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Combustion Chemistry and Dynamics in Nanoscale Environments

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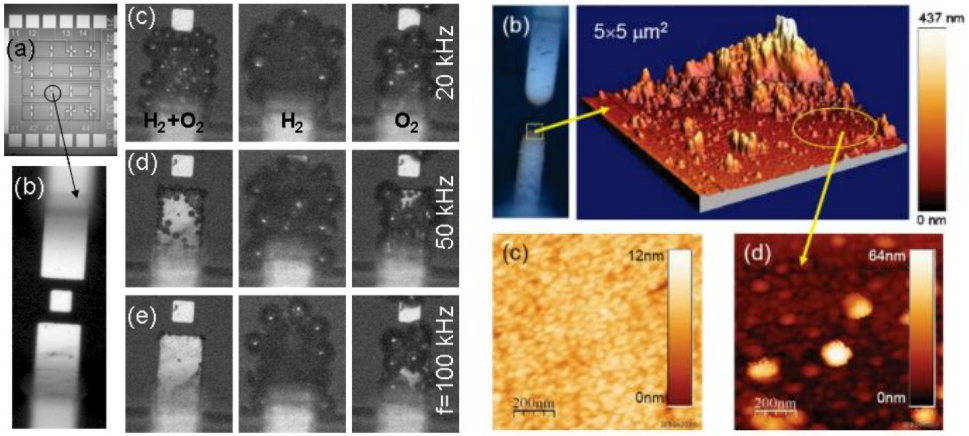
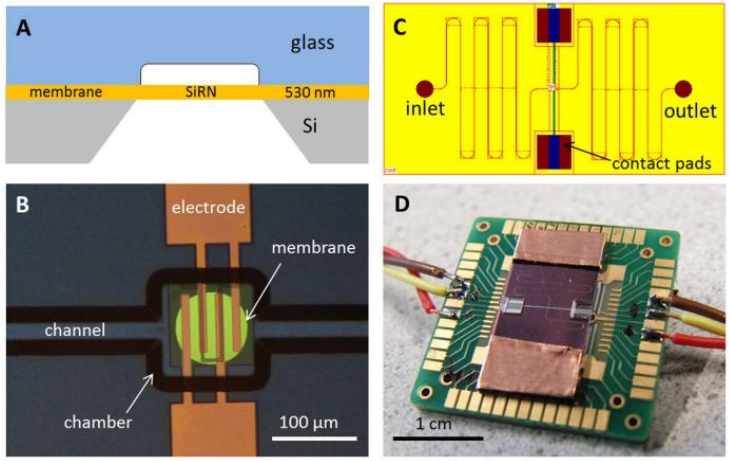
Motivation - An Accidental Discovery

- Spontaneous combustion between stoichiometric H_2/O_2 gases is observed for bubbles with sizes smaller than 150 nm generated by water electrolysis. "Exploding nanobubbles are the smallest combustion chambers realized in nature."
- Later, the authors demonstrated a fast and strong acutator that uses internal combustion of H_2 and O_2 as part of its working cycle. "This actuator is the first step to truly microscopic combustion engines and can be applied in microfluidics, micro/nano positioning, or compact sounds/ultrasound emitters."



Vitaly B. Svetovoy, et al., " Combustion of hydrogen-oxygen mixture in electrochemically generated nanobubbles " Physical Review E, 84, 035302, 2011.



Vitaly B. Svetovoy, et al., "New type of microengine using internal combustion of hydrogen and oxygen" Scientific Reports, 4, 4296, 2013

New Physics of Combustion in Nanoscale Environments

- What are the new physics of chemical reactions with heat release taking place in a nanoscale system which could be made of various nanomaterials with unique structure and geometry such as carbon-based nanostructures?
- Potential effects:
  - Mean-free-path (Knudsen number) effect

    e.g., the mean free path of hydrogen at room temperature and atmospheric pressure is about 110 nm.
  - Non-equilibrium fluid transport

    e.g., inhomogeneous fluid structure, slip (multilayer) boundary condition.
  - Increasingly important gas/wall interactions

    e.g., physical and chemical adsorption by wall.
  - Unique thermal, chemical and physical properties of the nanostructures acting as combustion carrier or reactor

Literature Review - Chemical Reactions in Nanoscale Environments

- A primary focus is on catalysis. Nanoparticle clusters and assemblies, nanowires, and carbon nanotubes are used as a carrier or directly for catalysis reactions. The high surface area and the dimensional effects of these nanocatalysts make them very promising.
- Interest has also been increasing in regard to the chemistry occurring in carbon nanotubes. Lu et al. (2008, 2010) studied the quantum dynamics of D + $H_2 \rightarrow$ HD + D exchange reaction and found the reaction probabilities are considerably higher in nanotubes with small diameters than in the gas-phase (unconfined). Andrei Khlobystov (2011) points out that nanotubes are much more than just passive containers, and the confinement at nanoscale can dramatically change the pathways of chemical reactions, often leading to unexpected products.
- Choi et al. (2010) coated a carbon nanotube with a thin shell of cyclotrimethylene trinitramine and ignited at one end using a laser. A combustion wave was found to propagate along the tube while the carbon nanotubes were intact. This wave propagated much faster than the theoretical flame speed of the fuel and created a strong electric current.

Objectives

The overall objective is to explore the new physics of combustion in nanoscale environments. The new knowledge to be developed will be crucial to future experimental, theoretical, and computational work necessary in this newborn field of “nanoscale combustion.”

