Direct Molecular Simulation:
Dissociation of Nitrogen from First Principles

Also see: Valentini, Schwartzentruber, Bender, Nompelis, Candler, AIAA Paper 2015-0474

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8th European Symposium on Aerothermodynamics, Lisbon 03/03/15
Motivation: Thermochemical Nonequilibrium

Finite-Rate Energy Exchange
Translational Rotational Vibrational Chemical

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Current CFD Modeling and Open Questions:

Example: Vibrational Energy Equation Source Term (rotation is similar)

\[
\frac{d\varepsilon_v}{dt} = \frac{\varepsilon^* - \varepsilon_v}{\tau_v} - k^{(D)}[N_2](\varepsilon_v^D - \varepsilon_v)
\]

Relaxation rate towards translational energy (equilibrium state)

Dissociation rate

Vibrational energy lost to dissociation

\[
k^{(D)} = k^{(D)}(\varepsilon_v, \varepsilon_r, \varepsilon_t, \ldots)
\]
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- Relaxation rate towards translational energy (equilibrium state)
- Dissociation rate
- Vibrational energy lost to dissociation

What is \(k^{(D)}\) and how it coupled to rotation/vibration? Is the standard approach valid?

\(Tr = Tt\) and \(k^{(D)} = k^{(D)}(\epsilon_v, \epsilon_r, \epsilon_t, \ldots)\) (Park two-temperature model)
Current CFD Modeling and Open Questions:

- What is $k^{(D)}$ and how it is coupled to rotation/vibration? Is the standard approach valid?
  \[ T_{r} = T_{t} \quad \text{and} \quad k^{(D)} = k^{(D)}[ (T_{t} T_{v})^{1/2} ] \quad (\text{Park two-temperature model}) \]

- What are the internal energy relaxation rates: $\tau_{r} (T)$ and $\tau_{v} (T)$?
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- Are rotation and vibrational energies even characterized by Boltzmann distributions?
  - is \(<\epsilon_v> \sim k_BTv\) (average energy ~ temperature) an appropriate model parameter?
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• What is the rotational and vibrational energy lost due to dissociation?

• We use a unique method (Direct Molecular Simulation – **DMS**) also called “CTC-DSMC”

• With additional **QCT** analysis, we answer many of these questions definitively (for N\(_2\)-N\(_2\))
All-Atom Molecular Dynamics of Shock Waves


All-Atom Molecular Dynamics of Shock Waves


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DMS vs. Pure Molecular Dynamics

- We can now directly verify DMS with pure MD (very important)
- We get *exact* agreement, for every case we run

Macroscopic profiles

Distribution functions

DMS vs. Quasi-Classical-Trajectory (QCT) Analysis

Quasi-Classical Trajectory (QCT) analysis for $k_D(T_t,T_r,T_v)$:

1) Generate 1 million molecules:

   - Randomly form pairs. Initialize trans, rot, and vib energies ($g$, $\varepsilon_r$, $\varepsilon_v$) from Boltzmann distributions at $T_t$, $T_r$, $T_v$. 
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2) For these pairs, randomize separation distance ($0 < b < b_{\text{max}}$) and all other impact parameters. Perform trajectories and record final atom positions and velocities.
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2) For these pairs, randomize separation distance ($0 < b < b_{\text{max}}$) and all other impact parameters. Perform trajectories and record final atom positions and velocities.

3) Multiply the average probability of dissociation by the hard-sphere collision rate:

$$k_D = \pi b_{\text{max}}^2 \sqrt{\frac{8kT_t}{\pi m}} \langle P_{\text{diss}} \rangle$$
DMS vs. Quasi-Classical-Trajectory (QCT) Analysis

Direct Molecular Simulation (DMS):

1) Generate 1 million molecules (within volume V):
   - Randomly form pairs. Initialize trans, rot, and vib energies (g, \( \varepsilon_r, \varepsilon_v \)) from Boltzmann distributions at Tt, Tr, Tv.

