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A Foundation for the Atomistic Simulation of Solid Rocket Propellants

April 18–20, 2023

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full screen

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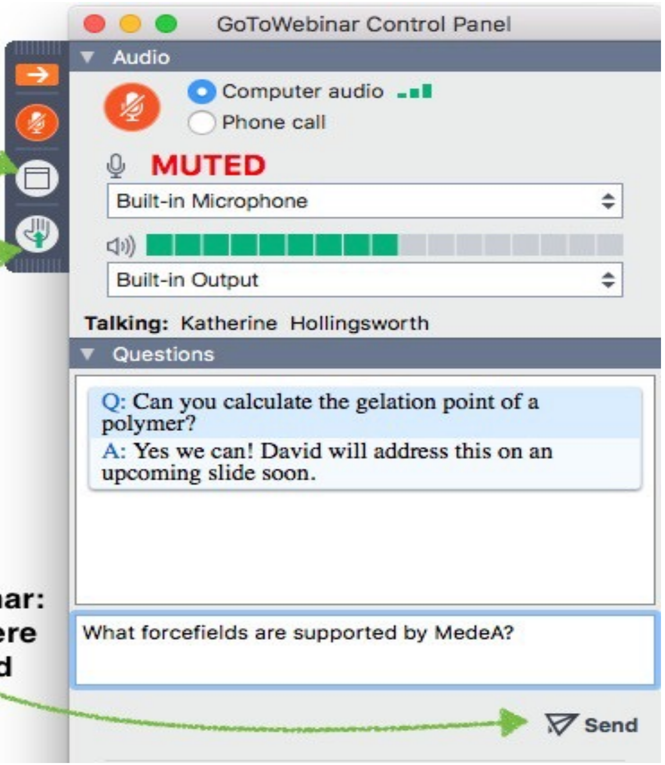

Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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Webinar Speakers

Katherine Hollingsworth ***Dr. Clive Freeman*** ***Presenter: Dr. Garrett Tow***

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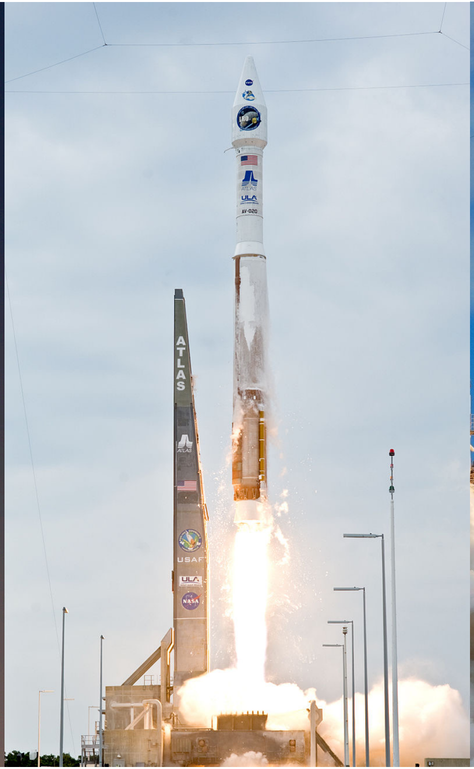
Solid Rocket Boosters

Ariane 5 – 116 Launches

Atlas V – 97 Launches



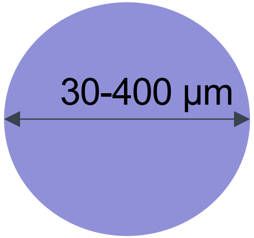
Space Shuttle – 135 Launches

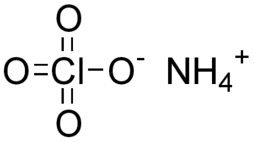
‘Conventional’ Solid Propellant

Formation of urethane cross-link

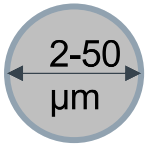
$$R_1-N=C=O + R_2-O-H \longrightarrow R_1-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_2$$

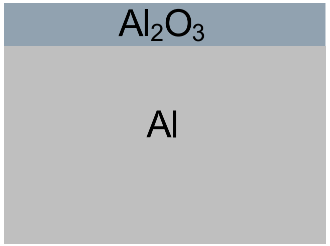
Ammonium Perchlorate (AP)



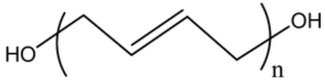


Aluminum (Al)



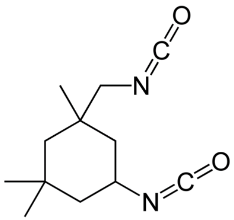


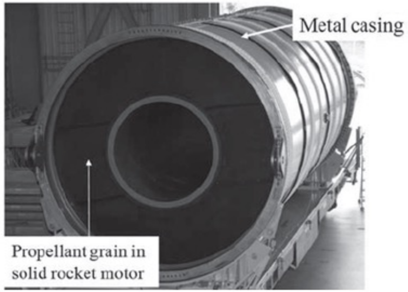
Hydroxyl-Terminated Polybutadiene (HTPB)



HTPB

Isophorone Diisocyanate (IPDI)





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Aging and Degradation of Elastomers

- Mechanical Aging
  - Cyclic thermal stress
  - Debonding of binder from particulate oxidizer
  - Voids
  - Microcracks

- Chemical Degradation
  - Thermo-oxidative cross-linking
  - Ozonolysis
  - UV radiation
  - $HClO_4$ mediated cross-linking

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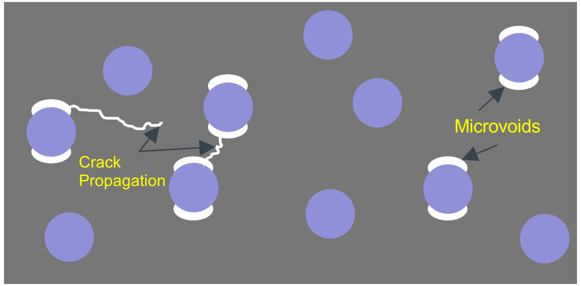
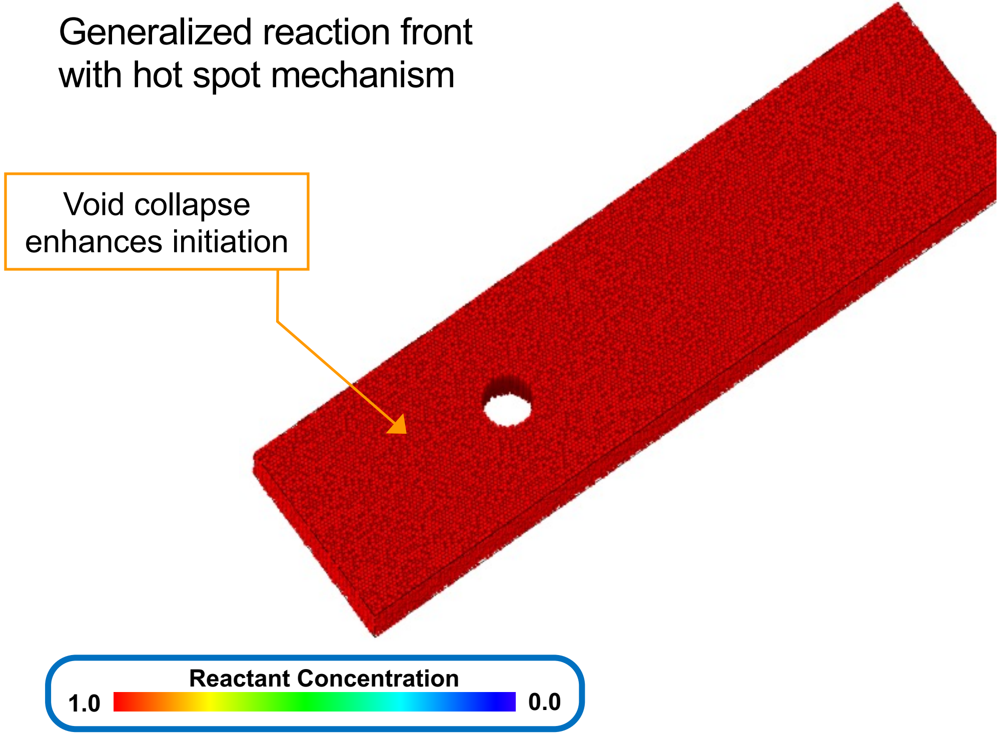
Polymer Delamination

Crack propagation from microvoids



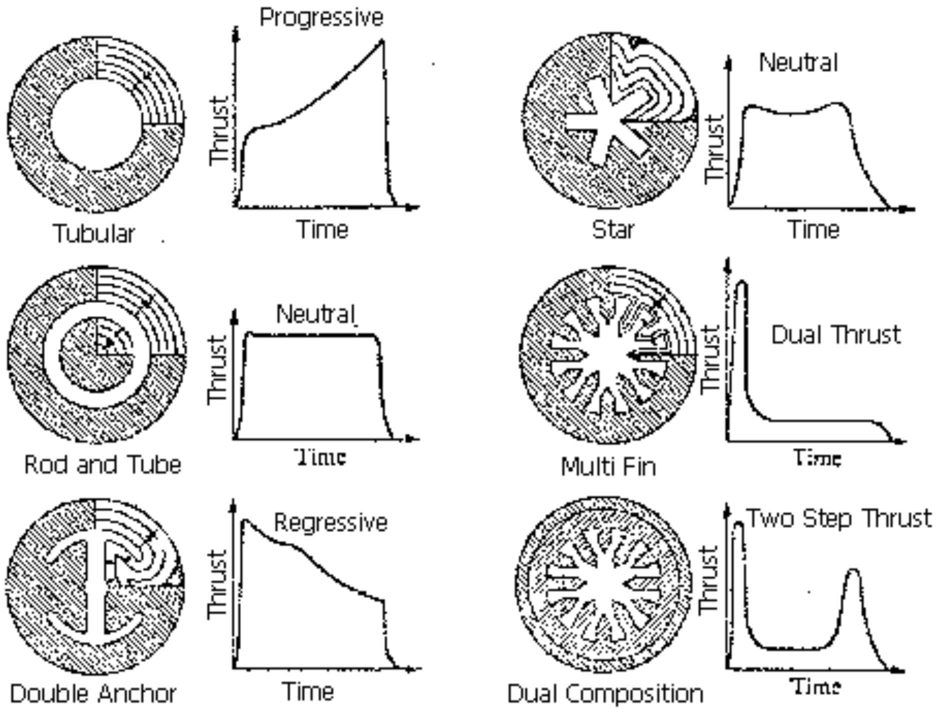
- Voids and cracks contribute to uneven burn.
- Uneven burn can lead to device failure.

