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Hydrocarbon and Water Desorption from Oxide Surfaces using Molecular Dynamics

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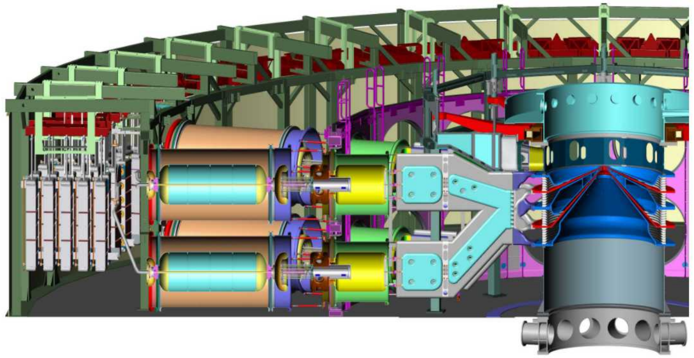
Motivation

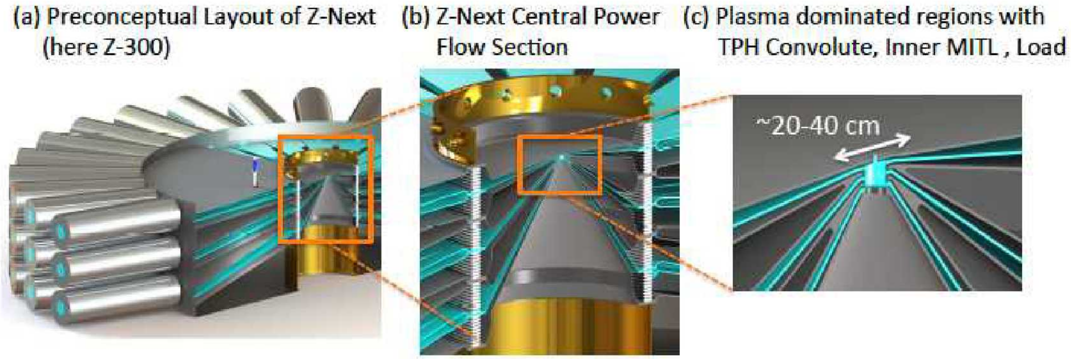
Sandia is the nation's leading laboratory for developing advanced **pulsed power technologies**

- Nuclear weapon physics
- Inertial confinement fusion

Pulsed power machines are unique environments for extreme environment research



Z



(a) Preconceptual Layout of Z-Next (here Z-300)

(b) Z-Next Central Power Flow Section

(c) Plasma dominated regions with TPH Convolute, Inner MITL , Load

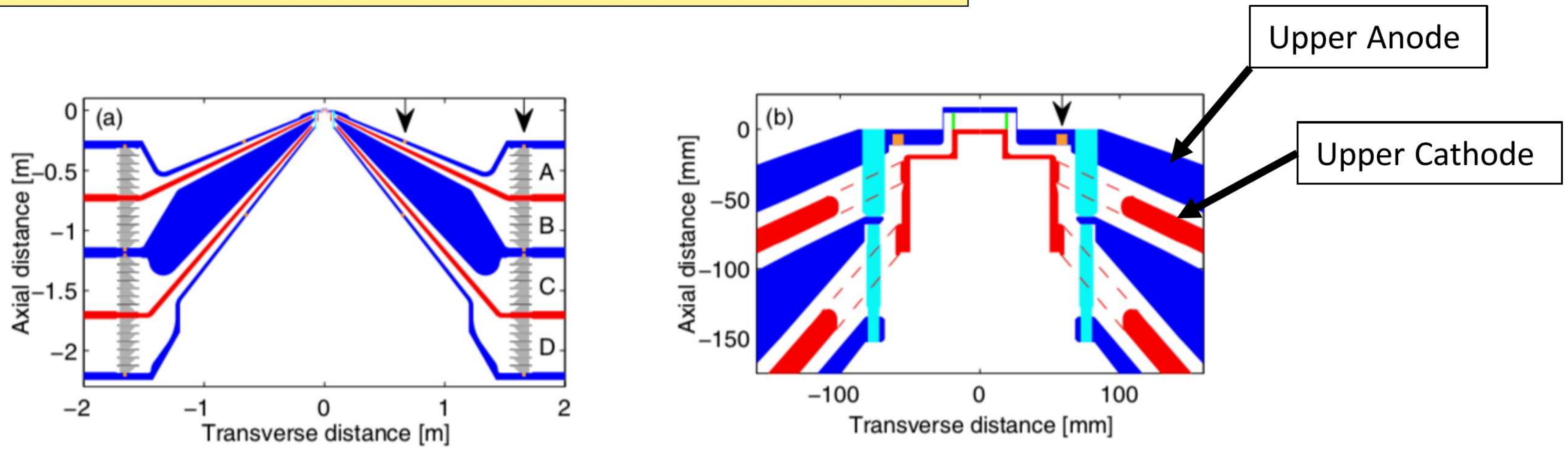
Z-Next

We want to confidently scale-up and design Next-Generation Pulsed Power Machines

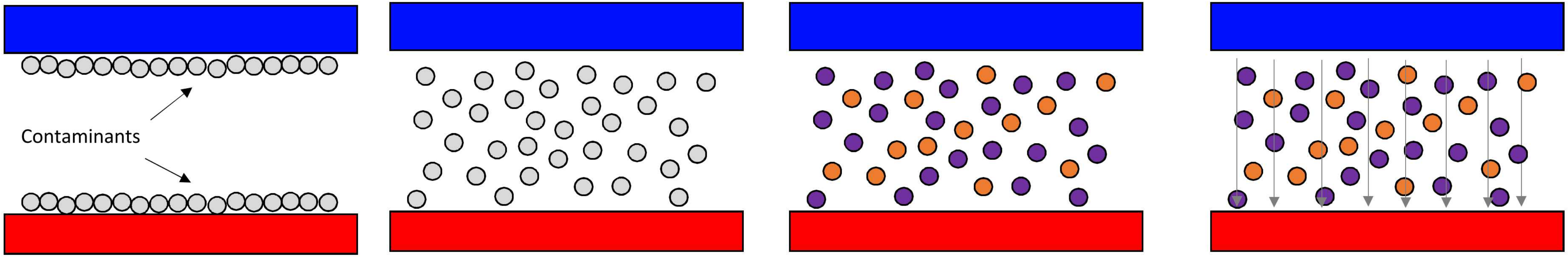
Power flow and current loss need to be addressed for scale-up design

- Current loss is observed from **plasma formation**

Current Understanding of Plasma Formation on Z

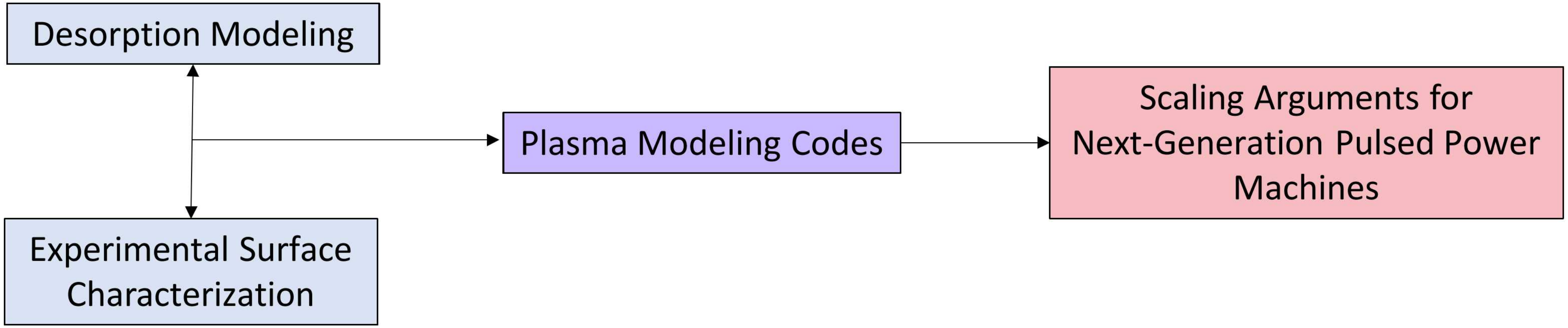


M. R. GOMEZ *et al.* PHYS. REV. ACCEL. BEAMS **20,** 010401 (2017)



Surfaces are heated → Contaminants desorb from the Surface → Plasma forms in the neutral layer → Plasma structures cross gaps and shunt current

Motivation

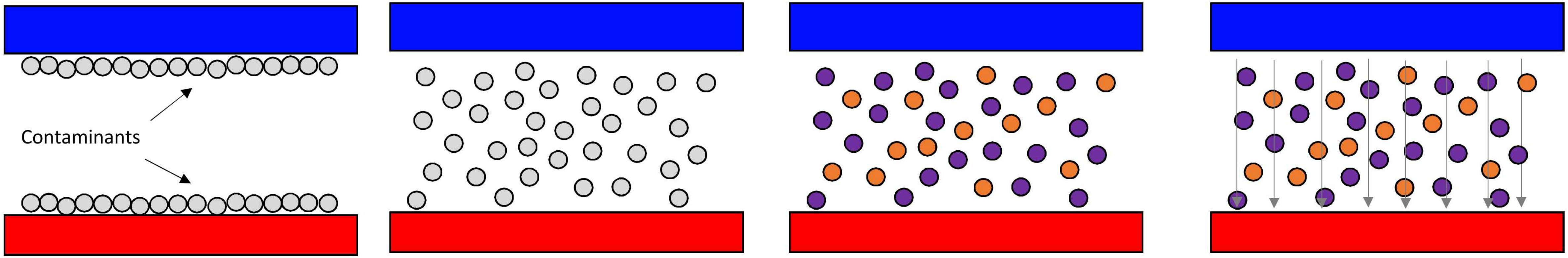


Desorption Modeling

Experimental Surface Characterization

Plasma Modeling Codes

Scaling Arguments for Next-Generation Pulsed Power Machines



Surfaces are heated → Contaminants desorb from the Surface → Plasma forms in the neutral layer → Plasma structures cross gaps and shunt current