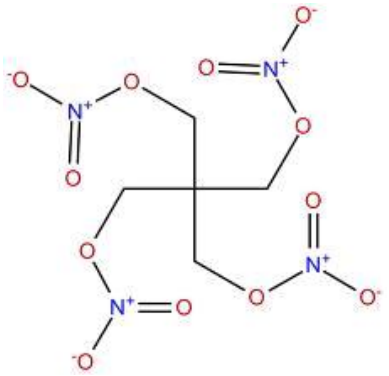
In this work, we investigated flame propagation of solid fuels along carbon-based nanostructures (carbon nanotubes - CNTs) using reactive molecular dynamics (MD) simulations:

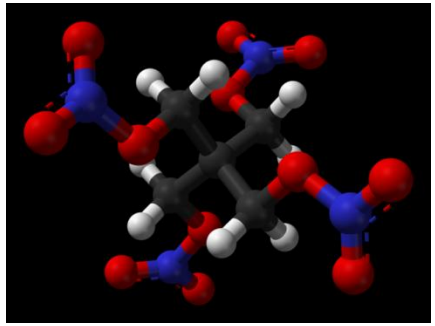
- Compute the transient flame propagation process;
- How does CNT affect the flame propagation speed?
- What is the fundamental mechanism for flame speed enhancement?
- What are the effects of CNTs length, diameter and structure?

These questions are answered by first-principle based reactive MD simulations which include both chemical (e.g. bond breaking and forming) and physical (e.g., thermal transport) changes at atomic level.

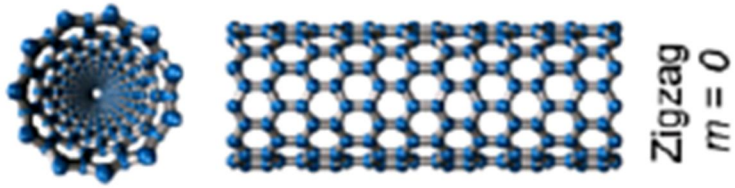
Flame Propagation of Solid Propellants along Carbon-based Nanostructures

- Atomic- and molecular-scale interactions become increasingly important when the scale is reduced to nano.
- The simulations are based on an open source code – Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) developed by Sandia National Lab.
- Pentaerythritol tetranitrate (PETN) $C_5H_8N_4O_{12}$
  - monopropellant, commonly used as a high explosive;
  - tetragonal crystal structure, two molecules per unit cell,
  - maximum theoretical density 1.77 kg/m^3 at room temperature



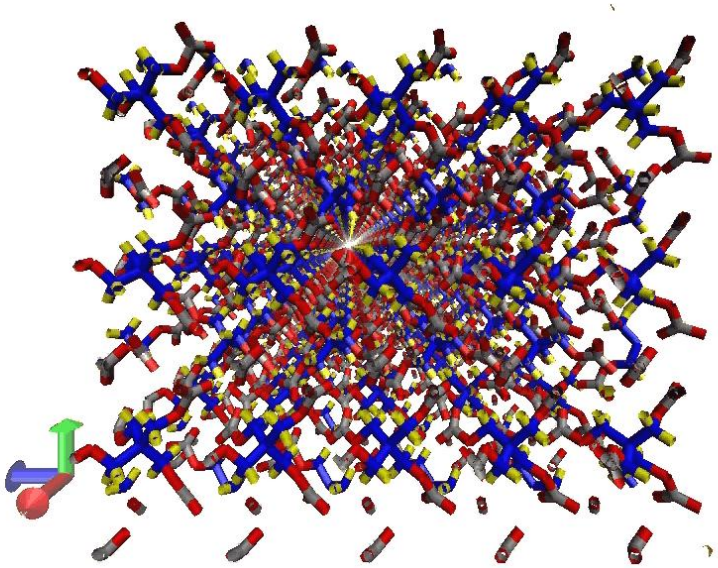


- Carbon-based nanostructures
  - single-wall carbon nanotubes
  - zigzag



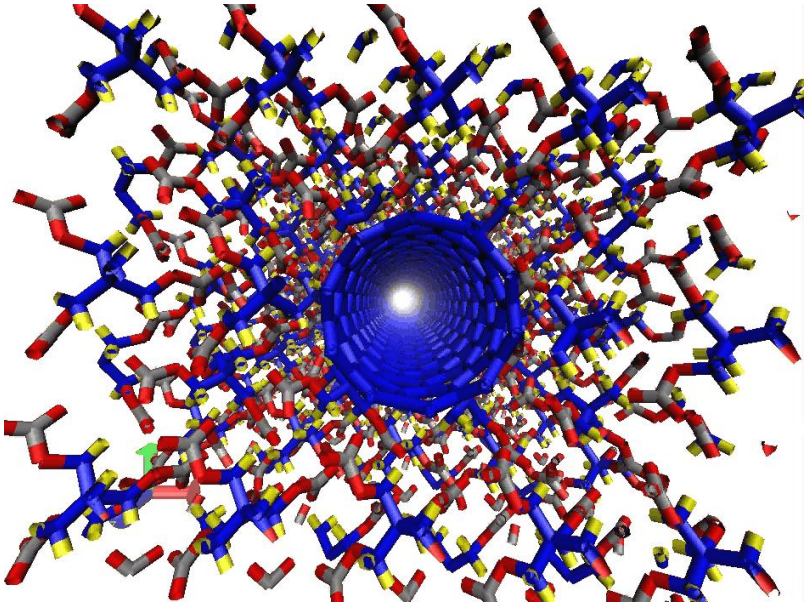
Structural Models

PETN



- Unit cell:
  9.2759 Å × 9.2759 Å × 6.6127 Å
- Computational domain:
  41 nm × 3 nm × 3 nm
- Flame propagation along the x axis (<100> direction)
- Number of PETN molecules: 1350
- Number of atoms: 39150