Generalized reaction front with hot spot mechanism



Animation provided by John Brennan and Jim Larentzos, ARL

Propellant Grain



https://www.nakka-rocketry.net/th_grain.html

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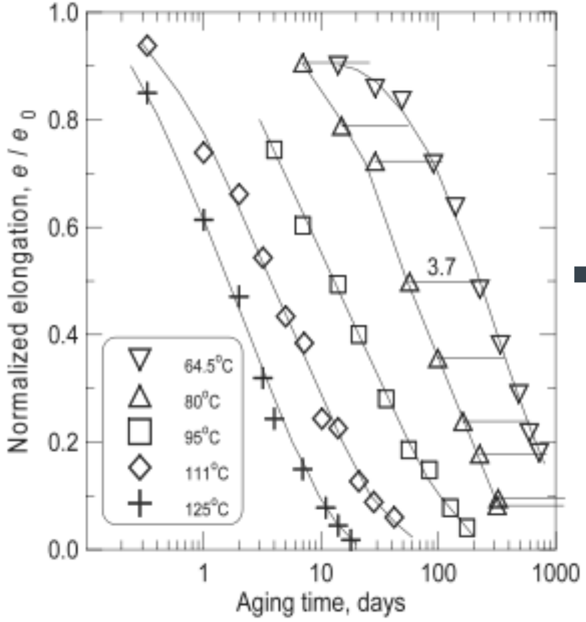
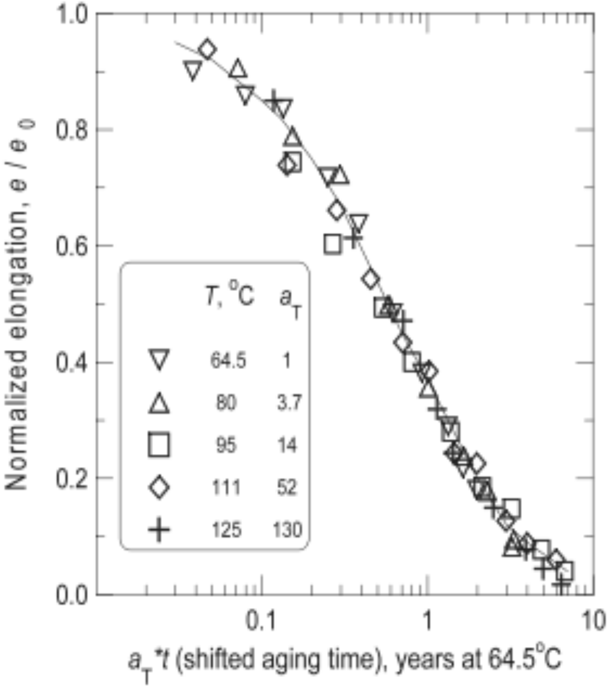
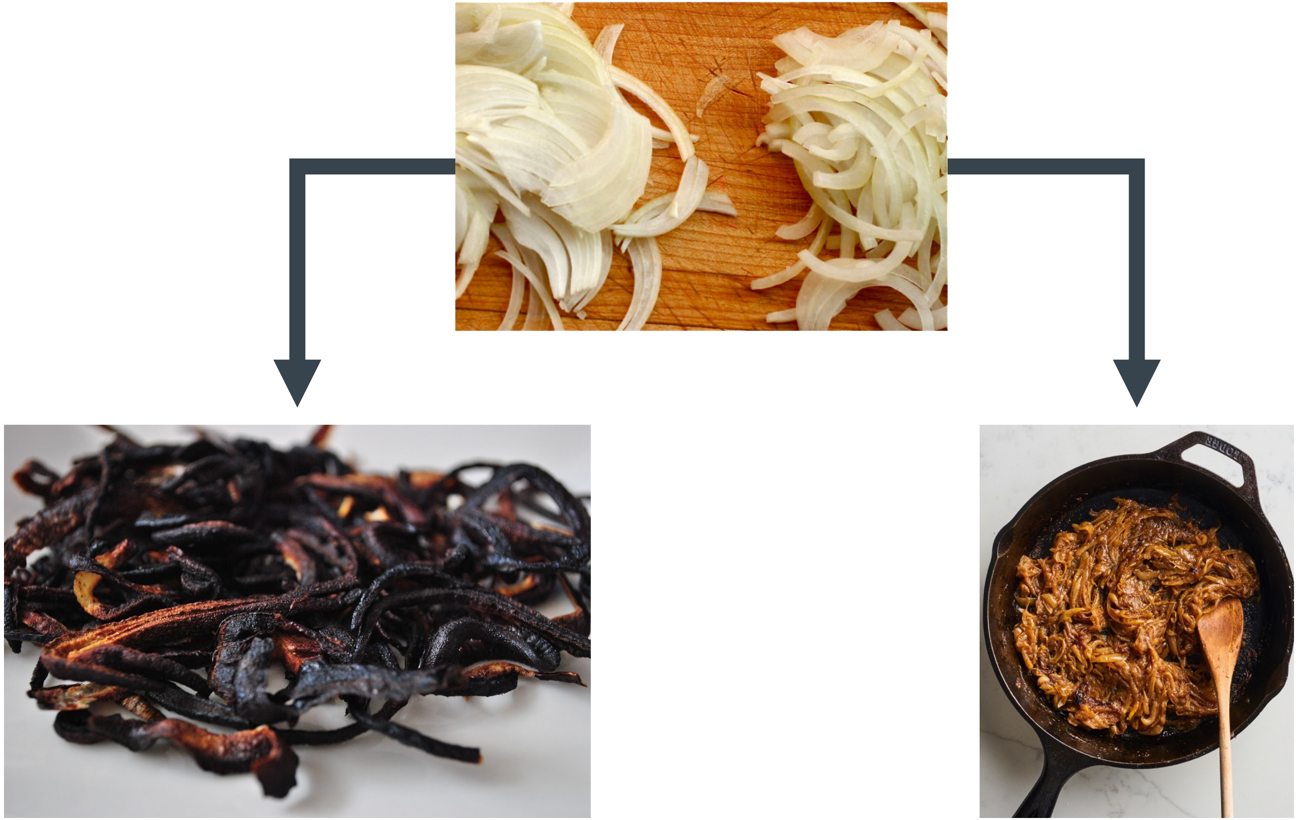
Accelerated Aging of Elastomers



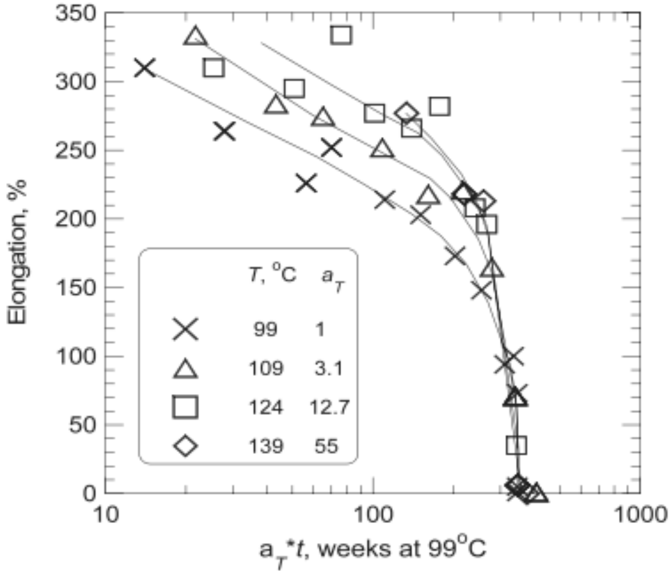


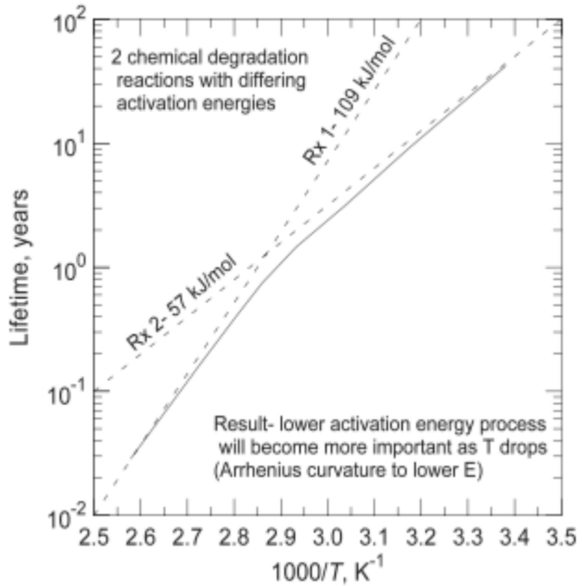
K. T. Gillen, R. Bernstein, and M. Celina (*2015*) CHALLENGES OF ACCELERATED AGING TECHNIQUES FOR ELASTOMER LIFETIME PREDICTIONS. Rubber Chemistry and Technology: March 2015, Vol. 88, No. 1, pp. 1-27.

Temperature Can Affect Distribution of Reaction Products



Temperature Can Affect Reaction Pathways



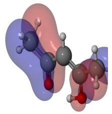


K. T. Gillen, R. Bernstein, and M. Celina (*2015*) CHALLENGES OF ACCELERATED AGING TECHNIQUES FOR ELASTOMER LIFETIME PREDICTIONS. Rubber Chemistry and Technology: March 2015, Vol. 88, No. 1, pp. 1-27.

AFOSR Proposal – Gordon and Maginn

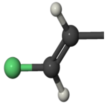
- **QM** – Activation Energies & Pre-Exponential Factors
- **MD** – Mechanical Properties via Classical Model
- **KMC** – Associate Time Scale with Degradation Extent

Tools: Different levels of description



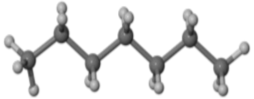
QM

- all or valence electrons



Semi-empirical QM

- valence electrons
- electron-electron interactions empirically parameterized

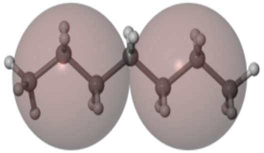


Forcefield (explicit H-atoms)

- all atoms
- non-reactive & reactive forcefields

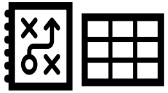
Forcefield (implicit H-atoms)

- groups containing 1 heavy atom (CHx groups)
- non-reactive forcefields



Forcefield (coarse-grained)

