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The Quantum-Kinetic Chemical Reaction Model for Navier-Stokes Codes

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Introduction

- Goal: Use NS to simulate upper-atmospheric flight
  - Chemical and thermal non-equilibrium
  - Reaction rates extrapolated

- Quantum-Kinetic reaction model
  - Originally proposed by Bird for DSMC
  - Phenomenological model based on colliding molecules
    - Uses microscopic data to calculate reaction rates
  - Reproduce equilibrium rates
    - Within uncertainty for temperature ranges measured
  - Model predicts rates in thermal non-equilibrium
  - Allows for closed-form solutions for use in Navier-Stokes (NS) and hybrid DSMC/NS codes

Current Study

- Test Q-K model in a NS simulation
  - Implement Q-K reaction models in a three-temperature NS code, DPLR
    - Obtain better agreement between DSMC and NS
    - Verify Q-K as a general chemistry model
  - Apply chemical reaction models to high-altitude flight test (BSUV)
  - Compare with previous studies: NS and DSMC

Quantum-Kinetic Model

- "QK Vib."
- Dissociation reaction rate:

$$k_{diss}\left(T,T_v\right)=\frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}}\left(\frac{T}{T_{ref}}\right)^{1-\omega}\left(\frac{2k_BT_{ref}}{m_r}\right)^{1/2}\left[\Phi_{vib}\left(T,T_v\right)+B\Psi_{vib}\left(T_v\right)\right]$$

$$\Phi_{vib}=\frac{1}{z_{vib}(T_v)}\sum_{i=0}^{i_d}Q\left[\frac{5}{2}-\omega,\frac{\theta_d-i\theta_v}{T}\right]\exp\left(-\frac{i\theta_v}{T_v}\right)$$

- Exchange reaction rate:

$$k_{exch}\left(T,T_v\right)=\frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}}\left(\frac{T}{T_{ref}}\right)^{1-\omega}\left(\frac{2k_BT_{ref}}{m_r}\right)^{1/2}\left(\exp\left(-\frac{C_1}{T_{av}\left(T,T_v\right)}\right)-\exp\left(-\frac{C_2}{T_{av}\left(T,T_v\right)}\right)\right)$$

$$C_1=i_a\theta_v\ ;\ i_a=\text{floor}\left(\frac{\theta_r}{\theta_v}\right)+1$$

$$C_2=i_d\theta_v\ ;\ i_d=\text{floor}\left(\frac{\theta_d}{\theta_v}\right)$$

$$T_{av}\left(T,T_v\right)=\frac{(3+2)T+2T_v}{(3+2)+2}$$

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Quantum-Kinetic Model

- "QK Rot."
- Dissociation reaction rate:

$$k_{diss}\left(T,T_r,T_v\right)=\frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}}\left(\frac{T}{T_{ref}}\right)^{1-\omega}\left(\frac{2k_BT_{ref}}{m_r}\right)^{1/2}\left[\Phi_{int}\left(T,T_r,T_v\right)+B\Psi_{int}\left(T_r,T_v\right)\right]$$

$$\Phi_{int}=\frac{1}{z_{vib}(T_v)z_{rot}(T_r)}\sum_{j=0}^{\infty}\left[(2j+1)\exp\left(-j\left(j+1\right)\frac{\theta_r}{T_r}\right)\sum_{i=0}^{i_d(j)}Q\left[\frac{5}{2}-\omega,\frac{\theta_d\left(j\right)-i\theta_v}{T}\right]\exp\left(-\frac{i\theta_v}{T_v}\right)\right]$$

$$i_d(j)=\Theta_d(j)/\Theta_v=U_m(j)/\Theta_v$$

$$\frac{U_m(j)}{D}=1+3.82\times10^{-5}j+3.80\times10^{-7}j^2+3.25\times10^{-8}j^3\quad(N_2)$$

$$\frac{U_m(j)}{D}=1+7.65\times10^{-4}j+3.46\times10^{-6}j^2+6.30\times10^{-9}j^3\quad(O_2)$$

$$\frac{U_m(j)}{D}=1+1.98\times10^{-4}j-1.89\times10^{-6}j^2+3.51\times10^{-8}j^3\quad(NO)$$