Motivation

Desorption Modeling

Exp
C

or
Power

Goal:

Confidently **scale-up and design** Next-Generation Pulsed Power Machines

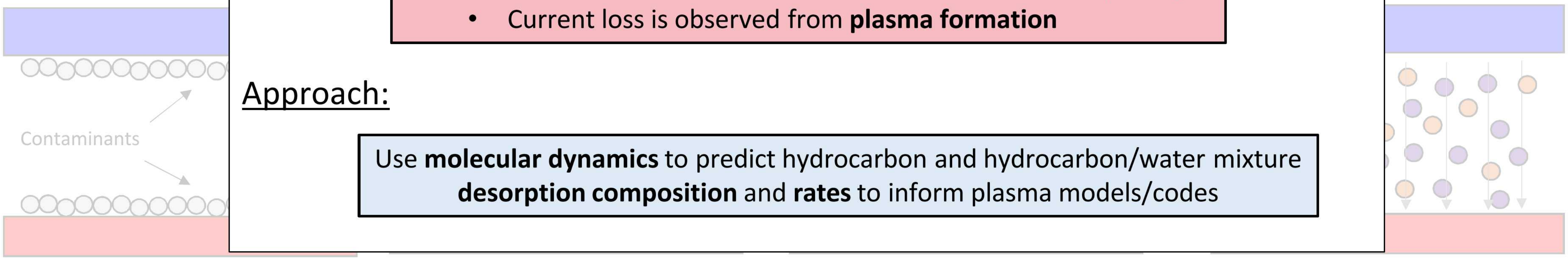
Problem:

Power flow and current loss need to be addressed for scale-up design

- Current loss is observed from **plasma formation**

Approach:

Use **molecular dynamics** to predict hydrocarbon and hydrocarbon/water mixture **desorption composition** and **rates** to inform plasma models/codes



Surfaces are heated → Contaminants desorb from the Surface → Plasma forms in the neutral layer → Plasma structures cross gaps and shunt current

Details of Desorption Modeling

Desorption Modeling

Lane, Leung, Thompson, and Cuneo, *J. Phys. Cond. Matt.*, **2018**

ClayFF (substrate) with SPC (water):

$$E_{\text{total}} = E_{\text{Coul}} + E_{\text{VDW}} + E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}}$$

$$E_{\text{Coul}} = \frac{e^2}{4\pi\epsilon_o}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}$$

$$E_{\text{VDW}} = \sum_{i\neq j} D_{o,ij}\left[\left(\frac{R_{o,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{o,ij}}{r_{ij}}\right)^{6}\right]$$

$$E_{\text{bond stretch } ij} = k_1(r_{ij} - r_o)^2$$

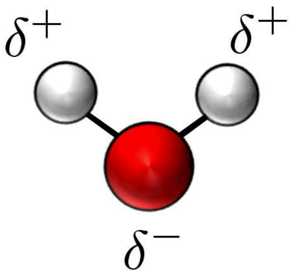
$$E_{\text{angle bend } ijk} = k_2(\theta_{ijk} - \theta_o)^2$$

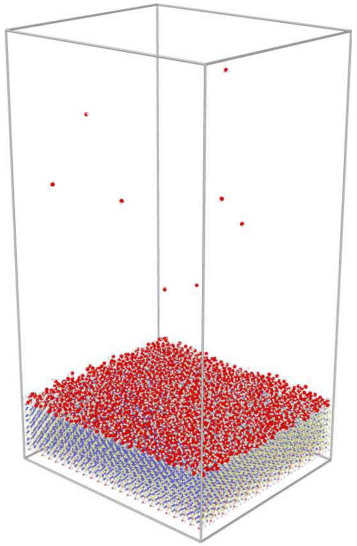
$$E_{\text{torsion}} = \sum_{n=1,5} A_n \cos^{n-1}(\phi)$$

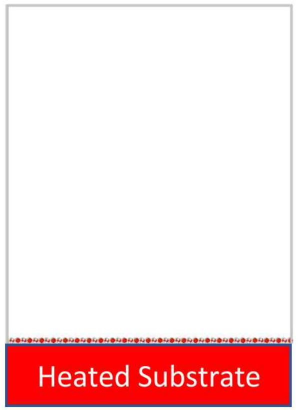
- ClayFF does well with water binding energies with metal oxides.
- SPC Water

Initial desorption studies of focused on **Water**:

- Composition
- Coverage
- Electrode Temperature







Temperature ramp from 300K to 1300K

Details of Desorption Modeling

Desorption Modeling

ClayFF with SPC with OPLS (hydrocarbons):

$$E_{\text{total}} = E_{\text{Coul}} + E_{\text{VDW}} + E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}}$$

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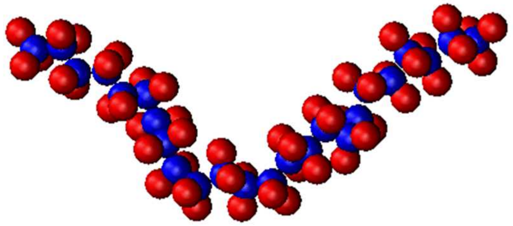
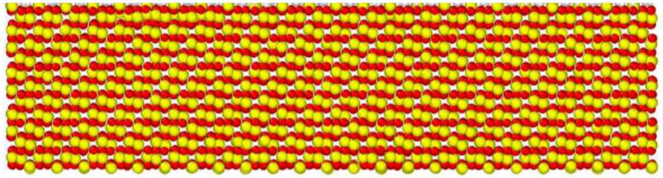
- ClayFF does well with water binding energies with metal oxides.
- SPC Water
- **OPLS Hydrocarbons**



Hydrocarbon (ex. $C_{24}H_{50}$)

α-Fe_2O_3 hematite (0001)