- beads containing 2-4 heavy atoms
- non-reactive forcefields



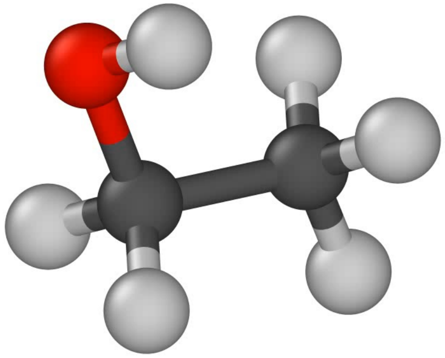
QSPR

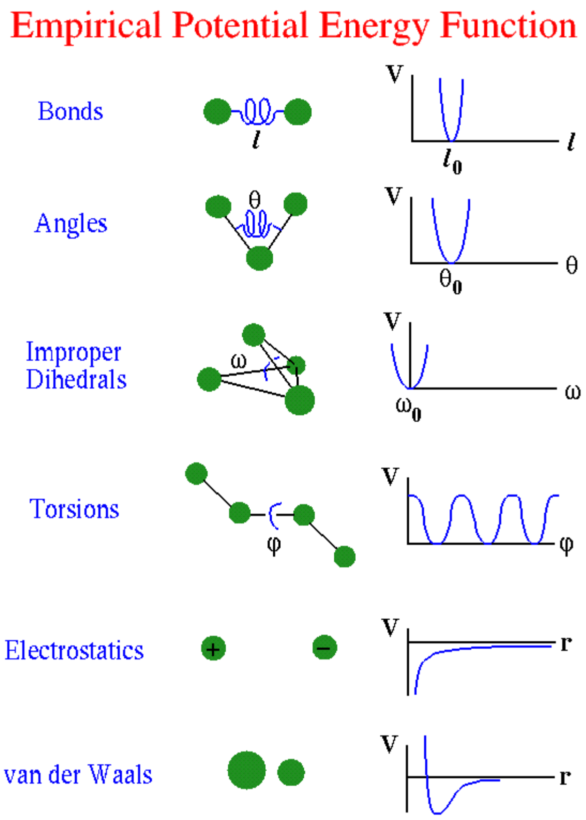
- correlations

Classical Molecular Modeling

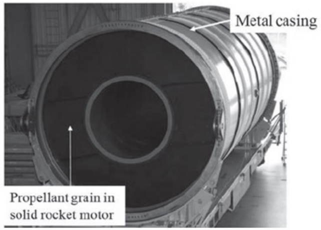
Use a 'Classical' Description

$$\mathbf{F} = \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t}$$

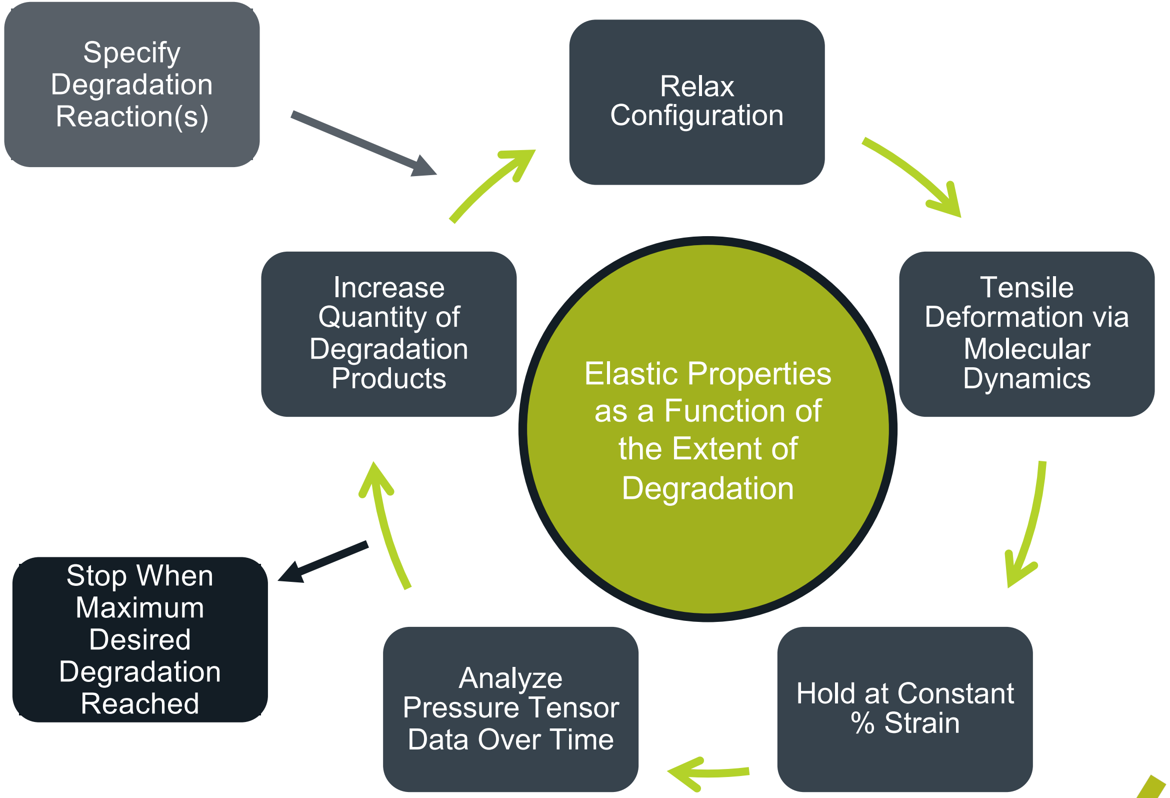




Desired Workflow for Classical Simulations



- Aging
- Degradation
- Embrittlement



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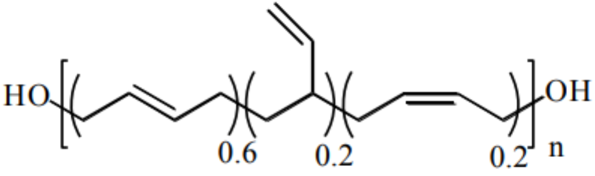
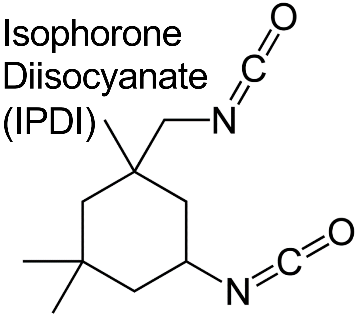
HTPB–IPDI Elastomer



Hydroxyl-Terminated
Polybutadiene
(HTPB)

Isophorone
Diisocyanate
(IPDI)



Poly bd® R-45M

TYPICAL PHYSICAL AND CHEMICAL PROPERTIES

Nonvolatile Material, wt.%	99.9
Viscosity, mPa.s @ 23 °C	7000
Viscosity, mPa.s @ 30 °C	4400
Hydroxyl Number, mf KOH/g	40.4
Hydroxyl Value, meq/g	0.72
Hydroxyl Functionality	2.2-2.4
Molecular Weight, M_n	2800
Polydispersity, M_w/M_n	2.2
Water, wt%	0.02
Specific Gravity @ 23 °C	0.899
Iodine Number, g/100g	400
Glass Transition Temperature, °C	-76

Technical Data Sheet

Poly bd® R45 HTLO

Property	Value	Unit
Molecular Weight (Mn)	2,800	g/mol
1,2 Vinyl	20	wt.%
Viscosity @ 30°C	5,000	cps
Tg	-75	°C
Specific Gravity @ 23°C	0.90	-
-OH (Groups/Chain)	2.5	-

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Free-Radical HTPB Characterization

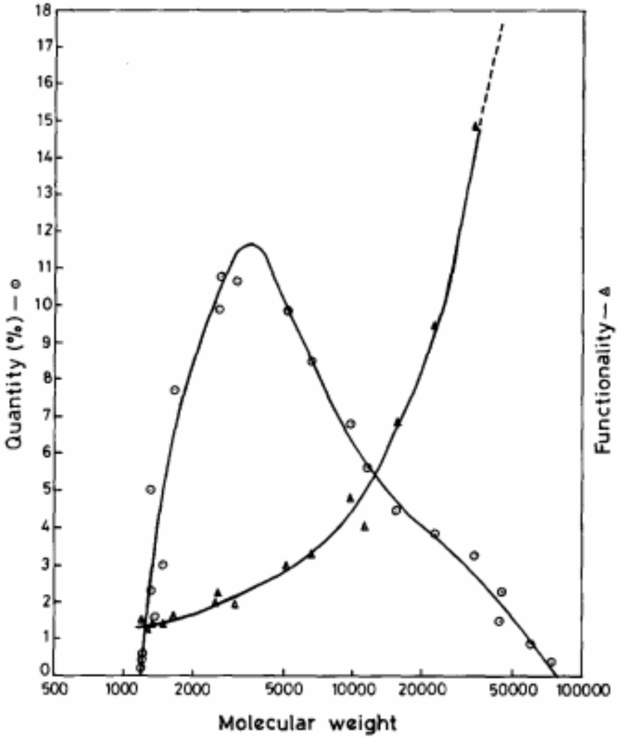
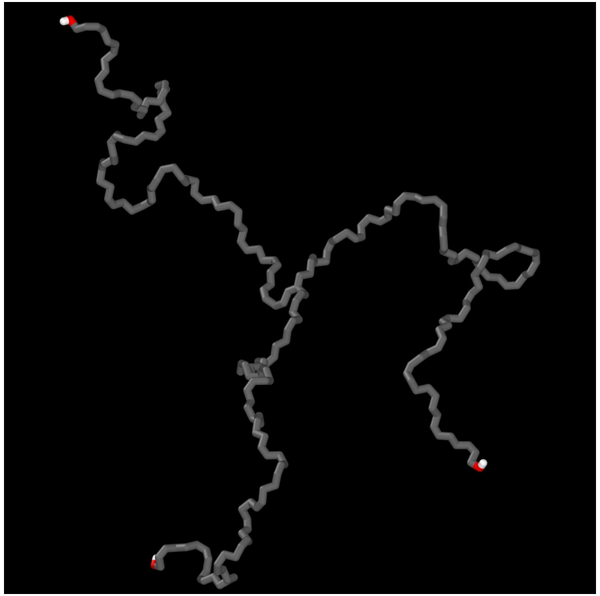


Figure 3 Functionality and molecular-weight distribution of a typical free-radical HTPB (prep. g.p.c.)

K.N. Ninan; V.P. Balagangadharan; K.B. Catherine. Studies on the functionality distribution of hydroxyl-terminated polybutadiene and correlation with mechanical properties. *Polymer* **1991**, *32*, 628–635.

HTPB Model - Simple

- Target 2,800 g/mol MW
- Target 2.5 Functionality
- System: cube with 8 nm edges
- Equilibrate for 1 microsecond



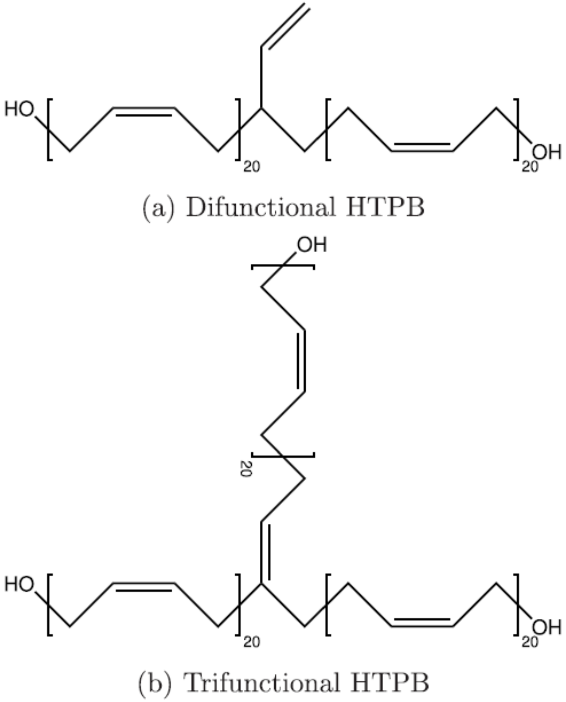
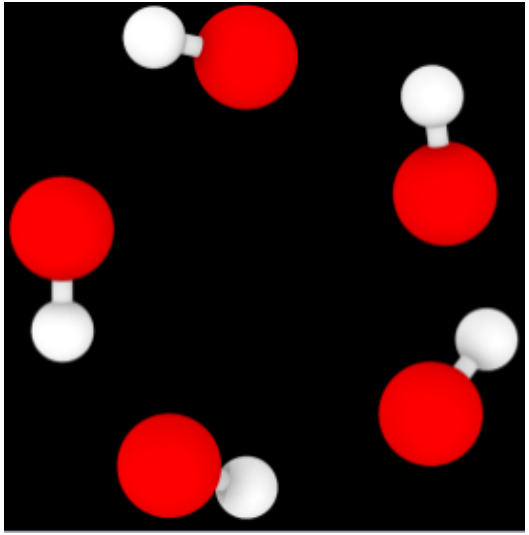
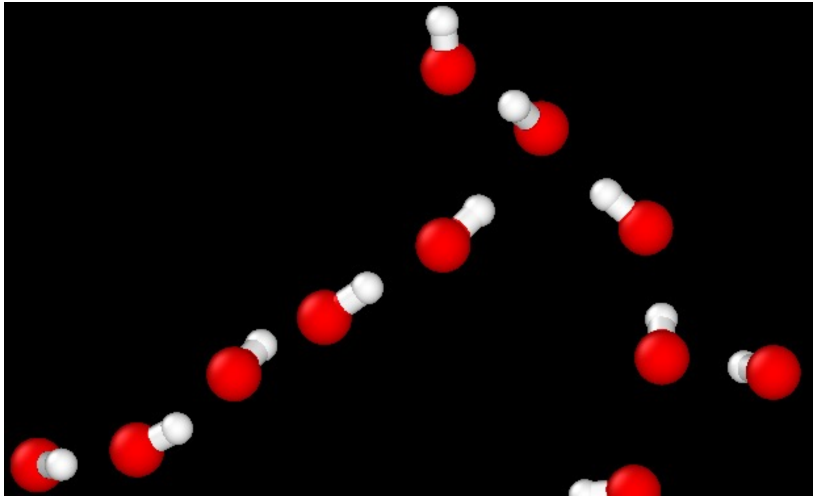


Figure 1. Model difunctional HTPB structure with a molecular weight of 2251.77 g/mol (a). Model trifunctional HTPB structure with a molecular weight of 3349.60 g/mol (b).