Quantum-Kinetic Model

- Exchange reaction rate:

$$k_{exch}\left(T,T_r,T_v\right)=\frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}}\left(\frac{T}{T_{ref}}\right)^{1-\omega}\left(\frac{2k_BT_{ref}}{m_r}\right)^{1/2}\left(\exp\left(-\frac{C_1}{T_{av}\left(T,T_r,T_v\right)}\right)-\exp\left(-\frac{C_2}{T_{av}\left(T,T_r,T_v\right)}\right)\right)$$

$$C_1=i_a\theta_v\ ;\ i_a=\text{floor}\left(\frac{\theta_r}{\theta_v}\right)+1$$

$$C_2=i_d\theta_v\ ;\ i_d=\text{floor}\left(\frac{\theta_d}{\theta_v}\right)$$

$$T_{av}\left(T,T_r,T_v\right)=\frac{3T+2T_r+2T_v}{7}$$

Computational Method

- Reaction Rates
  - Park ’90 and ’94 models
    - Modified Arrhenius equation
    - TTv model for dissociation
  - Q-K model
- Chemistry model
  - 5-species, 5-reaction air
  - Dissociation
    - Park or Q-K
  - Recombination
    - Park equilibrium curve fit
  - Endothermic exchange
    - Park or Q-K
  - Exothermic exchange
    - Park equilibrium curve fit

$$N_2 + M \leftrightarrow 2N + M$$

$$O_2 + M \leftrightarrow 2O + M$$

$$NO + M \leftrightarrow N + O + M$$

$$NO + O \leftrightarrow O_2 + N$$

$$N_2 + O \leftrightarrow NO + N$$

Computational Method

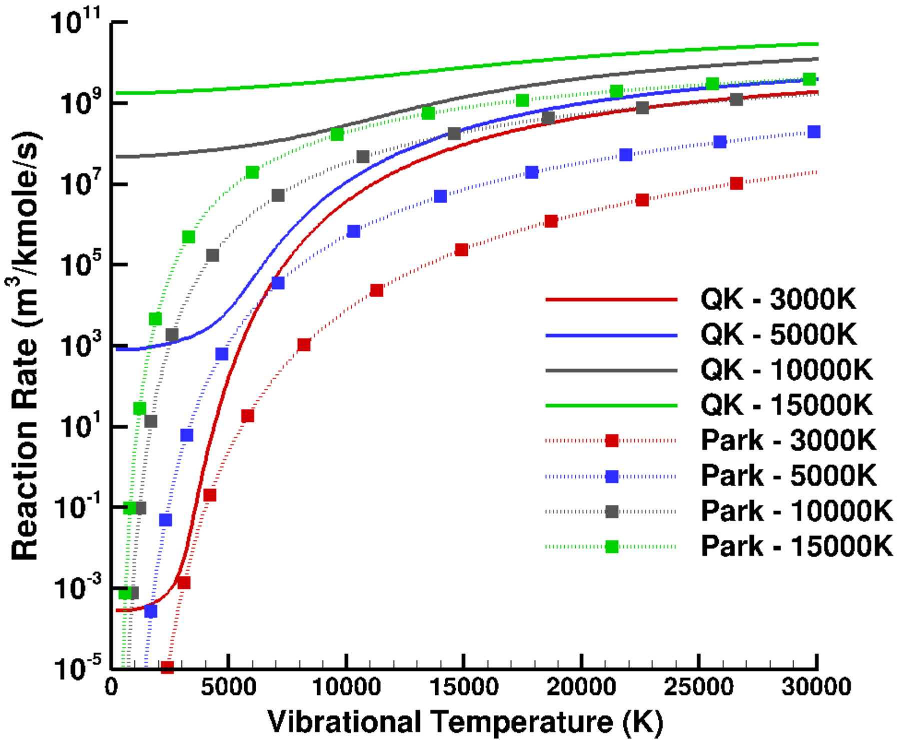
- Navier-Stokes: DPLR
  - Reacting, 2D NS equations based on finite volume formulation
  - Diffusive properties
    - Viscosity: Blottner-Wilke
    - Conduction: Eucken relation
    - Diffusion: Constant Lewis number
  - T-R-V non-equilibrium
    - Simple harmonic oscillator for vibrational energies
    - Rigid rotor for rotational energies
    - Collisional relaxation times based on:
      - Parker's model for rotational relaxation
      - Millikan and White for vibrational relaxation