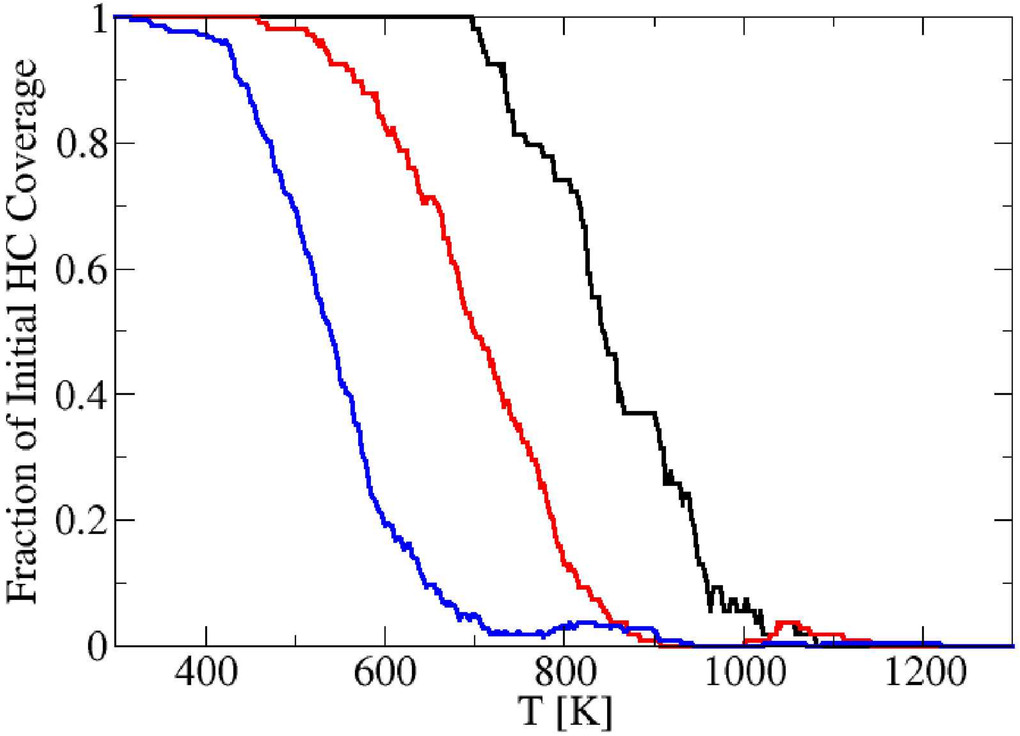
Side view of substrate

New Study focusing on:
- Chain length
- Chain architecture
- Mixtures

Chain Length Effect

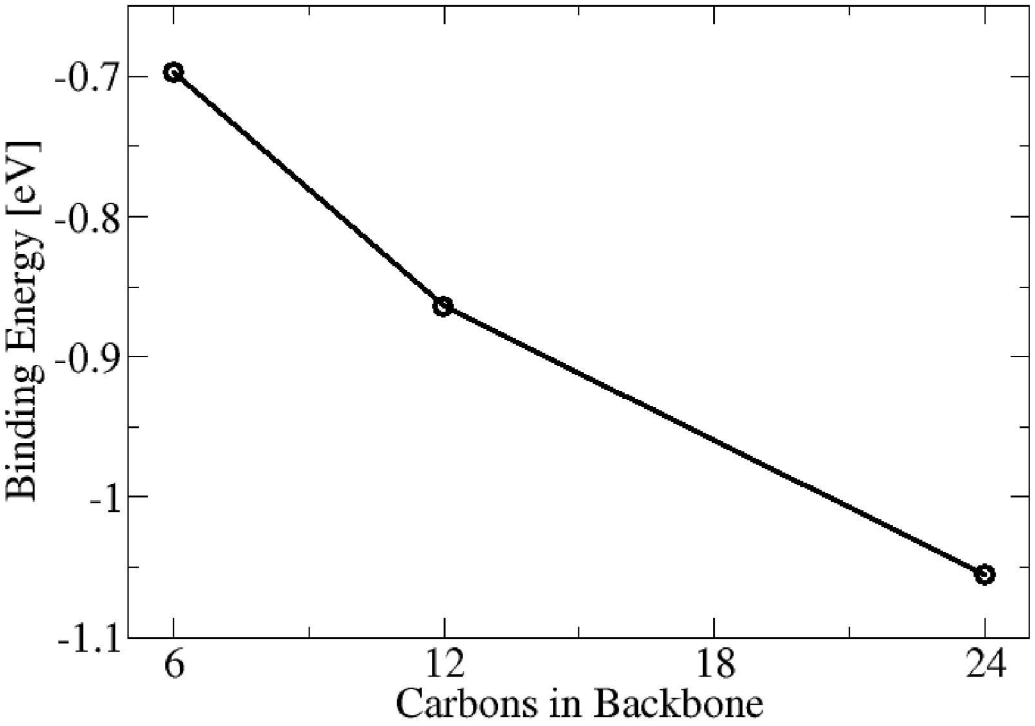
Ramp Rate: 2000K/ns
1296 Carbons Initially on Surface

- $n_{chains} = \{54\ C_{24}H_{50},\ 108\ C_{12}H_{26},\ 216\ C_6H_{14}\}$



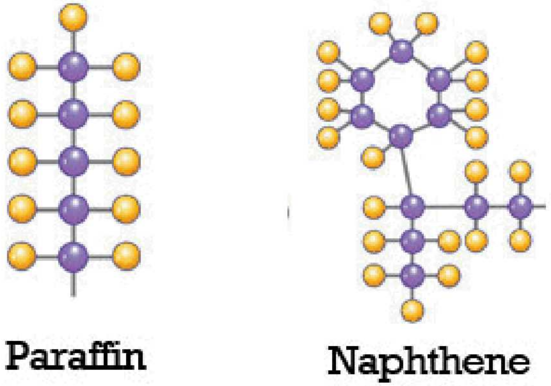
Instantaneous energy difference between initial and final state

Binding/Desorption energy vs Chain Length

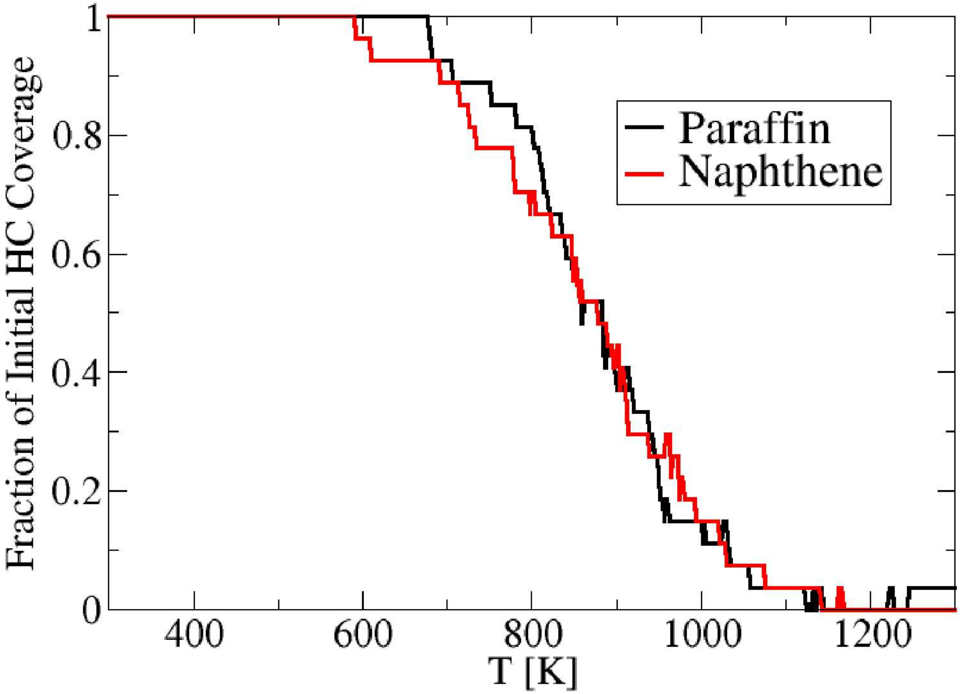


Longer chains more strongly adsorbed to surface due to increased vDW interactions

Chain Architecture Effect



More realistic representation of mineral oil found in Z-machine



Ramp Rate: 2000K/ns

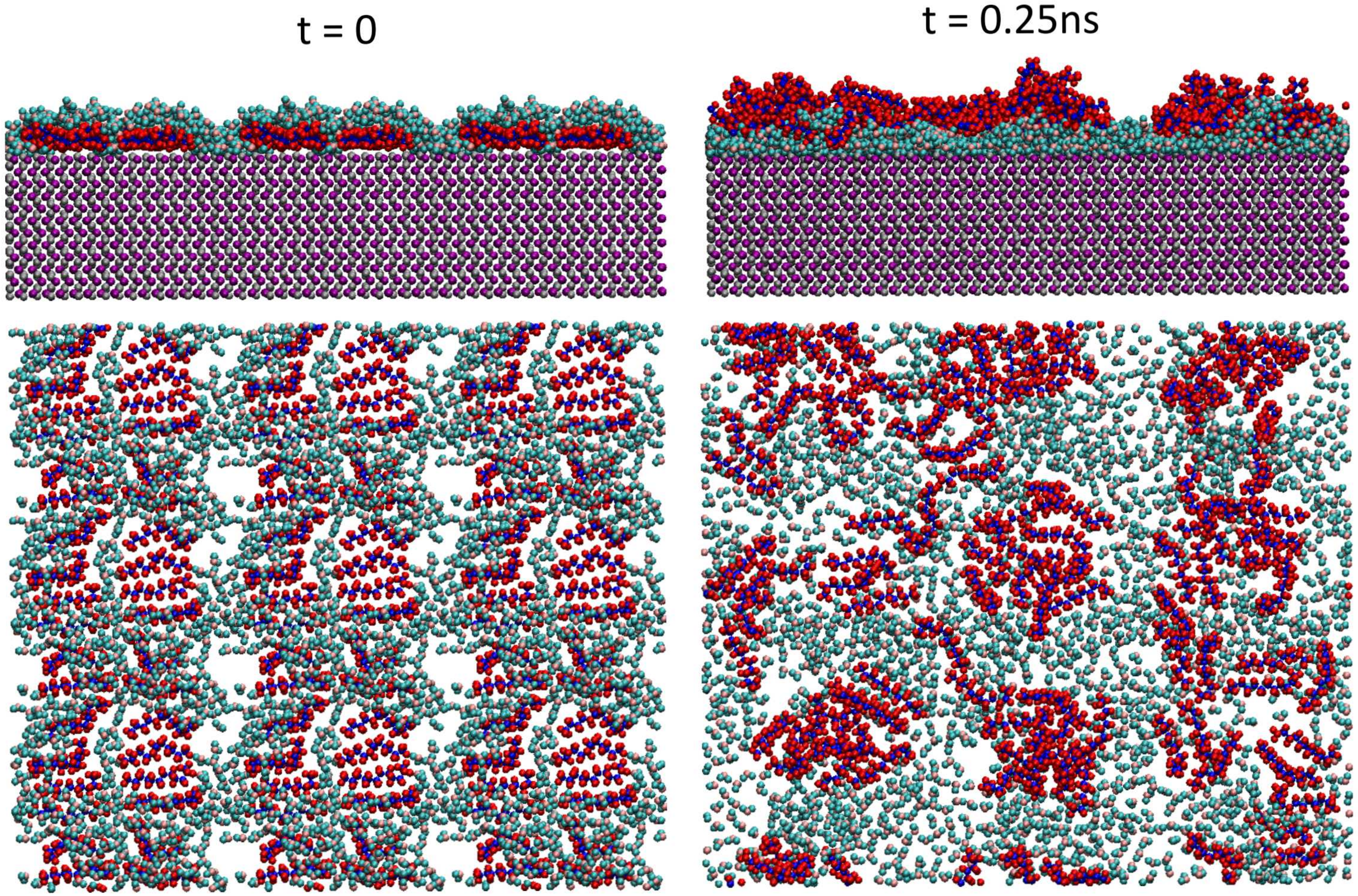
648 Carbons Initially on Surface

- n_{chains} = {27 $C_{24}H_{50}$ paraffin chains, 27 $C_{24}H_{48}$ naphthene chains}