Tow, G.M.; Maginn; E.J. Fully Atomistic Molecular Dynamics Simulations of Hydroxyl-Terminated Polybutadiene with Insights into Hydroxyl Aggregation. *Macromolecules* **2020**, *53*, 2594–2605.

Hydroxyl Aggregation Observed





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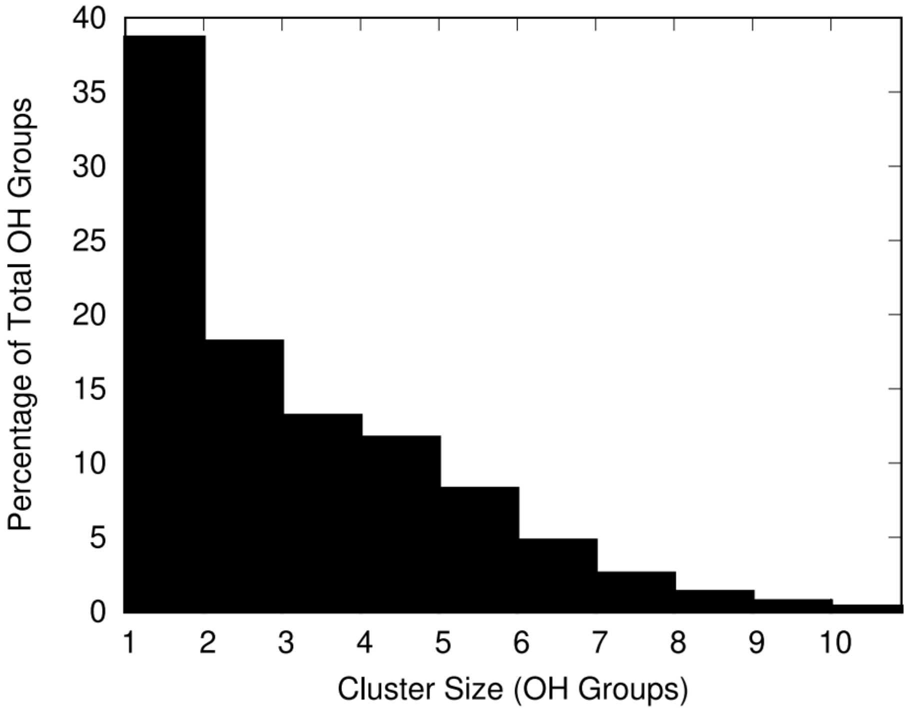
OH Cluster Sizes



- Experimental IR data indicates OH association due to wide O–H stretching peak indicating hydrogen bonding
- No experimental data on OH aggregation – contacted multiple authors

Tow, G.M.; Maginn; E.J. Fully Atomistic Molecular Dynamics Simulations of Hydroxyl-Terminated Polybutadiene with Insights into Hydroxyl Aggregation. *Macromolecules* **2020**, *53*, 2594–2605.

Spatial Distribution Impacts Stress-Strain

Macromelecules

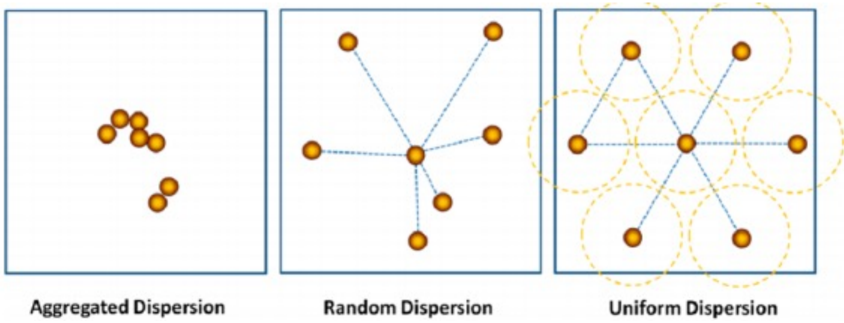
Article

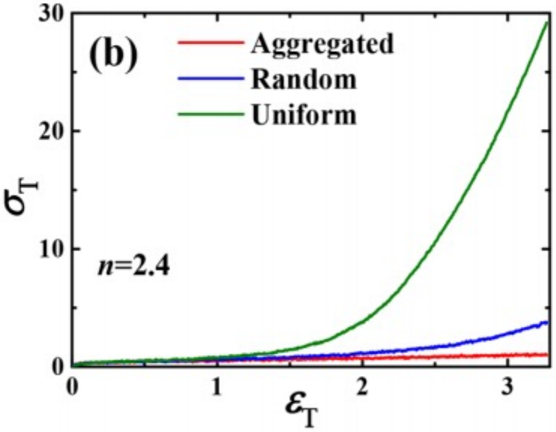
Cite This: *Macromolecules* 2019, 52, 121−134

pubs.acs.org/Macromolecules

Effects of Cross-Link Density and Distribution on Static and Dynamic Properties of Chemically Cross-Linked Polymers

Jianxiang Shen,[†] Xiangsong Lin,[†] Jun Liu,[‡] and Xue Li[*,§]



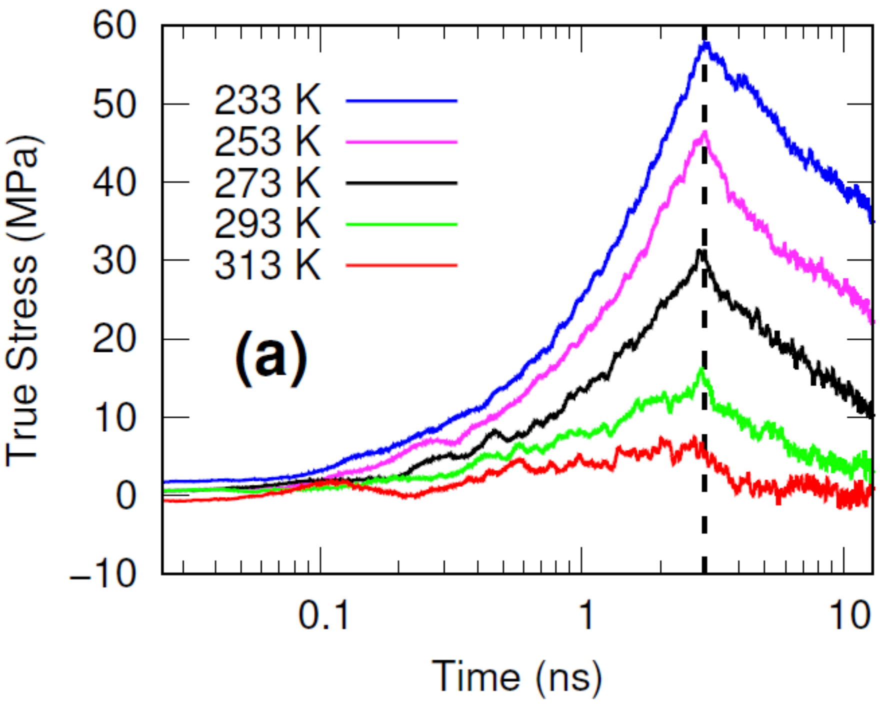


Cross-Linked HTPB–IPDI Systems

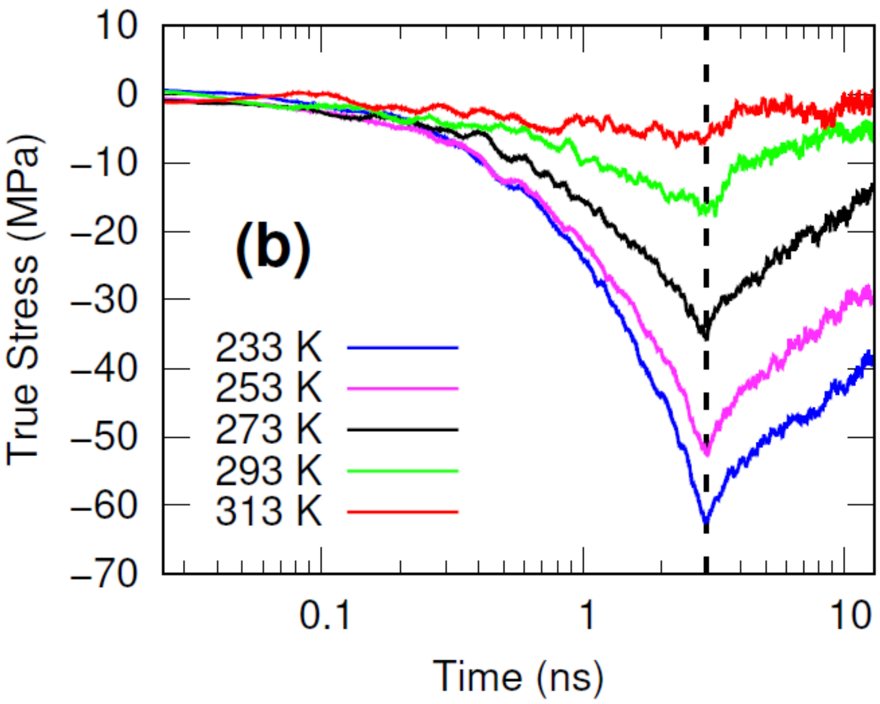
- Crosslink at 100%, 96%, 92%, and 88% NCO/OH ratio
- Quench to -40, -20, 0, 20, 40 Celsius
- 4 NCO/OH ratios, 5 temperatures, 5 initial configurations = 100 systems!
- Run 100 ns NPT relaxation, strain to 3% at 10^7 s^{-1}, hold at 3% strain

Stress vs Time for 1.00 NCO/OH Systems

Tensile



Compressive



Tow, G.M.; Maginn; E.J., “A Cross-Linking Methodology for Fully Atomistic Models of Hydroxyl-Terminated Polybutadiene and Determination of Mechanical Properties”, *Macromolecules* **2021** *54* (10), 4488-4496.