PETN + CNT

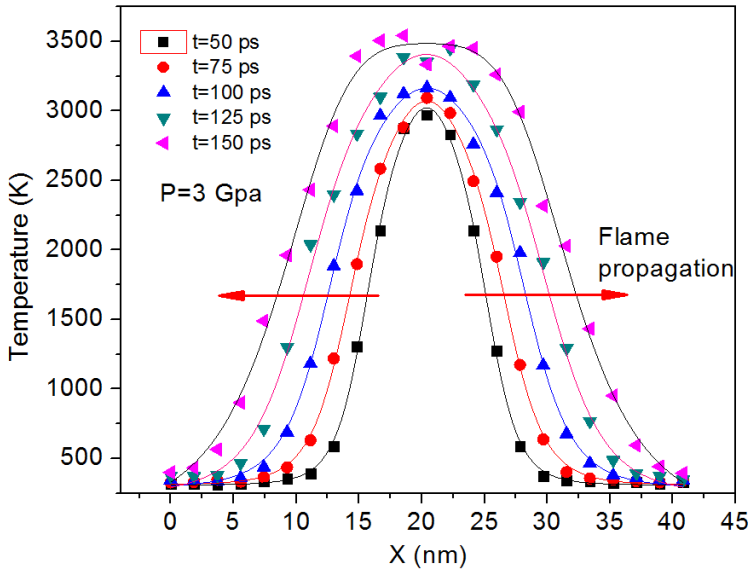


- Computational domain:
  41 nm × 3 nm × 3 nm
- Number of PETN molecules: 1215
- Number of atoms: 35 235
- Number of carbon atoms in CNT: 3800
- CNT structure: (10, 0)
- CNT outer diameter: 0.78 nm

Computational Methods

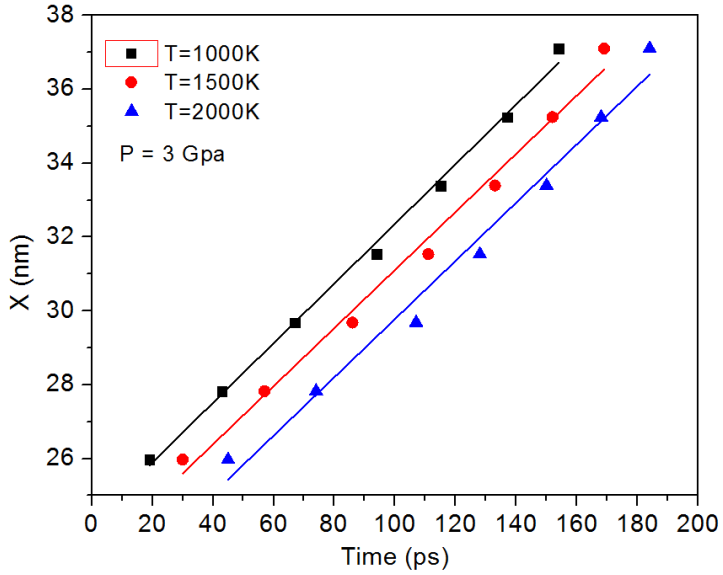
- **ReaxFF reactive force field** (van Duin et al. 2003, 2005, 2006; Budzien et. al. 2009)
- Initial energy minimization and system equilibration: NVT ensemble at 3K and 300K, respectively, for 2 ps.
- Temperature: $\frac{3}{2}k_b TN = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2$
- Pressure: $P = \frac{NK_b T}{V} + (\sum_{i=1}^{N} r_i F_i) / dV$
- A time step of 0.1 fs was used for all simulations.
- Ignition: An area in the middle (5 cells wide) was set to a high temperature of 2500 K for 2 ps to simulate an ignition source. The temperature of the rest areas remained at 300K.
- Periodical boundary conditions.
- Species identification: used a bond order value of 0.5 for all bonds (Sergeev et al., 2014).

