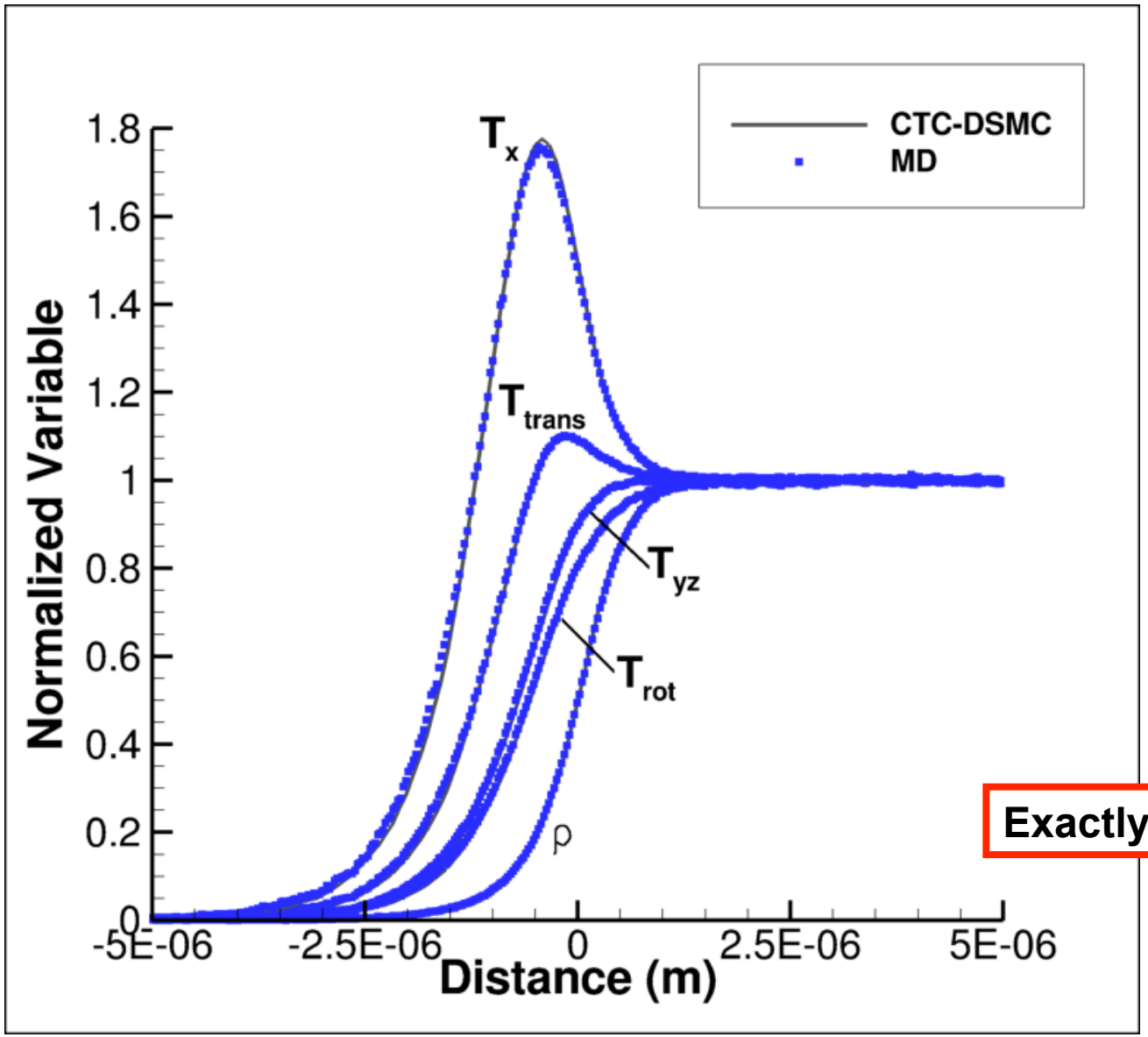


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- Inherently enables the use of **multiple PES** for different species and potentially for different collision energies (LJ → pure QM in theory)

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- >99% CPU time spent integrating collisions (DSMC move/sort/geom <1%). Thus perfectly suited for **GPU acceleration** (CPU handles move/sort/geom)
- Trajectory-DSMC ~100x more expensive than DSMC, but 2 weeks of GPU coding has found **speed-up of 10x per GPU**!