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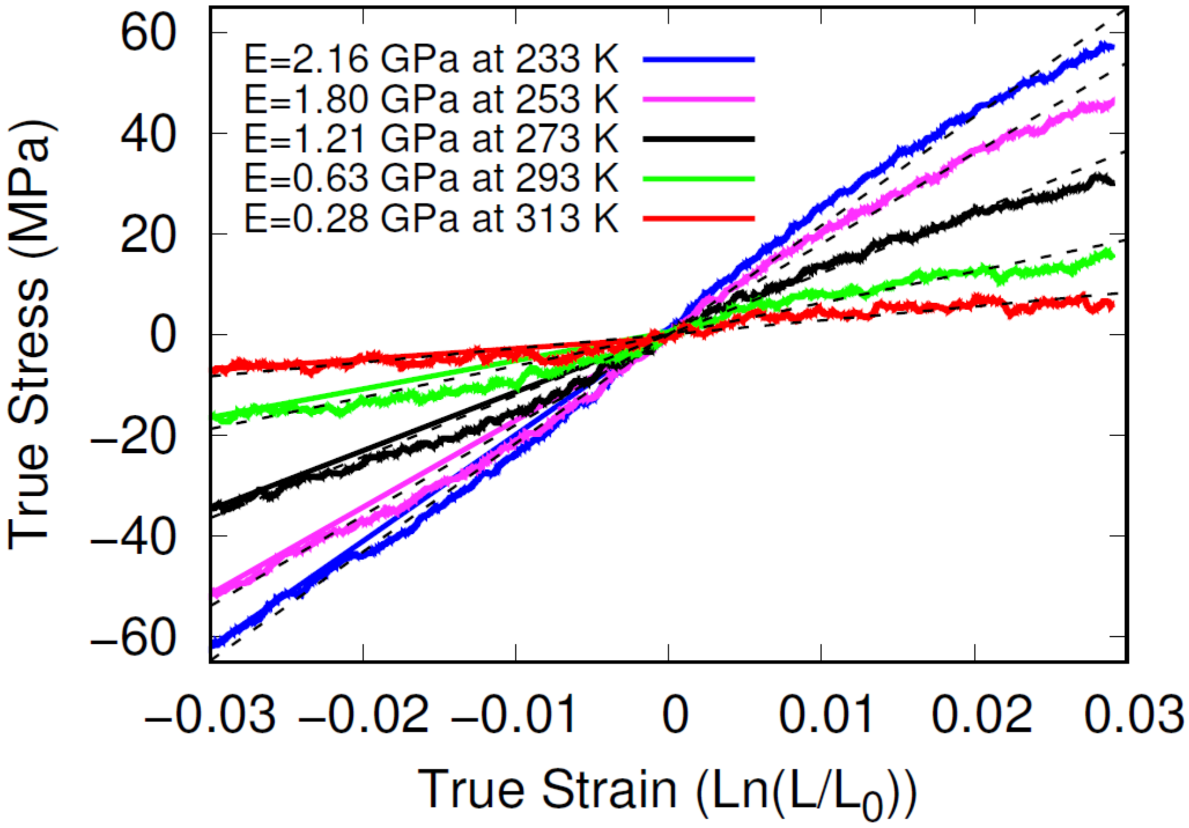
Young's Modulus for 1.00 NCO/OH Systems



Tow, G.M.; Maginn; E.J., "A Cross-Linking Methodology for Fully Atomistic Models of Hydroxyl-Terminated Polybutadiene and Determination of Mechanical Properties", *Macromolecules* **2021** *54* (10), 4488-4496.

Strain Rate Dependence

Using a Computational Strain Rate of 10^7 s^{-1}

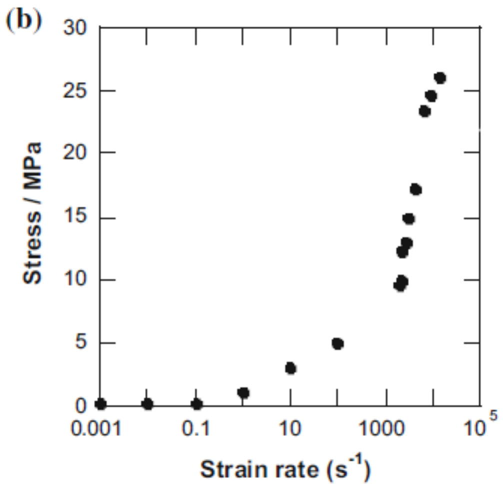


Fig. 7 Plasticized PVC
a stress–strain relationship at different strain rates and
b representative stress close to yield as a function of strain rate. Data from [153]

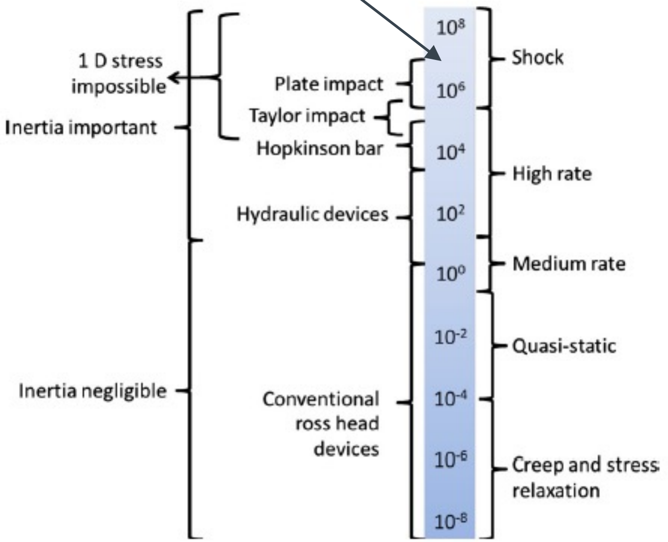
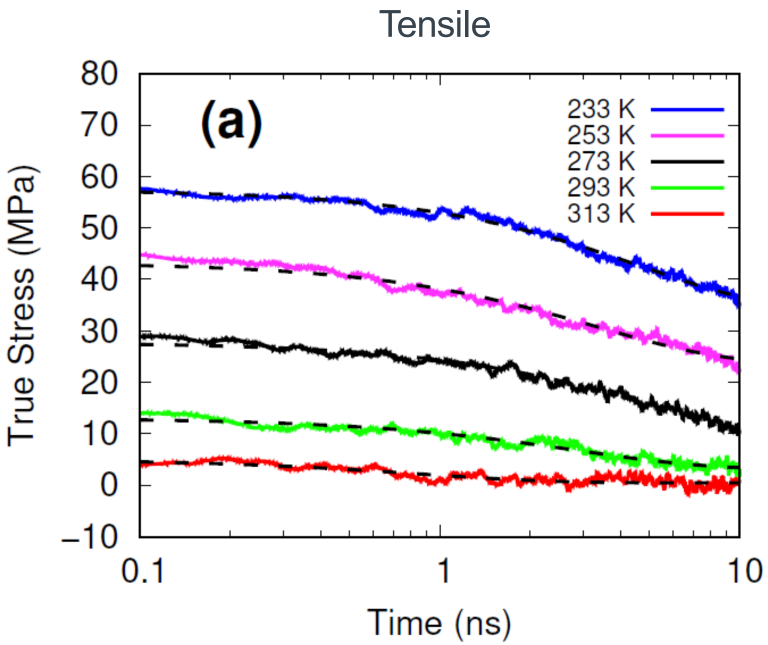


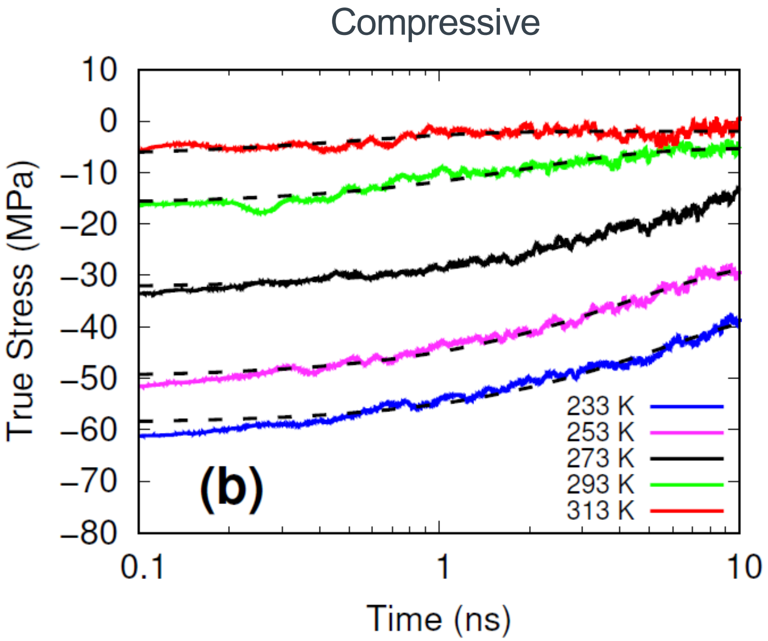
Fig. 1 Approximate division of strain rate regimes (in s^{-1}) and the experiments used to investigate these regimes. Further information on the various techniques can be found in Field et al. [36]

Siviour, C.R.; Jordan, J.L. High Strain Rate Mechanics of Polymers: A Review. *Journal of Dynamic Behavior of Materials* **2016**, 2, 15–32.

Stress Relaxation for 1.00 NCO/OH Systems

- Prony Series: $E(t) = E_\infty + \sum_{i=1}^{N} E_i e^{-t/\tau_i}$
  - We Use: $E(t) = E_\infty + E e^{-t/\tau}$





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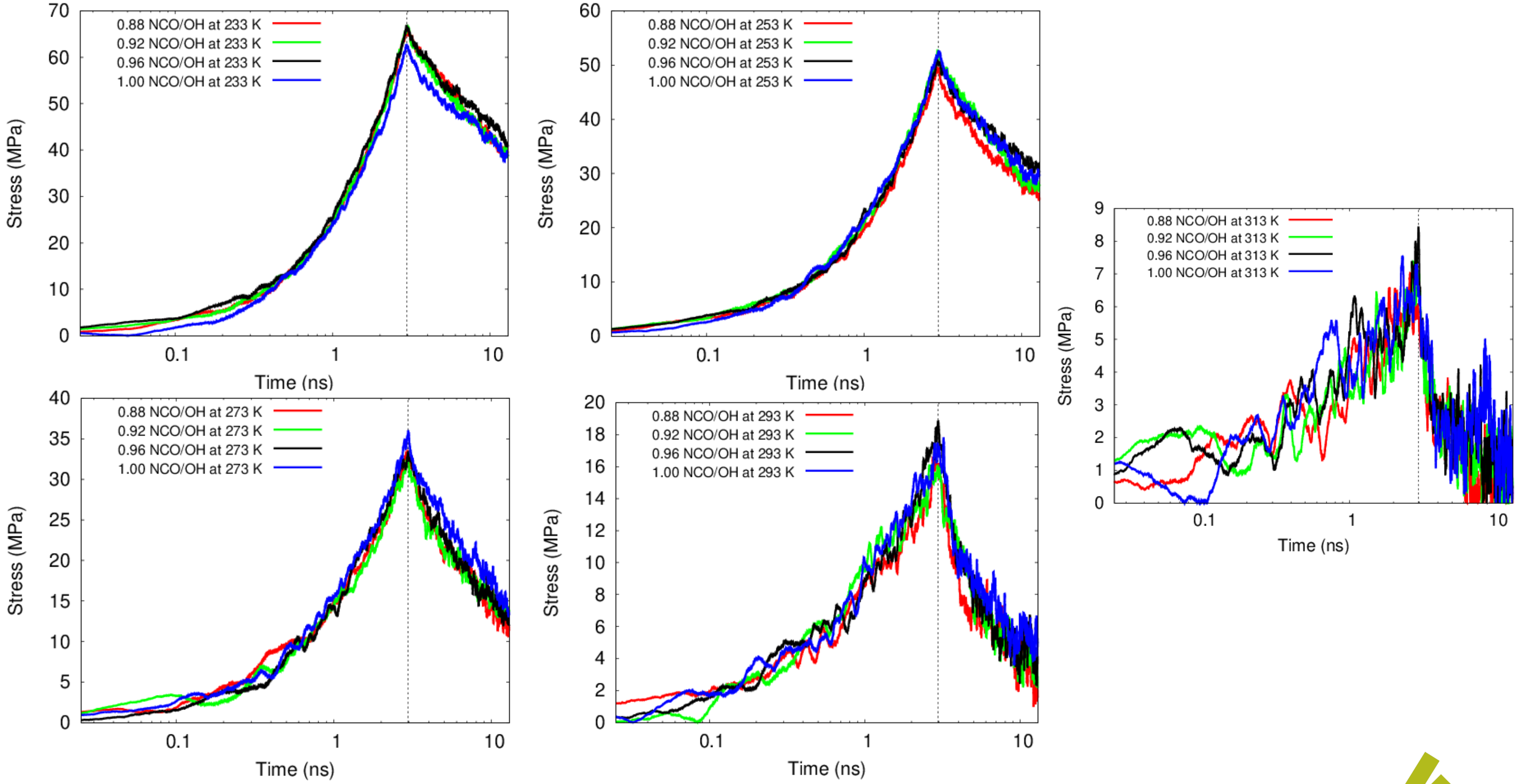
Effect of 0.88–1.00 NCO/OH Ratio



Tow, G.M.; Maginn; E.J., "A Cross-Linking Methodology for Fully Atomistic Models of Hydroxyl-Terminated Polybutadiene and Determination of Mechanical Properties", *Macromolecules* **2021** *54* (10), 4488-4496.