Computational Method

- DSMC: Icarus
  - Collision cross-section
    - General Larsen-Borgnakke model
    - Molecular properties based on Bird's data for VSS
  - Chemical reactions
    - Q-K model
  - T-R-V non-equilibrium
    - Simple harmonic oscillator for vibrational energies
    - Rigid rotor for rotational energies
    - Collisional relaxation times based on:
      - Parker's model for rotational relaxation
      - Millikan and White for vibrational relaxation

Reaction Rate Comparison

- Park model vs. Q-K model: thermal non-equilibrium
  - Dissociation
    - Q-K higher than Park
      - $N_2 + N_2 \rightarrow 2N + N_2$
    - Lower for other reactions
  - Exchange
    - Q-K usually higher than Park
- Correct behavior at low T_v
  - Rate is finite, not zero



$$N_2 + N_2 \rightarrow 2N + N_2$$

BSUV Flight Conditions

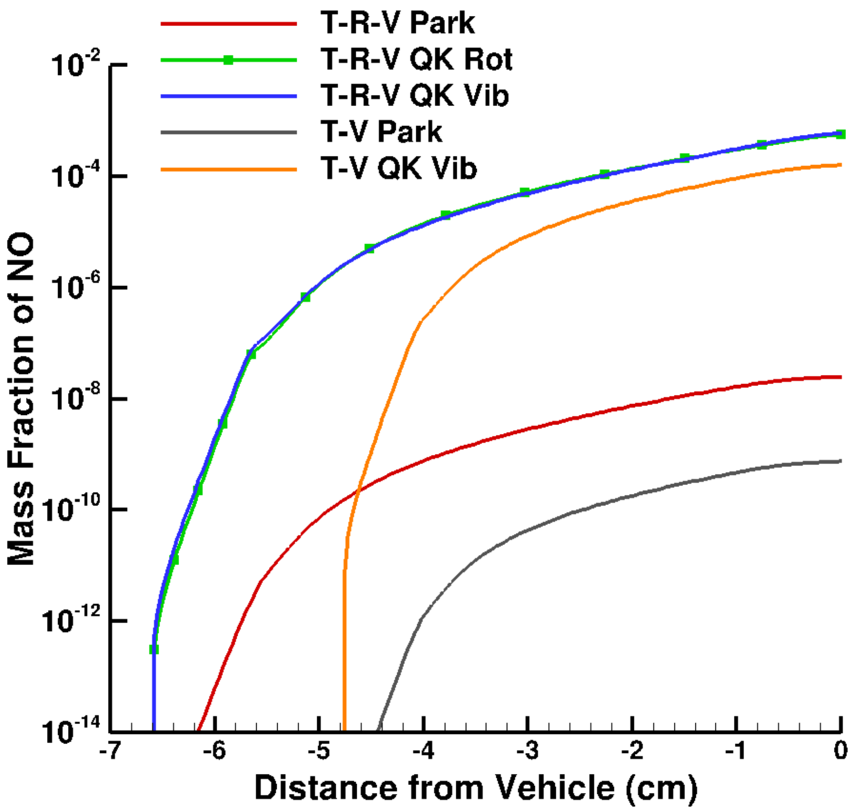
- Bow Shock UltraViolet (BSUV) flight 2
  - Measure stagnation line UV radiation: measured NO properties
  - Only simulate the nose of each vehicle
    - 0.1016 m (4 in.) radius
    - NS: 500 K isothermal wall
    - DSMC: 500 K diffuse wall

