
Direct Molecular Simulation of Hypersonic Flows

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¹ **FA9550-10-1-0563:** Fundamental Processes in High-Temperature Gas-Surface Interactions – AFOSR MURI FY2010

² **FA9550-10-1-0075:** AFOSR Young Investigator Program (YIP) FY2010

³ **FA9550-12-1-0202**

Outline

- Gas-Surface Interactions
 - Oxygen-Silica
 - Oxygen-Carbon
- Gas-Phase modeling
 - Direct Simulation Monte Carlo (DSMC)
 - All-atom Molecular Dynamics (MD) of shock waves
 - Trajectory-based DSMC of flow fields
- New Physical Models
 - “Direction-dependent” rotational relaxation
 - Rotation-Vibration coupling at high temperatures
- Summary and Remaining Challenges

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Finite-Rate Models for Gas-Surface Chemistry

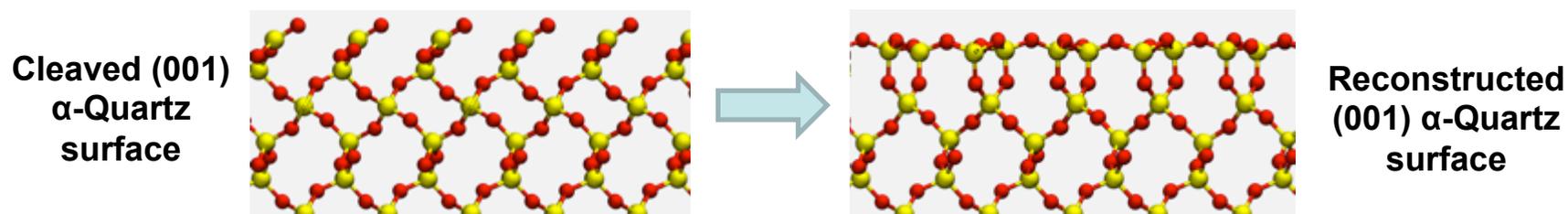
- Surface reactions now modeled similar to gas-phase reactions; this is required for nonequilibrium vehicle trajectories
- Models require activation energies and steric factors for each rate (rate parameters are now directly linked to physical chemistry)
- What are the precise mechanisms?
 - realistic surface structure, reactive chemical sites (“defects”)
- What are the rate parameters?
 - transition state energies, steric/geometrical effects
- *Beyond predicting existing TPS behavior, such modeling leads to fundamental understanding for new TPS design and potential control of gas-surface reactions*

Surface Catalytic Reactions

- (1) $O + [s] \rightarrow O_s$
- (2) $N + [s] \rightarrow N_s$
- (3) $O + O_s \rightarrow O_2 + [s]$
- (4) $N + N_s \rightarrow N_2 + [s]$
- (5) $O + N_s \rightarrow NO + [s]$
- (6) $N + O_s \rightarrow NO + [s]$
- (7) $O_{s,m} + O_s \rightarrow O_2 + 2[s]$
- (8) $N_{s,m} + N_s \rightarrow N_2 + 2[s]$
- (9) $O_{s,m} + N_s \rightarrow NO + 2[s]$
- (10) $N_{s,m} + O_s \rightarrow NO + 2[s]$
- (11) $O_s \rightarrow O + [s]$
- (12) $N_s \rightarrow N + [s]$

Atomistic Simulation of Silica Surfaces

- Silica is a main component in non-ablative/ablative TPS and SiO_2 oxide layers form on many TPS materials (i.e. SiC and UHTCs)
- We have developed a new $\text{ReaxFF}_{\text{SiO}}^{\text{GSI}}$ potential [1] for oxygen-silica systems and analyzed the surface structure of silica exposed to oxygen at high temp [2]

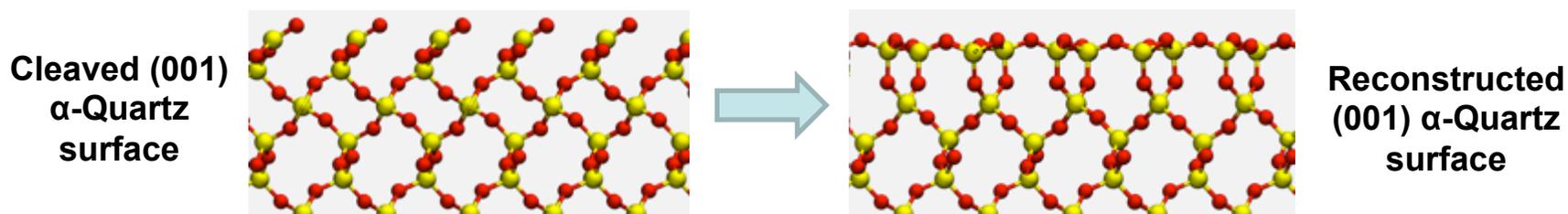


[1] Kulkarni, A.D., Truhlar, D.G., Srinivasan, S.G., van Duin, A.C.T., Norman, P., and Schwartzenruber, T.E., J. Phys. Chem. C (2013), 117, pp. 258-269.

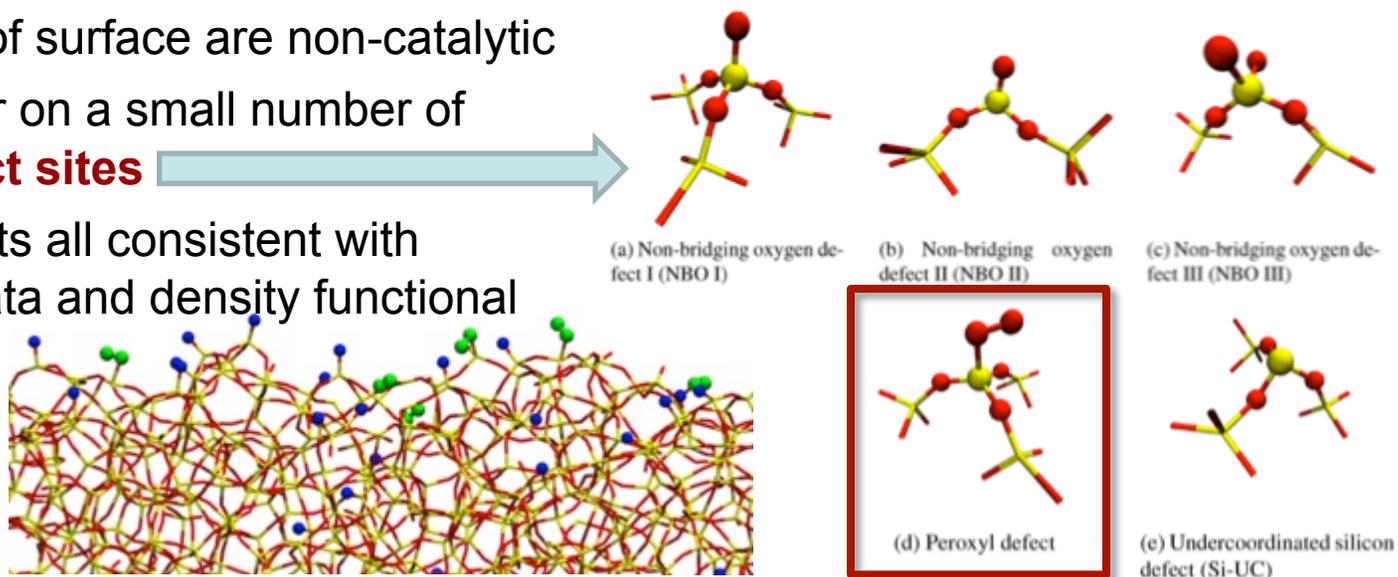
[2] Norman, P., Schwartzenruber, T.E., Leverentz, H., Luo, A., Paneda, R.M., Paukku, Y., and Truhlar, D.G., J. Phys. Chem. C (2013), 117, pp. 9311-9321.

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- Large portions of surface are non-catalytic
- Reactions occur on a small number of **chemical defect sites** 
- Predicted defects all consistent with experimental data and density functional theory (DFT)



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Vibrational Energy Accommodation to Surface

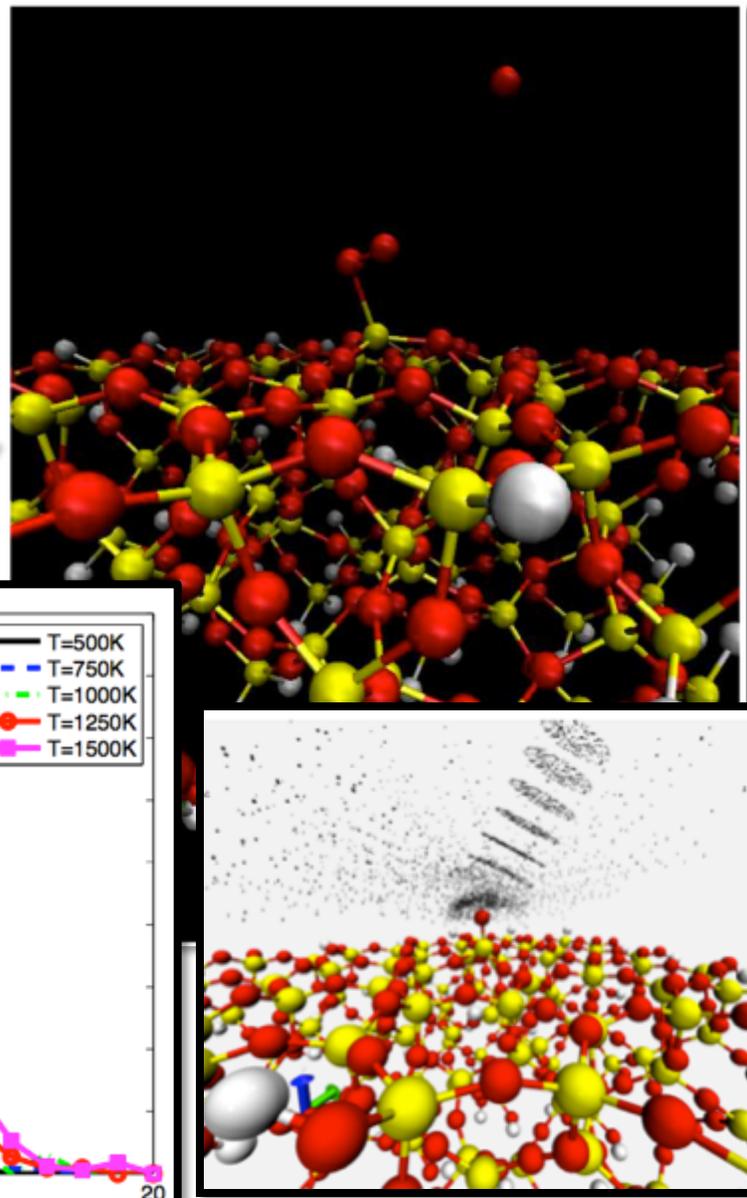
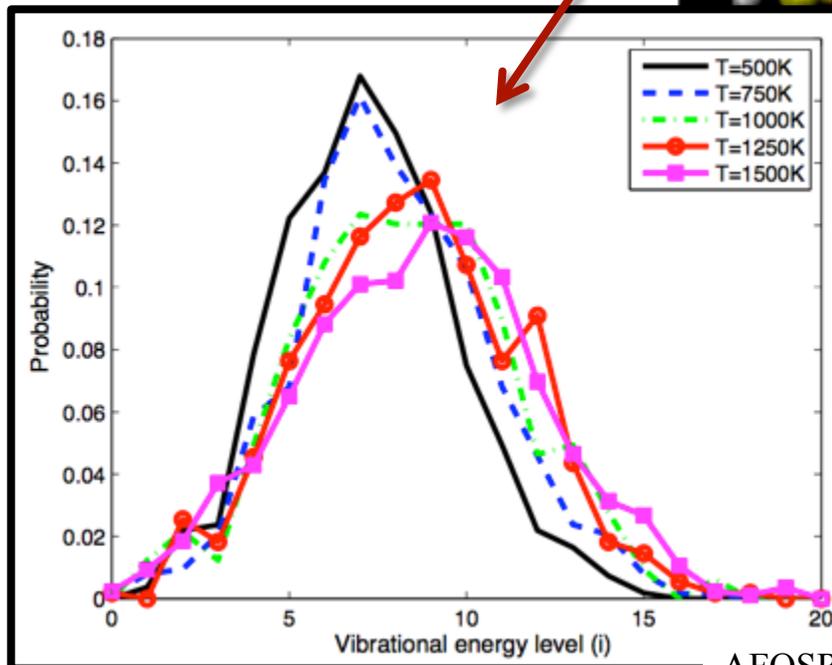
- Trajectories performed to determine activation energies and steric factors for each reaction mechanism (each defect chemistry)
- A finite-rate model has been developed
- Now investigating vibrational energy accommodation (β) to the surface
- Simulations clearly show that recombined molecules are vibrationally excited:

