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A reactive molecular dynamics study of phenol and phenolic polymers in extreme environments

PRESENTED BY

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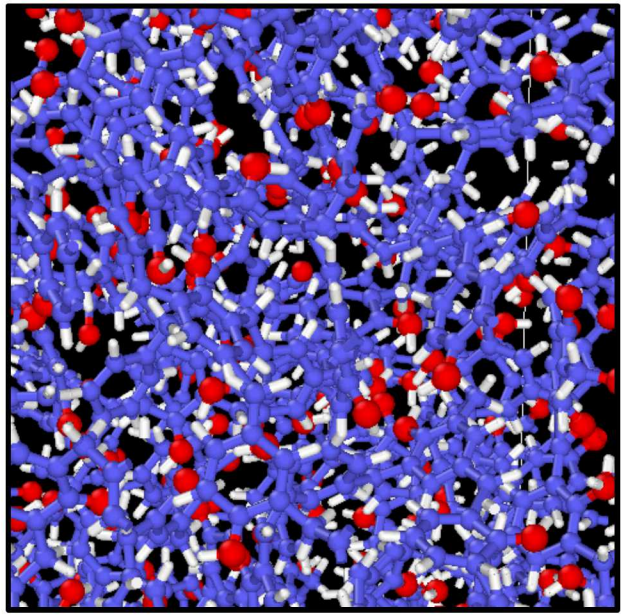
Intro/Rationale

Phenolic polymers

- Commonly used in extreme environments.
- Can vary greatly, depending on curing conditions, in crosslink extent, initial density, stoichiometry, molecular structure.

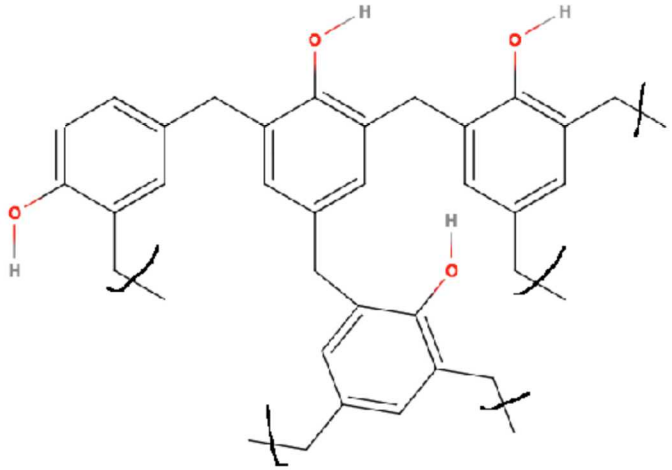
Reactive molecular dynamics (MD) can provide insight into
-Processes that occur during heating and shock.
-The relationship between molecular structure and density, shock response, and pyrolytic breakdown.



<u>Questions</u>

1.) Which reax parametrization is the most appropriate for modeling chemistry during pyrolysis and high pressure shock (yields the most accurate activation energies and reaction energies)?

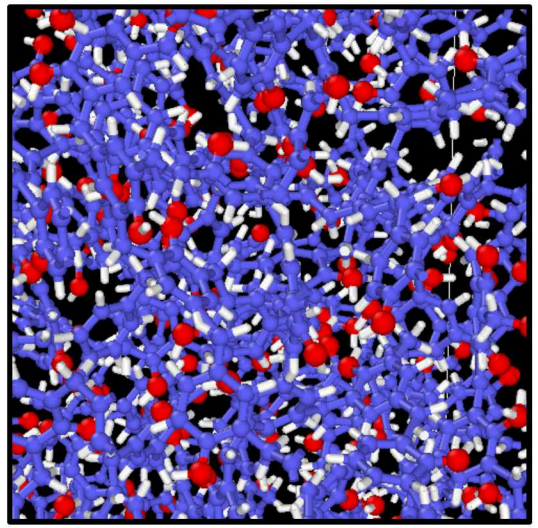
2.) Which is the most appropriate for phenolic shock (most accurately represents the intermolecular interactions of phenolics?