Mixtures: Initialization

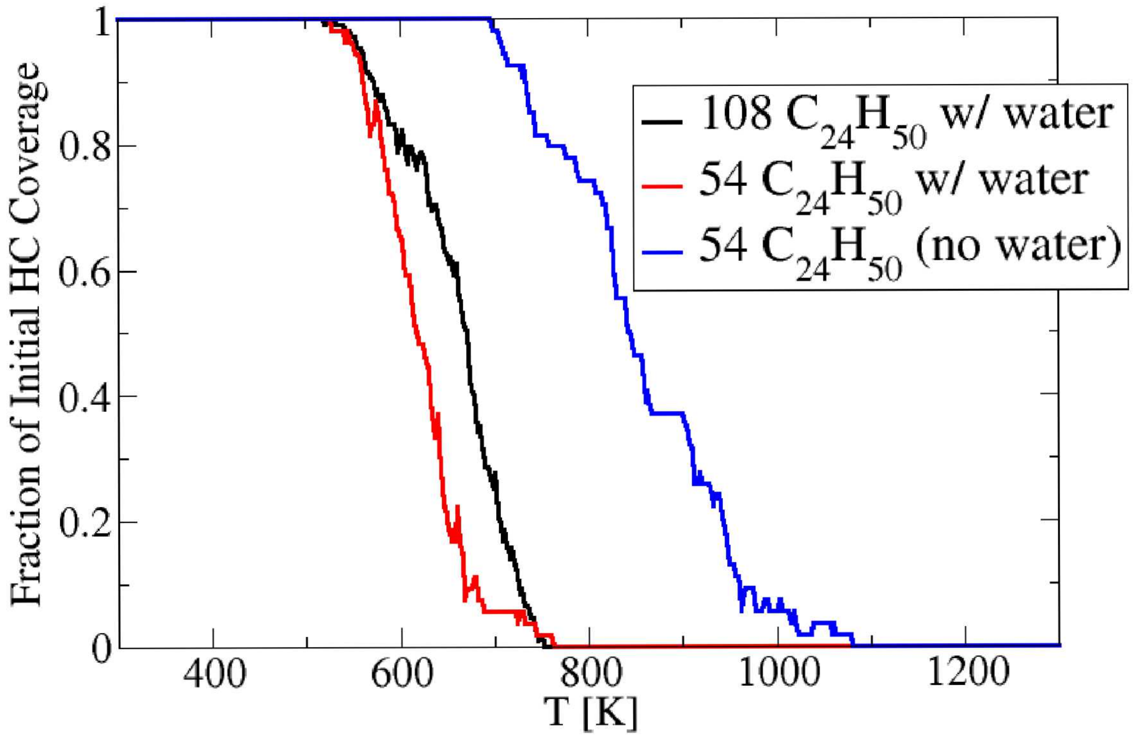
108 $C_{12}H_{26}$ chains (red/blue) / 192 water (pink/cyan) molecule mixture. Water is initially placed on top of the hydrocarbons at T = 100K. Simulation is ramped from 100K to 300K over the course of 0.25ns.

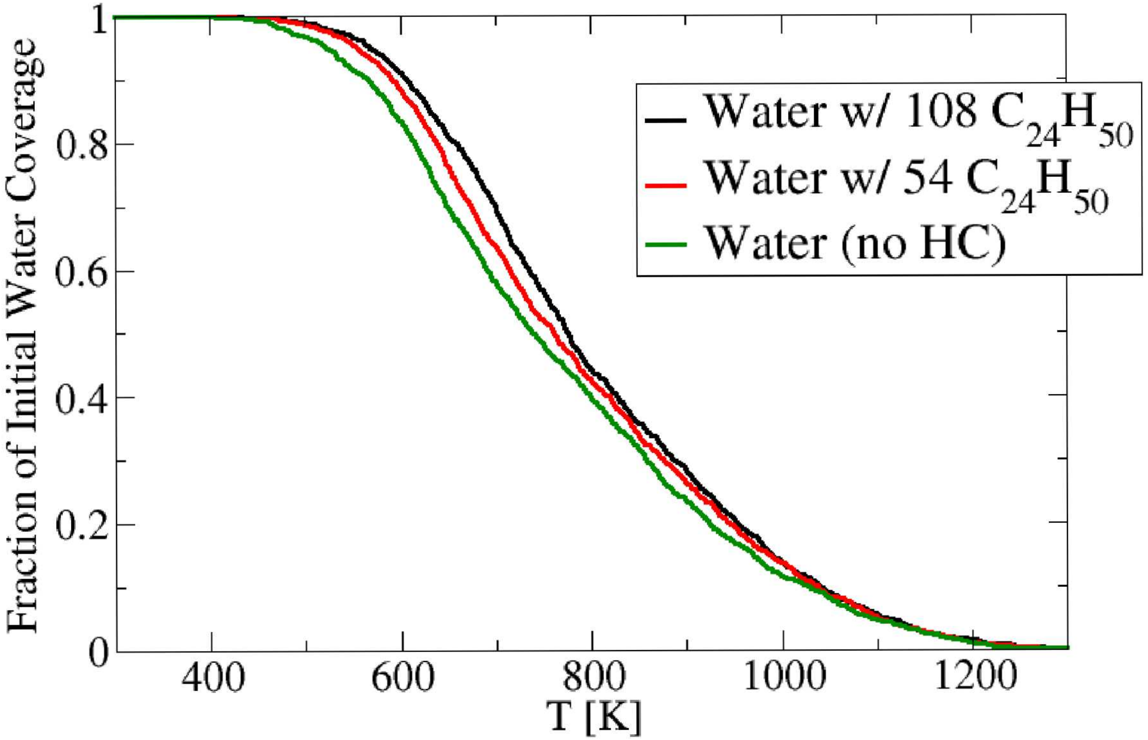
- The water moves to the surface causing the hydrocarbons to lift off the surface and sit atop the water.
- Hydrocarbons begin to phase separate from the water and form rafts.
- This simulation indicates the water's propensity to sit at the surface compared to the hydrocarbons is very strong



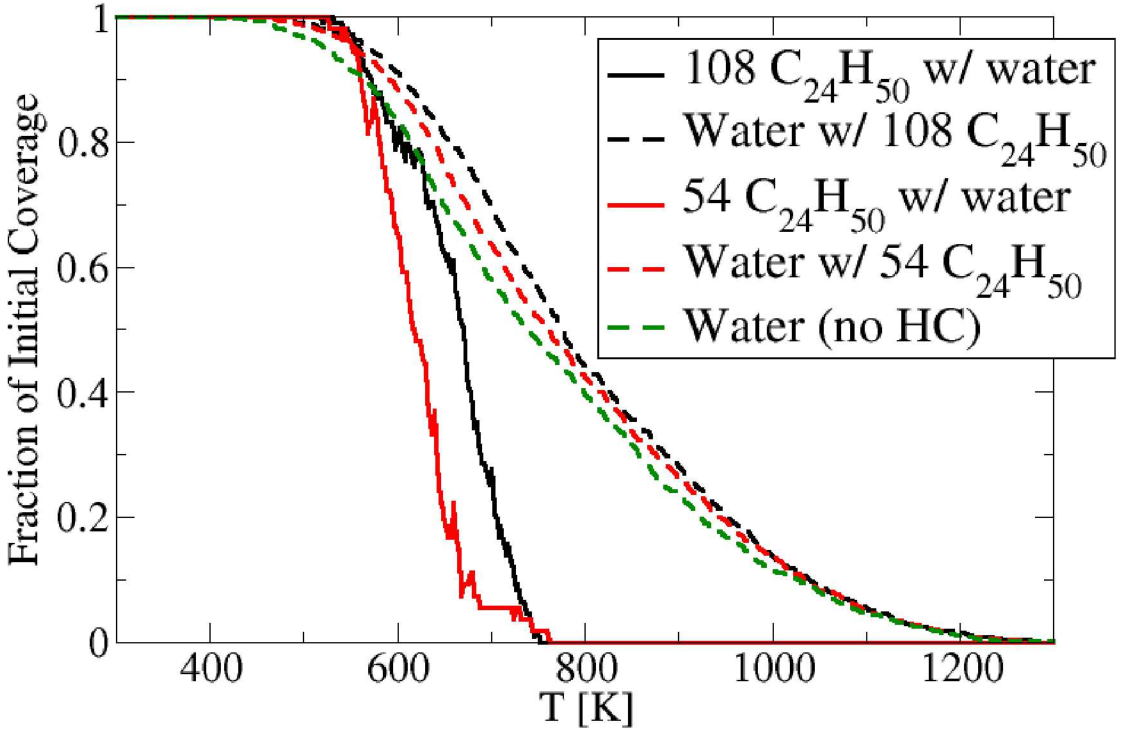
Top Row: Side view of substrate. Bottom Row: Bird's-eye view