$$\beta = q_r / h_D < 1$$

q_r = energy transmitted to surface

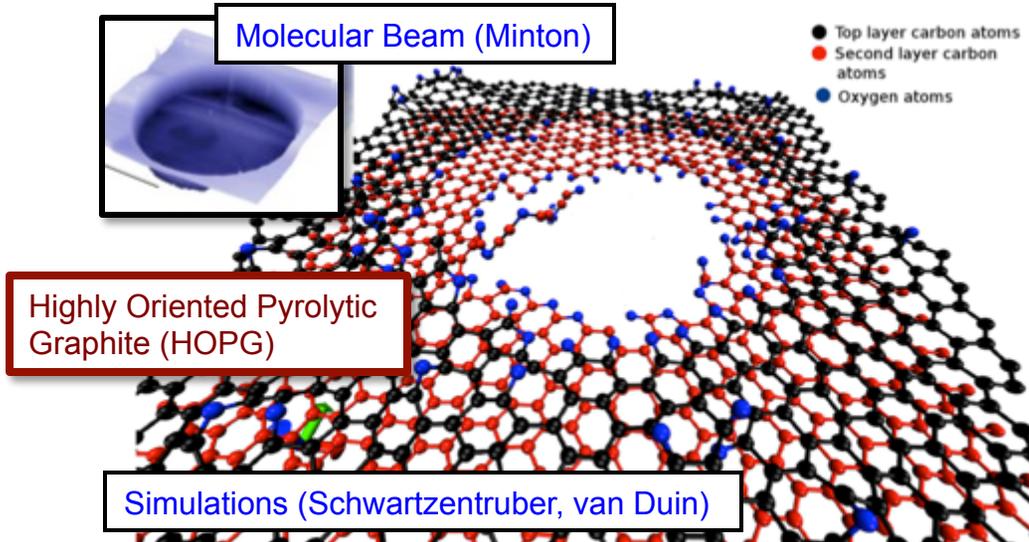
h_D = diss. enthalpy

What happens with a BL ??



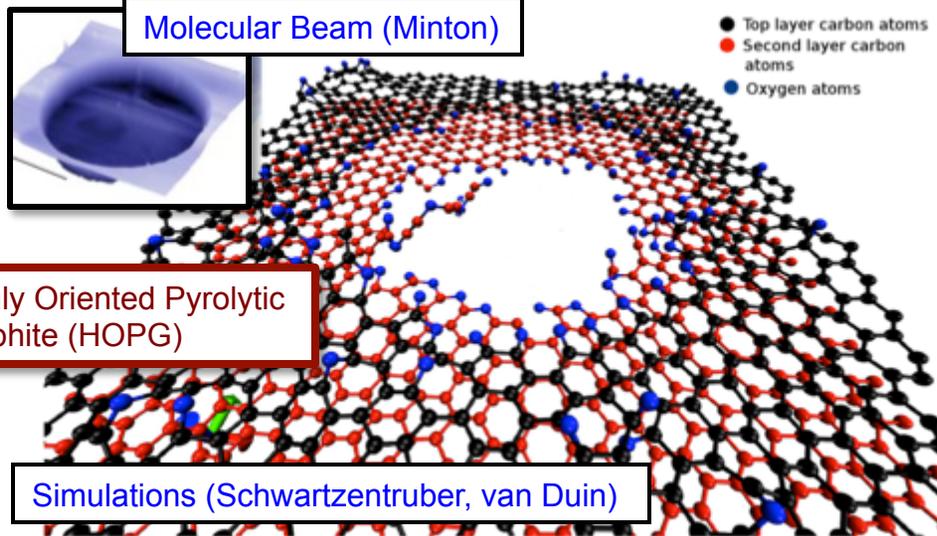
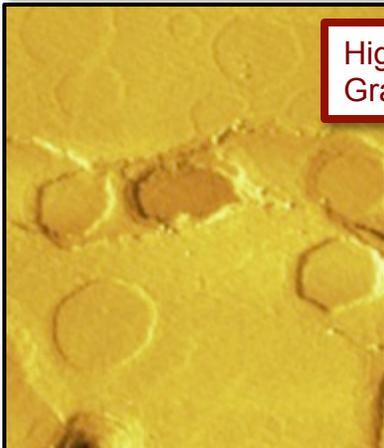
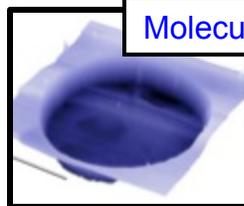
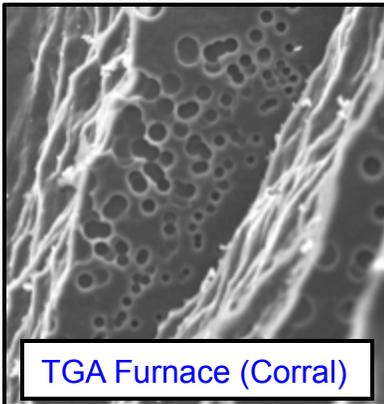
Carbon Oxidation

- “Etch pits” observed across a range of experimental facilities and carbon materials
- The same chemical reactions may be occurring on graphene edges, even for realistic fiber-based TPS