J. B. Scoggins et al. *Aerospace Sci. and Tech.* **66**, 177-192 (2017).

Reax parametrizations

ReaxFF – Bond order MD potential that handles chemistry.
Various parametrizations for different combinations of atoms under different conditions.

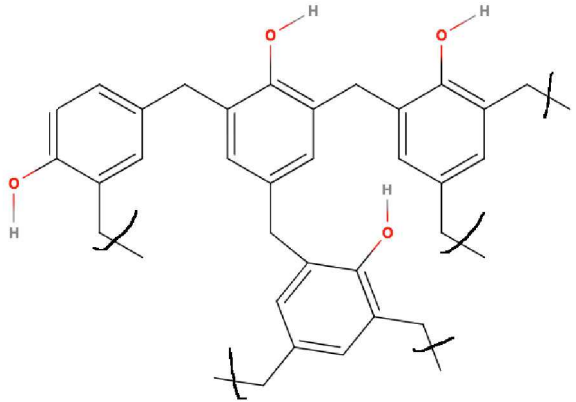


Parametrizations for H/C/O containing systems:

1.) CHO – commonly used for hydrocarbon reactivity.

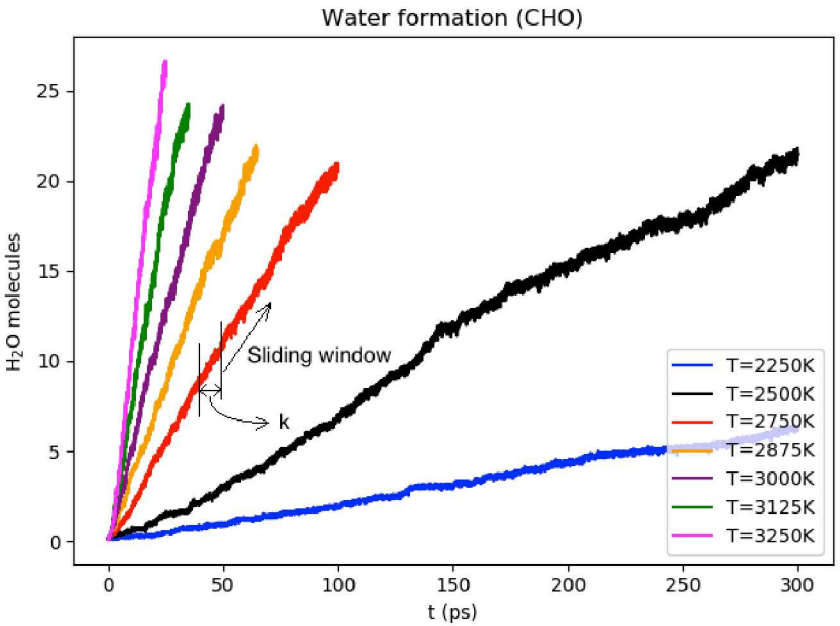
2.) Mattsson – Past success simulating polymers under chemistry-inducing shock (up to 60 GPa). Well tested for systems containing H and C.

