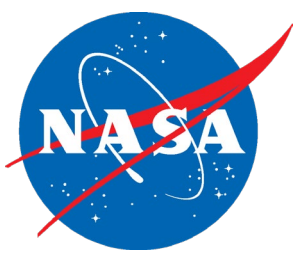
Discrete Rotational Energy for Polyatomic Molecules in Direct Simulation Monte Carlo

34th International Symposium on Rarefied Gas Dynamics
The University of Queensland
Brisbane, Australia

Derek S. Liechty
Aerothermodynamics Branch, NASA Langley Research Center
Dylan Crouse, Thomas Schwartzentruber
The University of Minnesota



Introduction

- The accurate prediction of internal energy relaxation becomes important when considering environments of vehicles entering atmospheres at high velocity.
- Direct simulation Monte Carlo (DSMC) has traditionally treated rotational energy with a continuous energy rigid rotor model.
  - Breaks down at low temperatures
  - Doesn’t account for physical stretching of bonds at high energy
- Previous works of Boyd and Gimelshein have addressed some of these issues, but either didn’t include polyatomic molecules or didn’t allow for centrifugal distortion.

Rigid Body Rotation of Polyatomic Molecules

- The classical kinetic energy of a rotor leads to the Hamiltonian

$$\widehat{H_r} = \frac{\widehat{J_a^2}}{2I_a} + \frac{\widehat{J_b^2}}{2I_b} + \frac{\widehat{J_c^2}}{2I_c}$$

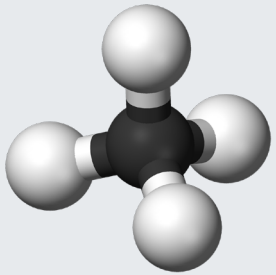
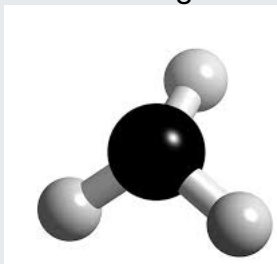
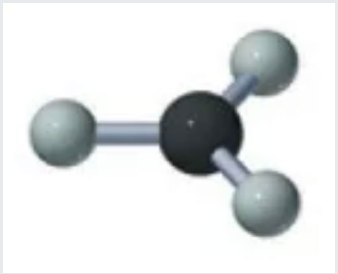
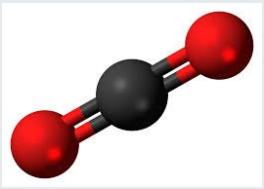
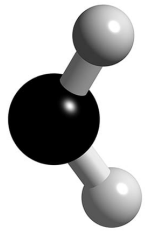
- The rotational motion of a rotor requires three quantum numbers
  - J is the rotational quantum number
  - M is the quantum number associated with projection of J onto space-fixed axis z
  - K is the quantum number associated with projection of J onto z-axis of molecule-fixed reference frame
- We define rotational constants about the principal axes:

$$\frac{\hbar^2}{2I_a} = hcA \qquad \frac{\hbar^2}{2I_b} = hcB \qquad \frac{\hbar^2}{2I_c} = hcC$$

Rigid Body Rotation of Polyatomic Molecules

Classification of Rotors

- Classification of Rotors is based on relative values of moments of inertia (or rotational constants)

Type	Spherical Top	Symmetric: Oblate Top	Symmetric: Prolate Top	Linear	Asymmetric
Relative Magnitudes Constants	$I_a = I_b = I_c$ $A = B = C$	$I_a = I_b < I_c$ $A = B > C$	$I_a < I_b = I_c$ $A > B = C$	$I_a = 0 < I_b = I_c$ $A = 0; B = C$	$I_a \neq I_b \neq I_c$ $A \neq B \neq C$
Examples	CH_4 	CH_3 	CH_3^+ 	CO_2 	CH_2 

Rigid Body Rotation of Polyatomic Molecules
Energy/Degeneracy

- Applying the definitions, energies and degeneracies of the different rotors become

Rotor Type	Energy	Degeneracy
Spherical	$\varepsilon_r = hcBJ(J+1)$	$g = (2J+1)^2$
Oblate	$\varepsilon_r = hc[BJ(J+1) + (C-B)K^2]$	$g = \begin{cases} 2J+1; K=0 \\ 2(2J+1); K \neq 0 \end{cases}$
Prolate	$\varepsilon_r = hc[BJ(J+1) + (A-B)K^2]$	$g = \begin{cases} 2J+1; K=0 \\ 2(2J+1); K \neq 0 \end{cases}$
Linear	$\varepsilon_r = hcBJ(J+1)$	$g = 2J+1$
Asymmetric – Nearly Prolate	$\varepsilon_r = hc\left[\frac{1}{2}(B+C)J(J+1) + \left(A - \frac{1}{2}(B+C)\right)K^2\right]$	$g = \begin{cases} 2J+1; K=0 \\ 2(2J+1); K \neq 0 \end{cases}$

