Institute for Shock Physics
Applied Sciences Laboratory

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World Class. Face to Face.

Quantum/Classical Simulations of Reactions at the Interfaces

Interfacial Dynamics: Ice-phobic Coatings and Chemistry under Extreme Conditions

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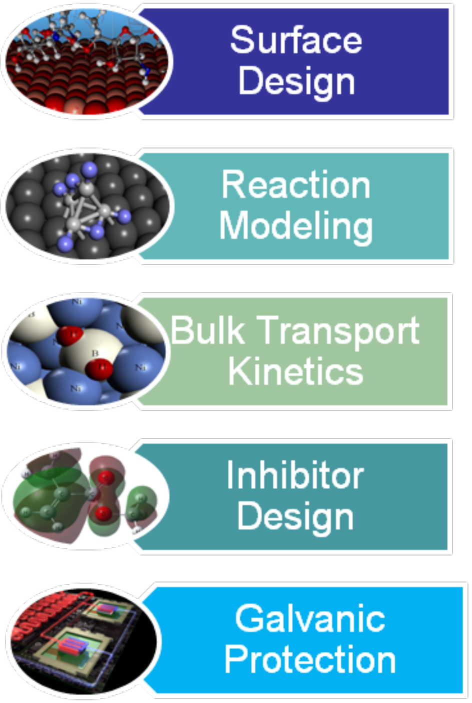
Overview

- Hydrophobic Coatings
  - Example: Ice-Phobic Composites
- Combustion and Detonation
  - Example: Al-Teflon Composite
    - Quantum Chemical Reactions
    - QM/MD and CPMD
- Simulations of Corrosion Reactions
  - Example: Stabilizing Mg-Alloys
- Challenges