Mixtures: Varying hydrocarbon concentration





Mixtures: Varying hydrocarbon concentration

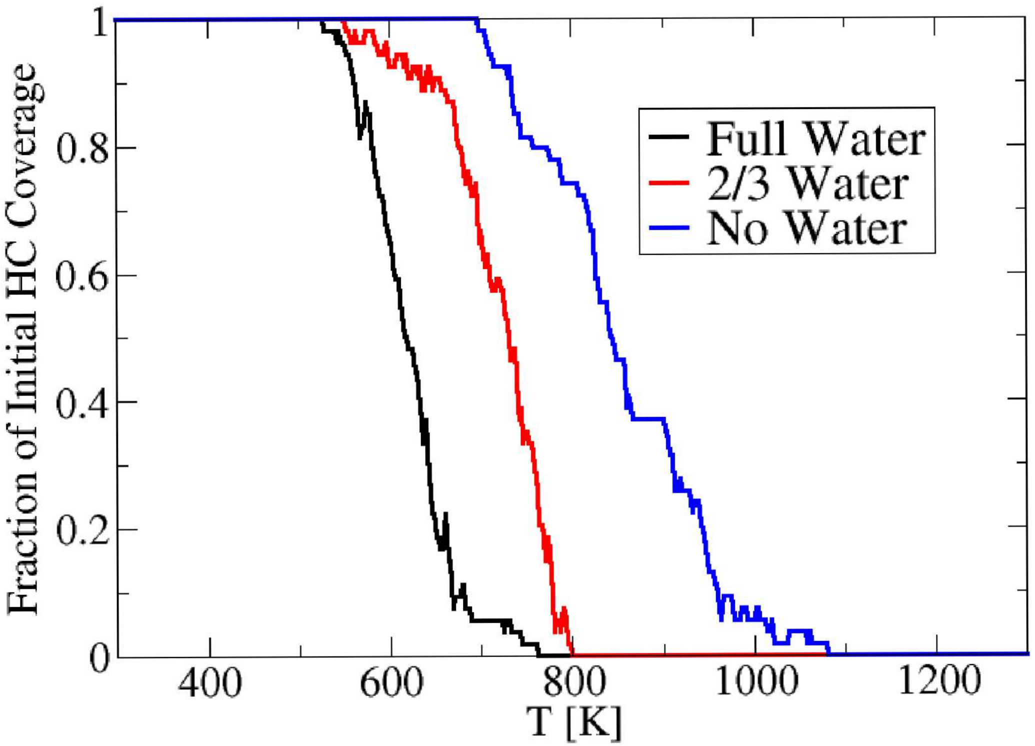


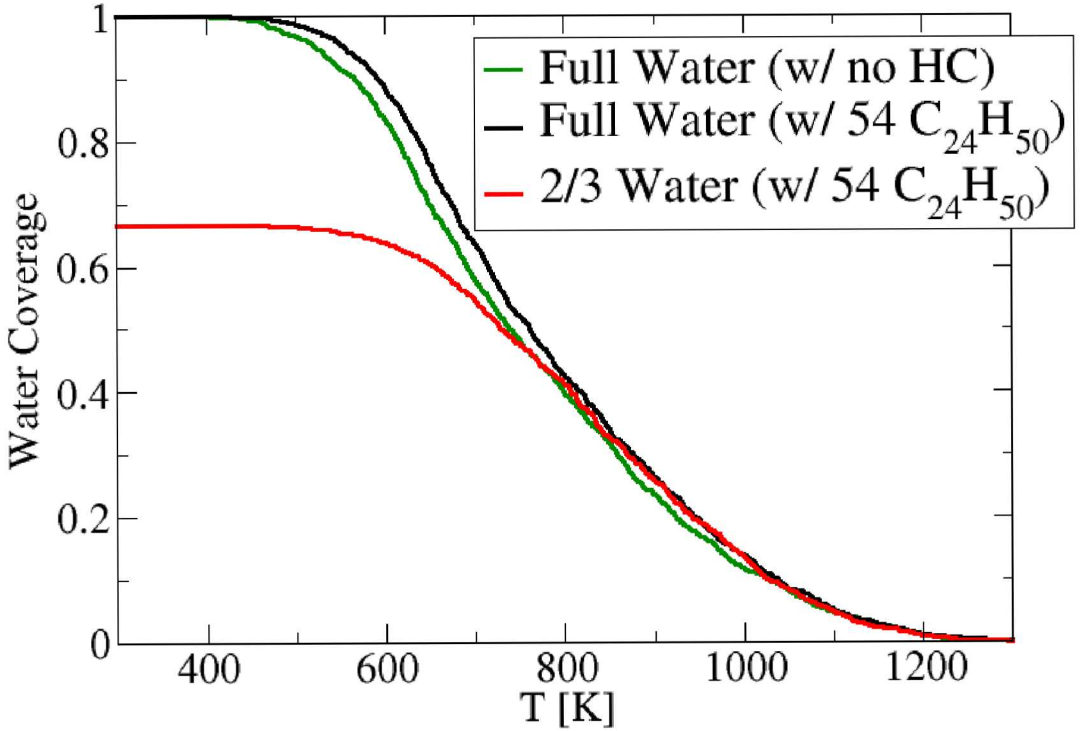
When 50% of water has desorbed:

No HC: 738K
“Low” HC concentration: 761K (~3.1% increase)
“High” HC concentration: 776K (~5.1% increase)

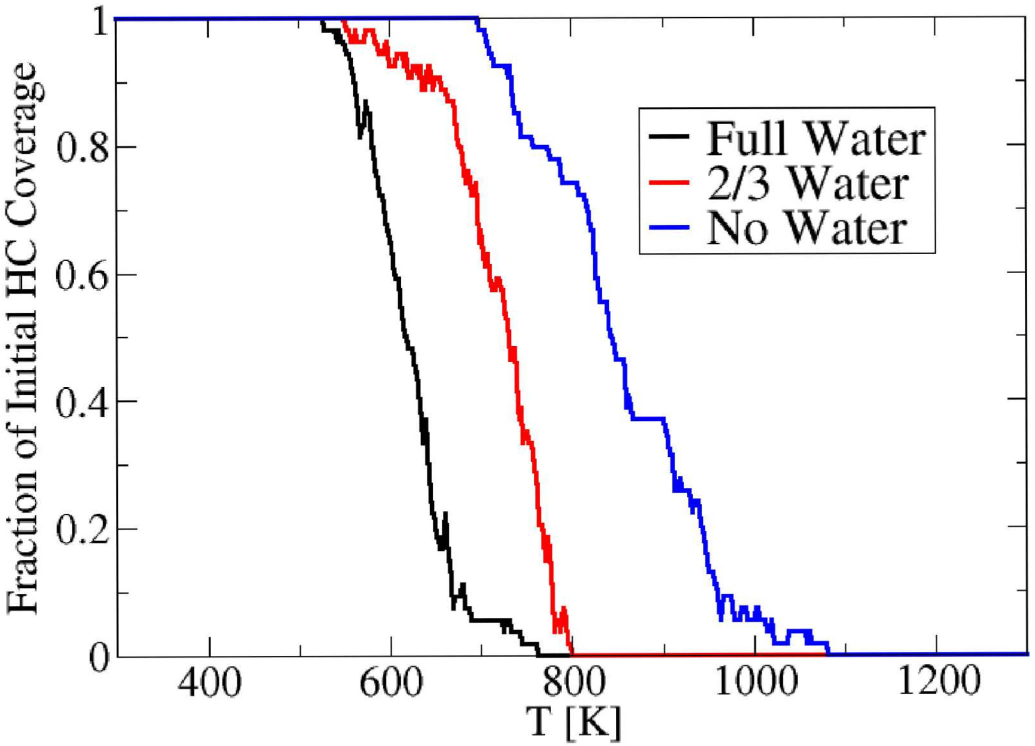
Increasing the hydrocarbon concentration/coverage on top of the water increases the desorption temperature

Mixtures: Varying water concentration





Mixtures: Varying water concentration



When 50% of hydrocarbon has desorbed:

No water: 843K
2/3 water coverage: 730K (~13.4% decrease)
Full water coverage: 617K (~26.8% decrease)

Increasing the water concentration/coverage on beneath the hydrocarbons decreases the desorption temperature

Conclusions: How Hydrocarbons affect desorption

Chain Length

- Longer hydrocarbons desorb slower then short hydrocarbons
- Supported by longer hydrocarbons having a higher desorption energy