(1.5) Choose a subset of these molecular pairs, based on the hard-sphere collision rate: \( \sim [g \pi (b_{\text{max}})^2] \)

2) For these pairs, randomize separation distance (0 < b < b_{\text{max}}) and all other impact parameters. Perform trajectories and record final atom positions and velocities.

(2.5) Volume still contains \( \sim 1 \) million molecule pairs, with a subset having new post-collision properties (atomic positions and velocities). New distributions (g, \( \varepsilon_r, \varepsilon_v \)) may not be Boltzmann. Return to (1.5).

3) Multiply the average probability of dissociation by the hard-sphere collision rate:
   
   DMS predicts the evolution of all energy distributions and dissociation processes (time-histories in this case).
Ab-Initio Potential Energy Surface (N4 system)

Available at http://comp.chem.umn.edu/potlib/


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By running a number of isothermal relaxations to various equilibrium temperatures, we can determine rotational and vibrational relaxation time constants for CFD.
For low $T (<10,000 \text{K})$ where experimental data is available (Millikan-White) excellent agreement is found (this is sensitive to the shape of the repulsive wall of the PES).

At higher temperatures it is in the range of prior empirical models (but *finally*… no longer empirical!)

### Vibrational Relaxation vs. Experiment

![Graph showing vibrational relaxation vs. experiment](image-url)
Quasi Steady-State (QSS) Dissociation

(a)

Graph showing temperature (T [K]) against time with various trajectories and dissociation reactions.

~500 Million Trajectories
Quasi Steady-State (QSS) Dissociation

~500 Million Trajectories

(a) $T [\text{K}]$

(b) $T [\text{K}]$

$\frac{[N_2]}{[N_2]_0}$
Quasi Steady-State (QSS) Dissociation

(a) $T [K]$ vs. time [s]

(b) $T [K]$ vs. time [s]

(c) $T [K]$ vs. time [s]

$\sim 500$ Million Trajectories

$\frac{[N_2]}{[N_2]_0}$
Distributions within the QSS Region

- Surprising to find noticeable depletion of $v > 30$ (for ‘low’ $T_t$ of 10,000K)
- Vibrational favoring $O(10^6)$, whereas rotational favoring only $O(10^2)$
Distributions within the QSS Region

- Now, significant depletion of \( \nu > 20 \)
- Vibrational favoring \( O(10^4) \) (more low \( \nu \) dissociation then at 10,000K)
Distributions within the QSS Region

- Dissociation from the entire \( \nu \) population
- Strong QSS state where \( T_{tr} \), \( T_{rot} \), \( T_{vib} \) are not equal
Distributions within the QSS Region

- Dissociation from the entire $v$ population
- Strong QSS state where $T_{tr}$, $T_{rot}$, $T_{vib}$ are not equal

Boltzmann distributions do not characterize dissociating nitrogen at any temperature (equilibrium QCT is not sufficient). Oxygen will exhibit much stronger nonequilibrium.
Dissociation rate predicted by DMS and QCT

DMS dissociation rate within QSS region is ~5x lower than QCT (at $T_r=T_v=T_t$)

This occurs almost uniformly across all temperatures, because at low T, even small departures from Boltzmann have a dramatic effect (strong favoring).
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We confirmed this by running pure QCT (at 10,000K), where the vib distribution was truncated for $v > 20$ and $v > 40$.

This exactly accounts for the 5x difference in $k_D$ (very interesting!)
Comparison of Dissociation Rates

(1) $k_D$ for $N_2-N_2$ from Jaffe et al. (QCT) is 3-5x lower than QCT-UMN. This could be due to the quantum data set and/or the PES fit.
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(2) DMS result for $N_2-N_2$ in QSS is quite close to the Appleton data.
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(2) DMS result for $N_2-N_2$ in QSS is quite close to the Appleton data.

(3) $k_D$ for N-N$_2$ from Panesi et al. (Master Eq.) is 4-5x higher than our N$_2$-N$_2$ DMS results. So N-N$_2$ dissociates faster than N$_2$-N$_2$. 