Highlights



Surface Design

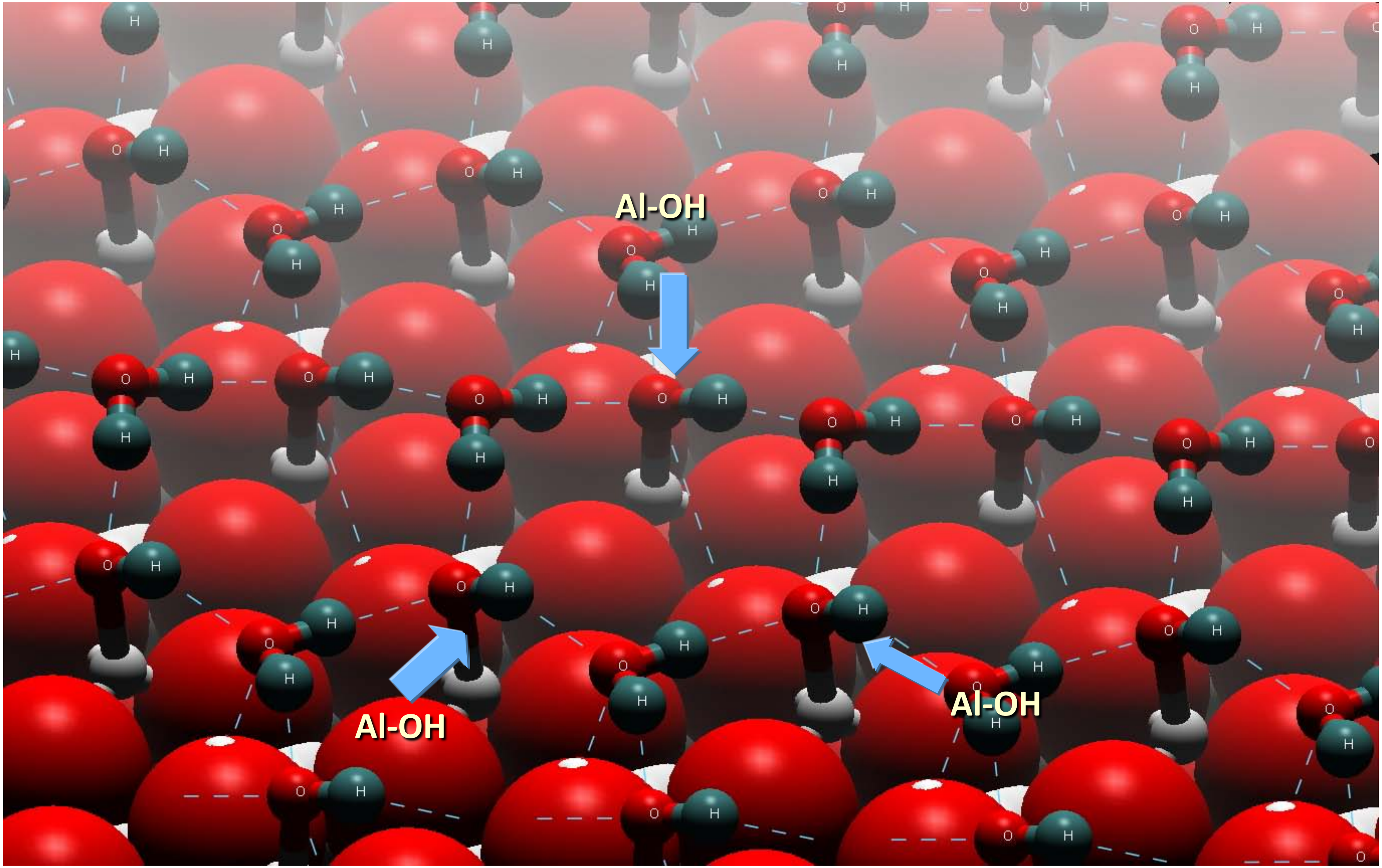
Reaction Modeling

Bulk Transport Kinetics

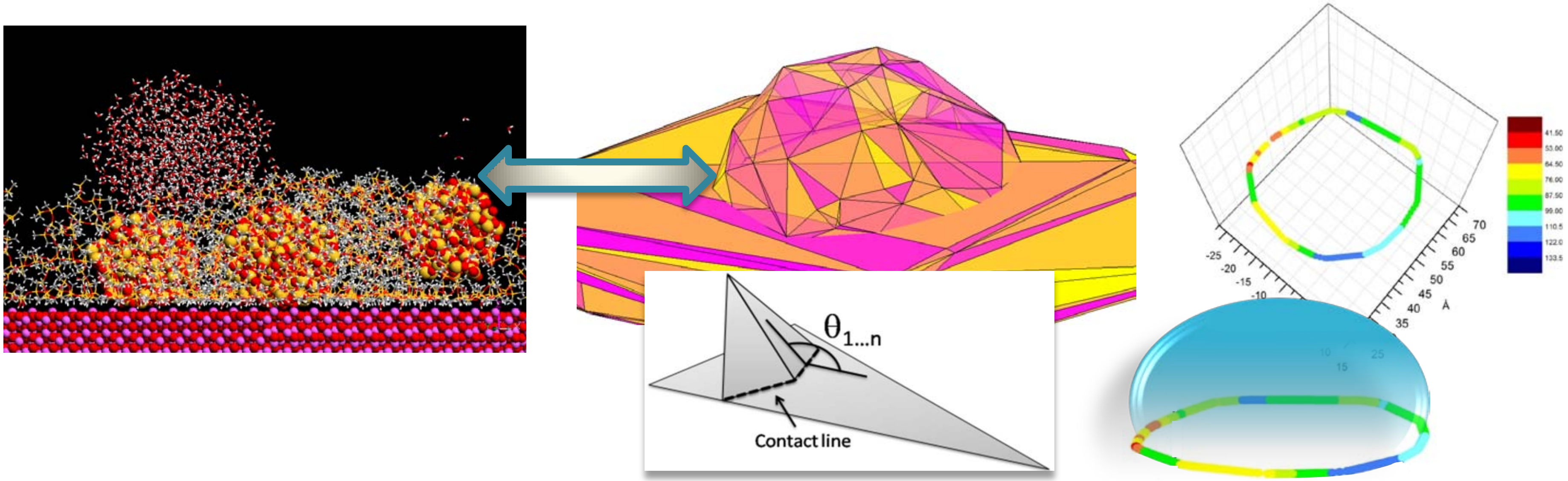
Inhibitor Design

Galvanic Protection

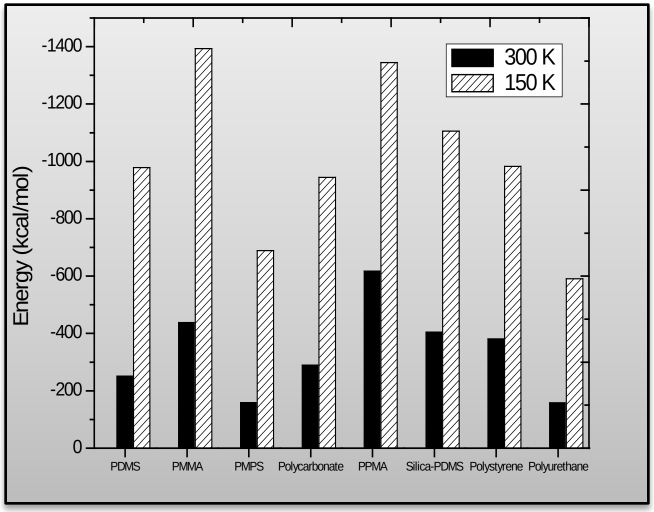
Example 1: Anti-Icing Coatings



Nanodroplet Simulations

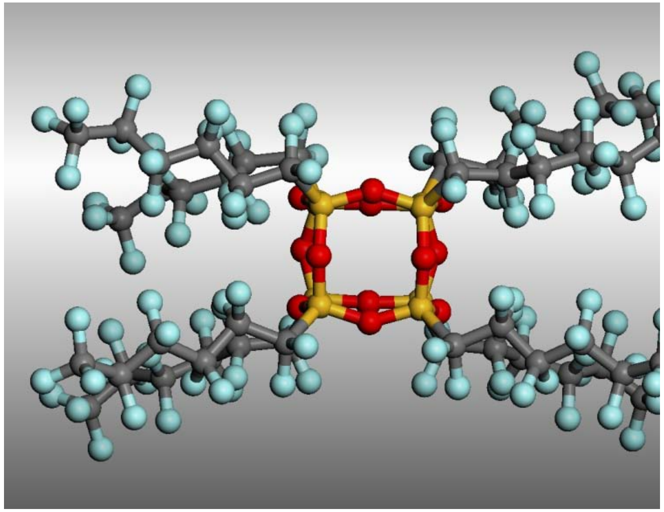