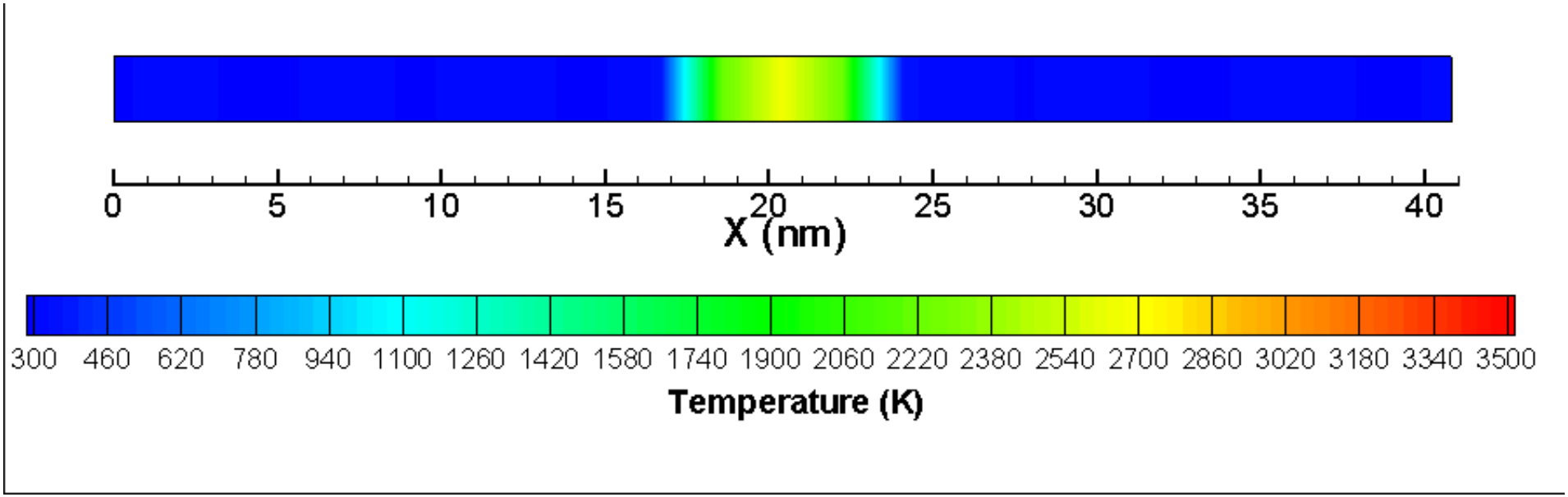
Flame Propagation of PETN



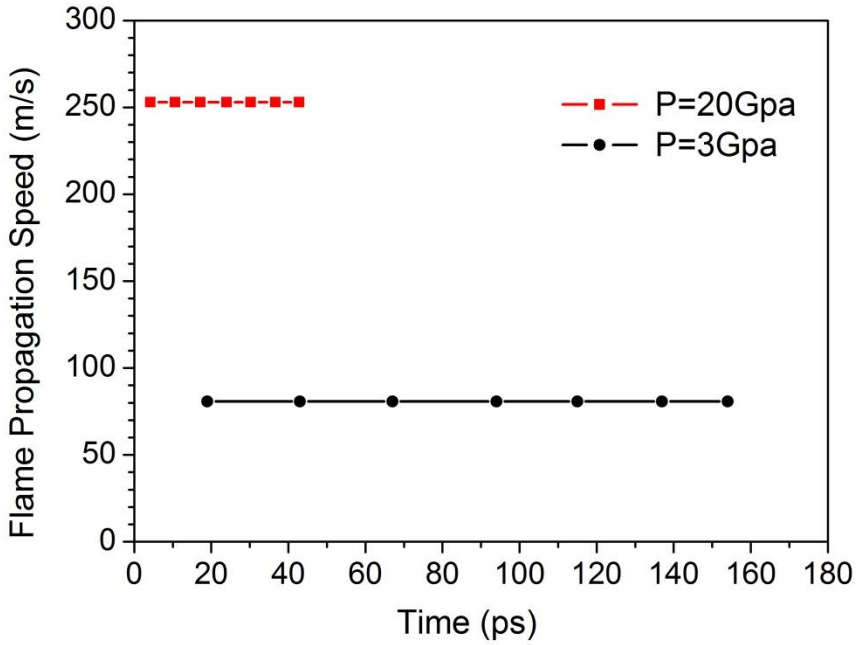
Flame Propagation

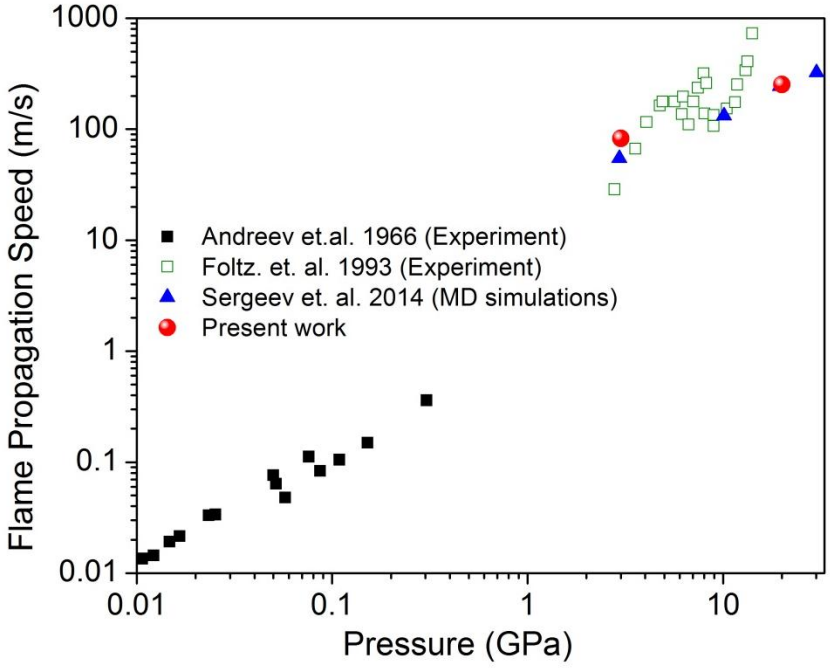
Current Time: 0 ps





Flame Propagation Speed of PETN

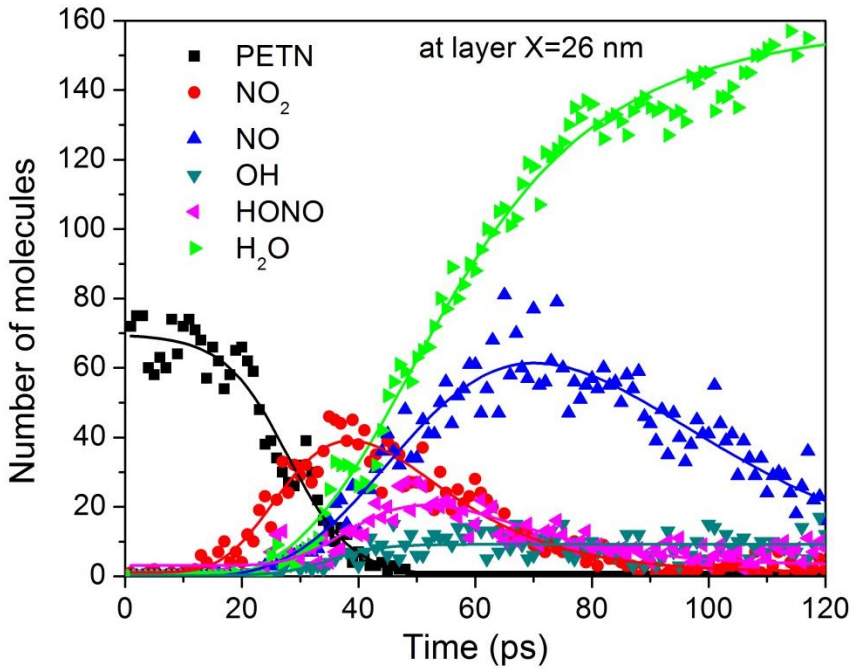


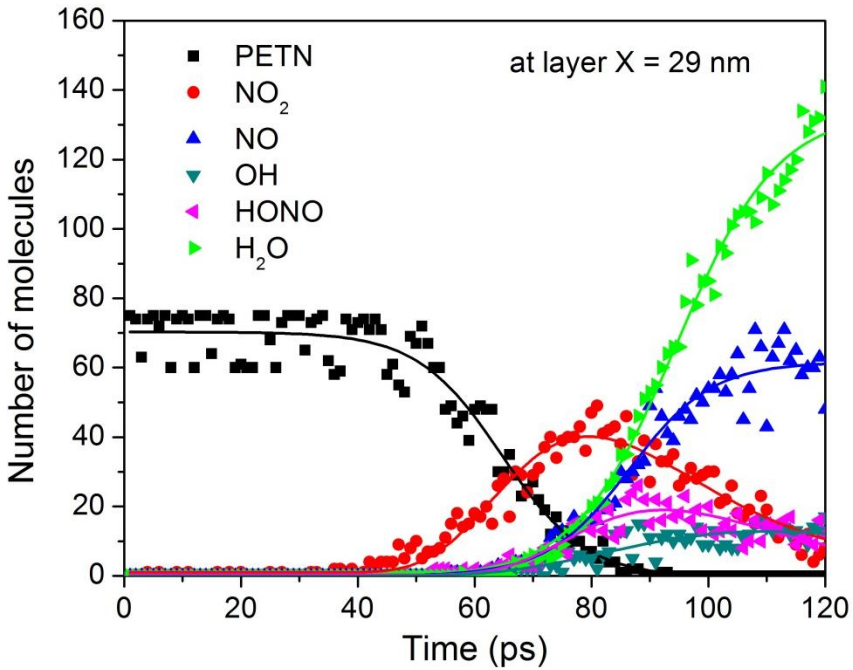


- Flame propagation speed is nearly constant as a function of time. It is independent of the temperature chosen as an indicator of flame front.
- The speed is about 80 m/s at 3 Gpa and 250 m/s at 20 Gpa.

- The computed flame speeds agree well with the measured values at high pressures confined in a diamond anvil cell.
- Shows a strong dependence on external hydrostatic pressure