87.5 km

Density (kg/m^3)	$5.33 \cdot 10^{-6}$
Velocity (m/s)	5100
Temperature (K)	186.87
Mass Fraction N_2	0.7663
Mass Fraction O_2	0.2337

87.5 km

- Mass Fraction of NO
  - Park 4-6 orders less
  - Higher T_t with Rot. Non-Eq results in more NO
  - QK Rot. rate reduces NO
- Comparisons
  - Current model predictions in the range of DSMC data
- Translational temperature
  - Rot. Non-Eq. results in higher T_t



Mass fraction of NO along the stagnation line at 87.5 km.

87.5 km

- Mass Fraction of NO
  - Park 4-6 orders less
  - Higher T_t with Rot. Non-Eq results in more NO
  - QK Rot. rate reduces NO
- Comparisons
  - Current model predictions in the range of DSMC data
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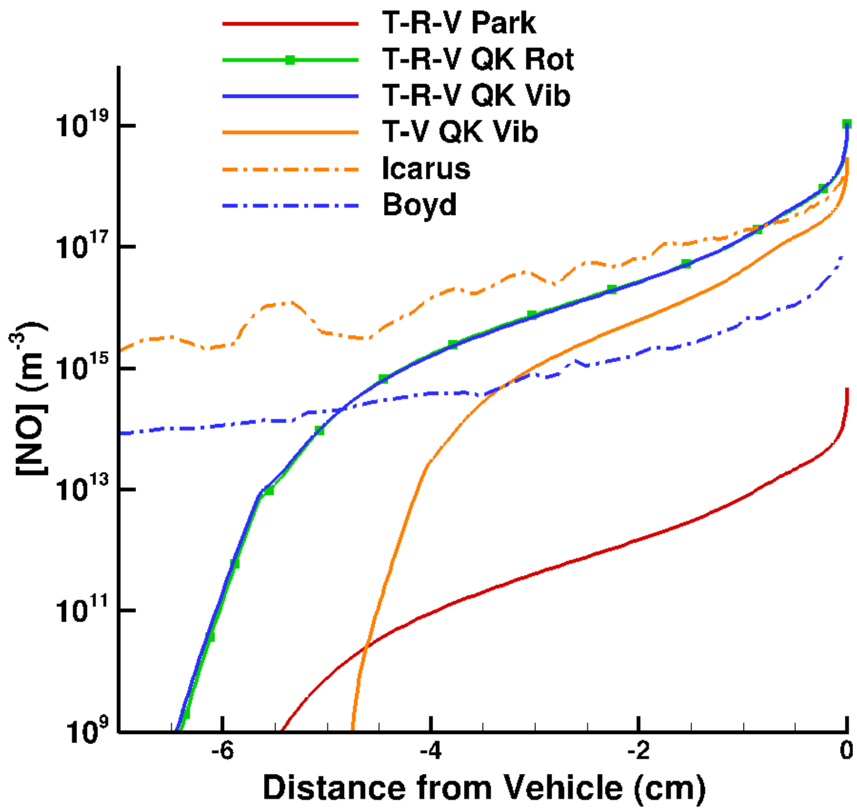

Particle density of NO along the stagnation line at 87.5 km.

Summary and Conclusions

- Quantum-Kinetic model versus Park model
  - Thermal equilibrium
    - Q-K predicts greater rates for some reactions, lesser rates for others
  - Thermal non-equilibrium
    - Q-K avoids the low dissociation rates observed with the TTv model in cases of strong thermal non-equilibrium
    - Effect of rotational energy is minimal on dissociation reaction rates
    - Q-K generally predicts greater rates for exchange reactions
- BSUV Simulations
  - Q-K models predict NO densities more consistent with previous studies compared to Park model
  - Current implementation lacks more detailed energy modeling