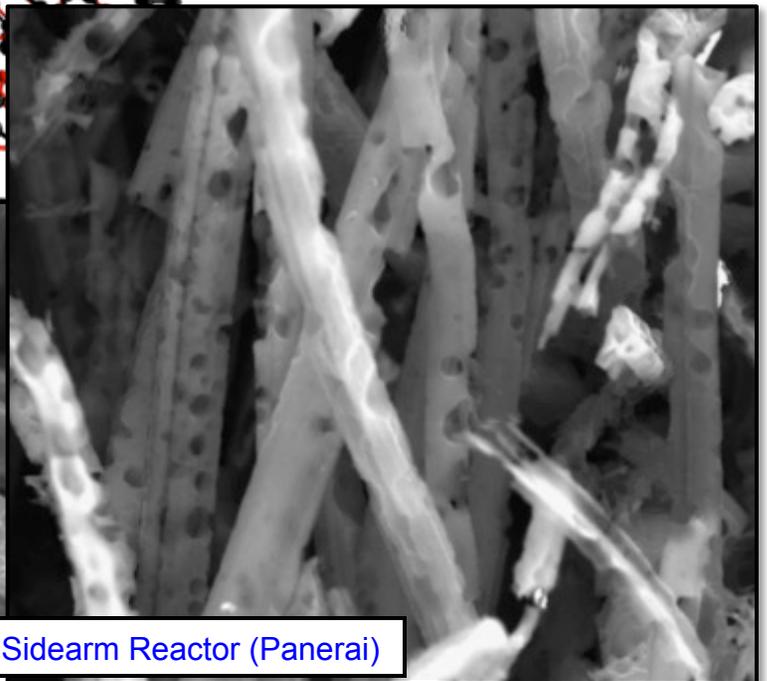
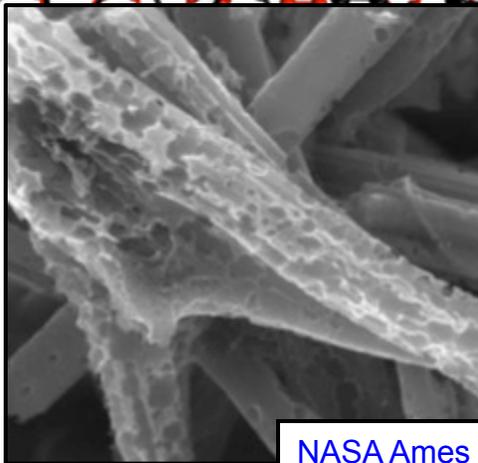
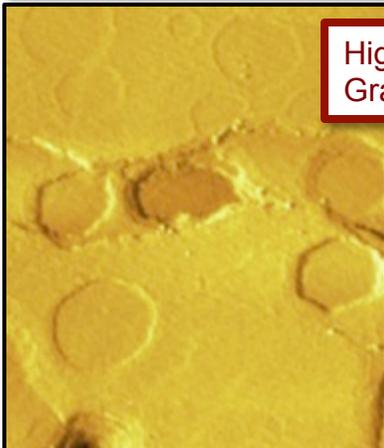
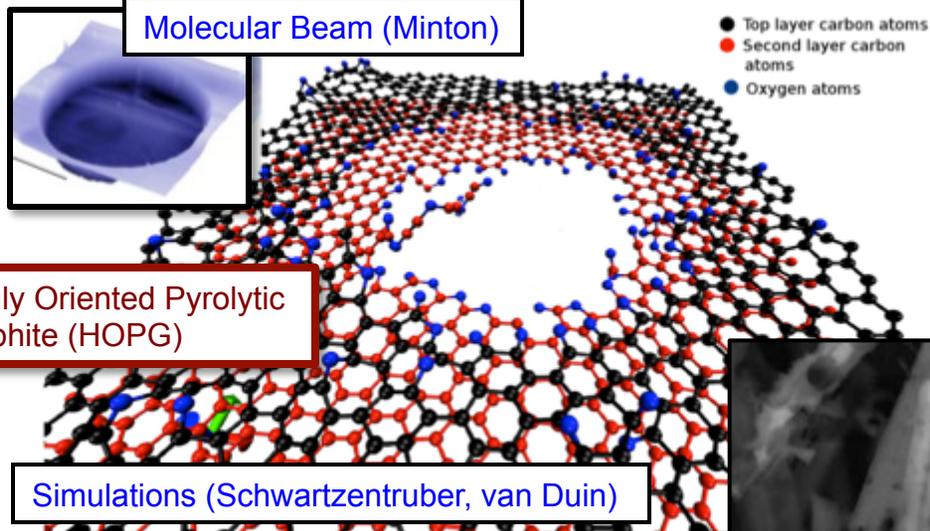
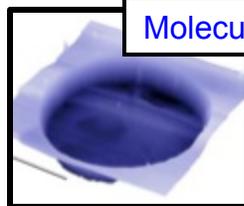
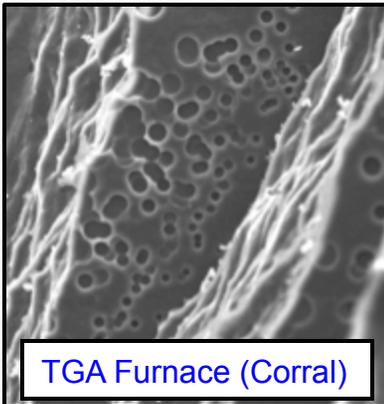
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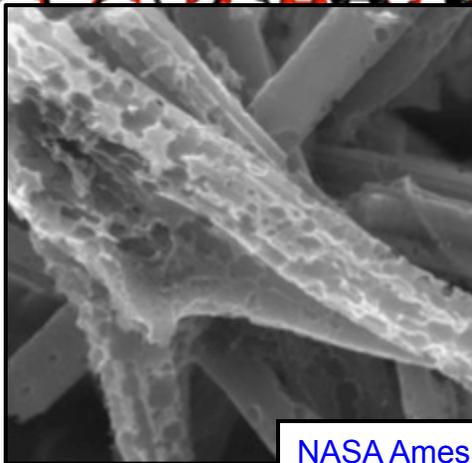
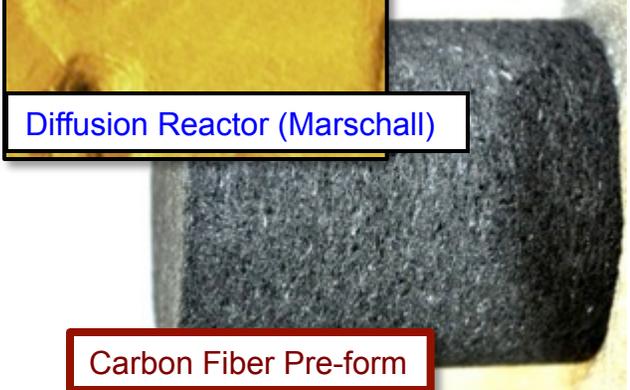
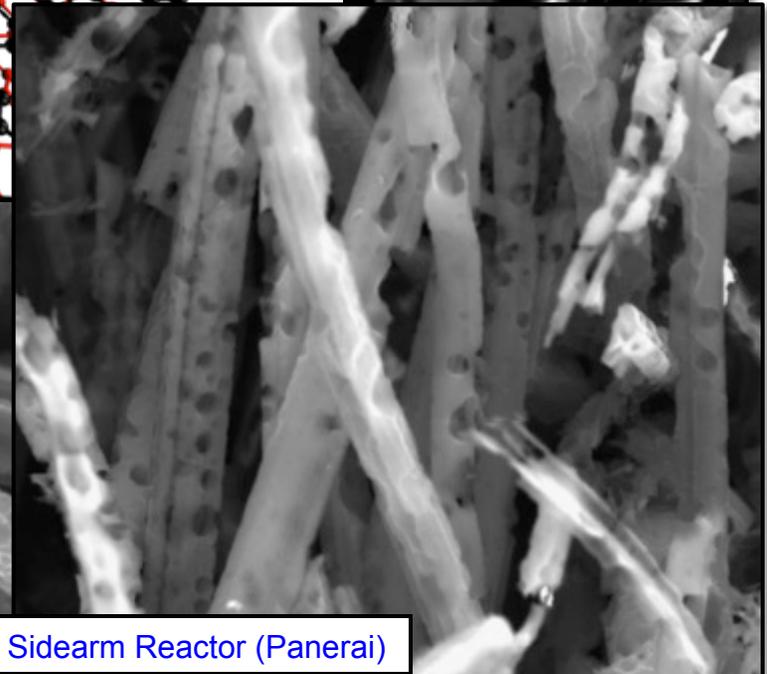
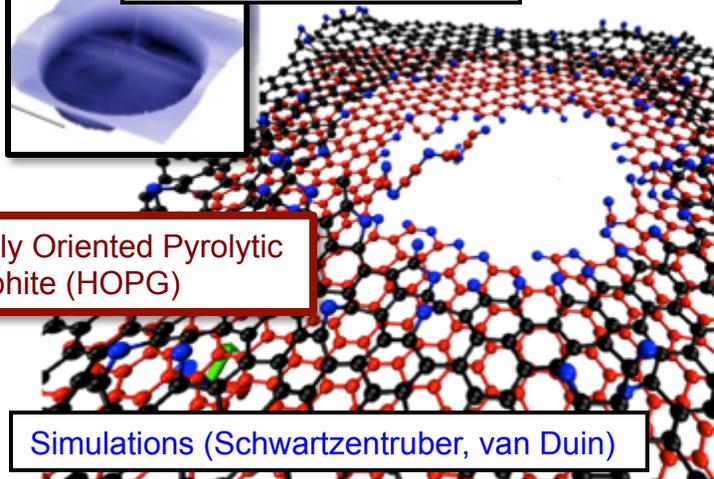
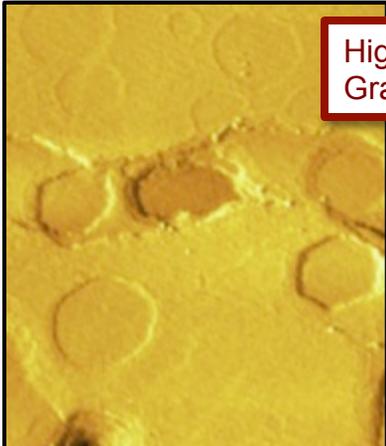
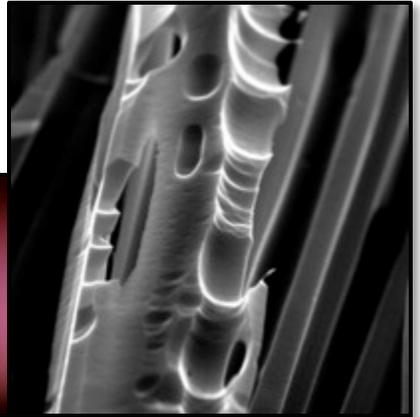
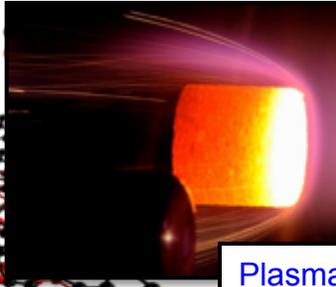
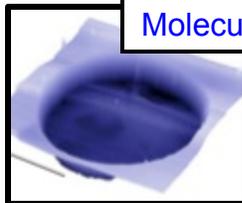
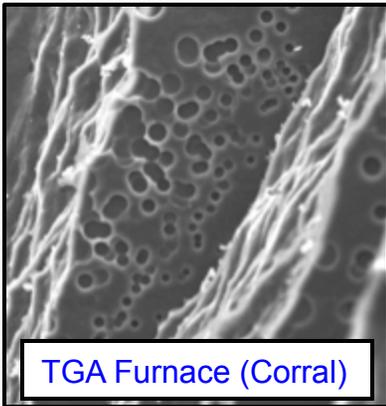
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Carbon Oxidation

Constructing a rate model for CFD requires knowledge of:

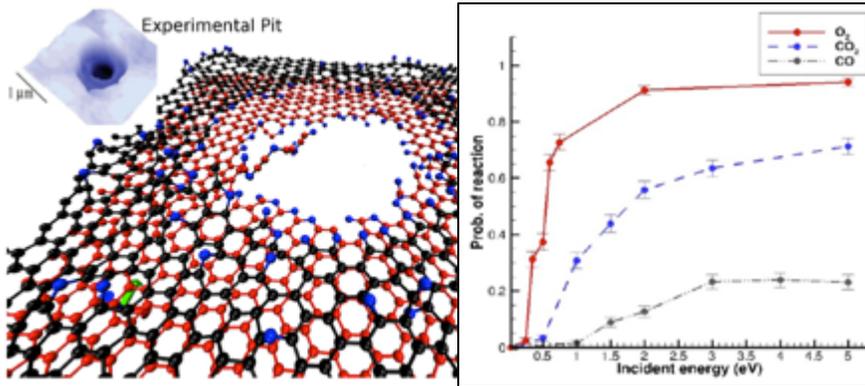
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- (2) The magnitude of the rates (real microstructure surface area, diffusion of reactive species to reactive sites)

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- (1) It seems possible that the same chemical reactions occurring on etch pit edges in molecular simulations of HOPG are actually occurring on real TPS microstructure.



Simulation trends agree with Molecular Beam observations:

- O₂ recombination occurs on entire surface (lowest activation energy)
- CO and CO₂ form only on etch pit edges with similar activation energies
- CO is less probable due to details of the mechanism

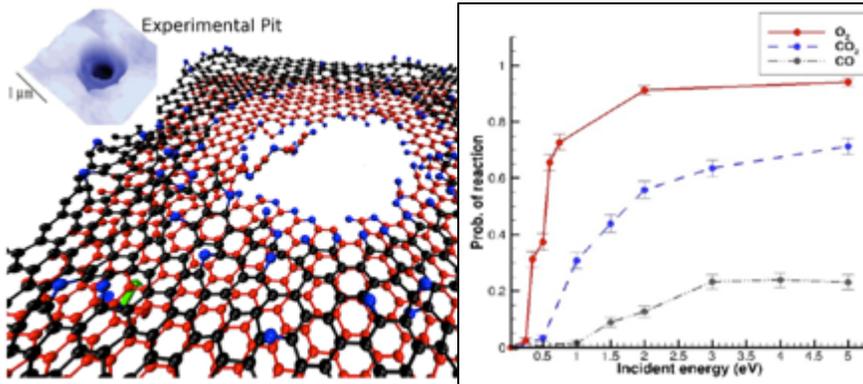
Poovathingal, Schwartzentruber, Srinivasan, van Duin, J. Phys. Chem. A (2013) 117, pp. 2692-2703

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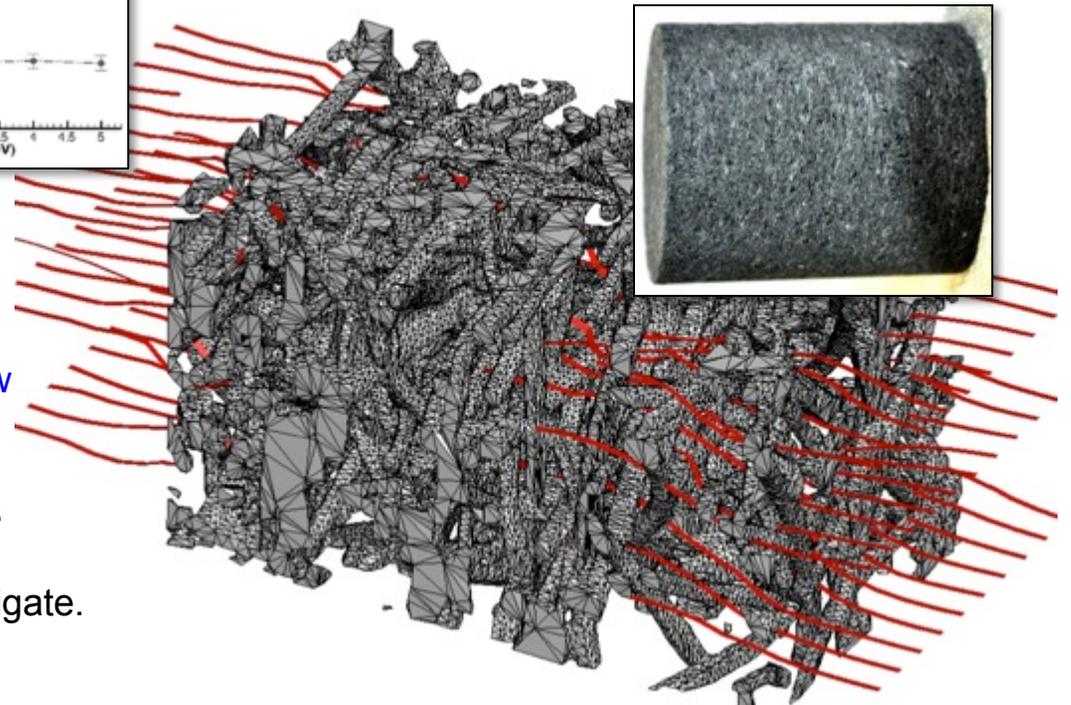
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Poovathingal, Schwartzentruber, Srinivasan, van Duin, J. Phys. Chem. A (2013) 117, pp. 2692-2703

- (2) It is now possible to image real TPS in 3D using tomography (Lawrence Berkley NL), triangulate a surface mesh, and simulate high-temperature diffusive and reactive flow using the DSMC particle method.