- Current nodes have 8 core-CPUs and 4 GPUs (= 50 core-CPU node…)

| Method | Speedup vs. Serial | Speedup/GPU |
|---|---|---|
| Serial | 1x | - |
| OpenMP | 7.14x | - |
| OpenMP + 1 GPU | - | - |
| OpenMP + 2 GPU | 33.24 | 13.05 |
| OpenMP + 4 GPU | 50.58 | 10.86 |

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- Stagnation line simulations using new surfaces within a year ($N_2$+$N_2$, $O_2$+$O_2$, $N_2$+$O_2$ – Truhlar UMN Chemistry and possibly $N_2$+N – NASA?)

# Summary and Conclusions

1) Pure Molecular Dynamics of normal shock waves is possible

2) MD simulations have been validated with all available experimental data for Ar, Ar-He, Xe-He, and $N_2$(rot) shock waves

3) New internal energy relaxation physics were found for $N_2$ rotational excitation/relaxation (ground vibrational state)
   - weaker temperature dependence than prior models
   - strong dependence on direction and degree of nonequilibrium

4) Demonstrated how a reduced-order model for DSMC/CFD can be constructed based on MD results (and we recommend its use)

5) Preliminary results show that trajectory-based DSMC exactly reproduces pure MD results at a cost ~100x slower than DSMC. However, trajectory-DSMC is perfectly suited for GPU acceleration with realistic 50x speedup on existing architectures.

# Challenges and Open Questions

1) Can we implement trajectory-DSMC such that 3-body collision rate is determined only by the PES (and exactly equals MD)?

2) Can we achieve GPU scalability (>10x per GPU) for complex PES?

**3) How do we go about model reduction for vibration, and rot-vib-diss coupling? What precisely should we look for?**

4) Chemistry is not entirely in our control… requires real collaboration. Will these PES agree with experiment for dissociating flows? What if they don't?

5) Experimental validation. Currently many CFD/DSMC and now MD calculations match the same experimental data sets (density/pressure traces). No way of distinguishing models. We need new data with hydrodynamic, internal energy state, and species fractions (even at a few points in a shock or expansion flow).

# Acknowledgments


- University of Minnesota researchers:
  - Dr. Paolo Valentini
  - Paul Norman
  - Chonglin Zhang
  - Savio Poovathingal
  - Byron Edgar

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# Questions?