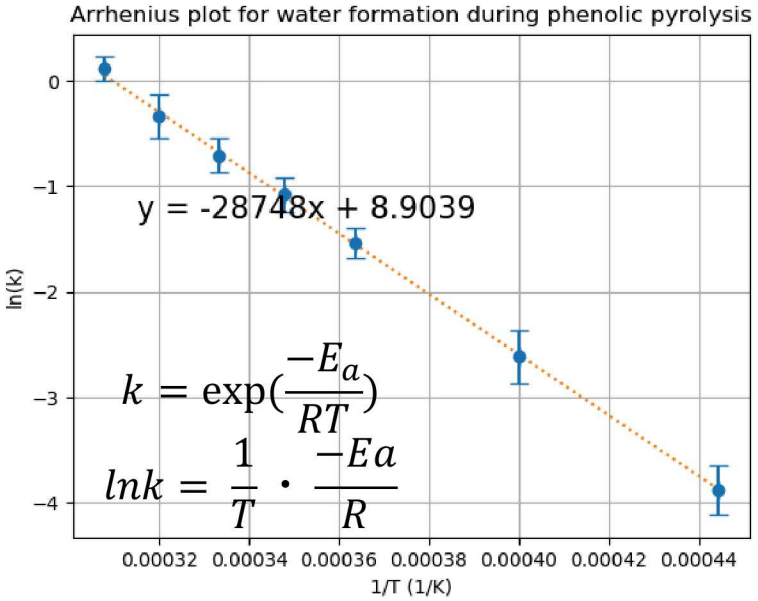
3.) Hydrogen Bond Augmented 2018 (HBA18) – Mattsson parametrization utilizing the O-H---O hydrogen bonding parameters from CHO. New hybrid parametrization – introduced to capitalize on the the strengths of the other two.



S. Plimpton *J. Comp. Phys.* **117**, 1-19 (1995).
A. C. T. van Duin et al. *J. Phys. Chem.* **105**, 9396-9409 (2001).
K. Chenoweth et al. *J. Phys. Chem. A* **112**, 1040-1053 (2008).
A. Harpale et al. *Carbon* **130**, 315-324 (2018).
T. R. Mattsson et al. *Phys. Rev. B* **81**, 054103 (2010).
J. Matthew D. Lane and N. W. Moore *J. Phys. Chem. A* **122**, 3962-3970 (2018).

Phenolic pyrolysis activation energies

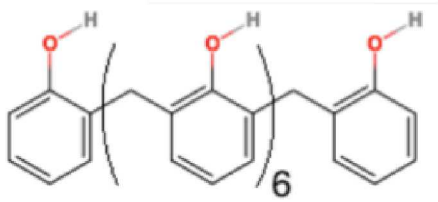




Water
-Abundant phenolic pyrolysis byproduct
-Formation kinetics studied with MD in the past.

”Global”
-Mass of all volatilizable species as a function of time
-Closer proxy to experimentally determined activation energies based on thermogravimetric analysis (TGA).
-Mass cutoff(s) based on heaviest gaseous products observed experimentally.

Methodology
1.) 16 linear chains – 15 instances.
2.) Water formation rates determined at various temperatures.
3.) Activation energies (E_a) extracted using the Arrhenius equation:



D. Jiang et al. *J. Phys. Chem. A* **113**, 6891-6894 (2009).
T. G. Desai et al. *Polymer* **52**, 577-585 (2011).
K. A. Trick et al. *Carbon* **33**(11), 1509-1515 (1995).
K. A. Lincoln *AIAA Journal* **21**(8), 1204 (1983).

Phenolic pyrolysis activation energies

NVT ensemble
1776 atoms – 16 linear phenolic chains
Periodic boundary conditions
15 instances
7-10 temperatures ranging from 2000 – 3250 K.
10s to 100s of ps per simulation
0.25 fs timestep

ρ = 1.25 g/cc	E_a (H_2O) (kj/mol)	E_a (Global) (kj/mol)	Source of variation
Exp, Jiang	----------	223-305	Temperature region and heating rates
Exp, Trick	----------	74-198	Temperature region and heating rates
Exp, Freidman	----------	192 - 293	Heating rate, method of determination
MD, Jiang	332 +/- 64	----------	
MD, Desai	286 +/- 46	----------	
This work, CHO	246 +/- 23	301 +/- 32	
This work, HBA18	135 +/- 5	210 +/- 12	
This work, Mattsson	130 +/- 6	191 +/- 13	