	300 K	150K	Experiment
PDMS	**103.86**	100.63	100-110
PMPS	**88.73**	85.79	90
PMMA	**67.8**	63.25	68-70
Polystyrene	**85.19**	77.85	84-88
Polycarbonate	**80.57**	65.78	79
Polyurethane	**77.76**	86.27	73
PDMS-Silica	**86.76**	89.25	93



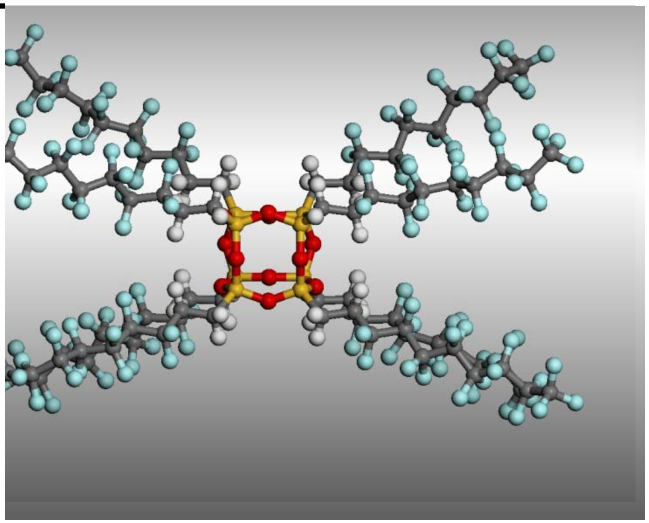
Contact angle and interfacial vdW forces change on freezing