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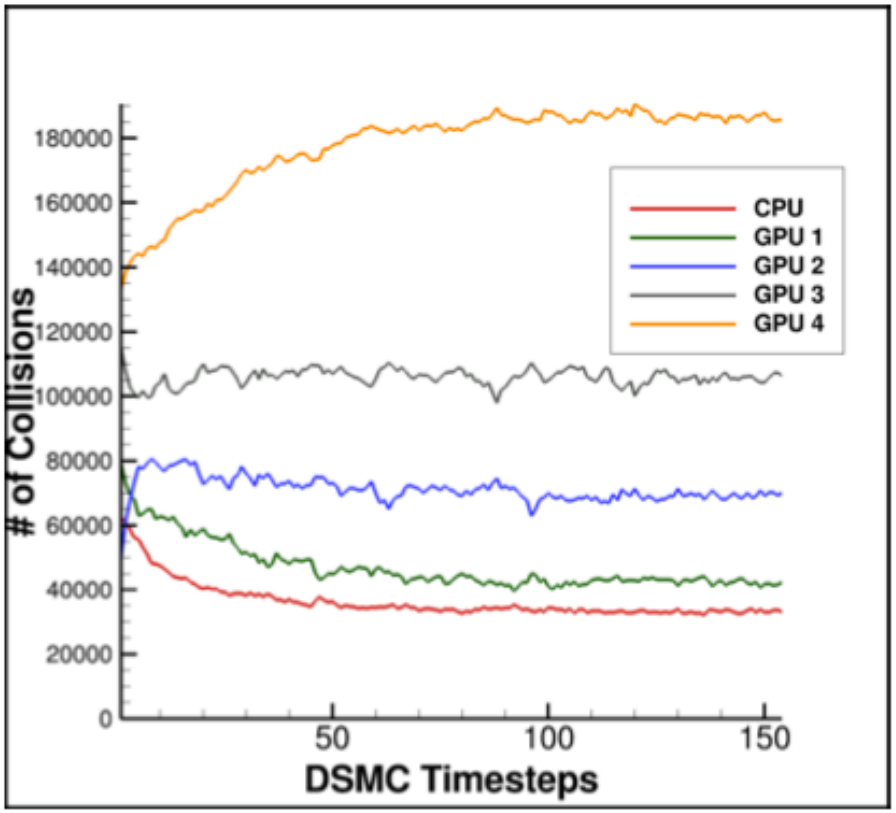
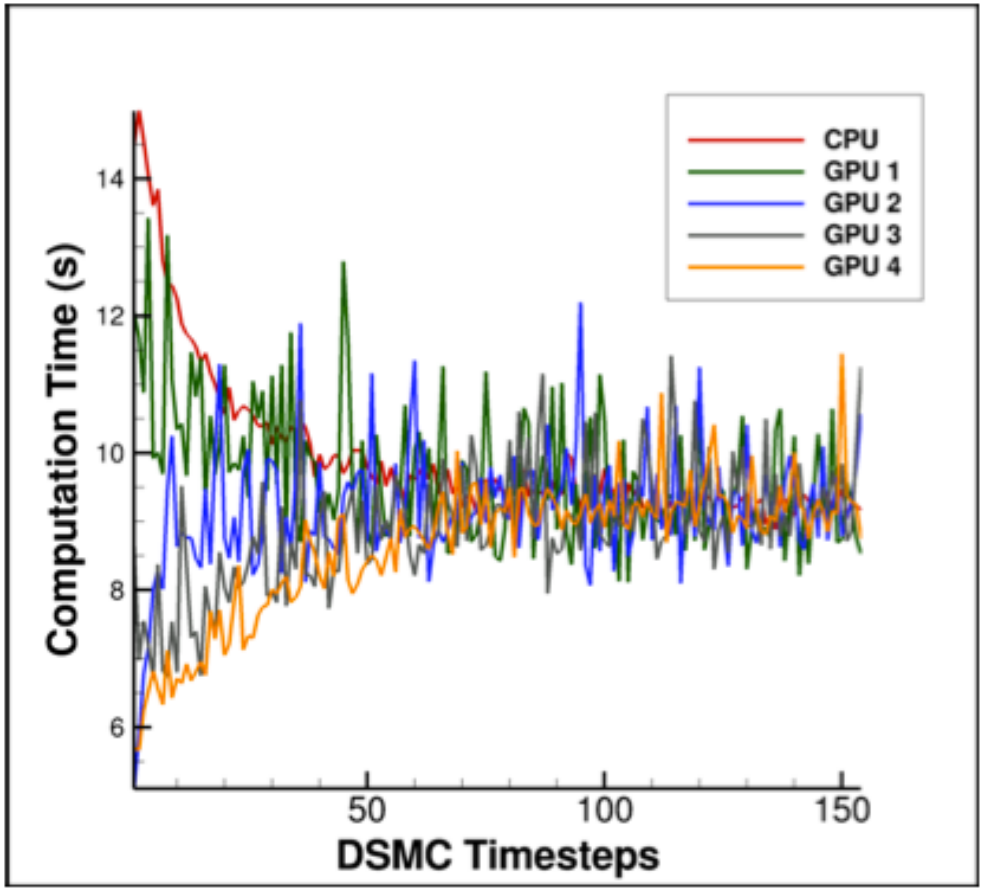
# GPU Load Balancing