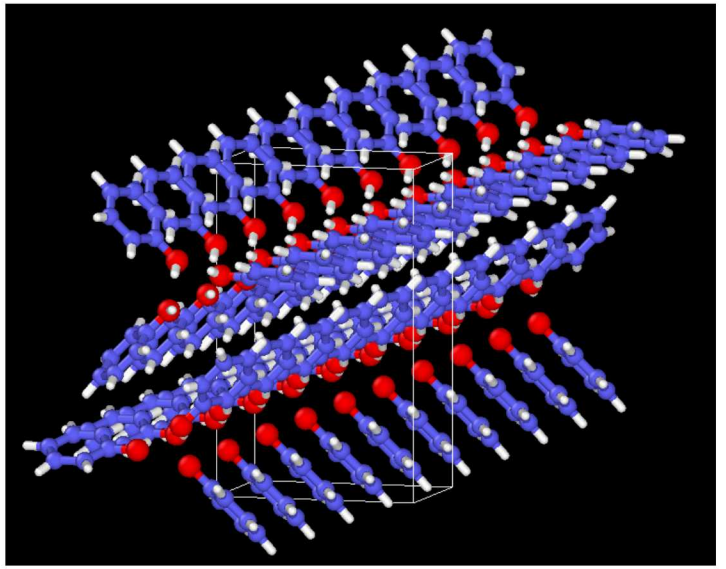
All reax parametrizations agree with experiment – variation too great to constrain MD results, which vary.

CHO 3250 K volatile evolution

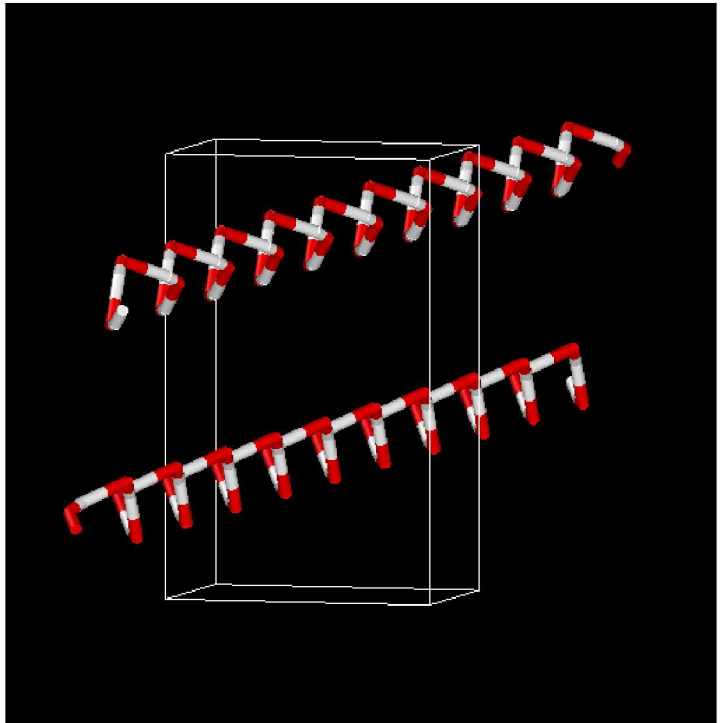
H. Jiang et al. *Carbon* **48**, 352-358 (2010).
K. A. Trick et al. *Carbon* **35**(3), 393-401 (1997).
H. L. Freidman *J. Polym. Sci. C* **6**(1), 183-195 (1964).

Crystalline phenol

Experimental crystal structure of phenol
-Characterized by hydrogen-bonded chains of molecules aligned parallel to crystallographic b axis, where the molecules are arranged in approximate threefold helices.