Tailored Roughness

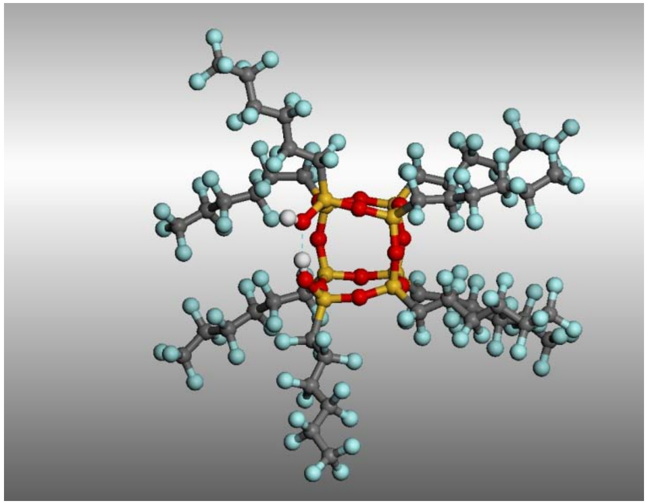


POSS-3

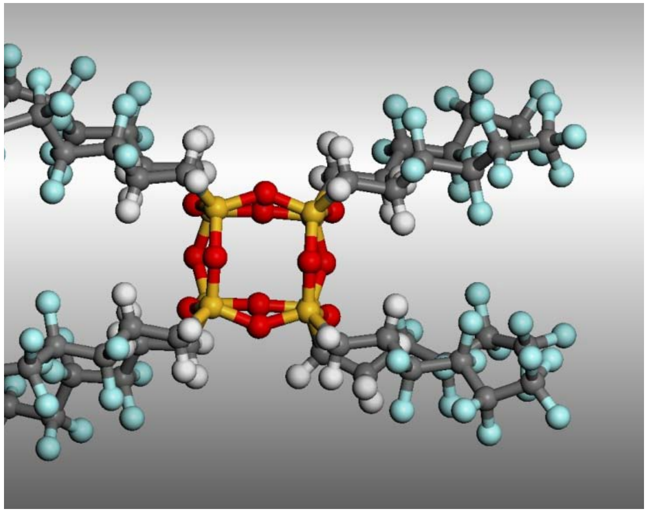
Molecular System	Contact Angle
POSS-3	103.5
POSS-4	82.2
POSS-5	60.3
POSS3-hydrolyzed	103.2
Polycarbonate	~80
Polycarbonate-POSS3	88.2
Polycarbonate-POSS5	97.1