Rigid Body Rotation of Polyatomic Molecules
Centrifugal Distortion

- Centrifugal force causes bonds to stretch slightly, increasing the moment of inertia, thus reducing rotational energy wrt rigid body

Rotor Type	Energy	Degeneracy
Spherical	$^{\varepsilon_r}/_{hc} = BJ(J+1) - D[J(J+1)]^2$	$g = (2J+1)^2$
Oblate	$^{\varepsilon_r}/_{hc} = BJ(J+1) + (C-B)K^2 - D_J[J(J+1)]^2 - D_{JK}J(J+1)K^2 - D_K K^4$	$g = \begin{cases} 2J+1; K=0 \\ 2(2J+1); K \neq 0 \end{cases}$
Prolate	$^{\varepsilon_r}/_{hc} = BJ(J+1) + (A-B)K^2 - D_J[J(J+1)]^2 - D_{JK}J(J+1)K^2 - D_K K^4$	$g = \begin{cases} 2J+1; K=0 \\ 2(2J+1); K \neq 0 \end{cases}$
Linear	$^{\varepsilon_r}/_{hc} = BJ(J+1) - D[J(J+1)]^2$	$g = 2J+1$

Not Included, Future Work

Modeling Discrete Rotational Energy in DSMC

Equilibrium Sampling

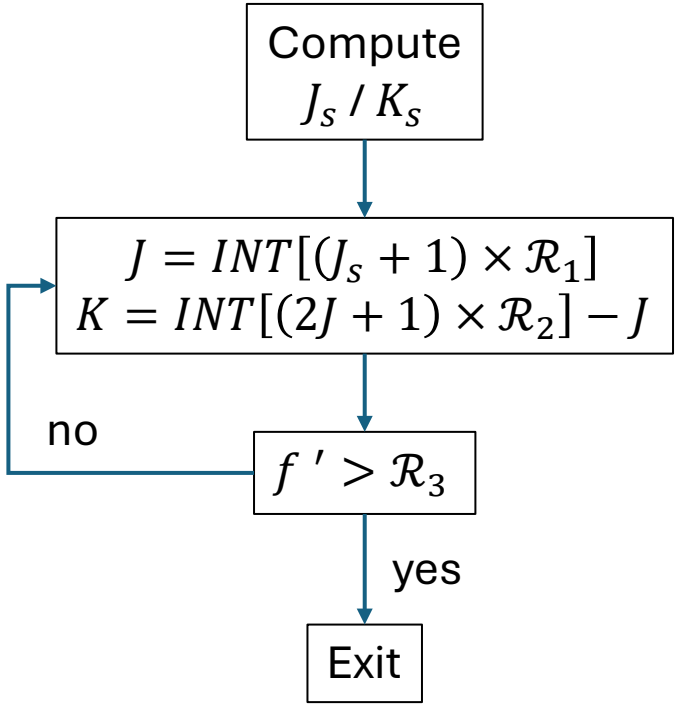
- Boltzmann distribution

$$f_{J,K} = \frac{N_{J,K}}{N} = \frac{g_J e^{-\frac{\epsilon_{J,K}}{kT}}}{\sum_j^{j_{max}} \sum_k^j g_j e^{-\frac{\epsilon_{j,k}}{kT}}} = \frac{g_J e^{-\frac{\epsilon_{J,K}}{kT}}}{Q_{J,K}}$$

- Acceptance/rejection scheme

$$f' = \frac{f}{f_{max}} = \frac{g_J e^{-\frac{\epsilon_{J,K}}{kT}}}{g_{J_s,K_s} e^{-\frac{\epsilon_{J_s,K_s}}{kT}}}$$

- J_s, K_s result in the maximum value of distribution function
- Details on computing max values in paper