Phenol crystal - re-equilibrated with each parametrization
-NPT ensemble
-123 K – ambient pressure
-0.1 fs timestep
-150 – 200 ps equilibration



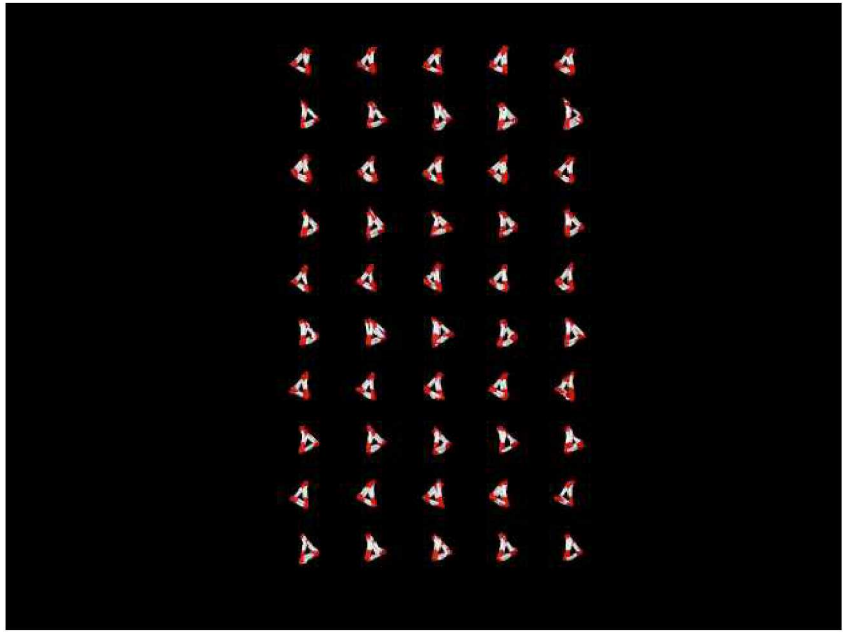
Density evaluated and compared with experiment.

Crystallinity evaluated based on
-Qualitative assessment of 3-fold helix retention
-Diffusion coefficient

V. E. Zavodnik et al. *Zh. Strukt. Khim.* **28**, 175 (1987).
David R. Allan et al. Acta Cryst. **B58**, 1018-1024 (2002).

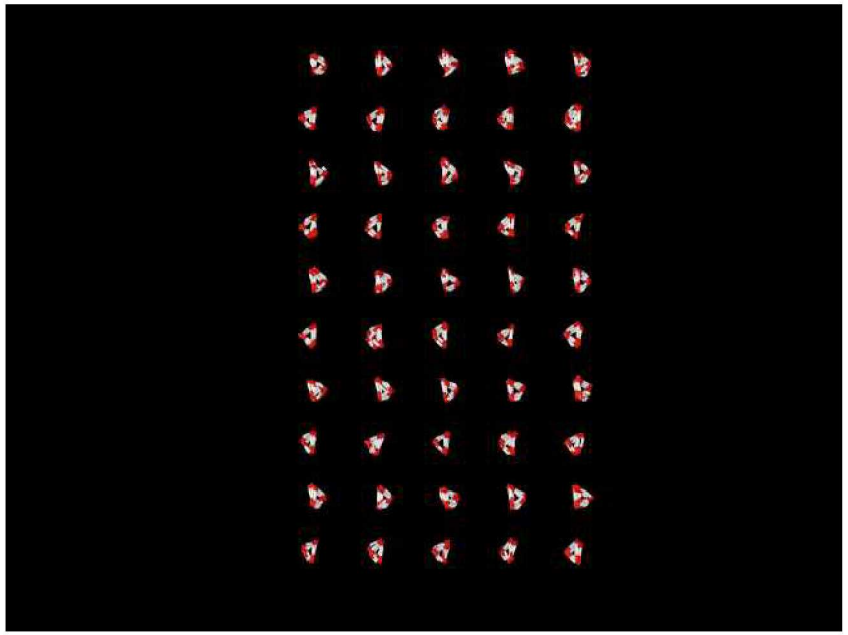
Crystalline phenol

Reax parametrization	Diffusion coefficient (Å²/ps)	Density (g/cc)
CHO	2.3 +/- 3.3 x 10^{-4}	1.432 +/- 0.003
HBA18	9.3 +/- 2.5 x 10^{-4}	1.200 +/- 0.003
Mattsson	9.8 +/- 0.4 x 10^{-3}	1.180 +/- 0.002
Zavodnik, Exp	----------	1.19