*There are certainly other reaction mechanisms observed in experiments (such thermal oxidation reactions) that we have yet to investigate.

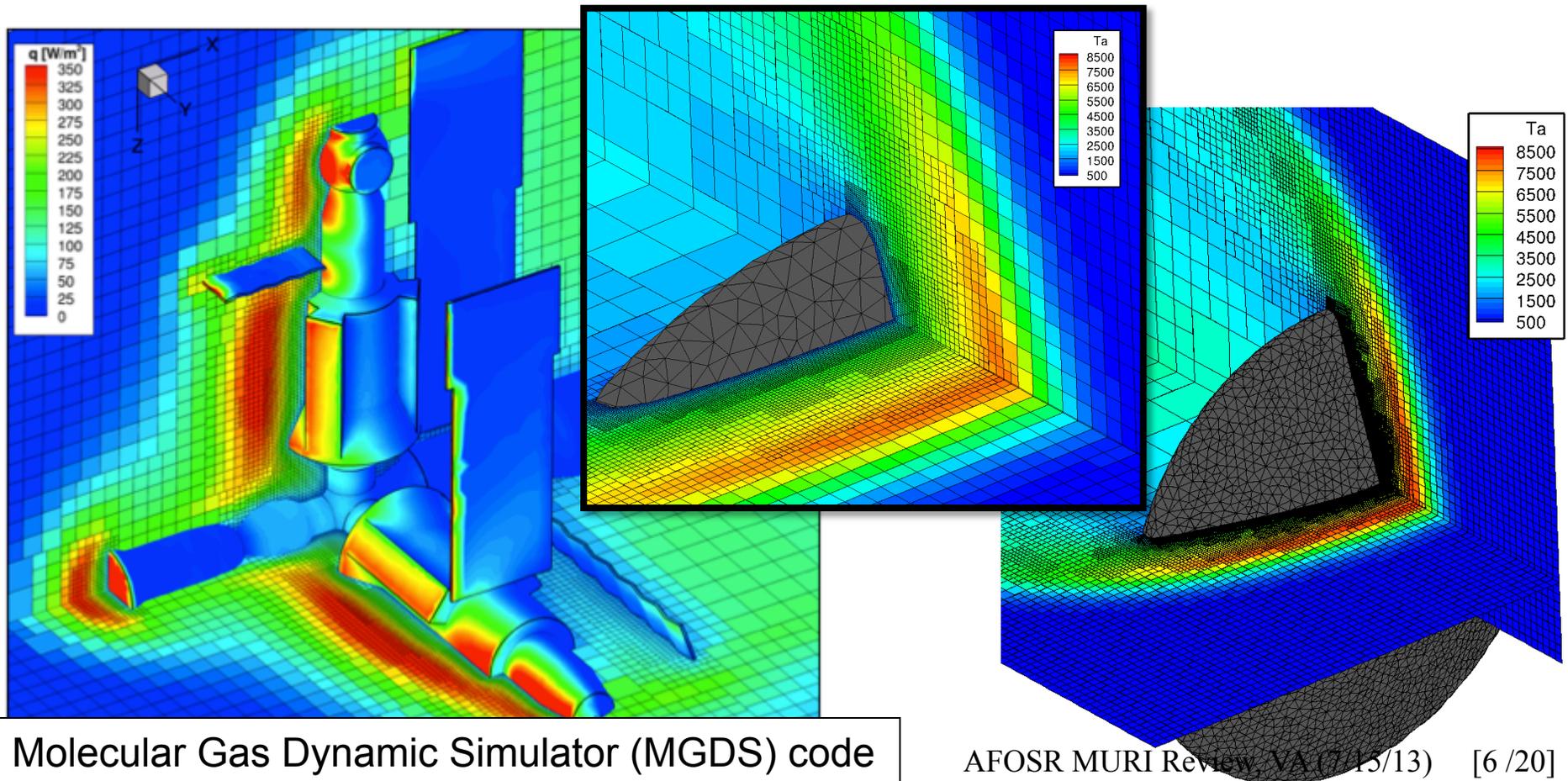


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Direct Simulation Monte Carlo (DSMC)

- 50-100 simulated molecules per cell (trivial calculations ~8-16 cores overnight)
- Currently, DSMC takes the same inputs as CFD (viscosity model, diffusion model, Millikan-White vibrational relaxation, dissociation $k_f(T, T_v)$ model, etc.)
- DSMC does not assume Maxwell-Boltzmann velocity and rot/vib distribution functions, rather, collision models are used (very flexible)



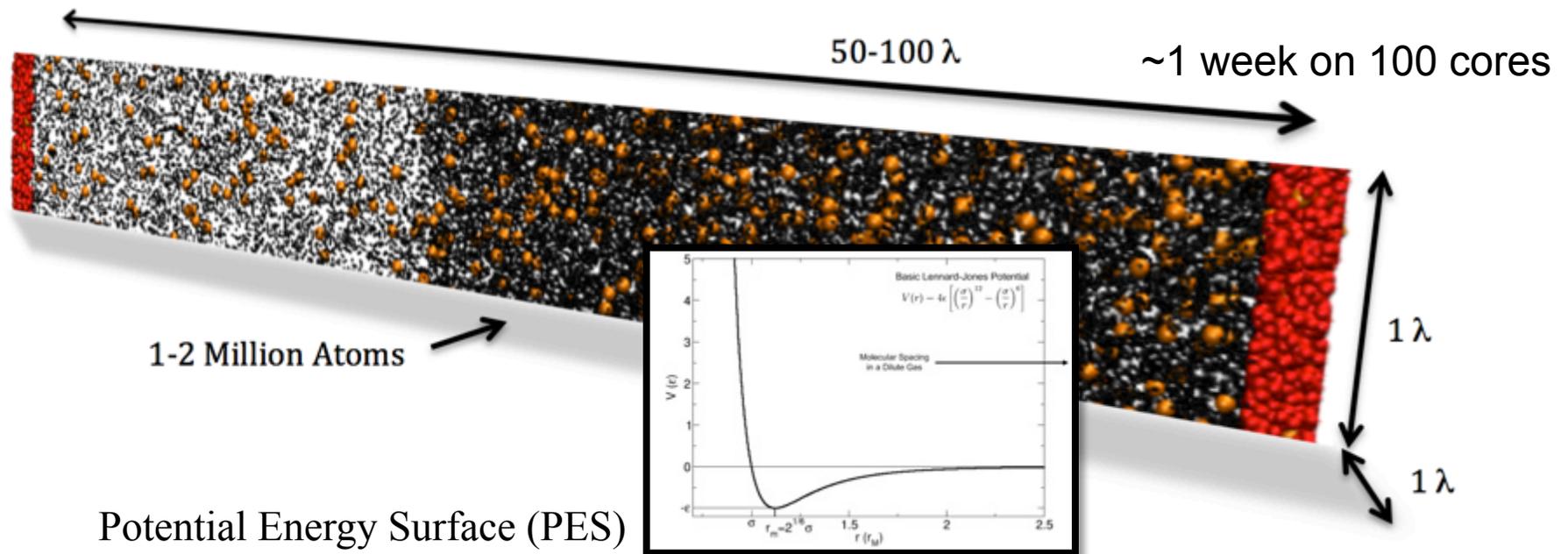
All-Atom Molecular Dynamics of Shock Waves

- No adjustable parameters: simple potentials for argon, helium, xenon, and nitrogen (vibrational ground state) are established

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

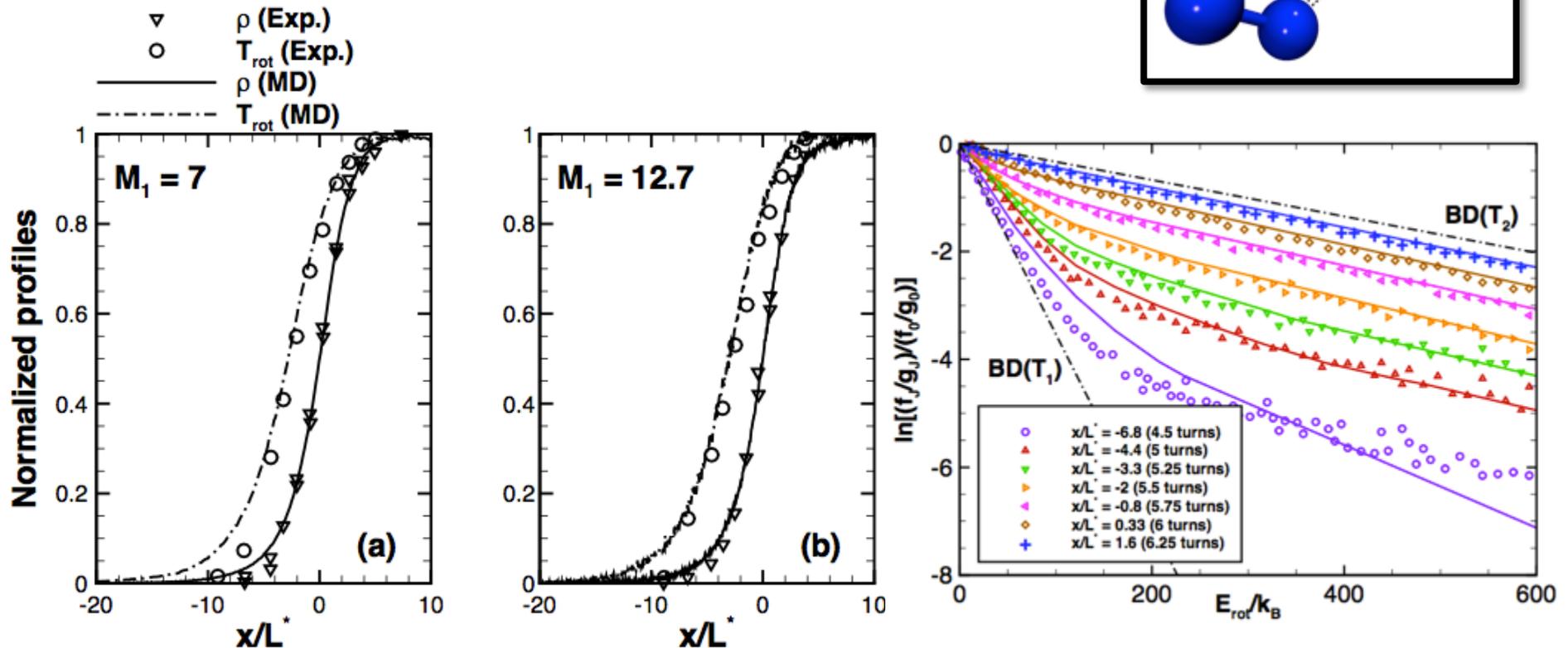
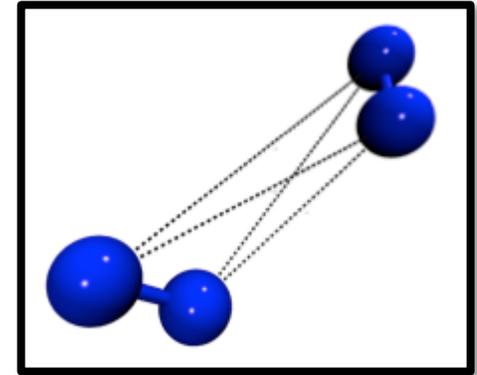
Valentini, and Schwartzentruber, "A Combined Event-Driven/Time-Driven Molecular Dynamics Algorithm for the Simulation of Shock Waves in Rarefied Gases", *Journal of Computational Physics*, 228 (2009) 8766-8778.