Chain Architecture

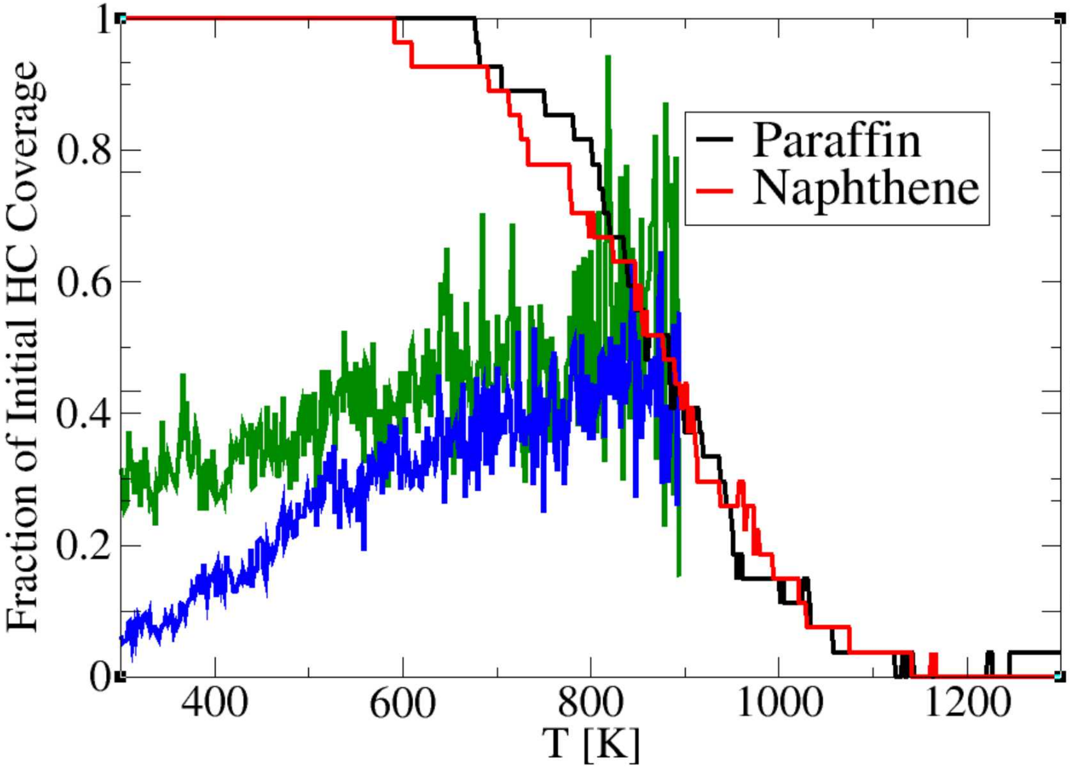
- C24 Naphthene and C24 Paraffin have similar desorption profiles
- Additional statistics and characterization of binding energy are necessary to further conclude any difference in the desorption as a function of chain architecture

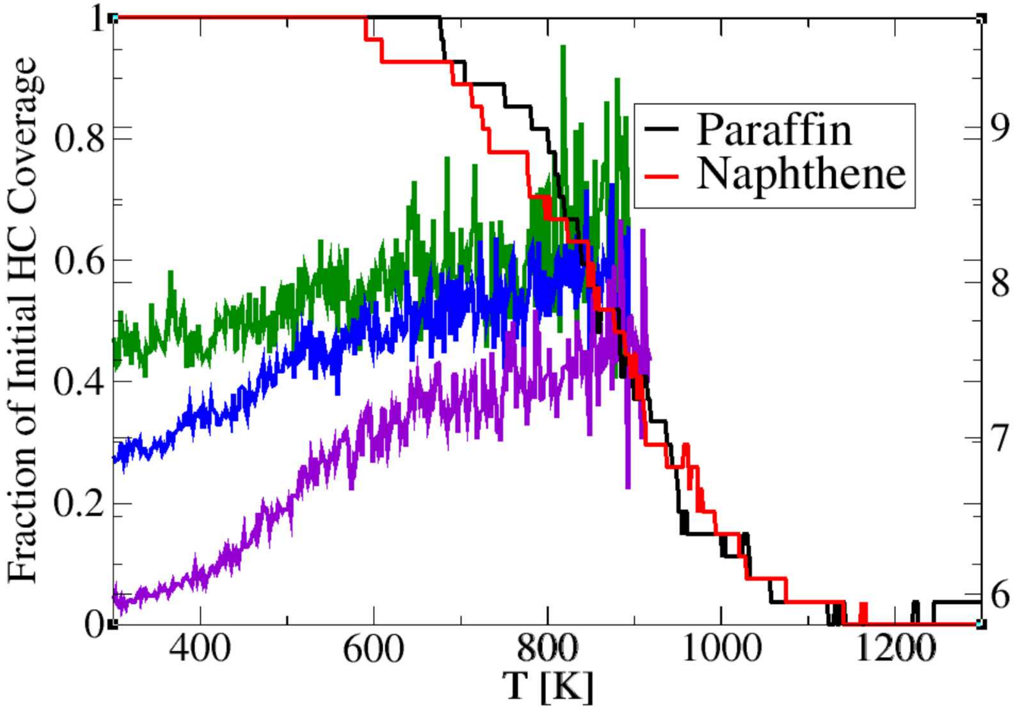
Mixtures

- Hydrocarbons are observed to sit on top of water due to water having a higher desorption energy/area than hydrocarbons
- Increasing the hydrocarbon concentration/coverage while keeping the water coverage the same increases the water desorption temperature (~ 3%-5% for coverages tested)
- Increasing the water concentration/coverage while keeping the number of hydrocarbons constant decreases the hydrocarbon desorption temperature (up to ~27% for full water coverage)

Supplementary Slides

Green: Carbons in cyclohexane (naphthene)
Blue: Carbons in backbone (naphthene)
Purple: Carbons (paraffin)

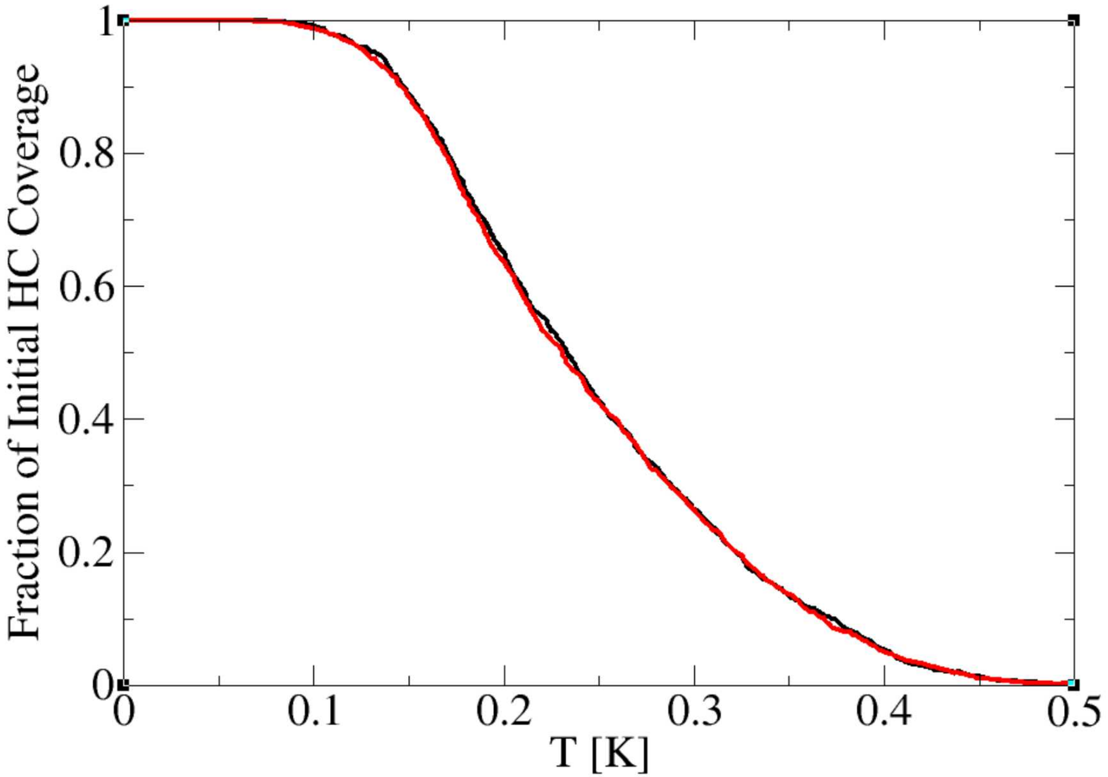




The right y-axis is height in Angstroms. Note the two y-axis are on slightly different scales

Water desorption from full monolayer

Black: Starting from initial ramp (100K to 300K, not equilibrated at 300K, so most chains laying flat)
Red: Equilibrated at 300K initially for > 1ns



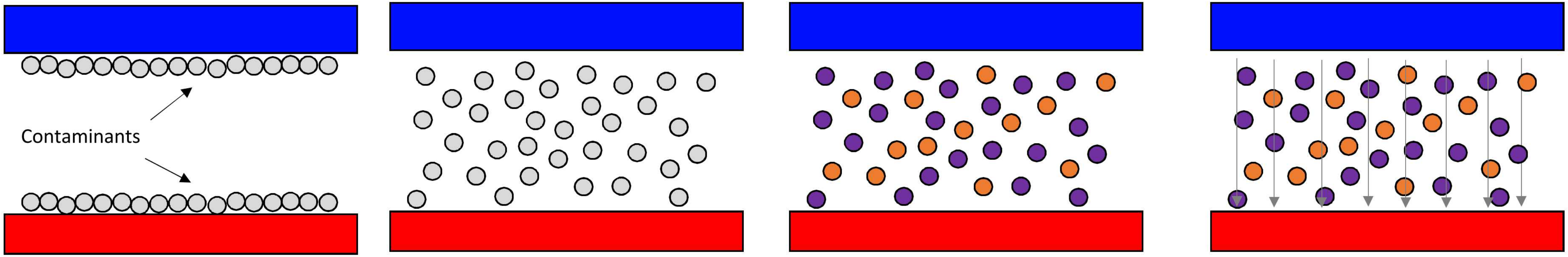
Current Understanding of Plasma Formation on Z

Accurate understanding of contaminant composition and **desorption processes** are necessary to inform plasma codes

Plasma modeling/codes

- Large investment to predict power flow phenomena
- Rely on **boundary conditions** at electrode boundary