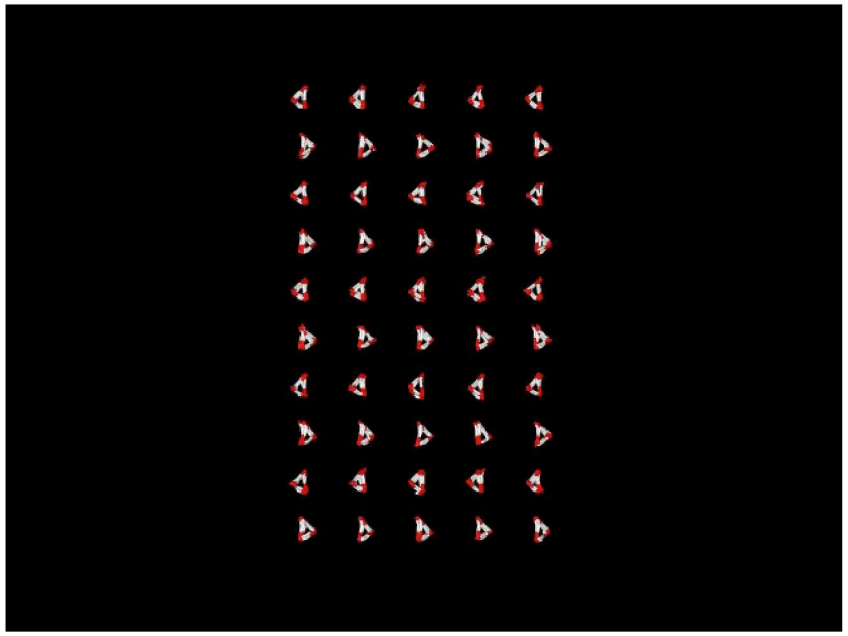


Mattsson

HBA18 captures H-bonding interactions from CHO to retain crystallinity. Density maintained due to Mattsson parameters.



