First Principles Based Reaction Kinetics for Decomposition of Hot Dense Liquid TNT from ReaxFF Multiscale Reactive Dynamics Simulations
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1. **AMORPHOUS LIQUID TNT PREPARATION AND THERMAL DECOMPOSITION**

The liquid TNT cell prepared using the scheme outlined in Section 2.2 (denoted *liquid 1*) reminisces some of the long range order that exists in the TNT crystal (see FIG. 1 below and FIG. 3 in the paper), while its density is very close to the measured one at 400K.

![FIG. 1: The energy-minimized TNT crystal supercell (left) and the liquid simulation cell at 1atm, 400K (right) shown in FIG. 2 in the paper are presented here from a different direction.](image)

In order to study the effect of liquid preparation scheme on its structure and thermal decomposition, a different approach was used to construct liquid TNT cell at 400K and 1 atm (denoted *liquid 2*):

- 36 TNT molecules were *randomly* placed in a unit cell (a, b, c = 23.64, 19.13, 20.79 Å) and the cell energy was minimized. Thereafter, the unit cell was 2x2x2 expanded, obtaining a 288 TNT molecules supercell with dimensions similar to those of *liquid 1* (a, b, c = 47.28, 38.26, 41.57 Å, density 1.444 gr/cm$^3$). The supercell energy was minimized using LAMMPS with ReaxFF LG-corrected potentials$^6$. The amorphous crystal cell obtained is plotted below in FIG. 2 and FIG. 3.

- The crystal was heated to 400K, beyond TNT’s measured melting point, then thermalized for 20 ps.

- Atmospheric pressure was applied at 400K via 30 ps long NPT simulation. The average density obtained was 1.35 gr/cm$^3$, ~6% lower than the measured one.

- Finally, the cell was thermalized at 400K for 2 ps and relaxed using NVE for additional 2 ps. See *liquid 2* cell in FIG. 4 and FIG. 5.

![FIG. 2: Two facets of energy-minimized amorphous TNT crystal supercell.](image)
The heat-up simulations for TNT liquid 2 were performed using the method described in Section 2.4, at 2250K, 2700K and 3500K. A comparison between the decay of the TNT molecules in liquid cells 1 and 2 is shown in FIG. 6 at these temperatures. The decay of liquid 2 is slightly slower compared to liquid 1 decay. This is expected due to the lower density, hence larger inter-molecular distances, in liquid 2 which decelerates inter-molecular reactions and decomposition.
FIG. 6: TNT molecules decay for \textit{liquid 2} (denoted in the legend by \textit{a - for amorphous}) and \textit{liquid 1} vs. simulation time, at various temperatures.

Thermal rate constants were calculated for the endothermic ($k_1$) and exothermic ($k_2$) stages of \textit{liquid 2} decomposition. In FIG. 7 Arrhenius plots of \textit{liquid 2} rate constants are compared to those of \textit{liquid 1}. The activation energy and pre-factor logarithm, $\ln(A_0 \text{ [sec}^{-1}])$, for $k_1$ are 35.2 kcal/mole and 33.4, and for $k_2$ 23.5 kcal/mole and 29.1, respectively. These values resemble those of the uncompressed \textit{liquid 1} (see Table 2 and Table 3 in the paper).

FIG. 7: Arrhenius plots for TNT \textit{liquid 1} and \textit{liquid 2} thermal decomposition. The endothermic stage rate constant ($k_1$) is plotted with full lines, whereas the exothermic stage rate constant ($k_2$) is plotted with dashed lines. Per liquid cell, the initial density is the density at 400K and 1 atm. Temperature range is 2250K-3500K.

Some dominant initial fragments created in the decomposition of liquid TNT at 2250K are plotted in FIG. 8 for \textit{liquid 2} and \textit{liquid 1}. It is seen that there are small differences in the decomposition characteristics of the two TNT liquid cells. In FIG. 9 the main initial fragments, NO and NO$_2$, are presented for heat-up simulations at various temperatures. It is seen that initially, in the uni- or bi-molecular reactions stage, the creation of the fragments is similar for
both liquid cells (density effect is small), whereas the reactions are slower in the later stages in the lower density liquid 2. This effect decreases with increasing temperature.