POSS-5



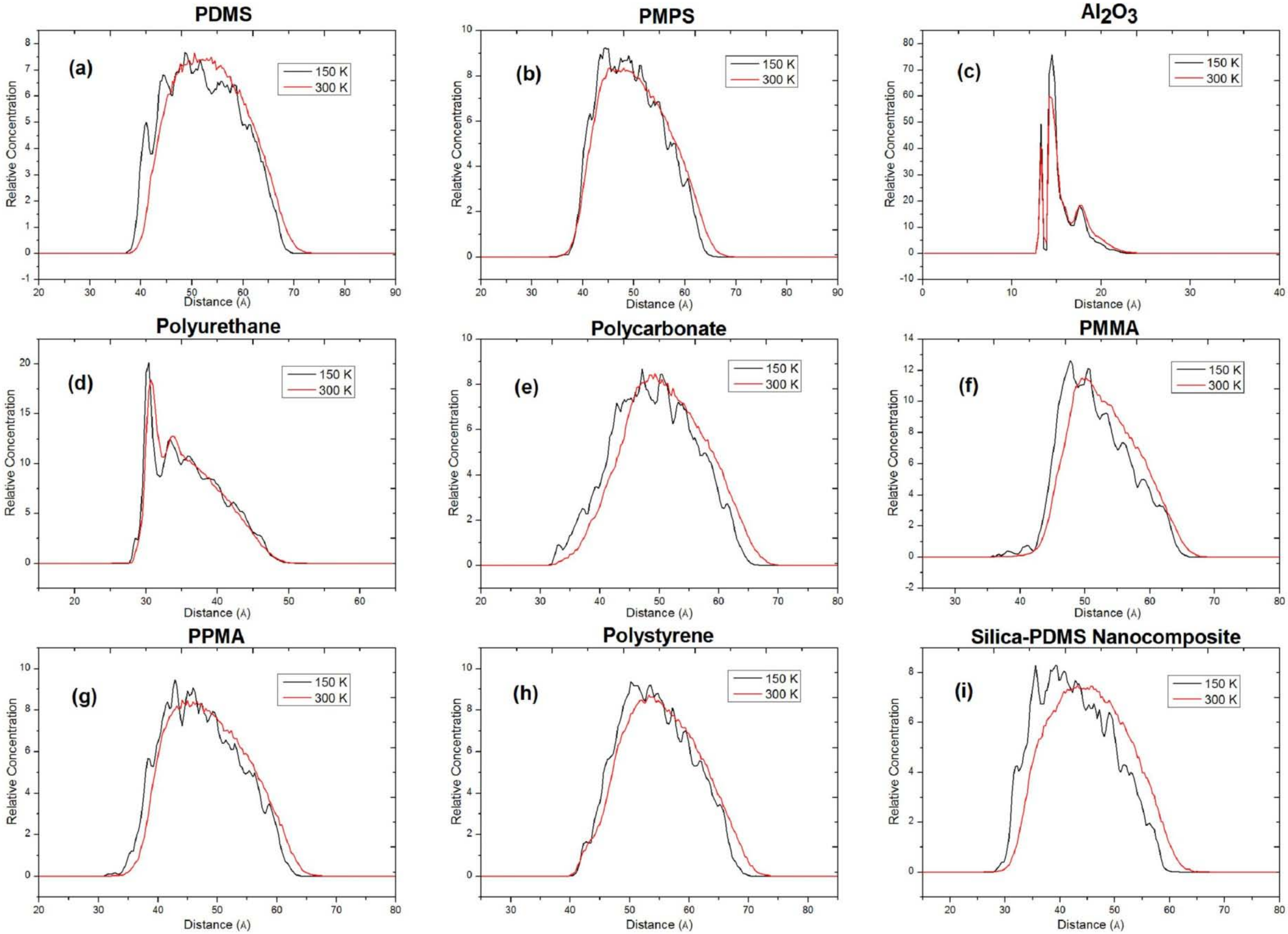
POSS-3 Hydrolyzed



POSS-4