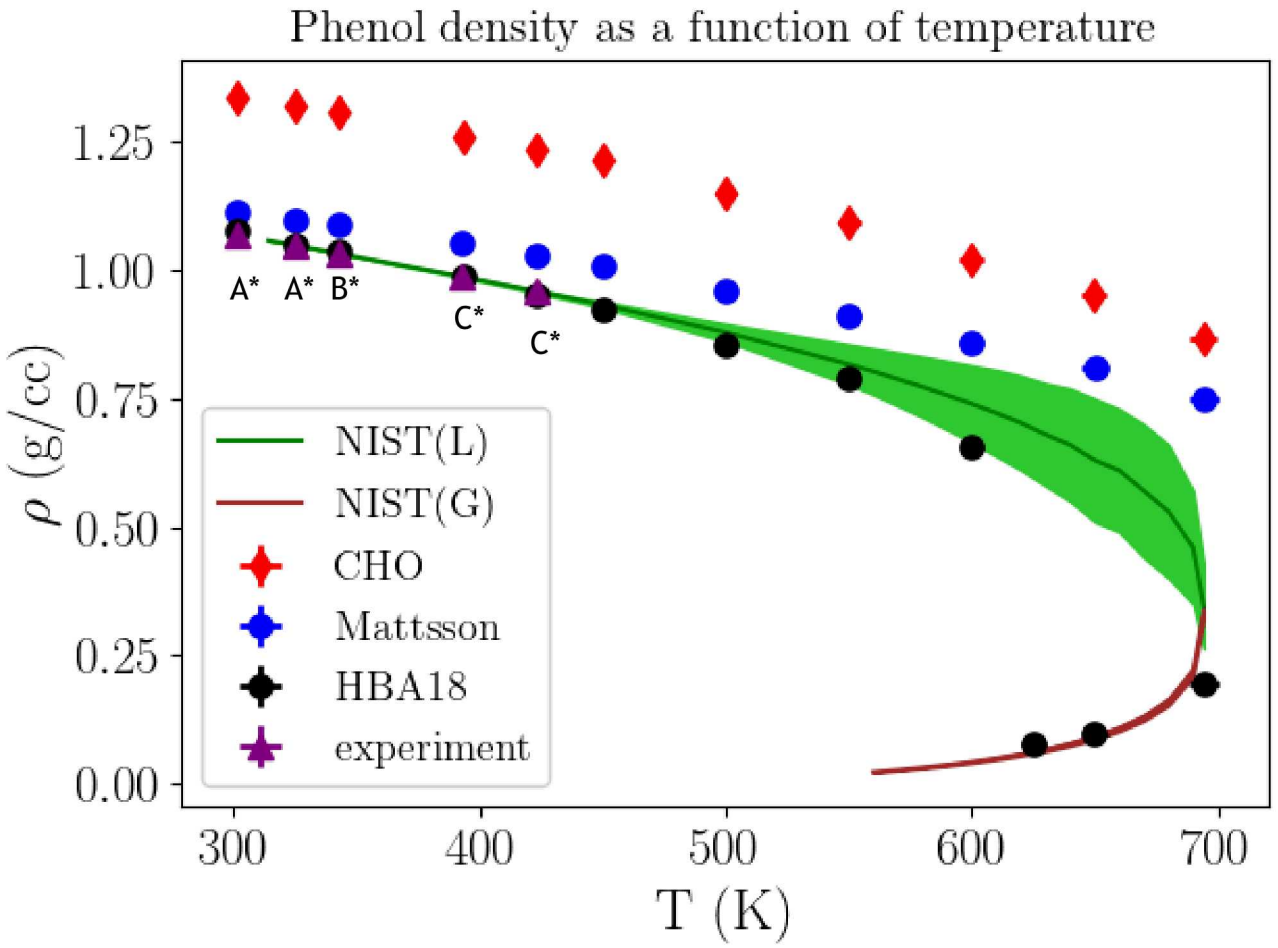
CHO



HBA18

V. E. Zavodnik et al. *Zh. Strukt. Khim.* **28**, 175 (1987).

Phenol density at various temperatures



Phenol equilibration - various points in P,T space along L/G coexistence curve.

Phenol data extracted from NIST web thermo data tables – derived from ThermoData Engine.

HBA18 agrees with experiment and the NIST model to a greater degree than the parametrizations from which it was derived.

A* R. B. Badachhape et al. *J. Chem. And Eng. Data* **10**, 143 (1965).
B* D. L. Cunha et al. *J. Chem. Eng. Data.* **58**, 2925-2931 (2013).
C* C. A. Buehler et al. *J. Am. Chem. Soc.* **54**(6), 2398-2405 (1932).
E.W. Lemmon et al. 2018 https://dx.doi.org/10.18434/T4JS3C
J. Chem. Inf. Model. **45**, 816-838 (2005).
J. Chem. Inf. Model. **47**, 1713-1754 (2007).
J. Chem. Inf. Model. **49**, 503-517 (2009).
J. Chem. Inf. Model. **49**, 2883-2896 (2009).

Conclusions

1.) All three MD parametrizations can accurately model phenolic pyrolysis based on activation energies.

2.) HBA18 is the most ideal reaxFF parametrization for studying shock:

- Accurately models crystalline phenol.
- Accurately models phenol across a range of temperatures relevant for shock.

Future work

Quantify energies associated with common product formation pathways for all three parametrizations and compare with quantum chemical calculations.