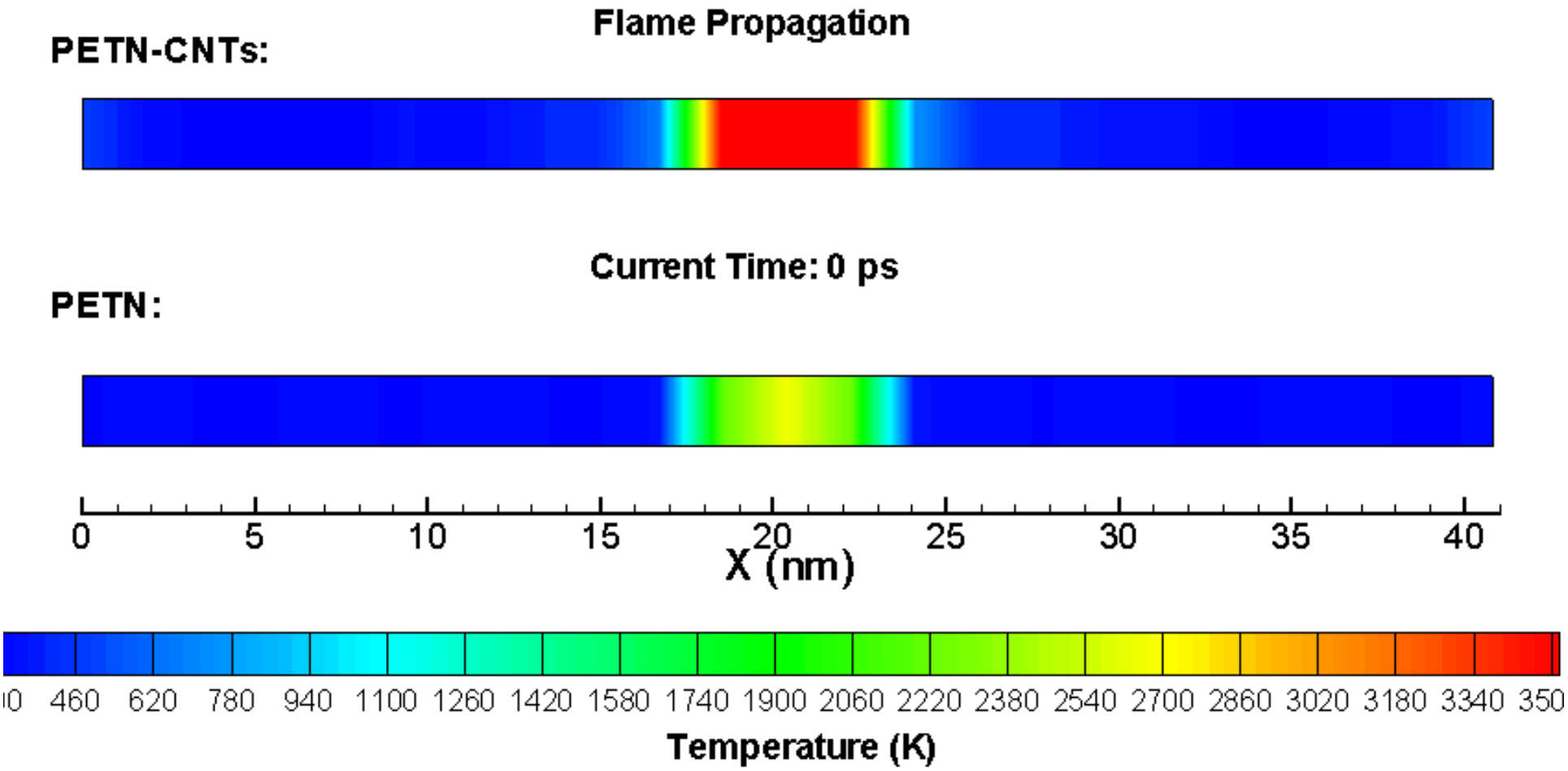
Species Profiles and Reaction Pathway



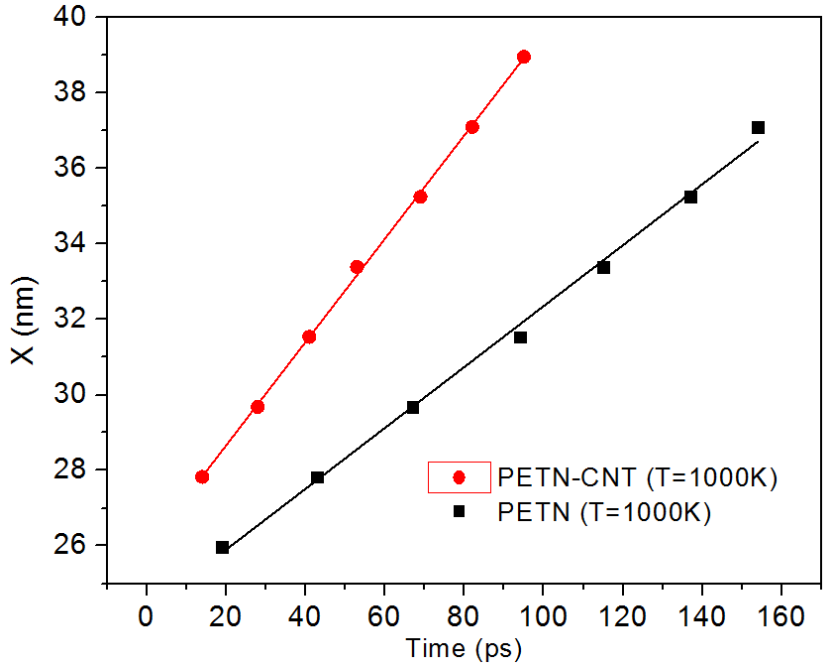


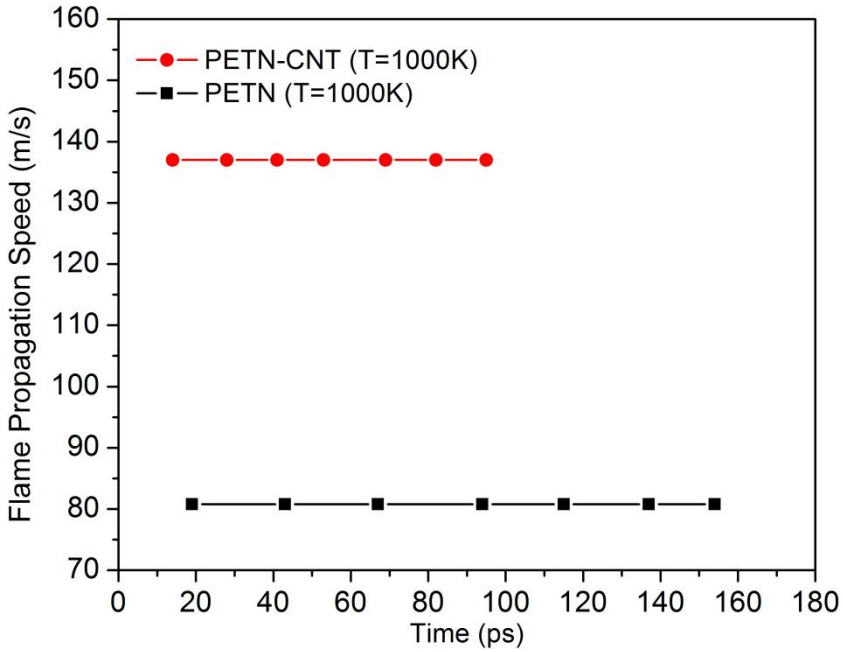
- NO_2 is the dominant initial product, indicating NO_2 − O bond, which has the weakest bond energy among all, breaks first during initiation.
- NO and HONO are other major initial products. They are formed after NO_2.
- Water formation begins after appearance of OH and NO.