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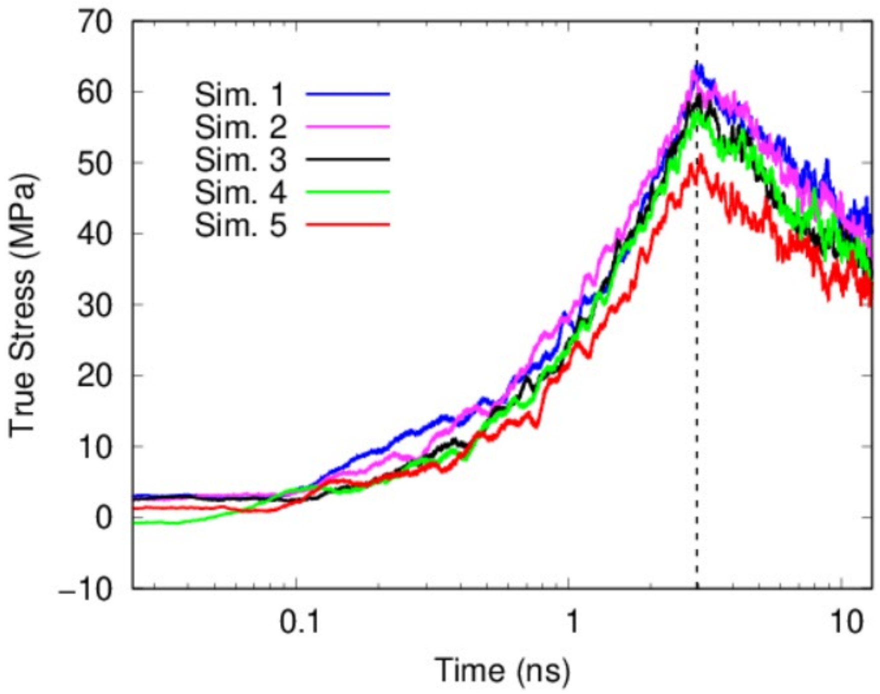
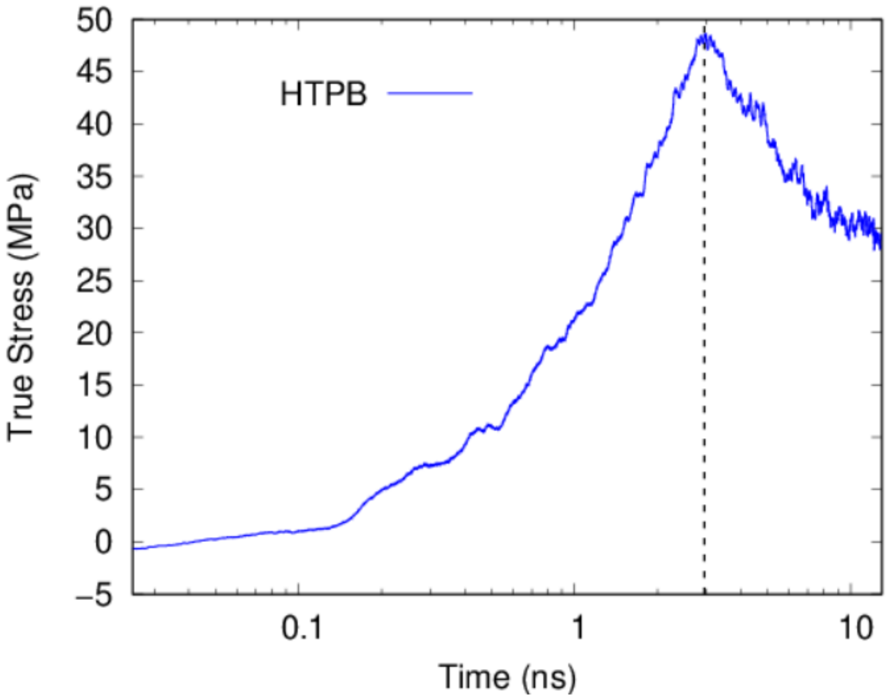
Effect of Cross-Linking

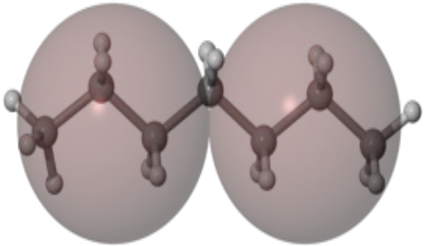




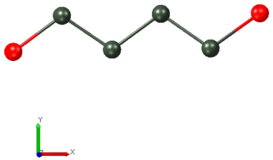
Tow, G.M.; Maginn; E.J., "A Cross-Linking Methodology for Fully Atomistic Models of Hydroxyl-Terminated Polybutadiene and Determination of Mechanical Properties", *Macromolecules* **2021** *54* (10), 4488-4496.

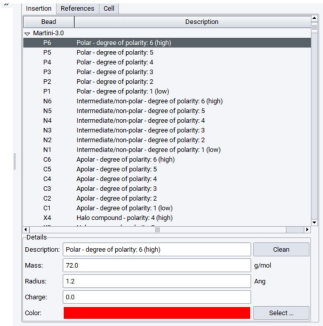
Future Direction for Assessing Elastic Properties

- Fast strain rates and short simulations inadequate
  - Only informs about the fastest relaxing modes in the system



- Need to map the atomistic model to a coarser-grained model
  - Coarse-grain monomers as beads
  - Even more aggressive coarse-graining may be necessary
  - Challenge is to retain chemical specificity of HTPB and degradation reactions
  - *MedeA Mesoscale Builder* (MARTINI 3 and SPICA forcefields)
  - Most *MedeA* tools used for atomistic models also apply to mesoscale models





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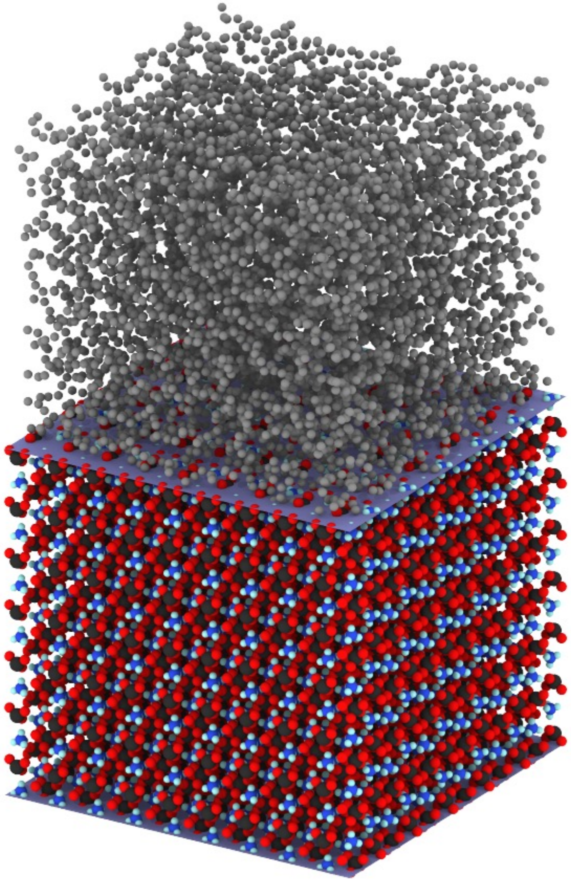
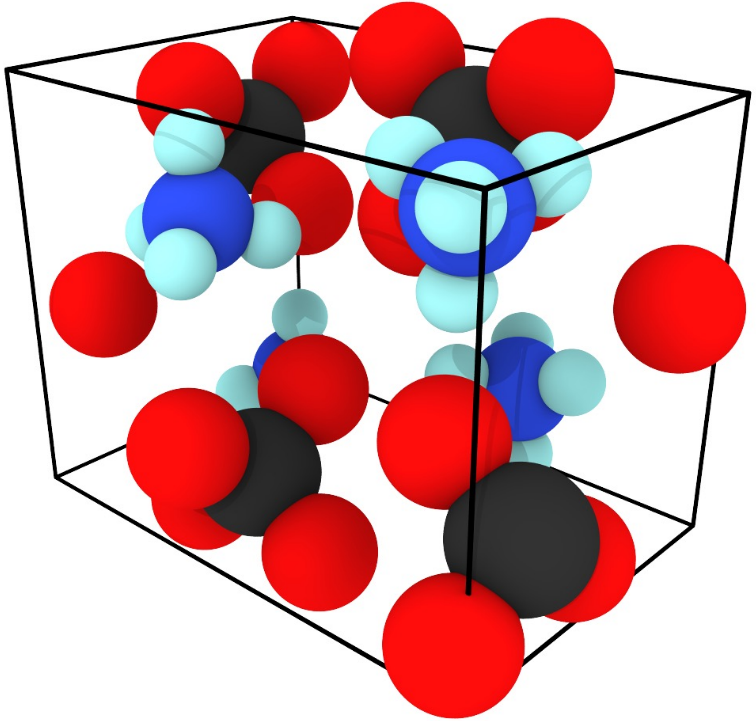
Models for Ammonium Perchlorate





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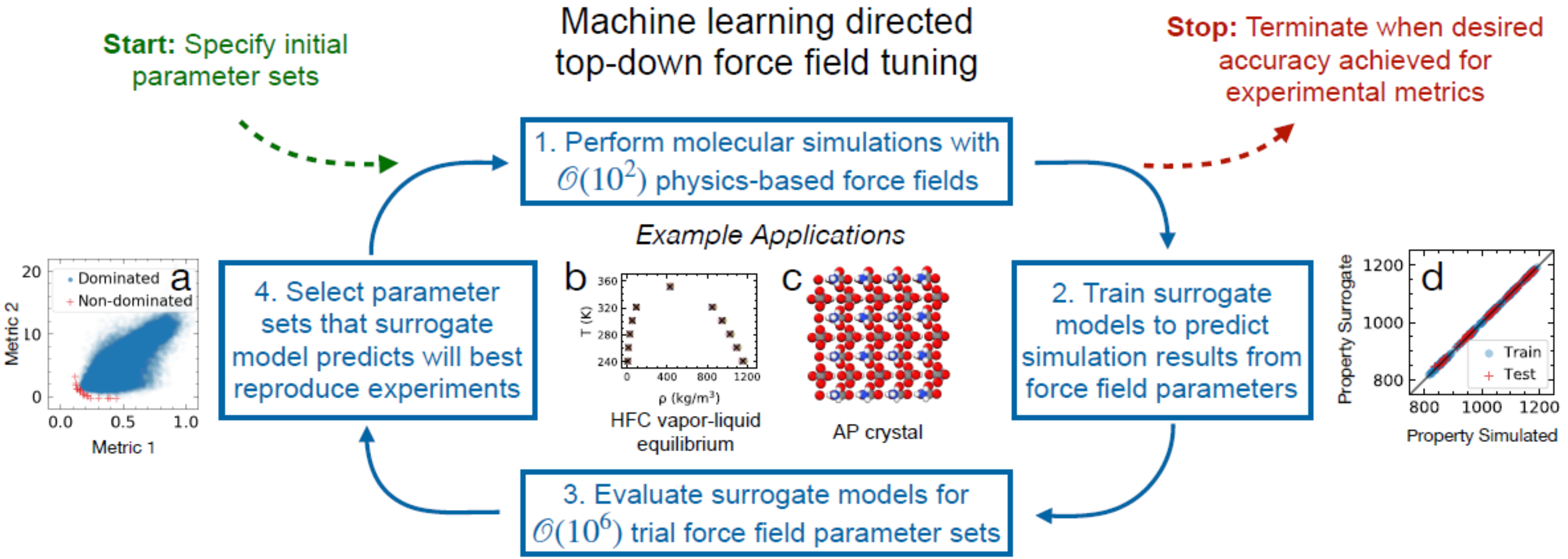
Machine Learning Directed Optimization of Classical Molecular Modeling Force Fields