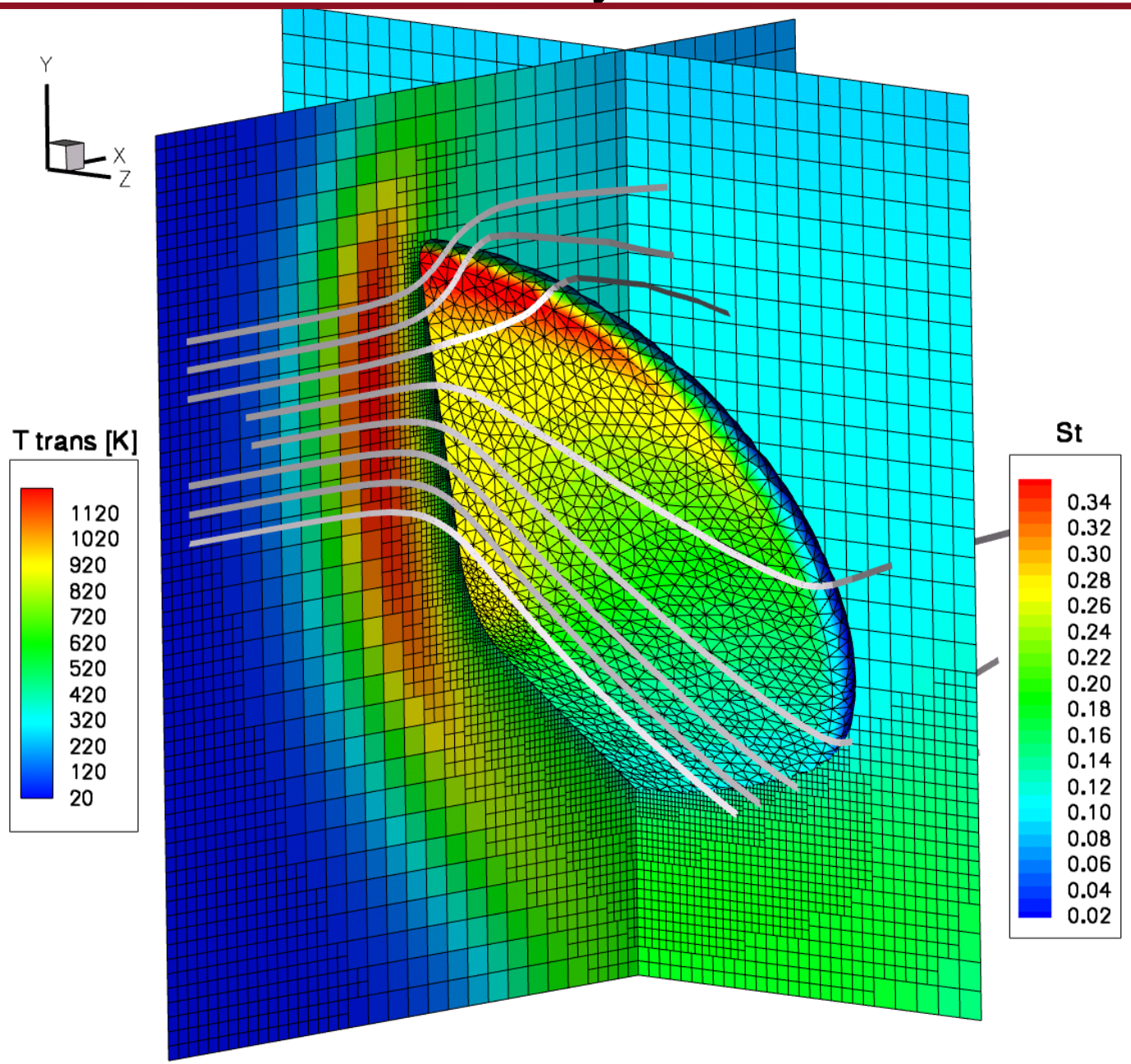



(a) Number of collisions vs. DSMC timestep

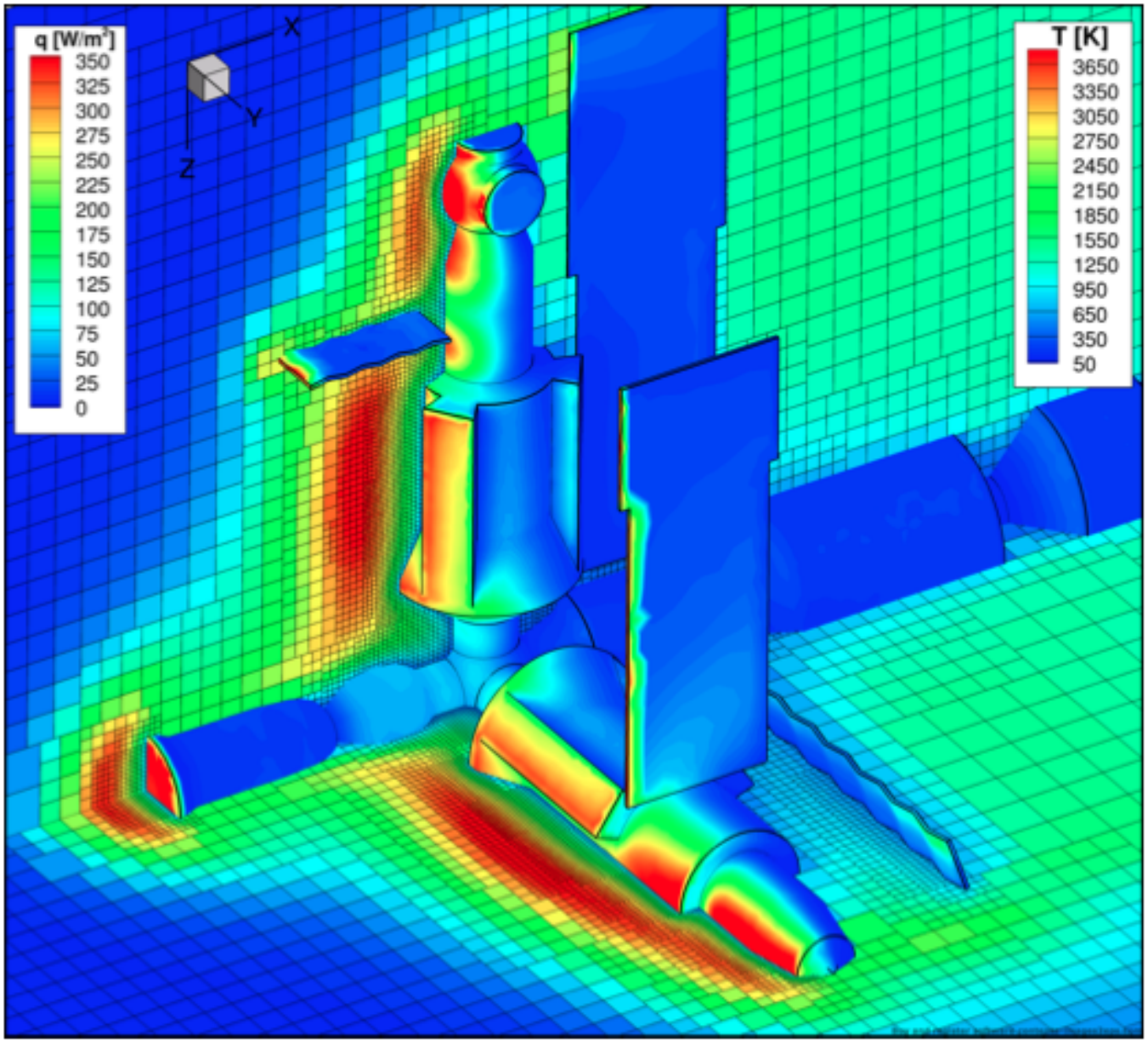



(c) Computational time vs. DSMC timestep

# DSMC Solution for Planetary Probe



# DSMC Solution for MIR Space Station



# Micro and Nanoscale Flows

- $\lambda$ and $\tau$ are constant so $\Delta x$ and $\Delta t$ are uniform
- Low T, so no gas-phase vibration/dissociation chemistry
- High thermal fluctuations compared to bulk flow velocity (large scatter)
- Requires subsonic (or far-field) boundary conditions and large domain sizes
- *Real* fluctuations in gas flow are present; nano-clusters may be "random walkers"