Finally, in FIG. 10 some small gaseous final products created in the thermal decomposition of the two liquid cells (1 and 2) at 2700K are plotted. H₂O and N₂ formation is delayed in liquid 2, whereas the carbon containing gases (CO and CO₂) are created faster. This can be understood, again, based on the higher proximity of the TNT molecules (and fragments) in denser liquid 1. Thus, in liquid 1 decomposition, both small gaseous fragments that do not contain carbon atoms (e.g. H₂O and N₂) and larger, carbon-rich clusters are created faster, while small carbon-containing fragments creation is delayed.
FIG. 10: Final gaseous products creation at 2700K for liquid 1 (dotted lines) and liquid 2 (full lines, denoted “a”).

2. PRESSURE AND POTENTIAL ENERGY EVOLUTION

The time evolution of the total pressure and potential energy as a function of density (see Table 1 in the paper) is presented in FIG. 11 and FIG. 12. Generally, the pressure increases with temperature and compression. In all cases, the pressure profiles reach an asymptotic limit. At low compressions (0 and 15%) the pressure increases, while it decreases at 30% compression. This density dependence can be explained by the formation of large clusters at high compression that causes reduction of the gaseous products and pressure (see Section 4 in the paper).

FIG. 11: Pressure vs. simulation time for various densities (ambient density – blue, 15% compression – green, 30% compression – red), plotted separately per constant temperature simulation (1800-3500K).
The variation of the system PE during the decomposition process is presented in FIG. 12. Although the simulations are carried out at a constant temperature (and kinetic energy), energy is consumed and released during the simulation due to chemical bond rupture and formation. The calculated PE profile can be divided into two parts: A short increasing part, which is related to the endothermic initial decomposition step, and a decreasing part, related to the exothermic reactions that take place following the initial part.

The influence of compression on the PE profile is demonstrated in FIG. 12. For all temperatures examined, the asymptotic potential energy reduces as the compression increases. This means that the final products are more stable at high compressions. This result can be explained by a more effective and complete decomposition of liquid TNT at these high pressures. A second observation is that the energy released (calculated as the difference between the asymptotic value of PE and the barrier energy) is larger at high compressions. In addition, at each temperature shown in FIG. 12, the PE reaches its maximal and asymptotic values faster as compression increases. This is in agreement with the liquid TNT decay rate increase as compression rises (see FIG. 4 in the paper).

The temperature dependence of the PE is presented in FIG. 13 for 30% compression. It is clear that the completion of the liquid TNT decomposition is faster at higher temperatures. The amount of energy released in the exothermic part of the PE is similar at all temperatures studied, with only ~2% variation between the lowest and highest temperatures.

**FIG. 12:** Potential energy vs. simulation time for various densities, plotted separately per constant temperature simulation (1800-3500K). \( t_{\text{max}} \) is the PE maximum, separating between the endothermic and exothermic stages in the decomposition reaction of liquid TNT. Energy units are kcal/mole, where “mole” here refers to a mole of simulation cells.
FIG. 13: Potential energy vs. simulation time for 30% compressed liquid TNT, at various temperatures.

3. **Bond Order Cutoff Values**

In order to determine whether a bond exists between every two atom pairs in the ReaxFF MD simulation, at each time step the calculated bond orders are compared with the relevant bond order cutoff values supplied within the fragments analysis code. The cutoff values used in the fragment analysis presented in this manuscript are given in Table 1 below.