Modeling Discrete Rotational Energy in DSMC

Post-Collision Sampling

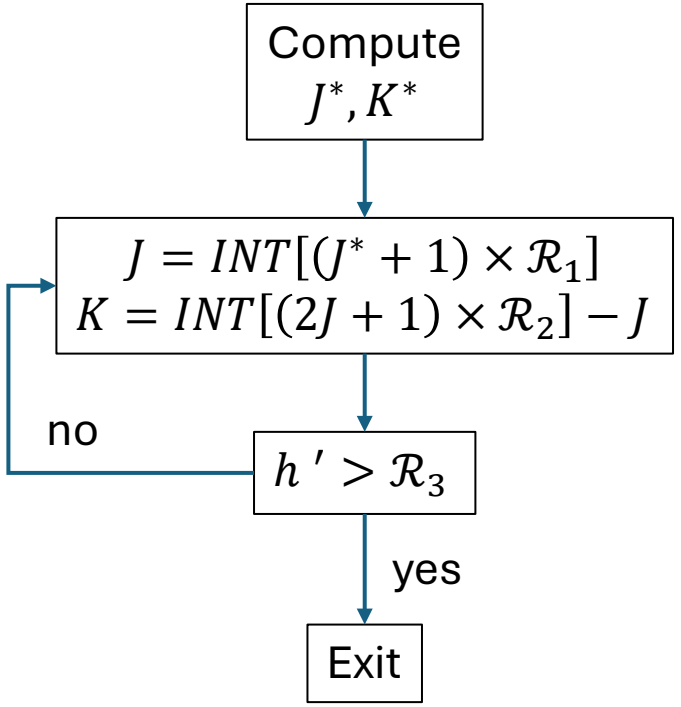
- Joint translational/rotational distribution function

$$h = \frac{g_J}{\Gamma\left(\frac{5}{2} - \omega_{A,B}\right)\sum_j^{j_{max}}\sum_k^j g_j e^{-\frac{\epsilon_{j,k}}{kT}}}\left(\frac{\epsilon_c - \epsilon_{J,K}}{kT}\right)^{\frac{3}{2}-\omega_{A,B}} e^{\left(-\frac{\epsilon_c}{kT}\right)}$$

- Acceptance/rejection scheme

$$h' = \frac{h}{h_{max}} = \frac{g_{J'}\left(\epsilon_c - \epsilon_{J',K'}\right)^{\frac{3}{2}-\omega_{A,B}}}{g_{J_s}\left(\epsilon_c - \epsilon_{J^*,K^*}\right)^{\frac{3}{2}-\omega_{A,B}}}$$

- J^*, K^* result in the maximum value of distribution function limited to the available collision energy
- Details on computing max values in paper



Results and Discussion

- Spectroscopic parameters

Species	Type	ζ_r	σ	A (cm^{-1})	B (cm^{-1})	C (cm^{-1})	D_J (cm^{-1})	D_{JK} (cm^{-1})	D_K (cm^{-1})
CH_4	Spherical	3	12	5.2412	5.2412	5.2412	1.09e-4	-	-
CH_3	Oblate	3	6	9.5779	9.5779	4.7428	1.05e-3	-1.9e-3	9.5e-4
CH_3^+	Prolate	3	6	9.3744	4.6114	4.6114	7.8e-4	-1.4e-3	6.0e-4
CO_2	Linear	2	2	0.0000	0.3915	0.0000	1.33e-7	-	-
CH_2	Asymmetric	3	2	73.8106	8.4504	7.1843	-	-	-

- DSMC parameters

Species	Type	MW (amu)	d_{ref} (m)	T_{ref} (K)	ω	α
CH_4	Spherical	16.0425	4.292e-10	273.0	0.688	1.419
CH_3	Oblate	15.0345	4.267e-10	273.0	0.684	1.418
CH_3^+	Prolate	15.034	4.267e-10	273.0	0.684	1.418
CO_2	Linear	44.0095	4.147e-10	273.0	0.632	1.259
CH_2	Asymmetric	14.0266	4.267e-10	273.0	0.684	1.418

Results and Discussion

Equilibrium Temperatures

- Integral temperature (integral)

$$T_r^r r = \frac{2\langle e_r \rangle}{\zeta_r R}$$

- Iterative method of Civrais*

$$f(T_r) = E_r^{DSMC} - E_r^{rr/cd}(T_r)$$

$$E_r^{rr/cd}(T_r) = \frac{\sum_{J=0}^{J_{max}} \sum_{K=0}^{J} \epsilon_{J,K} g_J e^{\left(-\frac{\epsilon_{J,K}}{kT}\right)}}{\sum_{J=0}^{J_{max}} \sum_{K=0}^{J} g_J e^{\left(-\frac{\epsilon_{J,K}}{kT}\right)}}$$