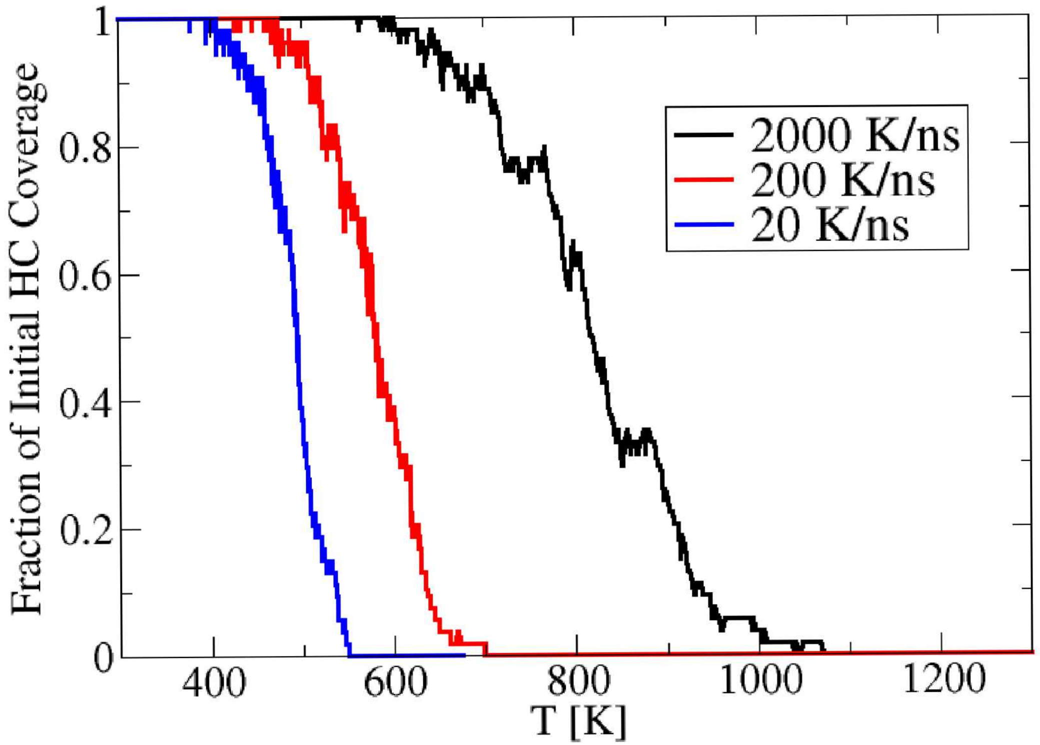
Evidence of hydrocarbons and will affect desorption composition and rates



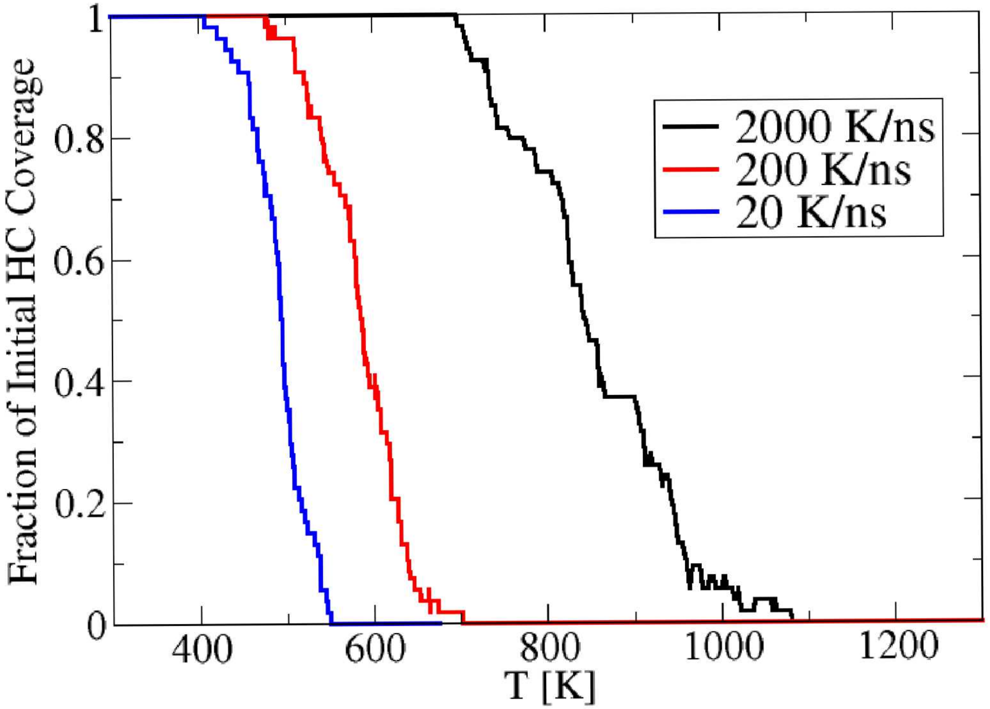
Surfaces are heated → Contaminants desorb from the Surface → Plasma forms in the neutral layer → Plasma structures cross gaps and shunt current