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<tr>
<th>Atom #1</th>
<th>Atom #2</th>
<th>Bond order cut off</th>
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</tr>
<tr>
<td>C</td>
<td>C</td>
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</table>

4. **Fragments Analysis: Initial and Intermediate Reactions**

Below, additional results for the initial and intermediate fragments formed during liquid TNT decomposition are shown, at ambient density and 30% compression. In FIG. 14, additional initial fragments created at 1800K are plotted (complementary to FIG. 8 in the paper), and in FIG. 15 - FIG. 17 fragments created at 2250K and 2700K are shown. A blow up of FIG. 15 (ambient...
density, 2250K - see FIG. 16) focuses on the initial decomposition reactions obtained: (1) Unimolecular NO₂ release; (2) TNT dimer decomposition, producing C₇H₅O₅N₂, C₇H₅O₅N₃ and NO₂. The vertical line (dashed, blue) represents t_max, the time when exothermic reactions initiate.

FIG. 14: Additional fragments at 1800K liquid TNT decomposition for ambient density (left) and 30% compression (right).

FIG. 15: A comparison between the initial fragments created at ambient density (left) and 30% compression (right) at 2250K.

FIG. 16: Blow up of FIG. 15 for ambient density liquid TNT at 2250K, focusing on the initial decomposition reactions.
5. **REAXFF PARAMETERS**


39 ! Number of general parameters
50.0000 !Overcoordination parameter
9.4514 !Overcoordination parameter
30.0000 !Valency angle conjugation parameter
216.4305 !Triple bond stabilisation parameter
12.4838 !Triple bond stabilisation parameter
0.0000 !C2-correction
1.0701 !Undercoordination parameter
7.5000 !Triple bond stabilisation parameter
11.9083 !Undercoordination parameter
13.3822 !Undercoordination parameter
10.4637 !Triple bond stabilization energy
0.0000 !Lower Taper-radius
10.0000 !Upper Taper-radius
2.8793 !Not used
33.8667 !Valency undercoordination
3.5895 !Valency angle/lone pair parameter
1.0563 !Valency angle
2.0384 !Valency angle parameter
6.1431 !Not used
6.9290 !Double bond/angle parameter
0.0283 !Double bond/angle parameter: overcoord
0.0570 !Double bond/angle parameter: overcoord
-2.4837 !Not used
5.8374 !Torsion/BO parameter
10.0000 !Torsion overcoordination
1.8820 !Torsion overcoordination
-1.2327 !Conjugation 0 (not used)
2.1861 !Conjugation
1.5591 !vdWaals shielding
0.0100 !Cutoff for bond order (*100)
### Valency Angle Conjugation Parameters
- Valency angle conjugation parameter: 5.2216
- Overcoordination parameter: 3.4021
- Overcoordination parameter: 38.5241
- Valency/lone pair parameter: 2.1533
- Not used: 0.5000
- Not used: 20.0000
- Not used: 5.0000
- Not used: 2.0000
- Version number: 6.5560

### Atomic Data
- Number of atoms: 6
- Atomic positions and other parameters are listed for each atom, including:
  - Atomic number
  - Atomic mass
  - Atomic radius
  - Bond order
  - Bond energy

### Bond Data
- Number of bonds: 10
- Bond order, bond length, bond energy, and other properties are listed for each bond, including:
  - Bond order
  - Bond energy
  - Bond length