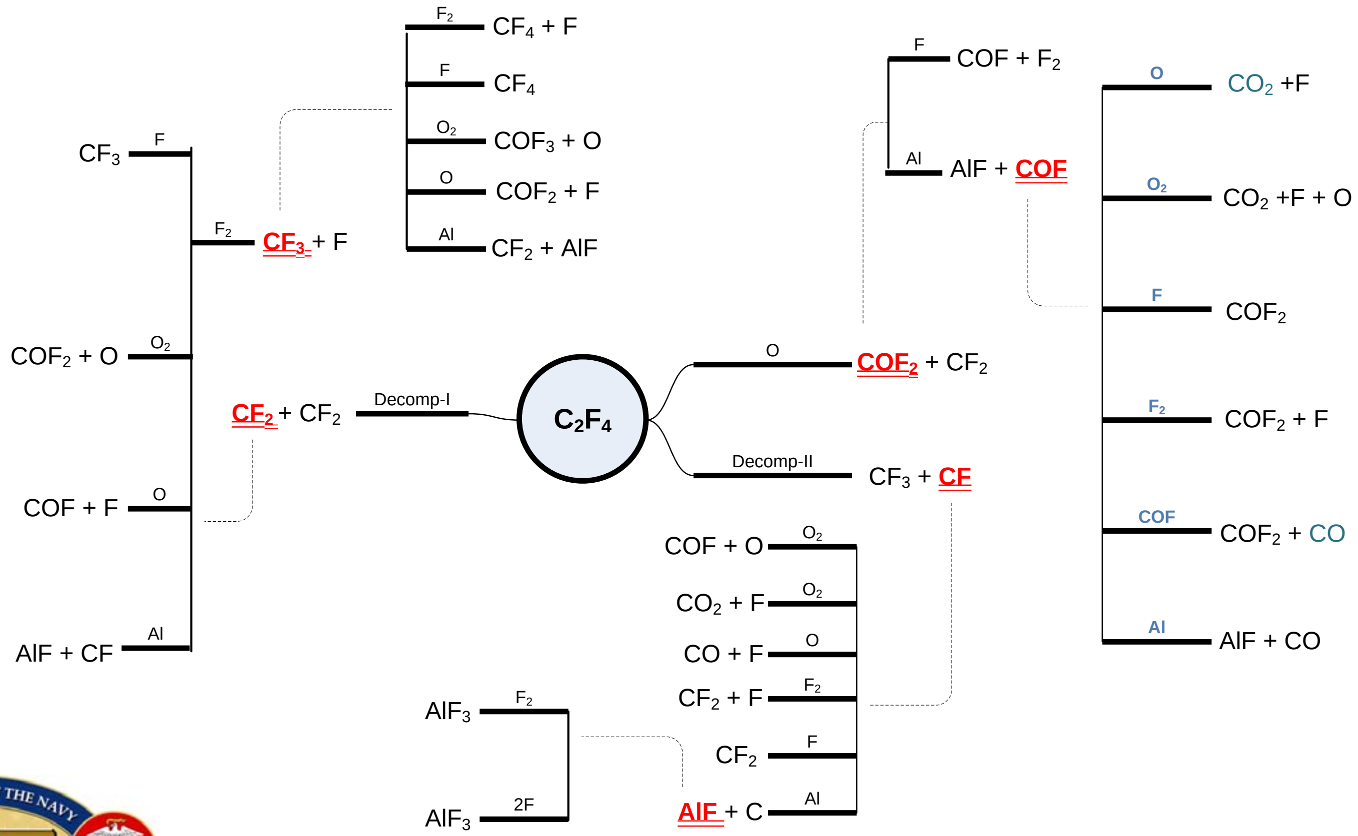
Simulation of water nanodroplet on polymeric coating at 300 K