Flame Propagation of PETN on CTN



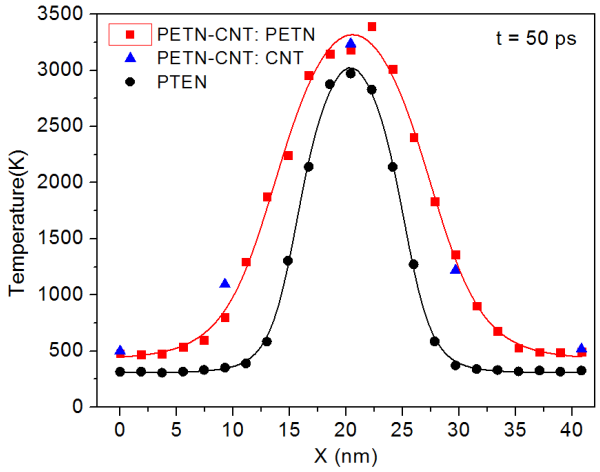
Flame Propagation Speed of PETN on CNT

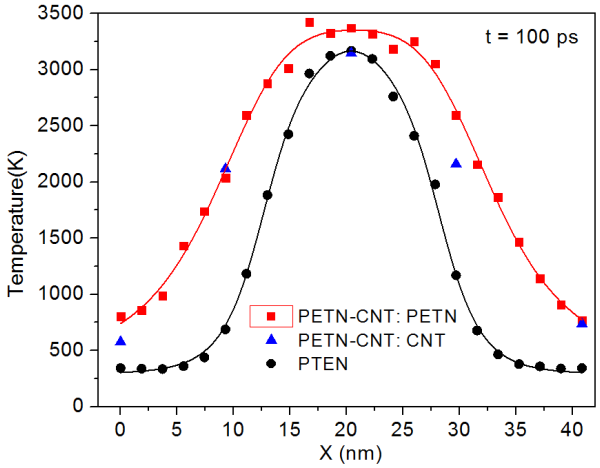


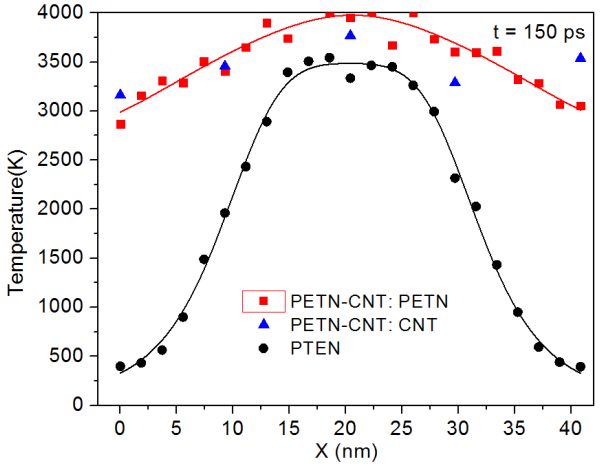


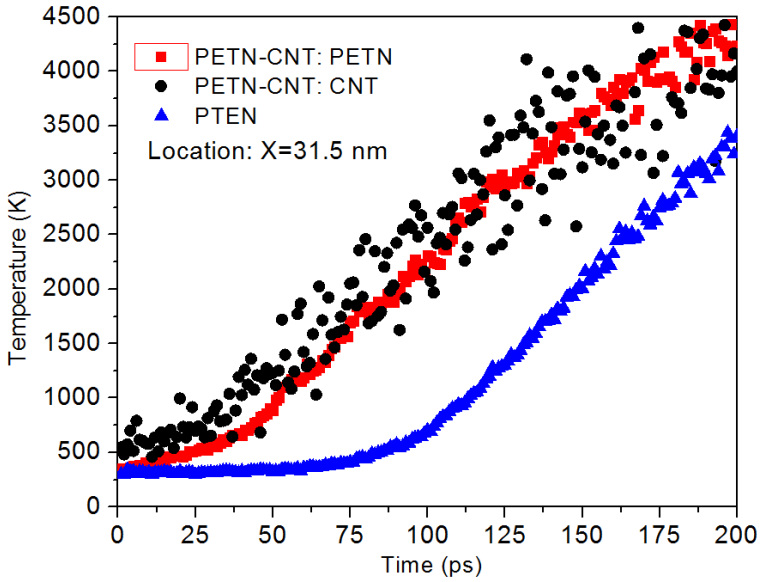
- The flame propagation speed of PETN on CNT is much faster than that of pure PETN (137 vs. 80 m/s), both at 3 Gpa.
- Such enhancement is speculated to be much more significant at lower pressures.