Valentini, Tump, Zhang, and Schwartzentruber, "Molecular dynamics simulations of shock waves in mixtures of noble gases", *Journal of Thermophysics and Heat Transfer*, Vol. 27, No. 2 (2013), pp. 226-234.



Diatomic Nitrogen (no vibrational excitation)

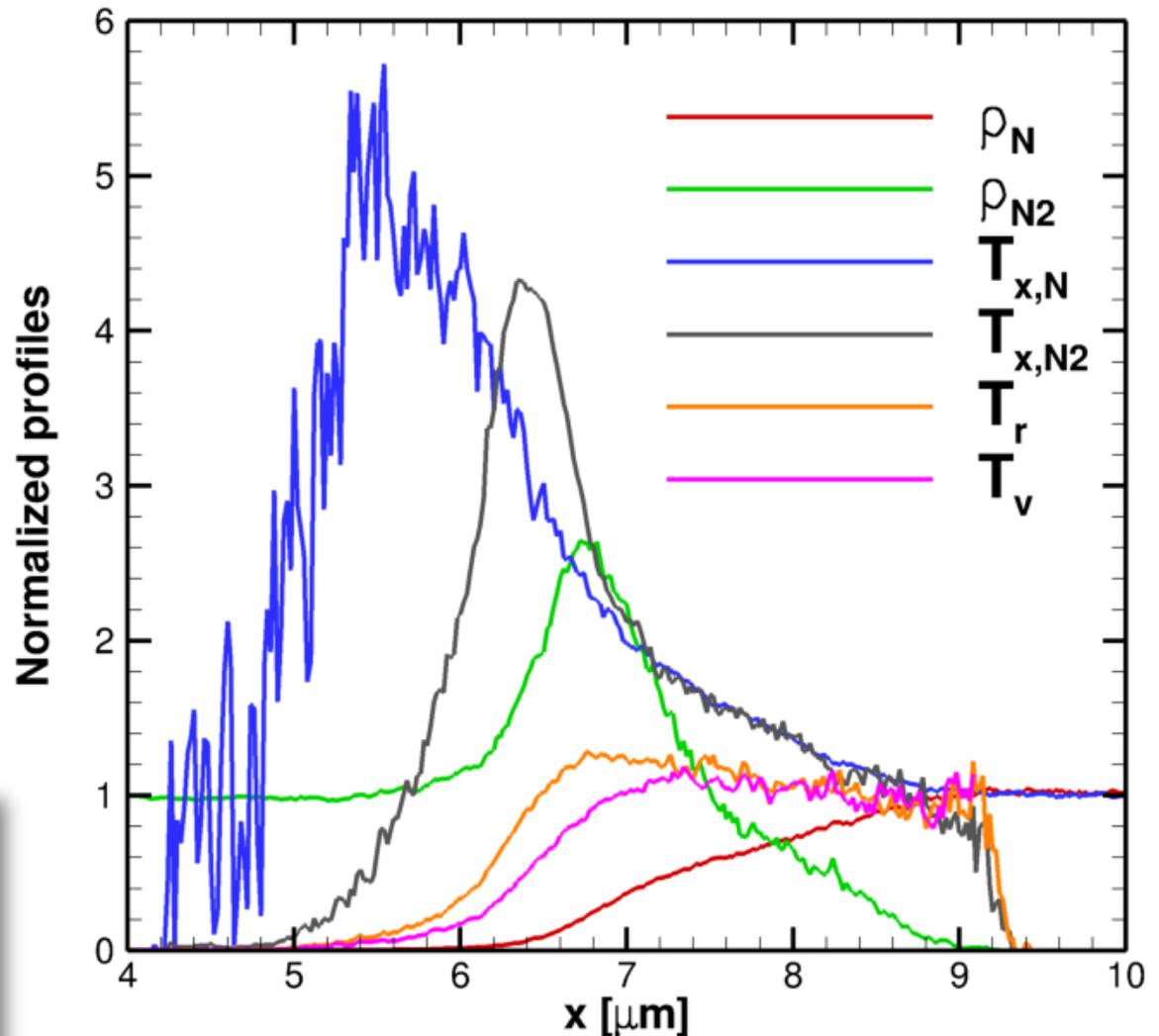
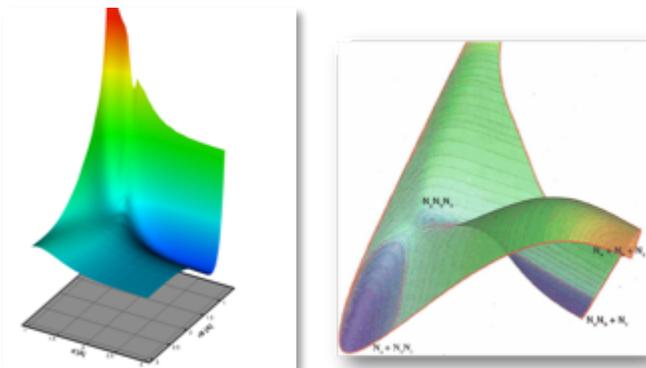
- MD validation with experimental data from Robben and Talbot (1966)
- PES involved rigid rotor molecules interacting with a site-to-site Lenard-Jones (LJ) potential



Valentini, Zhang, and Schwartzenruber, "Molecular dynamics simulation of rotational relaxation in nitrogen: implications for rotational collision number models", *Physics of Fluids*, 24, 106101 (2012).

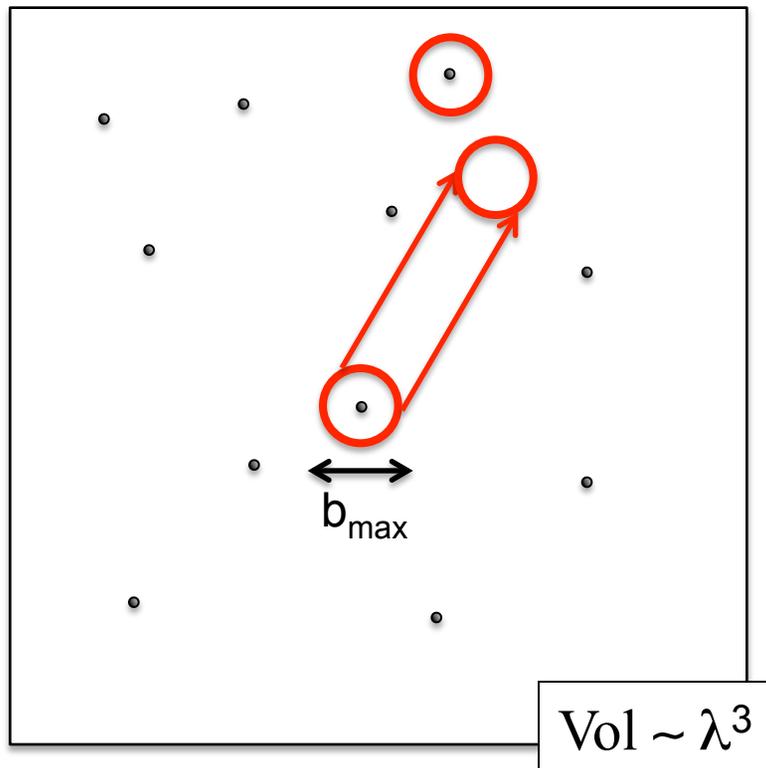
Preliminary MD of a Dissociating N₂ Shock Wave

- We now use a Morse-type potential that allows for dissociation
- We plan to use trajectory-based DSMC to handle dissociation for larger calculations (next slide)
- We plan to use new PES: [NASA Ames N3] and [Minnesota N4,O4,N2O2]



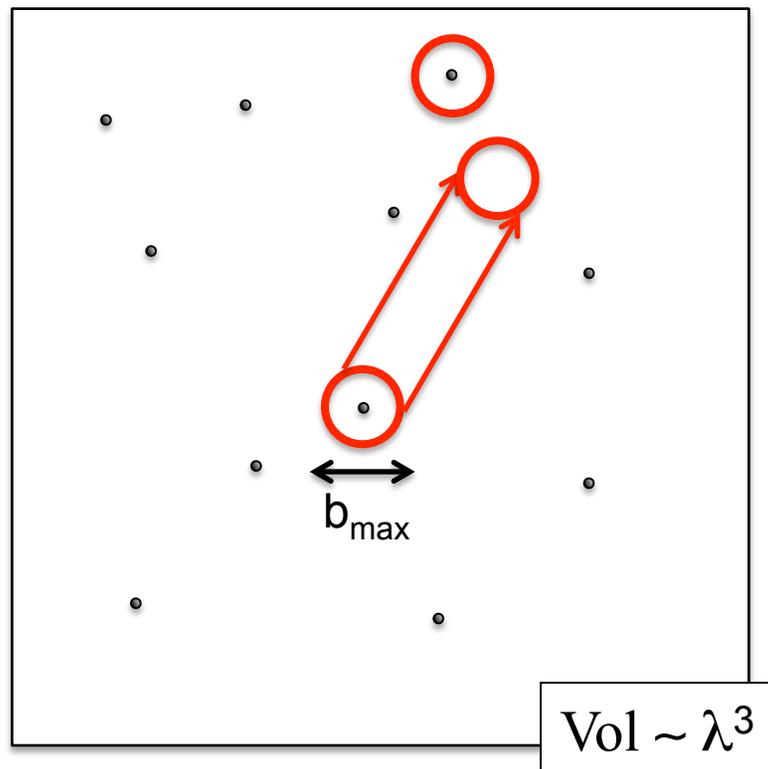
Trajectory Based DSMC (“CTC-DSMC”)

- Number of *trajectories* selected using a conservative hard-sphere cross-section

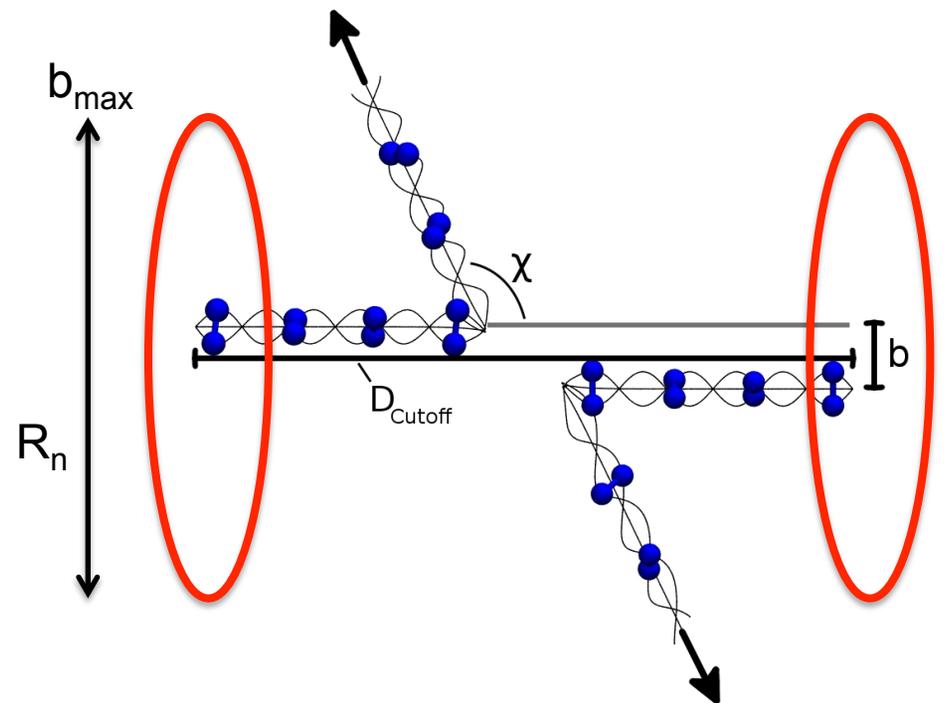


Trajectory Based DSMC (“CTC-DSMC”)