Acknowledgements

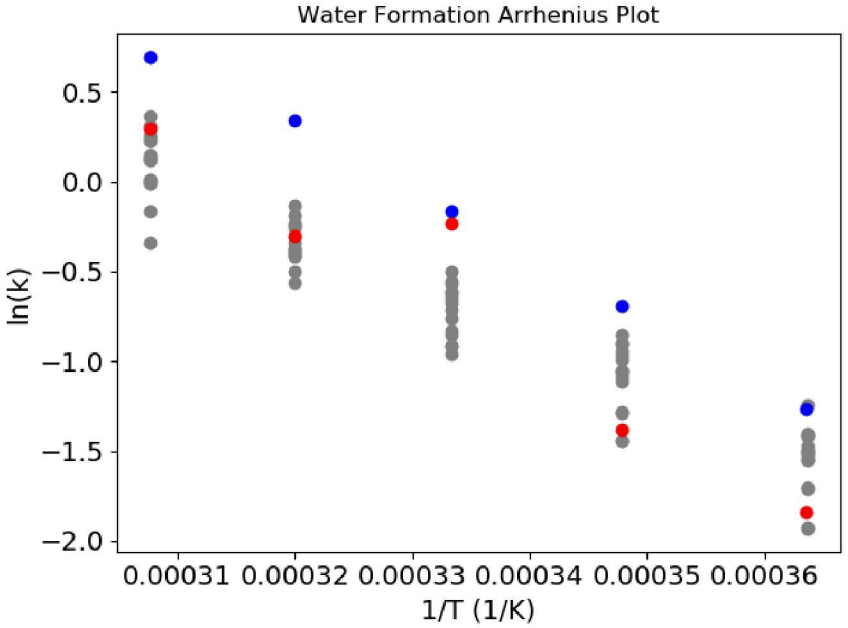
Sandia National Laboratories

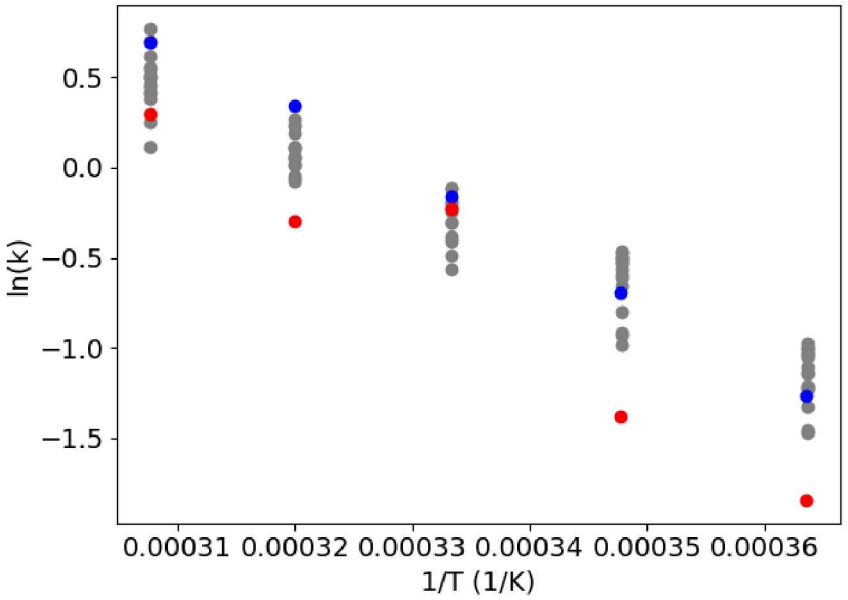
High Performance Computers

NIST

Dr. Kenneth Kronlein

Bonus slides





- D. Jiang et al. *J. Phys. Chem. A* **113**, 6891-6894 (2009).
- T. G. Desai et al. *Polymer* **52**, 577-585 (2011).