Temperature Profiles of PETN on CNT



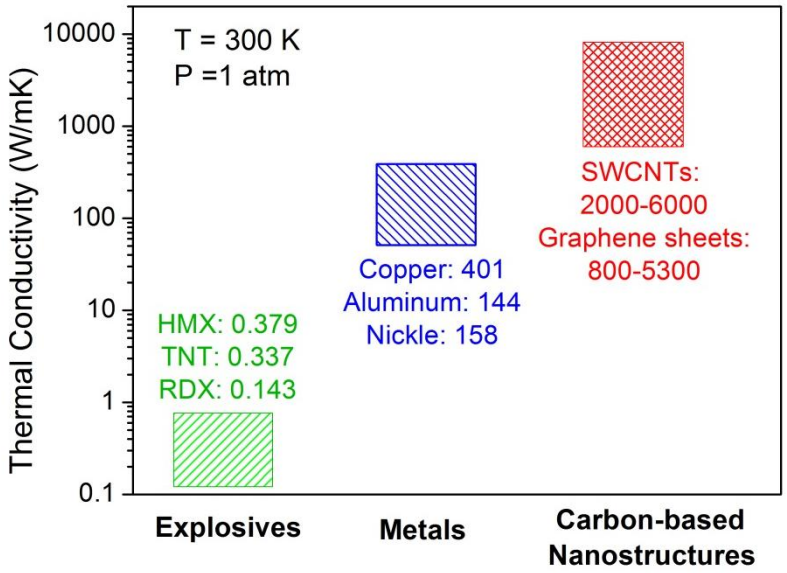


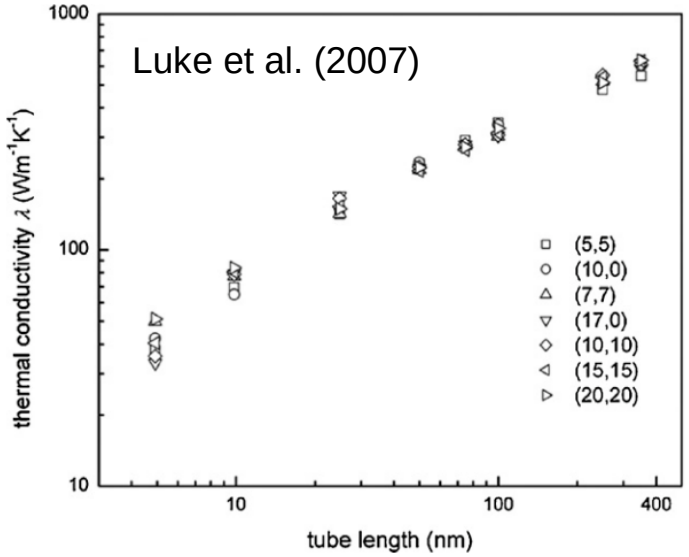




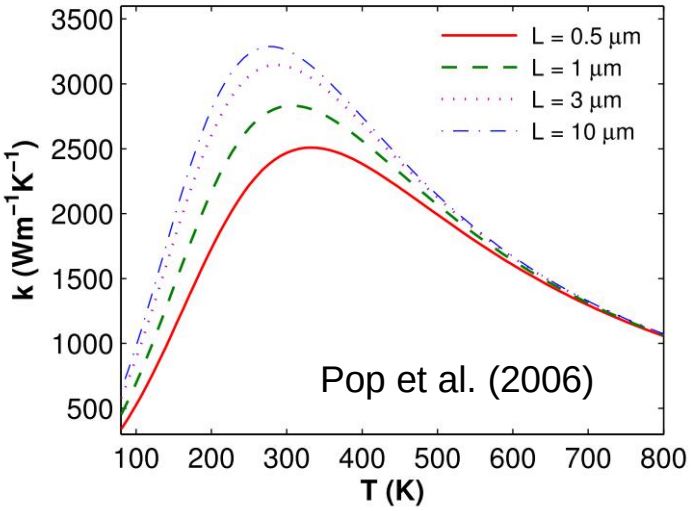
- The heat generated by PETN decomposition travels much faster in CNT than in PETN, which elevates the temperature of the unburned PETN. This is the main reason for flame speed enhancement.
- A heat pulse can propagate at speeds over 10 km/s in CNTs in the form of wave packets (Kim et al., 2007), much faster than typical flame speeds of fuels.

Thermal Transport in Carbon-based Nanostructures





- Thermal conductivity of CNTs: scattered results in the range between 2000-6000 W/m-K.
- Via a phonon conduction mechanism.
- Influenced by the number of phonon active modes, the boundary surface scattering, the length of phonon mean-free-path, and inelastic Umklapp-scattering.
- Depends on the diameter and length of the tubes, morphology, temperature, etc.



Conclusions

- The first MD simulations of flame propagation of monopropellant PETN on CNT based on first-principle derived reactive force field ReaxFF.
- For PETN, the computed flame speeds agree well with measured values using a diamond anvil cell. The speed is nearly constant as a function of time and is independent of the temperature chosen as flame front.
- For PETN on CTN, flame propagates much faster. This is attributed to faster heat propagation in CNTs via phonon transport than in PETN, which elevates the temperature of unburned PETN, causing flame speed to increase.
- Two potential applications of this phenomenon:
  - Carbon-based nanostructures may be used to improve propellant performance, e.g., faster burning rate, possibly change deflagration to detonation transition and shock sensitivity. The propellants may still have macroscopic dimensions but will exhibit microscopic features during burning.
  - Few other processes than combustion can produce a large temperature gradient which propagates very fast on carbon-based nanostructures on a small scale. This can generate a strong electric pulse to power MEME/NEMS devices as a result of thermoelectric (Seeback) effect.

Future Work

- Investigate the effect of pressure and various nanostructures on flame propagation using reactive MD simulations.
  - lower pressures (flame speed enhancement is expected to be a lot more significant at lower pressures)
  - various nanomaterials (single vs. multi-wall carbon nanotubes, graphene sheets)
  - length of CNTs (the mean-free-path of phonon is around 0.5 μm at room temperature)
  - diameters of CNTs (optimal ratio of fuel to CNT, competition between heat capacity and heat conductivity)
- Develop an experiment to further explore this phenomenon.
  - collaborate with Birck Nanotechnology Center on synthesis of various nanomaterials.
  - wet impregnation process to coat a layer of propellant on carbon-based nanostructures
  - develop a combustion chamber and measure flame speed

Acknowledgement

Graduate student: Guiyuan Mo

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