- Number of *trajectories* selected using a conservative hard-sphere cross-section
- If trajectories initialized with $(0 < b < b_{\max})$, where b_{\max} equals the hard-sphere cross-section, then *the PES determines the collision rate* (finite deflection angle)
- Also, *the PES determines the post collision states*

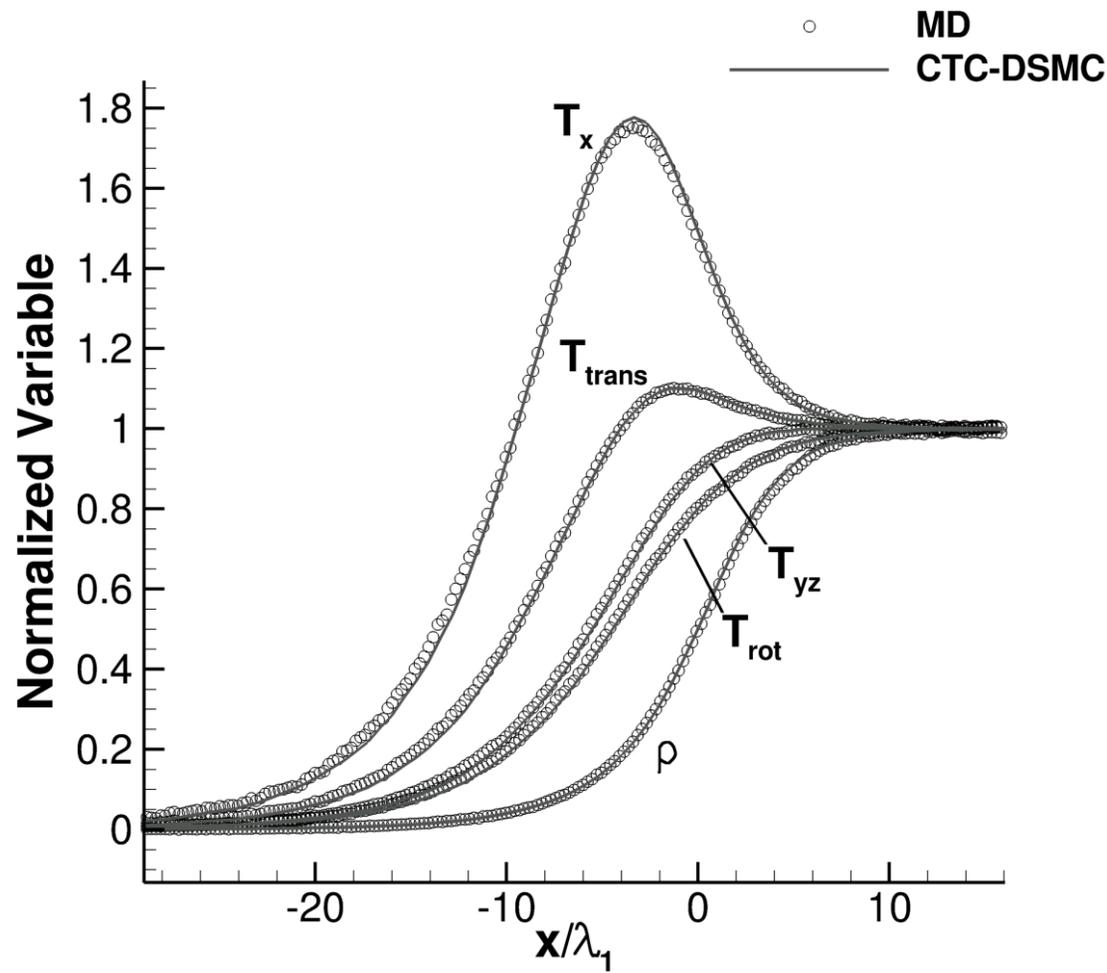


Only modeling input is the PES.



Trajectory-DSMC vs. Pure MD

- We can now directly verify CTC-DSMC with pure MD (crucial advancement)
- We aim for *exact* agreement (so far, so good)

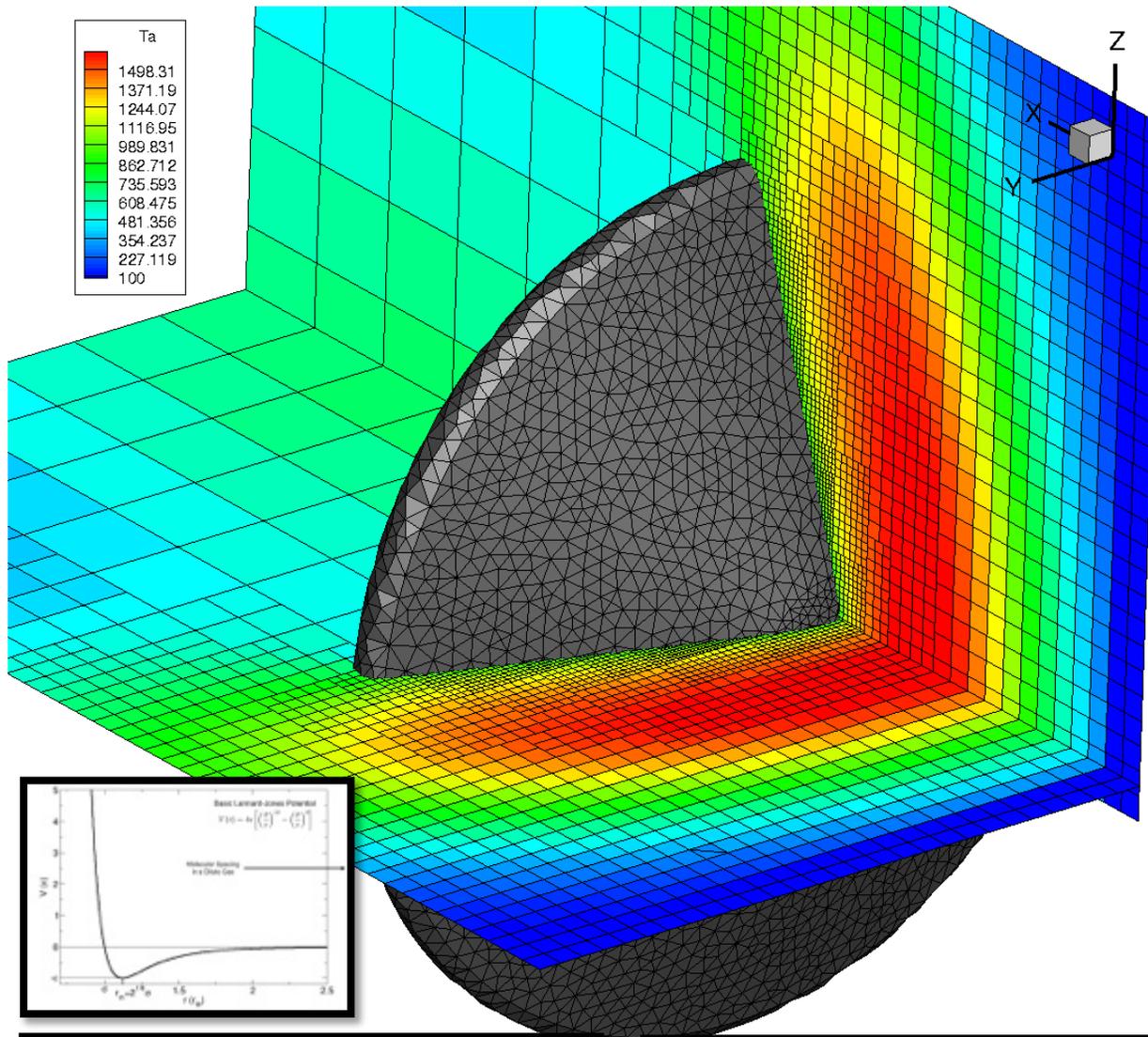


Norman and Schwartzenruber
“GPU-accelerated Classical
Trajectory Calculation DSMC
applied to shock waves”,
***Journal of Computational
Physics***, Vol. 247, 2013, pp.
153-167

Research on 3-body collisions:

Norman and Schwartzenruber
AIAA Paper 2013-1200, ASM
in Grapevine, Texas, 2013

3D CTC-DSMC is possible...

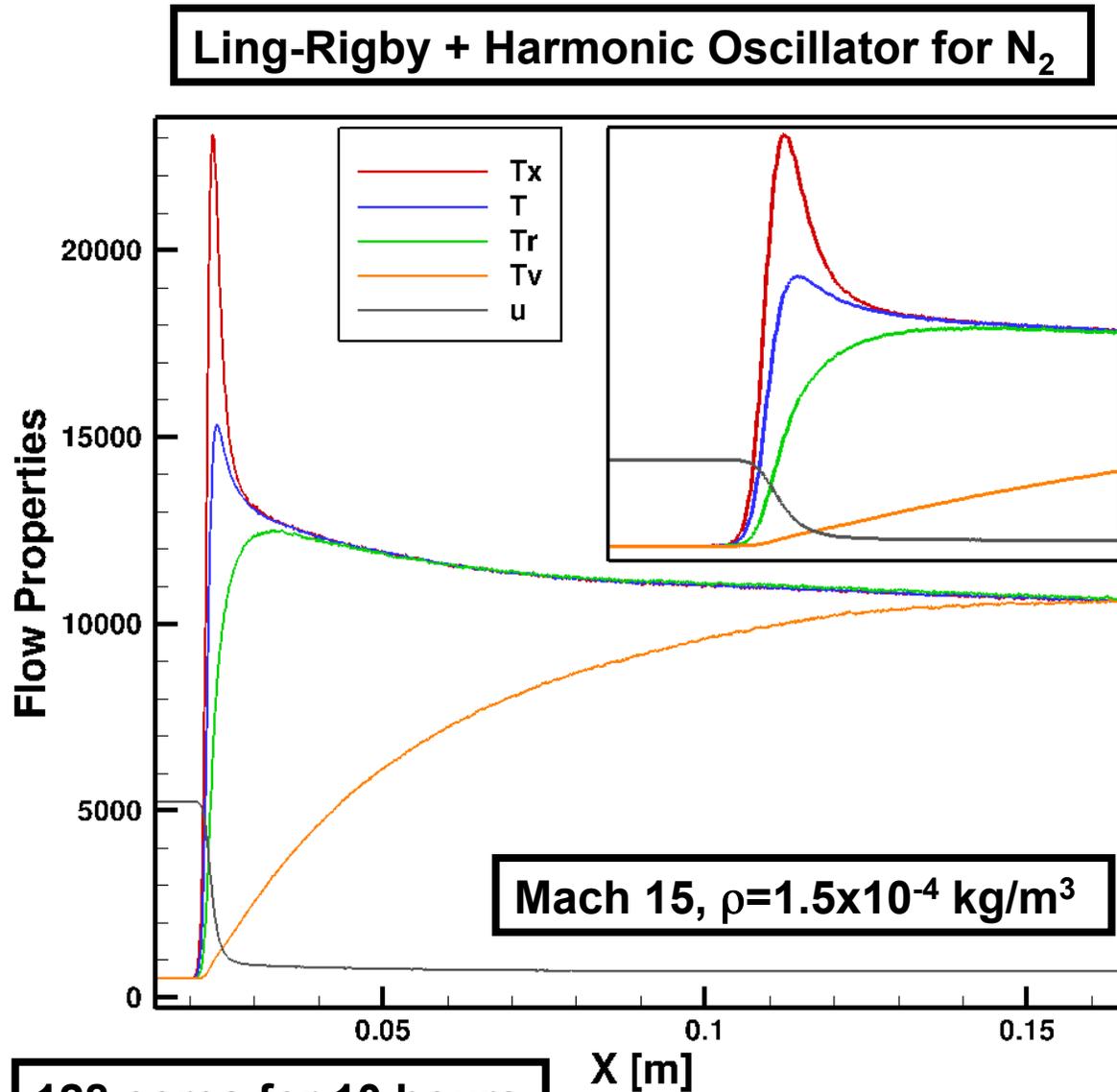


- 22 million particle DSMC-CTC calculation
- Trajectories replace the collision models in the Molecular Gas Dynamic Simulator (MGDS) code
- Number of trajectories is far larger than number of collisions using the DSMC-VHS model
- LJ potential accurately determines true collision rate in agreement with known value