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Formulation of CFD rot-vib-dissociation models

DMS simulations (and Master-equation simulations) contain all of the required data/information to formulate new models for CFD...

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\[
\frac{d\epsilon_v}{dt} = \epsilon^* - \epsilon_v - \frac{k(D)[N_2]}{\tau_v} (\epsilon^{D}_v - \epsilon_v)
\]

Require a model for the average vibrational energy lost due to dissociation (exactly predicted by DMS)

This parameter determines the precise QSS state \((T_{tr}, T_{rot}, T_{vib})\)
DMS Mixture Simulations for $\text{N}_2 + \text{N}_2$ and $\text{N}_2 + \text{N}$

DMS calculations can use a library of PESs (collision specific: N3, N4, etc.)
We use N4 PES (Truhlar group, Minnesota) with 3 or 4 N atoms

Direct simulation of dissociating nitrogen gas (~200 CPUs for 2 days)
Preliminary (simple) curve fits show $k^D_{\text{N}_3} = (3-5) \times k^D_{\text{N}_4}$ (in QSS)

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Why does DMS work?

Whereas state-resolved (master equation) analysis pre-computes all possible energy transitions, DMS only simulates the transitions that actually occur. This is a very, very, small subset of the total number of transitions. Ex: DMS calculations show that transitions of $\Delta v > 10$ can be ignored (?)
Conclusions

1) We have a new method (Direct Molecular Simulation – DMS) that provides a highly accurate and tractable approach to obtain all relevant nonequilibrium physics for these problems (and is fully consistent with QCT in the equilibrium-Boltzmann limit).

2) Rotational relaxation rates have been determined (see prior Valentini et al. publications).

3) Vibrational relaxation, Millikan/White + High-T corrections appear to be quite accurate!

4) Vibrational favoring is much stronger than rotational favoring.

5) QSS dissociation is ~5x slower than equilibrium QCT dissociation across a wide temperature range (even at 10,000K!) and such non-Boltzmann physics need to be accounted for when determining the dissociation rate.

6) All required information is produced by DMS simulations. Full time-histories during excitation and QSS region, including the internal energy lost due to dissociation, can be determined.

7) First results for full nitrogen system (N4 and N3) dissociation.
Direct Molecular Simulation: Dissociation of Nitrogen from First Principles

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Available Experimental Data (from 1960s and 70s)

Hanson and Baganoff (1972) inferred dissociation rates from end-wall pressure measurements in a shock tube.

A hypersonic flow model is required to infer reaction rates from the raw data.

Fig. 1 Pressure-gage data for $N_2$ at 2.1 torr.
Available Experimental Data (from 1960s and 70s)

Hanson and Baganoff (1972) inferred dissociation rates from end-wall pressure measurements in a shock tube.

Park (1988) re-interpreted the data using his T-Tv model (which includes vibrationally-favored dissociation).

Fig. 1 Pressure-gage data for $N_2$ at 2.1 torr.

\[ N + N + N_2 \xrightarrow{K_{r, N_2}} N_2 + N_2 \]


State-resolved DSMC and Master Equation

For a two body collision problem of molecules with internal structure (energy),

\[ N_2(j, \nu) + M \rightarrow N_2(j', \nu') + M \]

- **M**: atom or molecule without internal energy change
- \((j, \nu), (j', \nu')\): initial and final internal energy states
- The state-to-state cross section can be determined from:

\[
\sigma_R(g, j, \nu \rightarrow j', \nu') = \int_0^\infty \int_0^{2\pi} P_R(b, \epsilon; g, j, \nu \rightarrow j', \nu') b db d\epsilon ,
\]

where the integral could be obtained through a large number of trajectory calculations (QCT, CTC, etc.).
- The cross-section for transition from \((j, \nu)\) to all final quantum states,

\[
\sigma_R(g, j, \nu) = \sum_{j', \nu'} \sigma_R(g, j, \nu \rightarrow j', \nu') ,
\]

is analogous to the total cross-section (i.e. \(\sigma_T(g)\)) now with dependence on \(j, \nu\) (internal energy state).
State-resolved DSMC and Master Equation