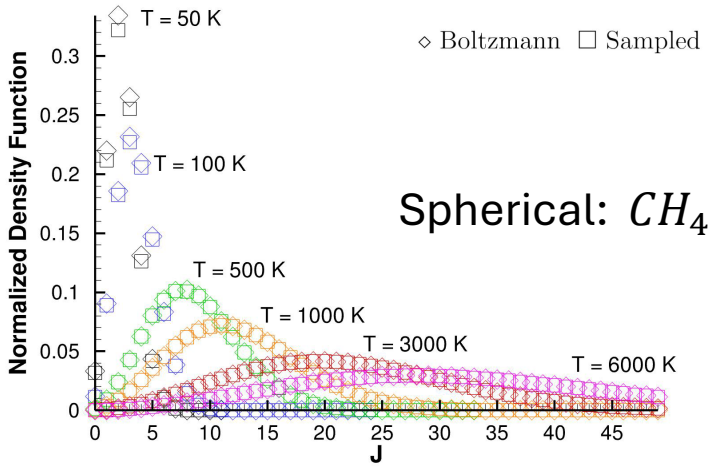
*Civrais, C.H.B., White, C., Steijl, R.: Vibrational modeling with an anharmonic oscillator model in direct simulation Monte Carlo. Journal of Thermophysics and Heat Transfer **37**(3) 534-548 (2023)

Species	T^{eq} (K)	$T^{integral}$ (K)	T^{rr} (K)	T^{cd} (K)
CH_4	50.00	48.74	50.00	49.99
	100.0	98.74	100.02	100.02
	500.00	498.85	499.95	500.08
	1000.00	998.70	999.98	999.62
	3000.00	2998.79	3000.13	3000.28
	6000.00	5999.38	5999.64	6000.34
CH_3	50.00	48.44	50.00	-
	100.00	98.46	100.00	-
	500.00	498.46	499.99	-
	1000.00	998.46	1000.03	-
	3000.00	2998.18	2999.61	-
	6000.00	5998.15	5999.76	-
CH_3^+	50.00	48.69	49.99	-
	100.00	98.68	100.00	-
	500.00	498.78	500.01	-
	1000.00	998.66	1000.21	-
	3000.00	2998.37	3000.19	-
	6000.00	5999.77	5999.57	-
CO_2	50.00	49.81	50.00	50.01
	100.00	99.85	100.00	100.02
	500.00	499.79	500.03	499.83
	1000.00	999.94	1000.07	1000.14
	3000.00	3000.22	2999.77	3000.09
	6000.00	5999.77	5999.57	5999.60
CH_2	50.00	44.56	50.00	-
	100.00	97.44	99.99	-
	500.00	497.56	500.03	-
	1000.00	997.64	1000.03	-
	3000.00	2997.53	3000.01	-
	6000.00	5997.74	6000.27	-