### Additional Parameters
- Number of off-diagonal terms: 6
- Additional parameters such as Ediss, Ro, gamma, rsigma, and rpi are listed for each parameter.
<p>| | | | | | |</p>
<table>
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|   | Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 74.0317 | 32.2712 | 0.9501 | 0.0000 | 0.1780 | 10.5736 | 1.0400 |
| 1 | 2 | 70.6558 | 14.3658 | 5.3224 | 0.0000 | 0.0058 | 0.0000 | 1.0400 |
| 2 | 1 | 76.7339 | 14.4217 | 3.3631 | 0.0000 | 0.0127 | 0.0000 | 1.0400 |
| 1 | 2 | 0.0000 | 0.0000 | 6.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 2 | 0.0000 | 3.4110 | 7.7350 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 2 | 2 | 0.0000 | 27.9213 | 5.8635 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 1 | 65.3104 | 6.3897 | 7.5000 | 0.0000 | 0.2000 | 10.0000 | 1.8525 |
| 3 | 1 | 71.9855 | 28.5708 | 6.4252 | 0.0000 | 0.2000 | 0.0000 | 1.8525 |
| 1 | 2 | 65.8892 | 45.0000 | 1.6598 | 0.0000 | 0.2000 | 10.0000 | 1.8525 |
| 3 | 1 | 73.1057 | 25.8227 | 4.2145 | 0.0000 | 0.2000 | 0.0000 | 1.8525 |
| 4 | 1 | 65.8759 | 40.9838 | 2.4369 | 0.0000 | 0.2000 | 0.0000 | 1.8525 |
| 2 | 1 | 56.3039 | 17.3681 | 5.3095 | 0.0000 | 0.9110 | 0.0000 | 1.0400 |
| 2 | 1 | 71.5505 | 11.1820 | 3.7129 | 0.0000 | 0.9110 | 0.0000 | 1.0400 |
| 1 | 2 | 0.0000 | 0.0019 | 6.3000 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 3 | 72.3642 | 37.8942 | 1.1566 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 1 | 3 | 90.0000 | 45.0000 | 0.5719 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 1 | 3 | 70.4331 | 14.4055 | 7.1593 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 1 | 3 | 83.8833 | 23.3345 | 2.3433 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 1 | 3 | 84.0407 | 45.0000 | 1.0695 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 4 | 1 | 65.8759 | 40.9838 | 2.4369 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 3 | 56.3039 | 17.3681 | 5.3095 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 3 | 82.3474 | 13.5165 | 3.4896 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 1 | 4 | 68.4330 | 19.3525 | 2.1625 | 0.0000 | 1.7325 | 0.0000 | 1.0440 |
| 1 | 4 | 86.2893 | 37.5587 | 1.2660 | 0.0000 | 1.7325 | 0.0000 | 1.0440 |
| 1 | 4 | 74.2404 | 12.0540 | 0.7195 | 0.0000 | 0.5355 | 0.0000 | 2.5279 |
| 2 | 4 | 84.1185 | 45.0000 | 1.3826 | 0.0000 | 0.5355 | 0.0000 | 2.5279 |
| 2 | 4 | 78.7133 | 24.6250 | 3.8202 | 0.0000 | 0.5355 | 0.0000 | 2.5279 |
| 2 | 4 | 56.3036 | 14.1532 | 3.3914 | 0.0000 | 0.2000 | 0.0000 | 2.1689 |
| 2 | 4 | 74.2404 | 12.0540 | 0.7195 | 0.0000 | 0.5355 | 0.0000 | 2.5279 |
| 2 | 4 | 82.7133 | 24.6250 | 3.8202 | 0.0000 | 0.5355 | 0.0000 | 2.5279 |
| 2 | 4 | 56.3036 | 14.1532 | 3.3914 | 0.0000 | 0.2000 | 0.0000 | 2.1689 |

<p>|   | Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n   |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.0000 | 48.4194 | 0.3163 | -8.6506 | -1.7255 | 0.0000 | 0.0000 |
| 1 | 1 | 0.0000 | 63.3484 | 0.2210 | -8.8401 | -1.8081 | 0.0000 | 0.0000 |
| 2 | 1 | 0.0000 | 45.0000 | 1.0695 | 0.0000 | 0.7472 | 0.0000 | 1.2639 |
| 1 | 3 | 82.3474 | 13.5165 | 3.4896 | 0.0000 | 0.0000 | 0.0000 | 1.0400 |
| 0 | 2 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0 | 1 | -0.0002 | 85.8794 | 0.3236 | -3.8134 | -2.0000 | 0.0000 | 0.0000 |</p>
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! Nr of hydrogen bonds: at1; at2; at3; Rhb; Dehb; vhb1

4 3 2 3 2.0000 -5.0000 3.0000 3.0000
3 2 4 1.7753 -5.0000 3.0000 3.0000
4 2 3 1.3884 -5.0000 3.0000 3.0000
4 2 4 1.6953 -4.0695 3.0000 3.0000

13