Bridgette J. Befort[a,1], Ryan S. DeFever[a,1], Garrett M. Tow[a], Alexander W. Dowling[a], and Edward J. Maginn[a,2]

[a]Department of Chemical Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States



https://github.com/dowlinglab/ap-fffit

B.J. Befort, R.S. DeFever, G.M. Tow, A.W. Dowling, and E.J. Maginn, “Machine Learning Directed Optimization of Classical Molecular Modeling Force Fields“, *Journal of Chemical Information and Modeling* **2021** *61* (9), 4400-4414

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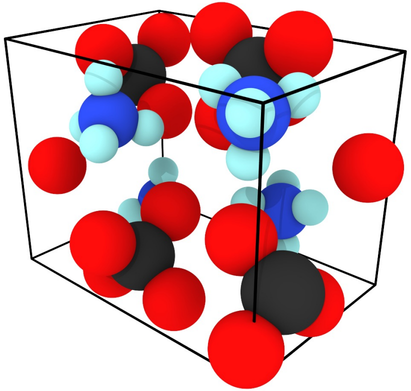
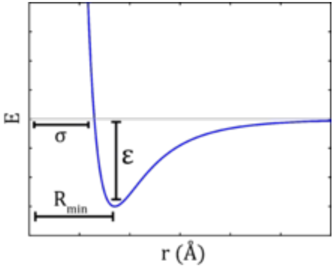
Optimization Objectives



- Mean Absolute Percent Error (MAPE) of Lattice Parameters at 10, 78, 298 K.
- Unit Cell Mean Distance (UCMD) – deviation from the experimentally observed unit cell atomic positions at 10 K.
- Variable Parameters = Lennard-Jones Parameters

Static Parameters:
- Harmonic bonds
- Harmonic angles
- Partial charges



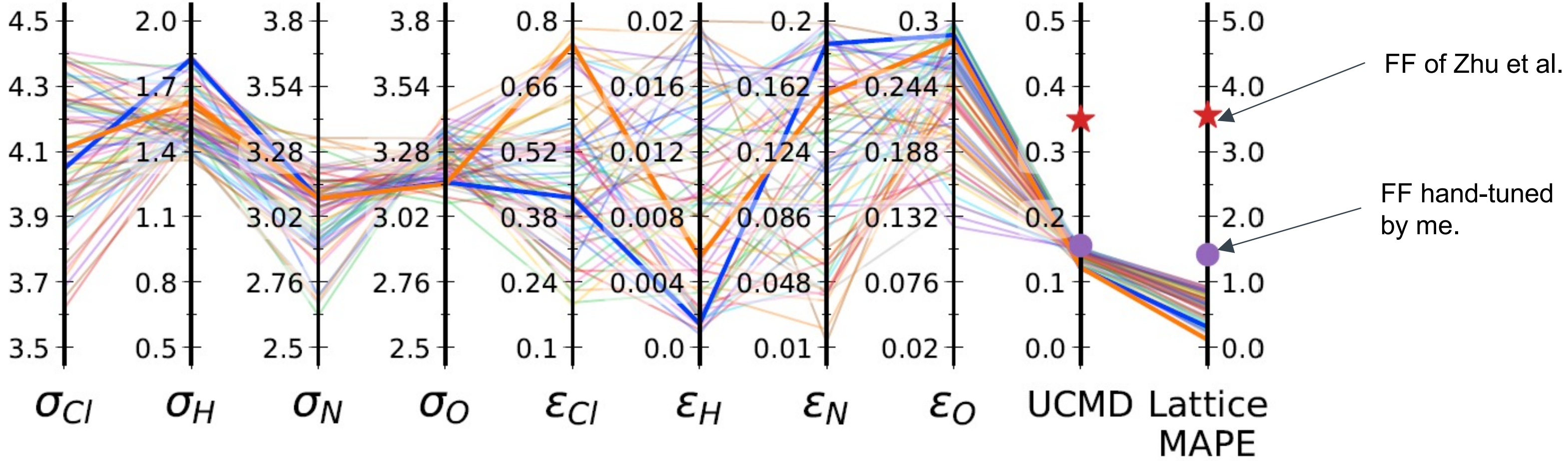
$$U^{\mathrm{LJ}}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Pauli Repulsion | Dispersion

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

Suffering from Success



$$U^{\mathrm{LJ}}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Pauli Repulsion

Dispersion

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

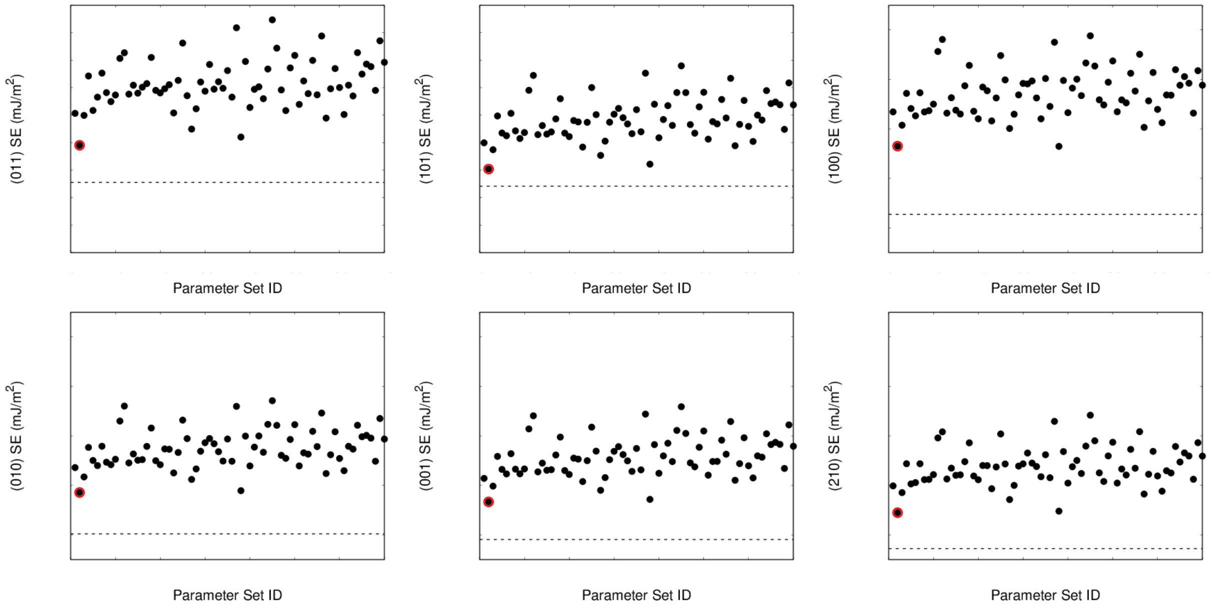
How to pick which force field?

Performance on other metrics?

Transferability?

B.J. Befort, R.S. DeFever, G.M. Tow, A.W. Dowling, and E.J. Maginn, “Machine Learning Directed Optimization of Classical Molecular Modeling Force Fields“, *Journal of Chemical Information and Modeling* **2021** *61* (9), 4400-4414

AP Surface Energies Compared to DFT Simulation



Relative Surface Energies

QM: (210)<(001)<(010)<(100)<(101)<(011)
MD: (210)<(001)<(010)<(101)<(011)<(100)

Agreement for the lowest-energy crystal facets.

In-Chul Yeh and Garrett M. Tow, “Force Field Parameters for Ammonium Perchlorate Validated using Surface Energies and Applied to Interactions with Polymer Binder”, *in preparation*.

AP–HTPB Interfacial Energy

Influence of HTPB Variants on the Wettability of Ammonium Perchlorate

D. Ramirez[1] and J. Kalman[2]
California State University, Long Beach, Long Beach, California, 90840, United States of America

Figure 4 – Test sample of orthorhombic AP with reference angle θ depicted ($\theta = 77.3°$).

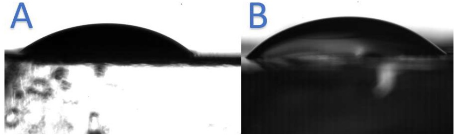


Figure 6 - Implementation of diffused light and covering of crystal thickness. (A) Masking of the interface by refracted light B) Clearly defined interface post-experimental setup modification.

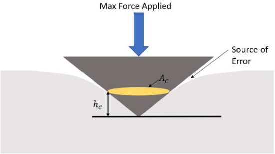


Figure 7 - Diagram of the nanoindentation method showing the source of values and error.

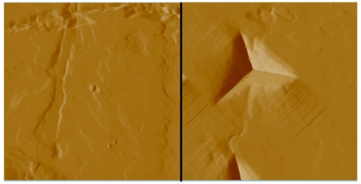
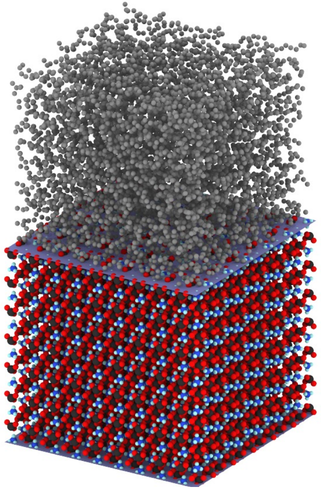


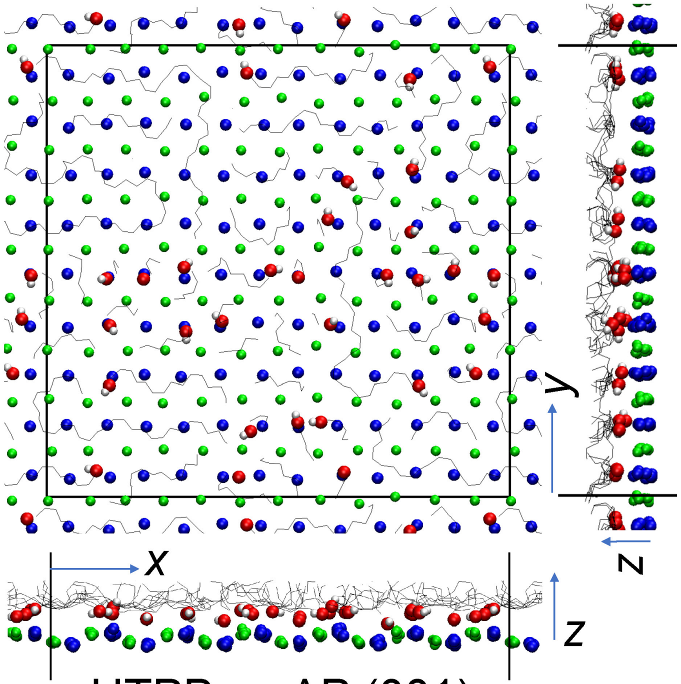
Figure 14 – Left: Surface topography pre-indentation showing surface roughness, Right: Post indentation with visible crystal dislocations.