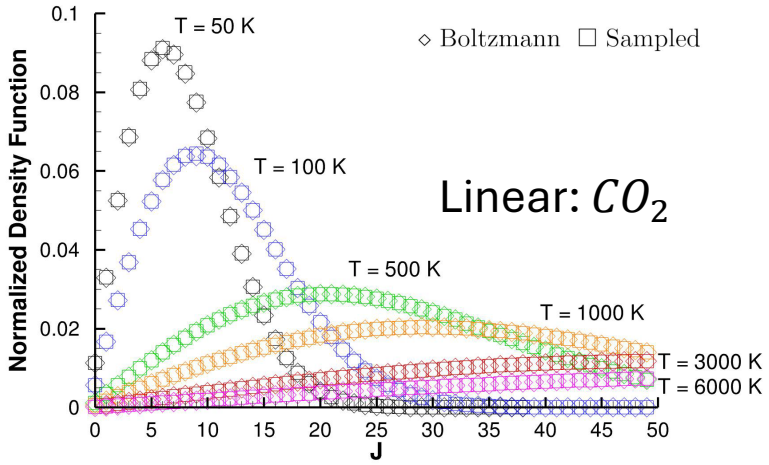
Results and Discussion

Equilibrium Distribution of Energy Levels

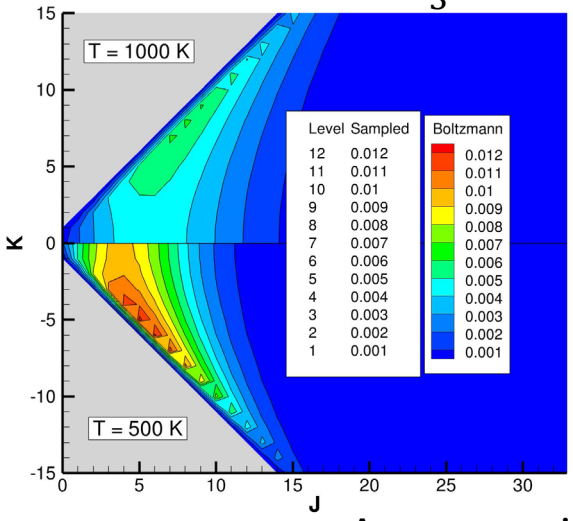
Spherical: CH_4



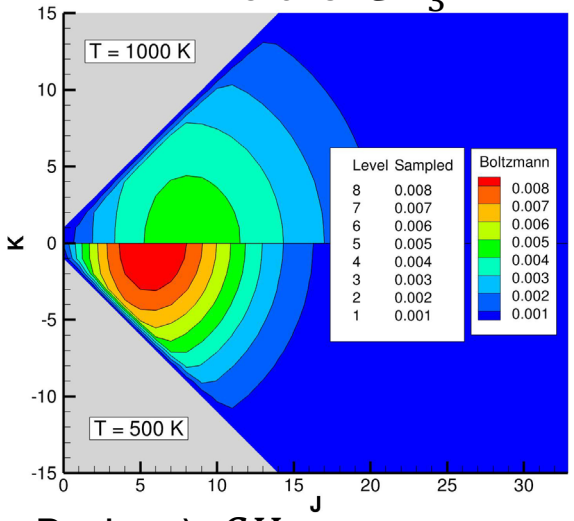
Linear: CO_2



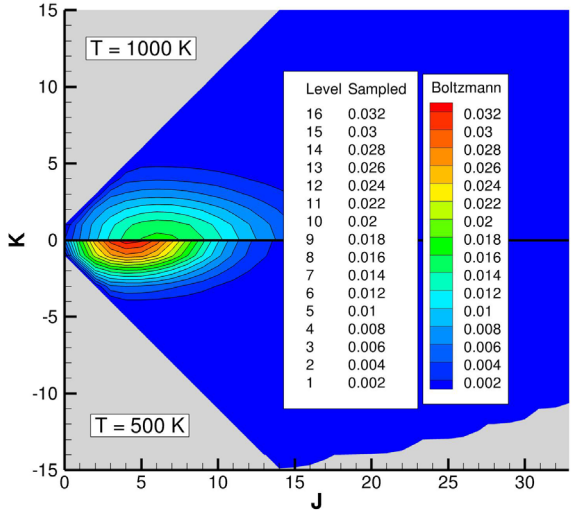
Oblate: CH_3



Prolate: CH_3^+



Asymmetric (Near-Prolate): CH_2



Results and Discussion

Thermophysical Properties: Specific Heat

- Expected value

$$c_v = \left(\frac{\partial e}{\partial T}\right)_V \qquad e = RT^2 \frac{\partial}{\partial T}[\ln(Q)]$$

  - We'll define

$$S_0 = \sum_{J=0}^{\infty} \sum_{K=0}^{J} g_J e^{\left(-\frac{\epsilon_{J,K}}{kT}\right)} = Q_r$$

$$S_1 = \sum_{J=0}^{\infty} \sum_{K=0}^{J} g_J \left(\frac{\epsilon_{J,K}}{k}\right) e^{\left(-\frac{\epsilon_{J,K}}{kT}\right)}$$

$$S_2 = \sum_{J=0}^{\infty} \sum_{K=0}^{J} g_J \left(\frac{\epsilon_{J,K}}{k}\right)^2 e^{\left(-\frac{\epsilon_{J,K}}{kT}\right)}$$

$$c_v = R \frac{S_0 S_2 - S_1^2}{S_0^2 T^2}$$

- Sampled value – variance of energy

$$c_v = \frac{\langle (\Delta e)^2 \rangle}{kT^2} = \frac{\langle e^2 \rangle - \langle e \rangle^2}{kT^2}$$