- In DSMC, we use the transition probability:
  
  \[ P_R(g, j, v \rightarrow j', v') = \frac{\sigma_R(g, j, v \rightarrow j', v')}{\sigma_R(g, j, v)} \]

- From kinetic theory, we obtain state-to-state transition rates \( k_f(j, v \rightarrow j', v'; T) \) by integrating cross sections over equilibrium distribution for velocity \( (g) \),

  \[ k_f(j, v \rightarrow j', v'; T) = 4\pi \left( \frac{\mu}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^{+\infty} \sigma_R(g, j, v \rightarrow j', v') g^3 \exp \left( -\frac{\mu g^2}{2k_B T} \right) dg \]
State-resolved approach  \( P_R(g, j, v \rightarrow j', v') \ k_f(j, v \rightarrow j', v'; T) \)

- For \( \text{N}_2 + \text{N} \) collisions, there are 9390 (~10^4) rovibrational states, in the ground the electronic level, and \( \mathcal{O}(10^8) \) state-to-state reactions to consider. Recently accomplished by a number of groups using the N3 PES (Panesi, Jaffe, Schwenke, Magin, J. Chem. Phys., 2013)

- For the \( \text{N}_2 + \text{N}_2 \) collisions there are \( \mathcal{O}(10^{16}) \) rovibrational combinations. The situation becomes increasing intractable as one considers multi-species systems (\( \text{N}_2, \text{O}_2, \text{NO}, \text{N}, \text{O} \)) and excited electronic states (i.e. oxygen)...

- Even representing 10 energy levels with 1 ‘bin’, the number of rovibrational transitions would still be \( \mathcal{O}(10^8) \) for just \( \text{N}_2 + \text{N}_2 \)! Additionally, for DSMC, you need to store each transition probability for a specific relative velocity (g).
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  Additionally, for DSMC, you need to store each transition probability for a specific relative velocity (\( g \)).

- DMS simulates the same trajectories as required to determine cross-sections, however, \emph{embeds} these trajectory calculations \emph{within a flow field simulation} (“on-the-fly”)

- A DMS simulation only performs the collisions (state-transitions) that \emph{actually occur}. This is a very, very, very, small subset of the total number of possible transitions, noted above.

- The \( g,j,v \) states resulting from a collision become the initial states of the molecule’s next collision (all other impact parameters are randomized – as in a real dilute gas)
State-resolved approach  \( P_R(g,j,v \rightarrow j',v') \)  \( k_f(j,v \rightarrow j',v'; T) \)

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- DMS is fundamental simulation approach meant as a validation tool for reduced-order models, and may provide guidance towards model reduction (i.e. how to bin states ?)
2D-AxiSym and 3D DMS is possible...

- Only N atoms (no rot/vib decoupling)
- No transport properties or rates
- No DSMC collision models
- No state-resolved cross-sections

Currently: 50x DSMC cost (simple PES) – 10,000x DSMC cost (ab-initio PES)
Internal Energy Excitation/Dissociation at 10,000 K

\[ T_i = 10,000 \, \text{K} \]
Internal Energy Excitation/Dissociation at 20,000 K

$T_t = 20,000 \text{ K}$

Graphs showing temperature ($T$) and time ($t$) with various parameters and data points.
Choice of conservative $b_{\text{max}}$
Dissociation in function of internal energy (rot+vib)
Vibrational energy lost (QCT vs. DMS)
Direct Molecular Simulation (DMS)

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

\[ P_{\text{collision}} = \frac{W_p \sigma g \Delta t}{\text{Vol}_{\text{cell}}} \]
(Statistically exact for hard-spheres)

\[ \sigma = \pi (b_{\text{max}})^2 \]

Direct Molecular Simulation (DMS)

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

\[
P_{\text{collision}} = \frac{W_p \sigma g \Delta t}{\text{Vol}_{\text{cell}}} \\
(\text{statistically exact for hard-spheres})
\]

\[
\sigma = \pi (b_{\text{max}})^2
\]