Lennard-Jones for Argon

128 cores for 10 hours

CTC-DSMC for Rotating/Vibrating N₂



128 cores for 10 hours

- All-atom simulation (each trajectory integrates the motion of 4 N atoms)
- Simulation operates only atom positions and velocities
- No rotational or vibrational energies are defined (post-processed only)
- No Z_R , Z_V , σ_{VHS} , or Borgnakke-Larsen collision models
- Essentially **automates** the trajectories required to converge **state-to-state cross-sections**

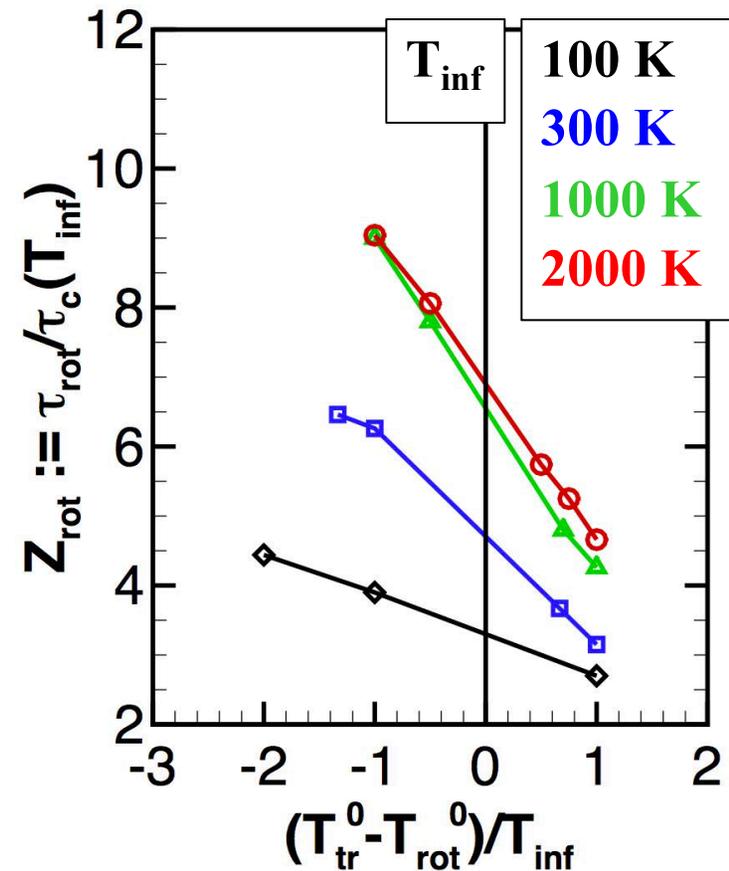
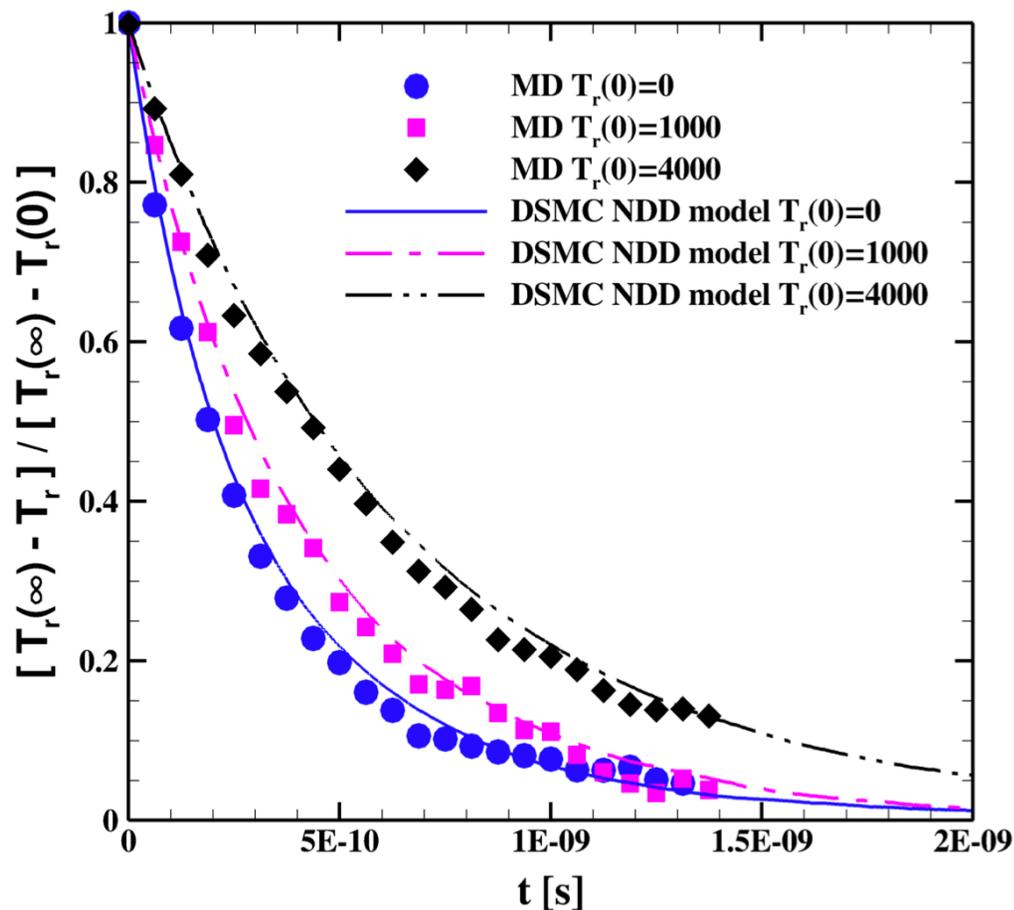
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“Directional” Dependence of Rotational Relaxation

- Pure MD relaxation, shock, and expansion simulations clearly show that rotational relaxation rates (τ_R and Z_R) depend strongly on the **degree of nonequilibrium and the direction-to the equilibrium state**

[Compressing flows = fast excitation] [Expanding flows = slow de-excitation]



A New Rotational Model for DSMC and CFD

- A simple phenomenological model, easy to implement and computationally efficient (called the NDD model), reproduces pure MD for a range of compressing and expanding flows
- Parameterized for nitrogen

$$p_{rot}^{NDD}(\varepsilon_t, \varepsilon_r) = \min\left\{C_n C_a \tilde{p}_{rot}(\varepsilon_t, \varepsilon_r), \frac{1}{2}\right\}$$

$$\tilde{p}_{rot}(\varepsilon_t, \varepsilon_r) = \frac{\Gamma\left(\frac{\zeta_t}{2}\right)\Gamma\left(\frac{\zeta_r}{2}\right)}{\Gamma\left(\frac{\zeta_t}{2} + n\right)\Gamma\left(\frac{\zeta_r}{2} - n\right)Z_r^\infty} \left[1 + \left(\frac{\zeta_t}{2} + n - 1\right)\frac{k_B T^*}{\varepsilon_t}\right] \left(\frac{\varepsilon_t}{\varepsilon_r}\right)^n$$

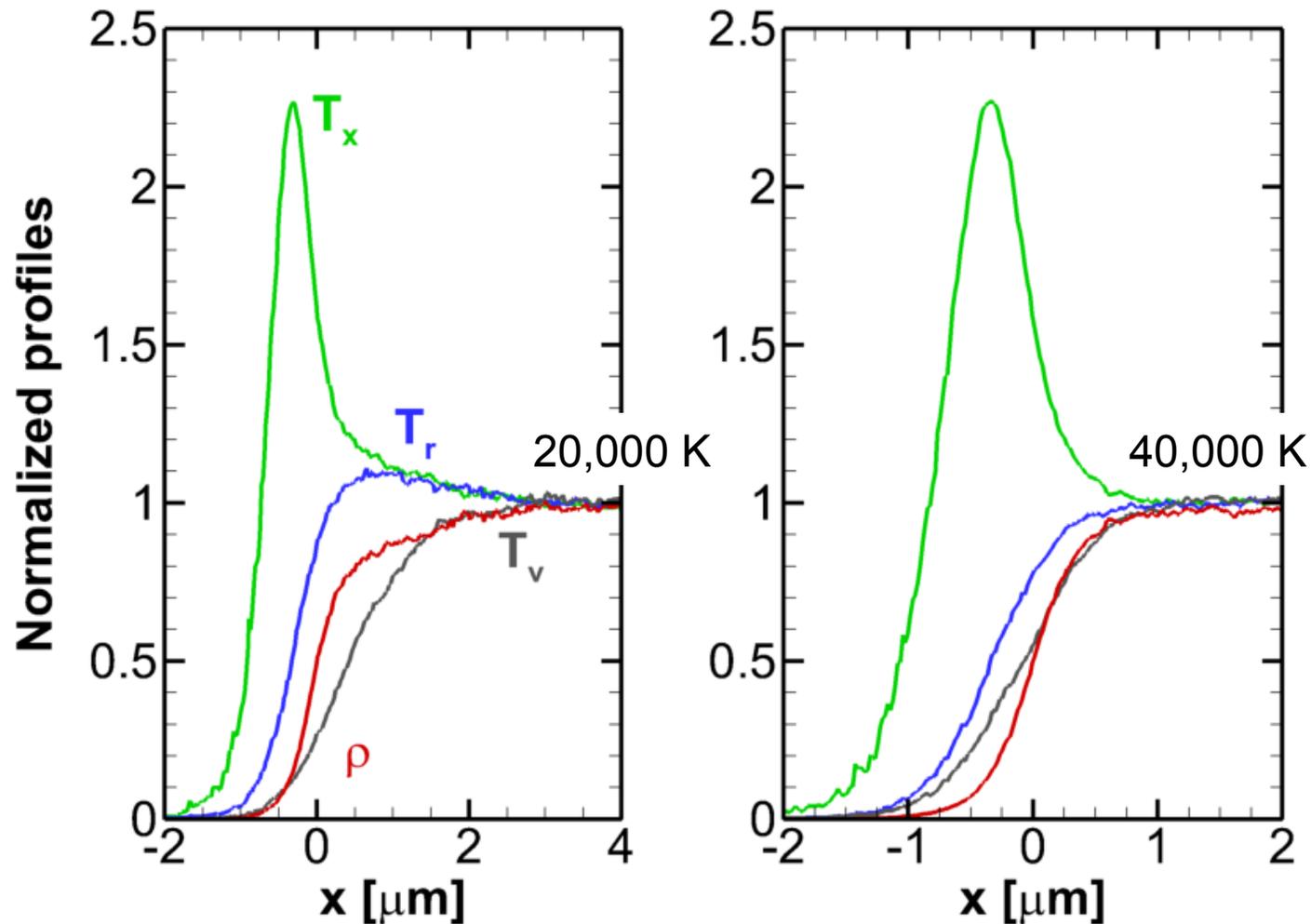
- In the continuum limit the model integrates to the following (for use in CFD):

$$Z_{rot}(T_t, T_r) = \frac{Z_r^\infty}{1 + \frac{T^*}{T_t}} \left(\frac{T_r}{T_t}\right)^n$$