Species	T^{eq} (K)	$c_v^{integral}/R$	c_v^{rr}/R	$c_v^{rr,sampled}/R$	c_v^{cd}/R	$c_v^{cd,sampled}/R$
CH_4	50.00	1.50000	1.50000	1.50017	1.50104	1.50208
	100.00	1.50000	1.50000	1.49955	1.50208	1.50390
	500.00	1.50000	1.50000	1.50148	1.51061	1.51179
	1000.00	1.50000	1.50000	1.49979	1.52178	1.52017
	3000.00	1.50000	1.50000	1.50000	1.57347	1.57090
	6000.00	1.50000	1.50000	1.50102	1.59840	1.59711
CH_3	50.00	1.50000	1.50144	1.50156	-	-
	100.00	1.50000	1.50040	1.50074	-	-
	500.00	1.50000	1.50002	1.50051	-	-
	1000.00	1.50000	1.50000	1.49985	-	-
	3000.00	1.50000	1.50000	1.50020	-	-
	6000.00	1.50000	1.50000	1.49986	-	-
CH_3^+	50.00	1.50000	1.50011	1.50022	-	-
	100.00	1.50000	1.50003	1.49976	-	-
	500.00	1.50000	1.50000	1.49988	-	-
	1000.00	1.50000	1.50000	1.49941	-	-
	3000.00	1.50000	1.50000	1.49941	-	-
	6000.00	1.50000	1.50000	1.50037	-	-
CO_2	50.00	1.00000	1.00000	0.99987	1.00012	1.00048
	100.00	1.00000	1.00000	1.00065	1.00024	1.00039
	500.00	1.00000	1.00000	1.00010	1.00121	1.00057
	1000.00	1.00000	1.00000	1.00004	1.00243	1.00251
	3000.00	1.00000	1.00000	1.00027	1.00744	1.00830
	6000.00	1.00000	1.00000	1.00012	1.01213	1.01299
CH_2	50.00	1.50000	1.72933	1.72905	-	-
	100.00	1.50000	1.51295	1.51339	-	-
	500.00	1.50000	1.50001	1.49979	-	-
	1000.00	1.50000	1.50000	1.49989	-	-
	3000.00	1.50000	1.50000	1.50000	-	-
	6000.00	1.50000	1.50000	1.49994	-	-

Results and Discussion

Thermophysical Properties: Enthalpy

- Expected value

$$h_{int} \equiv e_{int}$$

  - From previous definitions

$$h_r = R\frac{S_1}{S_0}$$

- Sampled value

$$h = \langle e \rangle$$

Species	T^{eq} (K)	$h^{integral}/R$	h^{rr}/R	$h^{rr,sampled}/R$	h^{cd}/R	$h^{cd,sampled}/R$
CH_4	50.00	1.50000	1.46230	1.46221	1.46281	1.46248
	100.00	1.50000	1.48115	1.48114	1.48219	1.48242
	500.00	1.50000	1.49623	1.49655	1.50149	1.50174
	1000.00	1.50000	1.49811	1.49805	1.50882	1.50823
	3000.00	1.50000	1.49937	1.49940	1.53401	1.53416
	6000.00	1.50000	1.49969	1.49984	1.56852	1.56861
CH_3	50.00	1.50000	1.45292	1.45310	-	-
	100.00	1.50000	1.47684	1.47688	-	-
	500.00	1.50000	1.49543	1.46548	-	-
	1000.00	1.50000	1.49772	1.49769	-	-
	3000.00	1.50000	1.49924	1.49909	-	-
	6000.00	1.50000	1.49962	1.49954	-	-
CH_3^+	50.00	1.50000	1.46110	1.46076	-	-
	100.00	1.50000	1.48058	1.48026	-	-
	500.00	1.50000	1.49612	1.49635	-	-
	1000.00	1.50000	1.49806	1.49799	-	-
	3000.00	1.50000	1.49935	1.49918	-	-
	6000.00	1.50000	1.49968	1.49959	-	-
CO_2	50.00	1.00000	0.99624	0.99617	0.99630	0.99646
	100.00	1.00000	0.99812	0.99847	0.99824	0.99853
	500.00	1.00000	0.99962	0.99959	1.00023	1.00042
	1000.00	1.00000	0.99981	0.99994	1.00103	1.00117
	3000.00	1.00000	0.99994	1.00007	1.00362	1.00365
	6000.00	1.00000	0.99997	0.99996	1.00718	1.00711
CH_2	50.00	1.50000	1.33684	1.33683	-	-
	100.00	1.50000	1.46152	1.46156	-	-
	500.00	1.50000	1.49269	1.49267	-	-
	1000.00	1.50000	1.49635	1.49646	-	-
	3000.00	1.50000	1.49878	1.49877	-	-
	6000.00	1.50000	1.49939	1.49943	-	-