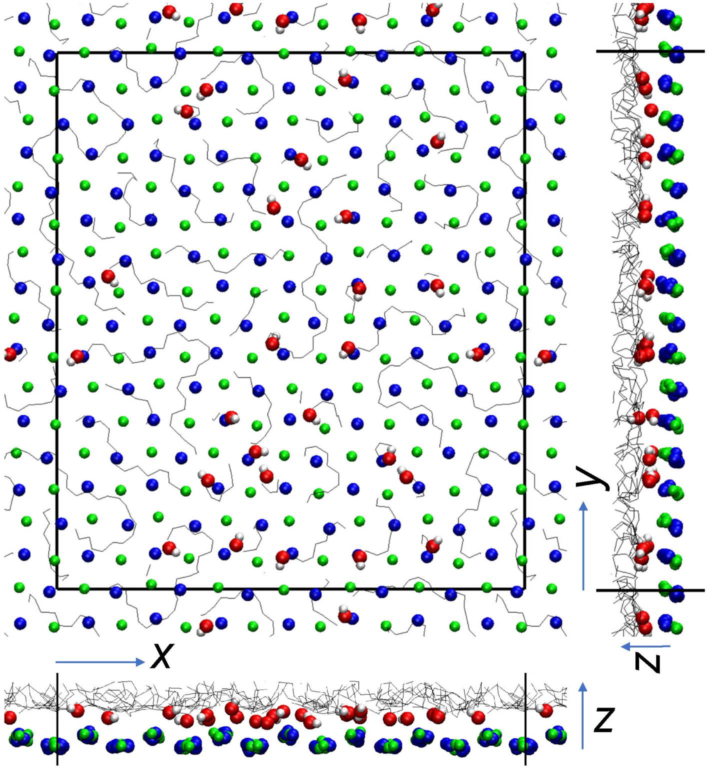
(210): MD ~18% higher than expt.
(001): MD ~10% higher than expt.

MD agrees with experiment that (210)>(001) for AP–HTPB interfacial energy

Hydroxyl Interactions with AP Surfaces



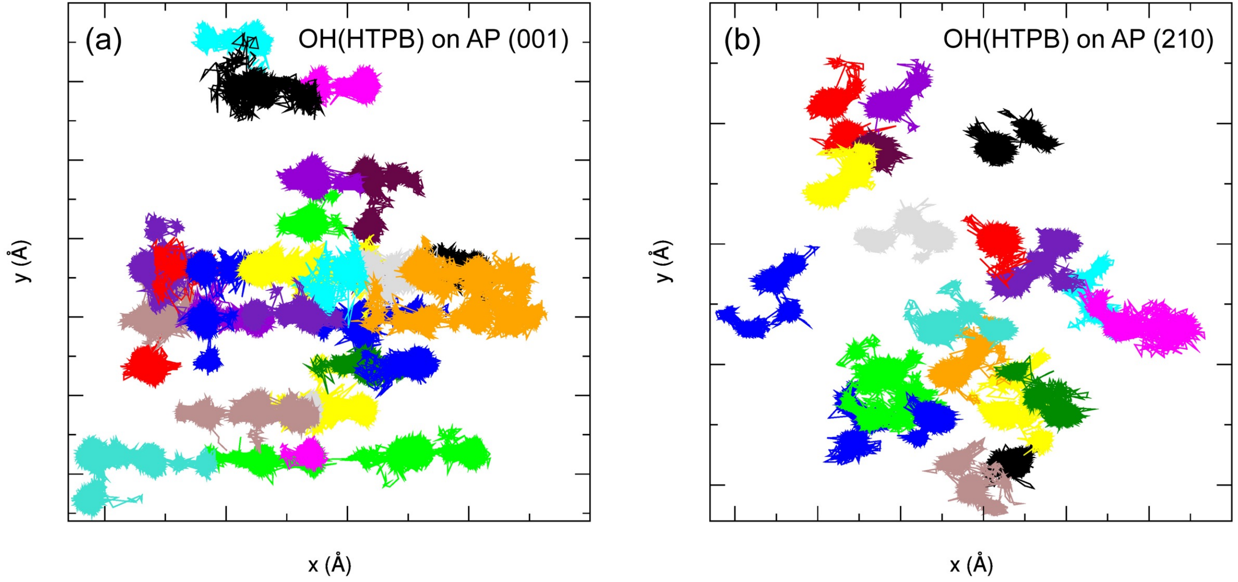
HTPB on AP (001)

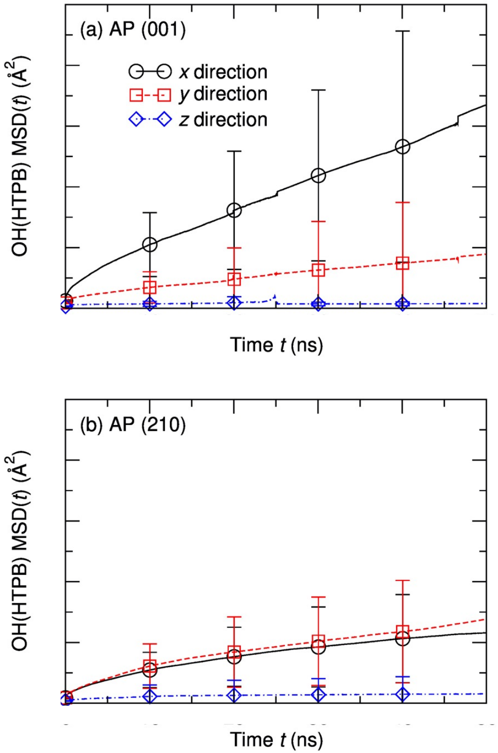


HTPB on AP (210)

In-Chul Yeh and Garrett M. Tow, “Force Field Parameters for Ammonium Perchlorate Validated using Surface Energies and Applied to Interactions with Polymer Binder”, *in preparation*.

OH Diffusion Behavior at AP Surfaces

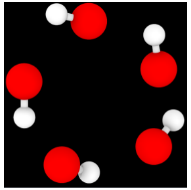


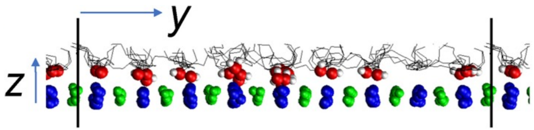


In-Chul Yeh and Garrett M. Tow, "Force Field Parameters for Ammonium Perchlorate Validated using Surface Energies and Applied to Interactions with Polymer Binder", *in preparation*.

Outstanding Questions

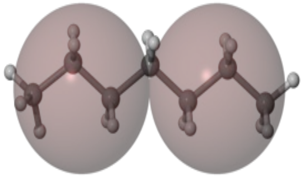
- Impact of the spatial distribution of hydroxyl groups on cross-linking
  - OH association in bulk HTPB
  - OH adsorption on AP surfaces
  - Additives that enhance or disperse OH clustering?

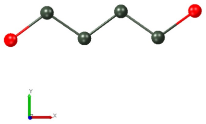


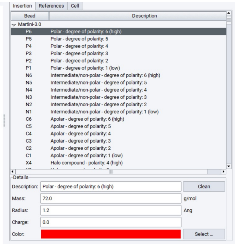


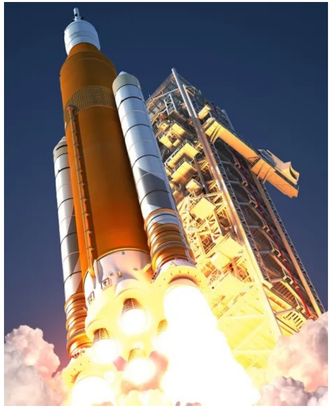
- Accelerated equilibration methods
  - Monte Carlo, parallel tempering, Hamiltonian replica exchange
  - Difficult to fully equilibrate due to sluggish polymer dynamics and self-assembly behavior

- Access to mesoscale time and length scales
  - *MedeA Mesoscale Builder* (MARTINI 3 and SPICA forcefields)
  - Longer timescale needed for elastic property evaluation









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Acknowledgments

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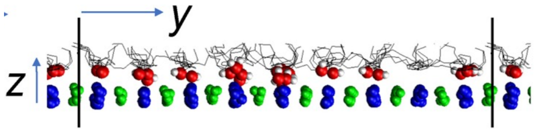
In-Chul Yeh, ARL



Funding and
Computational Resources

DOD HPC MODERNIZATION PROGRAM

CRC CENTER FOR RESEARCH COMPUTING

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Relevant *MedeA* Modules

MedeA Environment: Materials Modelling and Simulation Environment

***MedeA Molecular Builder*:** Create 3D molecular models. Import and edit molecular systems or build them stepwise using the *MedeA* molecular fragment library.

MedeA Amorphous Materials Builder: Create condensed phase models based on system chemical composition and target density. It eliminates lengthy mixing and amorphization simulations through realistic sampling of the translational, rotational, and conformational degrees of freedom of component species.

***MedeA* Polymer Builder:** Creates models of isolated polymer chains, providing a foundation for building more complex models. Examples include bulk polymers, blends, solutions, or multiphase systems incorporating one or more interfacial regions.

***MedeA LAMMPS*:** Focuses on the efficient execution of computational tasks using computational hardware ranging from massively parallel facilities to laboratory-scale workstations and GPU-enabled clusters.

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Relevant *MedeA* Modules

***MedeA* Thermoset Builder:** Applies state-of-the-art methods for creating complex topologies of polymer networks in order to create strain-free molecular models with experimentally observed crosslink densities.

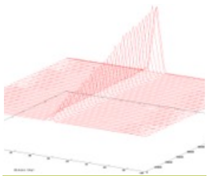
***MedeA* Stack Layer Builder:** Prepares interface systems comprising two or more layers of materials. Combines individual layers of amorphous and crystalline nature, solids, liquids, partially ordered liquid crystal systems and vacuum regions.

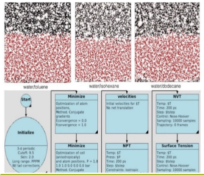
MedeA Mesoscale Builder: Creates models for simulations on the time and length scale of microseconds and tens of nanometers. Mesoscale bead definitions and parameters are provided for the MARTINI and SPICA forcefields.

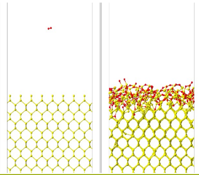
***MedeA* Diffusion:** Automatically calculate diffusivity from mean square displacement

MedeA Deformation: Evaluates the stress-strain relationships of materials beyond the elastic regime, which can be used to extract mechanical properties of materials including Young's modulus, yield strength, ultimate strength, fracture strength, and shear strength.

MedeA MT: Calculates in a fully automatic manner elastic, mechanical and thermodynamic properties of crystalline, polycrystalline, and amorphous materials.







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Related *MedeA* Webinars

Multiscale Modeling of Polymers Using the MedeA Environment:

https://www.materialsdesign.com/webinars/recorded/MedeA-Training-Multiscale-Modeling-of-Polymers-Using-the-Med

Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers:
https://www.materialsdesign.com/webinars/recorded/theodorou-polymer-2022

Mesoscale Simulations:

https://www.materialsdesign.com/webinars/recorded/Mesoscale-Simulations

Elasticity and Beyond: Predicting Mechanical Properties with MedeA:

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Using MedeA to Study Formation and Properties of Polymer Networks:
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Question and Answer Session

Dr. Clive Freeman

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Dr. Garrett Tow

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Questions about Materials Design Webinars

Katherine Hollingsworth

khollingsworth@materialsdesign.com

materials design

info@materialsdesign.com

www.materialsdesign.com

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Innovation by Simulation