Zhang, Valentini, and Schwartzentruber, “A Nonequilibrium-Direction-Dependent Rotational Energy Model for use in Continuum and Stochastic Molecular Simulation”, *AIAA Paper 2013-1202*

Rotation-Vibration Coupling at High Temperature

- At sufficiently high temperatures, rotation equilibrates with vibration first, not translation (pure MD simulations using Ling Rigby + HO for N₂)



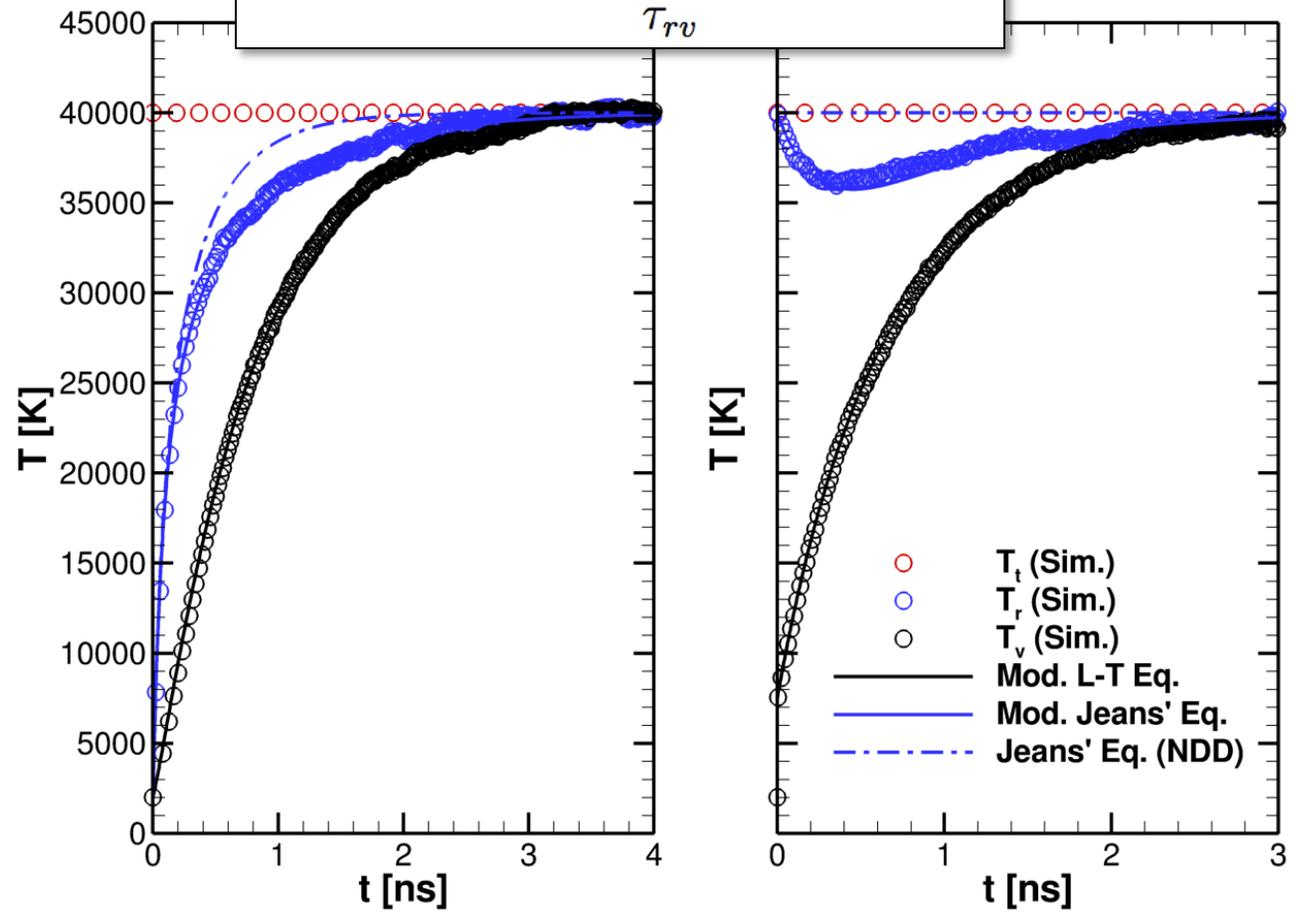
Rotation-Vibration Coupling at High Temperature

Proposed Modification:

$$\frac{d(\frac{1}{2}\zeta_r T_r)}{dt} = \frac{\frac{1}{2}\zeta_r T_t(t) - \frac{1}{2}\zeta_r T_r(t)}{\tau_r} + \Omega \quad \frac{d(\frac{1}{2}\zeta_v T_v)}{dt} = \frac{\frac{1}{2}\zeta_v T_t(t) - \frac{1}{2}\zeta_v T_v(t)}{\tau_v} - \Omega$$

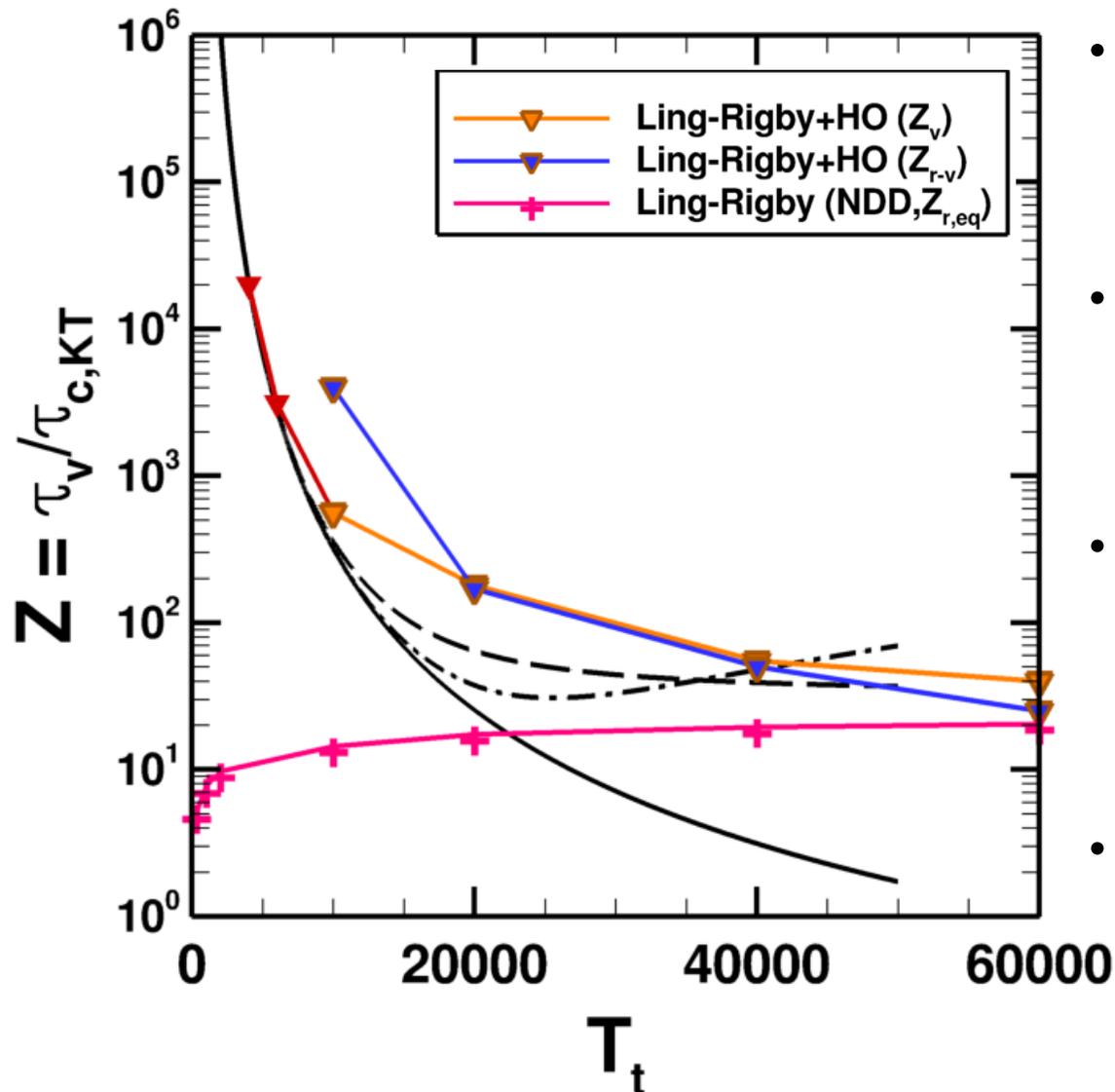
$$\Omega = \frac{\frac{1}{2}(\zeta_r + \zeta_v)T_v(t) - \frac{1}{2}(\zeta_r + \zeta_v)T_r(t)}{\tau_{rv}}$$

- Pure MD simulations predict very interesting physics that no current model can reproduce; at high temperatures rot-vib exchange becomes important
- Pure MD simulations suggest an intrinsic coupling that can only be captured using τ_R , τ_V , and τ_{R-V}
- PES ranging from HO to AHO reduce the temperature at which this occurs



Rotation-Vibration Coupling at High Temperature

- A number of studies (based on computational chemistry) predict that τ_v and τ_R approach one another at high temperatures



- This indicates that rotation should be considered in addition to vibration in CFD
- Furthermore, we are proposing a modification (τ_{R-v}) is also required
- We have used simplified potential energy surfaces (PES), however, we expect these trends to be correct
- We are now repeating the analysis with MURI PES

Summary

- We are using DSMC for real TPS microstructure to simulate diffusion, surface area, and surface reactions
- MURI team is working on understanding representative atomistic surfaces (i.e. etching) for carbon oxidation
- By combining the above modeling with new experimental data from MURI team (with new Exp. data), we hope to increase our understanding of realistic carbon-based TPS considerably
- Gas-phase modeling capabilities include: independent trajectories, pure MD, trajectory-based DSMC, state-resolved DSMC, DSMC, and CFD.
- MD modeling led to construction of a new “direction-dependent” rotational energy model and proposed correction for rotational-vibrational coupling.
- Having a full range of models is ideal in order to fully interpret both ab-initio and experimental data. I think these models are in place.

Challenges

- Ideally the modeling framework would look like:
 - computational chemistry – state-resolved cross-sections – thermally averaged state-resolved rates – reduced order CFD models
- Generating a state-resolved model is extremely complex and computationally expensive. Will need model-reduction, but how to do this?
-
- Rare events for MD, CTC-DSMC, DSMC, and converging cross-sections, present computational challenges
- Carbon-based (realistic) TPS oxidation is a highly complex, multiscale process. Our modeling approaches do not fully overlap as they do for gas-phase processes.
 - could be many dominant ‘mechanisms’ with complex, evolving, microstructure

Direct Molecular Simulation of Hypersonic Flows

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² **FA9550-10-1-0075:** AFOSR Young Investigator Program (YIP) FY2010

³ **FA9550-12-1-0202**