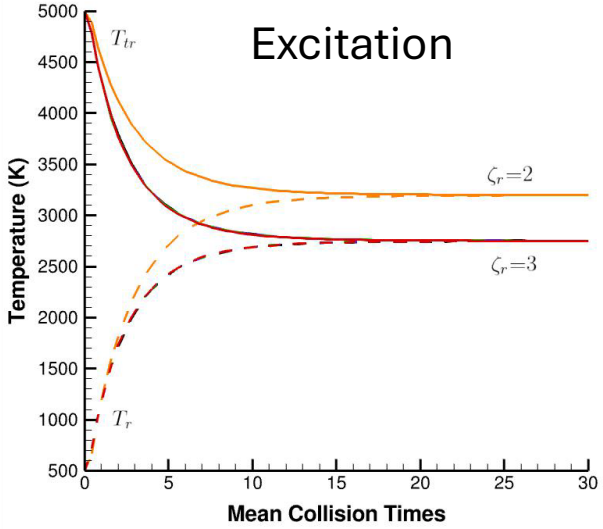
Results and Discussion

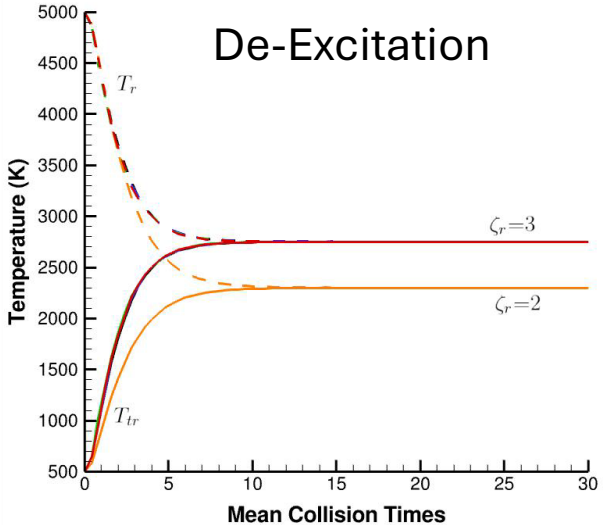
Adiabatic Relaxation: Equilibrium Temperature

- Excitation and de-excitation of rotational energy
- Equilibrium temperature

$$T_{eq} = \frac{\zeta_{tr,i} T_{tr,i} + \zeta_{r,i} T_{r,i}}{\zeta_{tr,f} + \zeta_{r,f}}$$

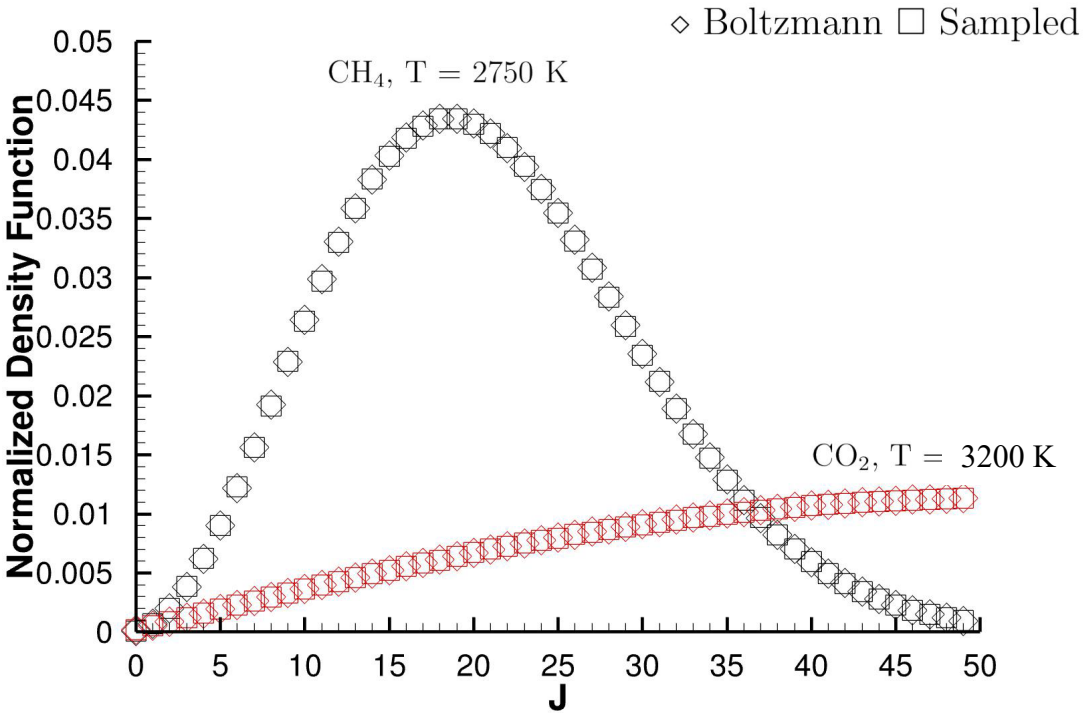
  - Excitation
    - $T_{eq} = 2750$ K for $\zeta_r = 3$
    - $T_{eq} = 3200$ K for $\zeta_r = 2$
  - De-Excitation
    - $T_{eq} = 2750$ K for $\zeta_r = 3$
    - $T_{eq} = 2300$ K for $\zeta_r = 2$