C24, “high” coverage

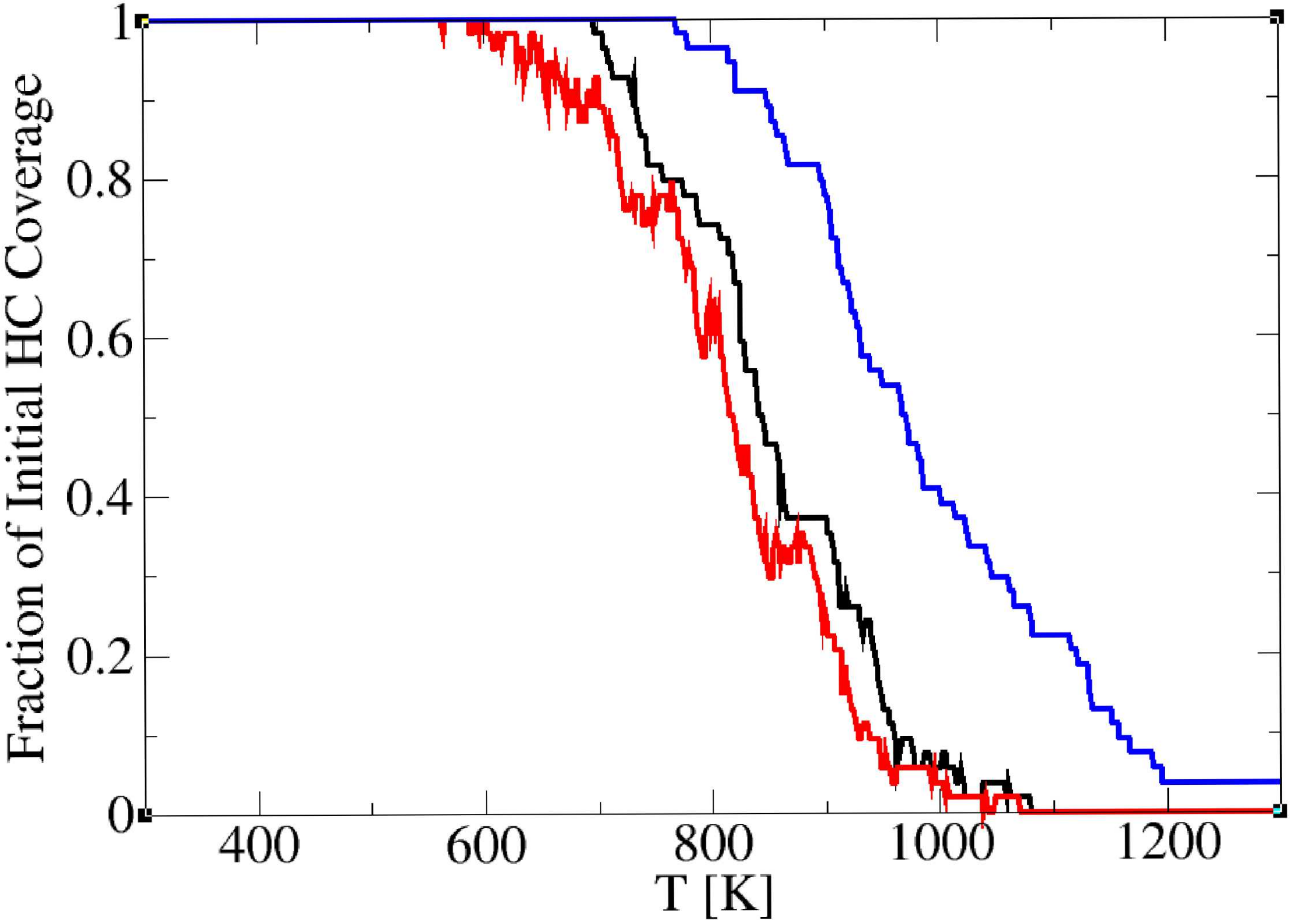
8 Angstroms



20 Angstroms



Black: 8 Angstroms
Red: 20 Angstroms
Blue: Full Evaporated



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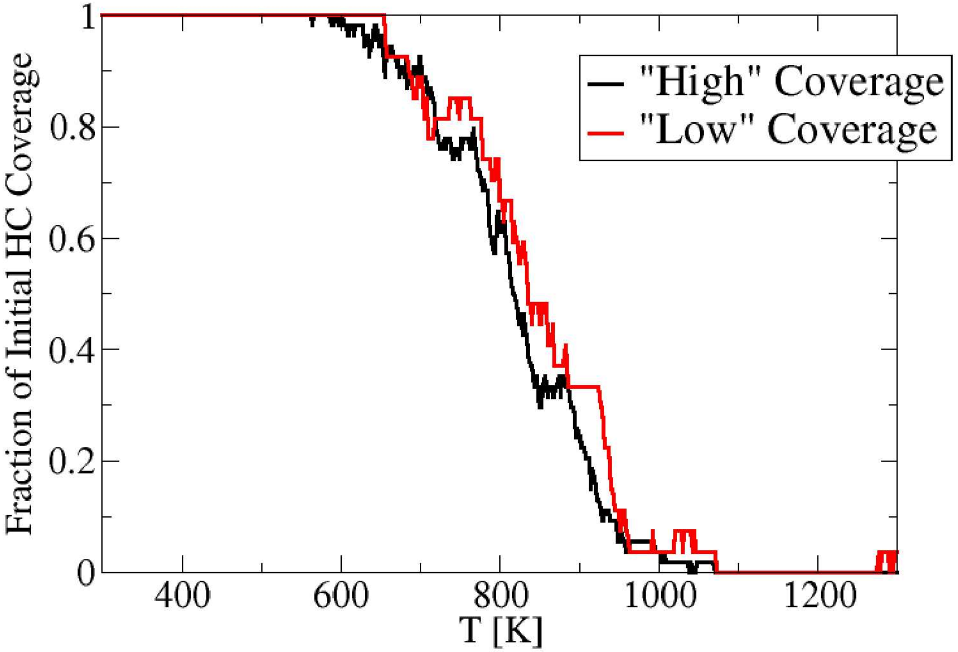
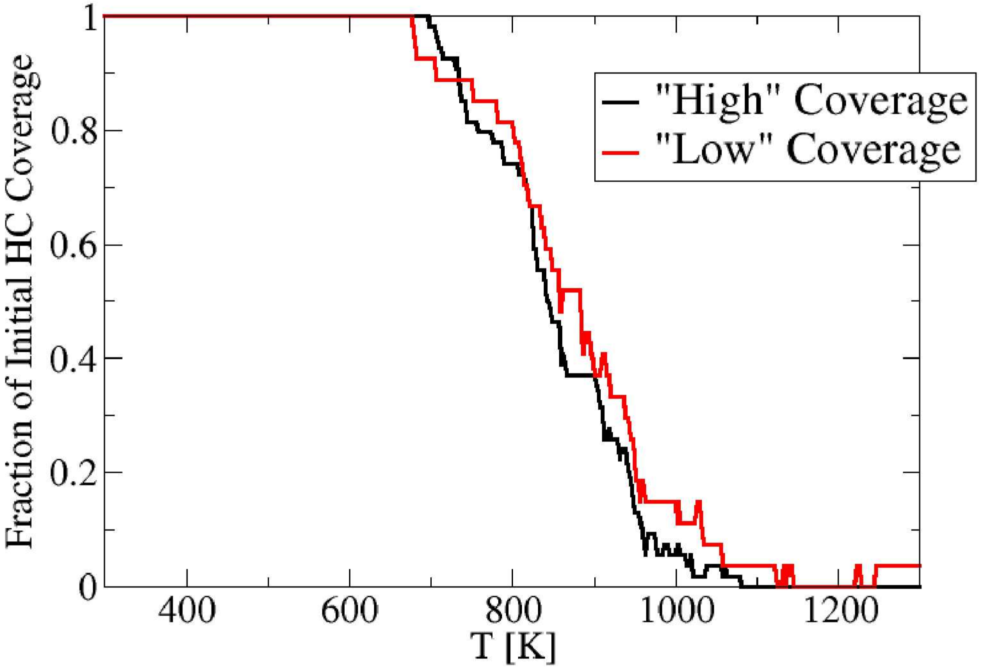
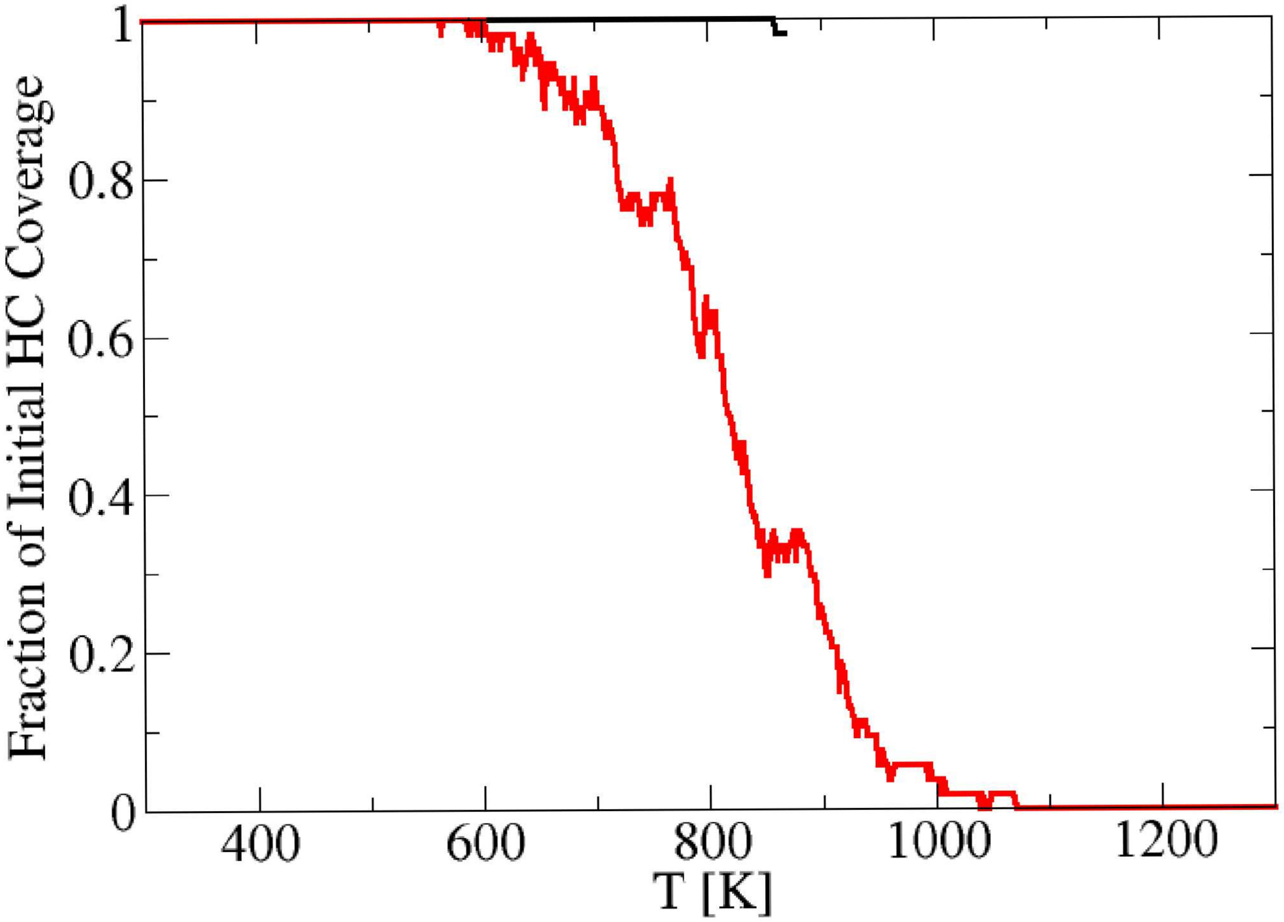


20 Angstroms





Binding Energies:

Non-React. ~ -1.055 eV
ReaxFF Oxide -> React. ~-1.824 eV

Details of Desorption Modeling

Desorption Modeling

Previous Work (Non-Reactive MD):

$$E_{\text{total}} = E_{\text{Coul}} + E_{\text{VDW}} + E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}}$$

$$E_{\text{Coul}} = \frac{e^2}{4\pi\epsilon_o}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}$$

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- SPC Water
- **OPLS Hydrocarbons**

Reactive MD (ReaxFF)

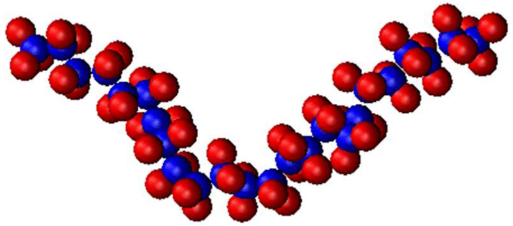
$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

- Allows bond-breaking/reactivity
- “Oxide” force-field (Aryanpour [2010])
- Electrostatic energy

$$E(\mathbf{q}) = \sum_{i=1}^{N}\left[\chi_i q_i + \eta_i q_i^{2} + \mathrm{Tap}(r_{ij})k_c\frac{q_i q_j}{(r_{ij}^3 + \gamma_{ij}^{-3})^{1/3}}\right]$$

- At each timestep, charges are adjusted to minimize energy

New Study focusing on:
- Chain length
- Chain architecture
- Mixtures



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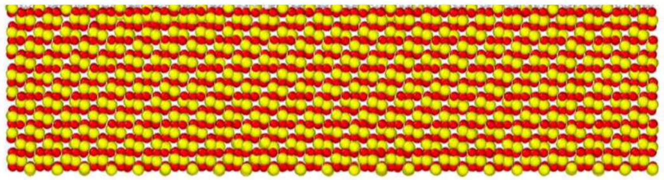

Side view of substrate