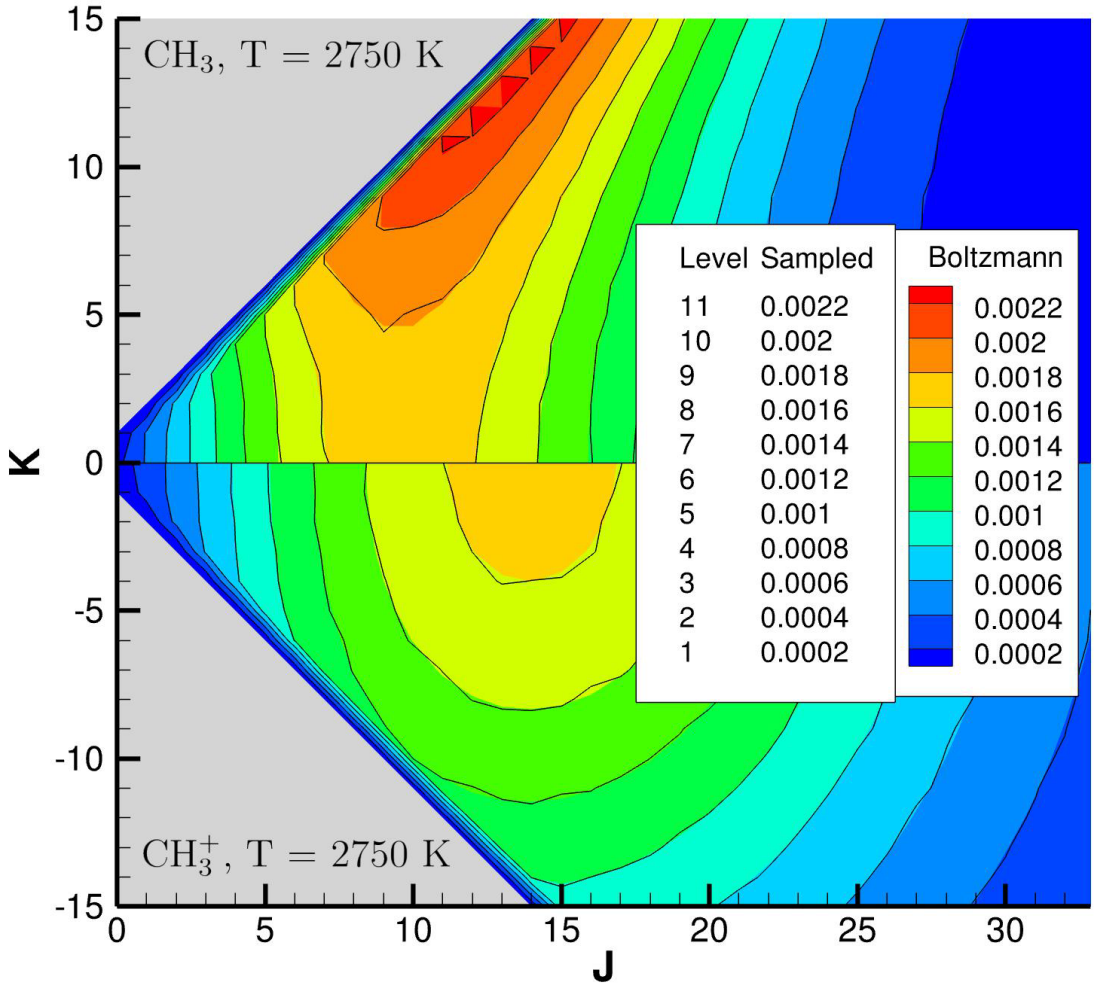




Results and Discussion

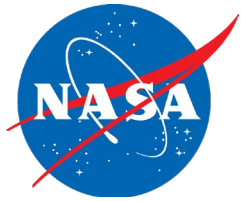
Adiabatic Relaxation: Energy Level Distribution





Conclusions

- A discrete rotational energy model for polyatomic molecules has been successfully implemented and verified within DSMC.
  - Post-collision and equilibrium sampling procedures successfully reproduce theoretical distributions, specific heat, and enthalpy.
  - Effectively reproduced theoretical equilibrium in systems initially in thermal non-equilibrium.
- Sampled values of rigid rotor model accurately captured deviations at low-temperature missed by continuous energy model.
- Addition of centrifugal distortion demonstrated the model's capability to account for bond stretching at high rotational energies



Questions?