Supercooled Water/Icing

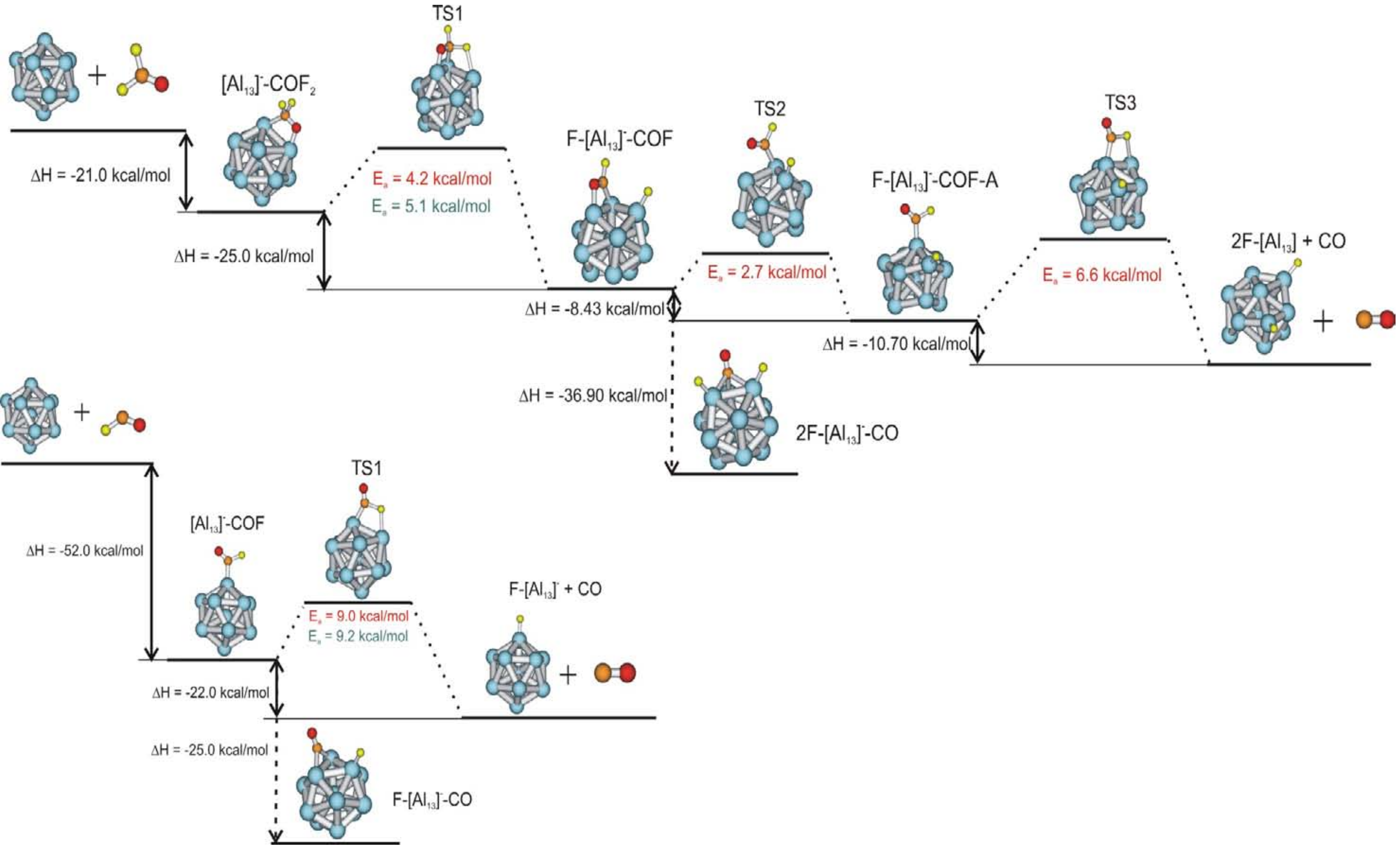


Example 2: Chemistry of Al-Teflon Composites in Extreme Condition

$(C_2F_4)_n + O_2 + Al \rightarrow AlF_3 + CO + CO_2$

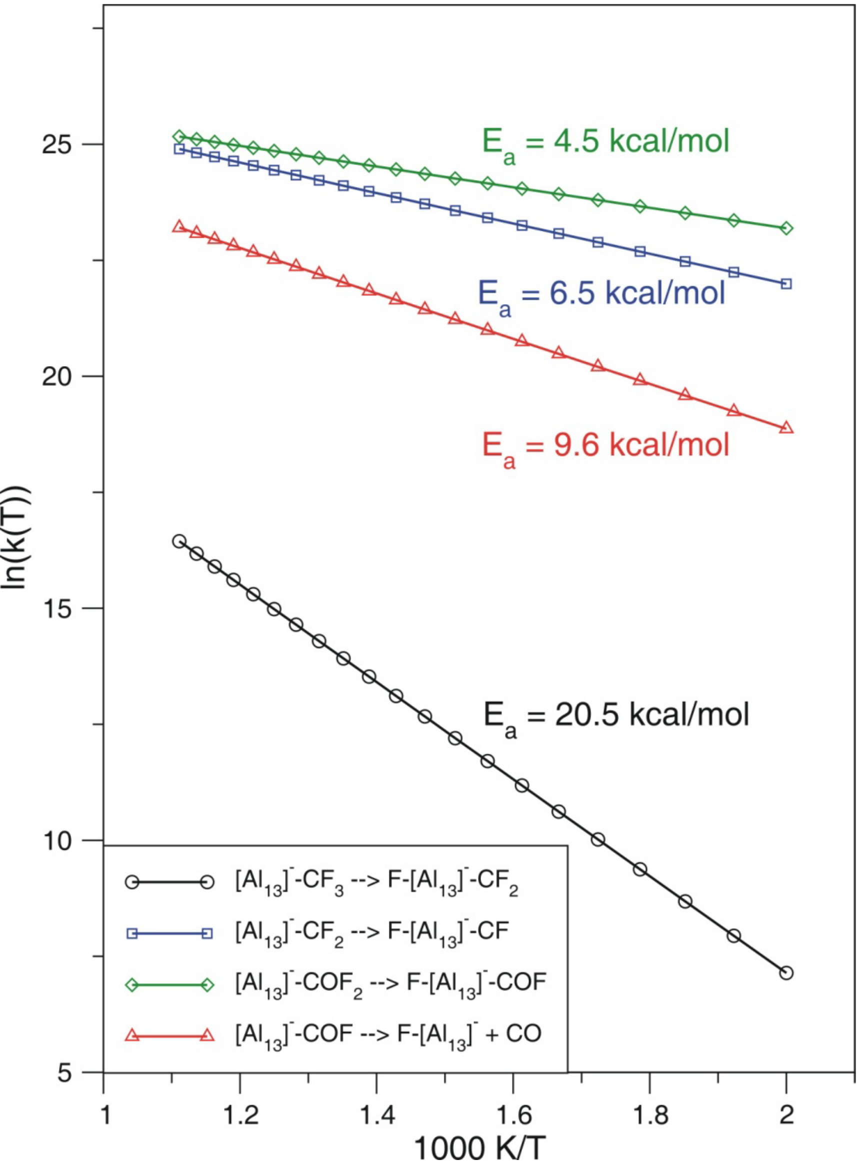


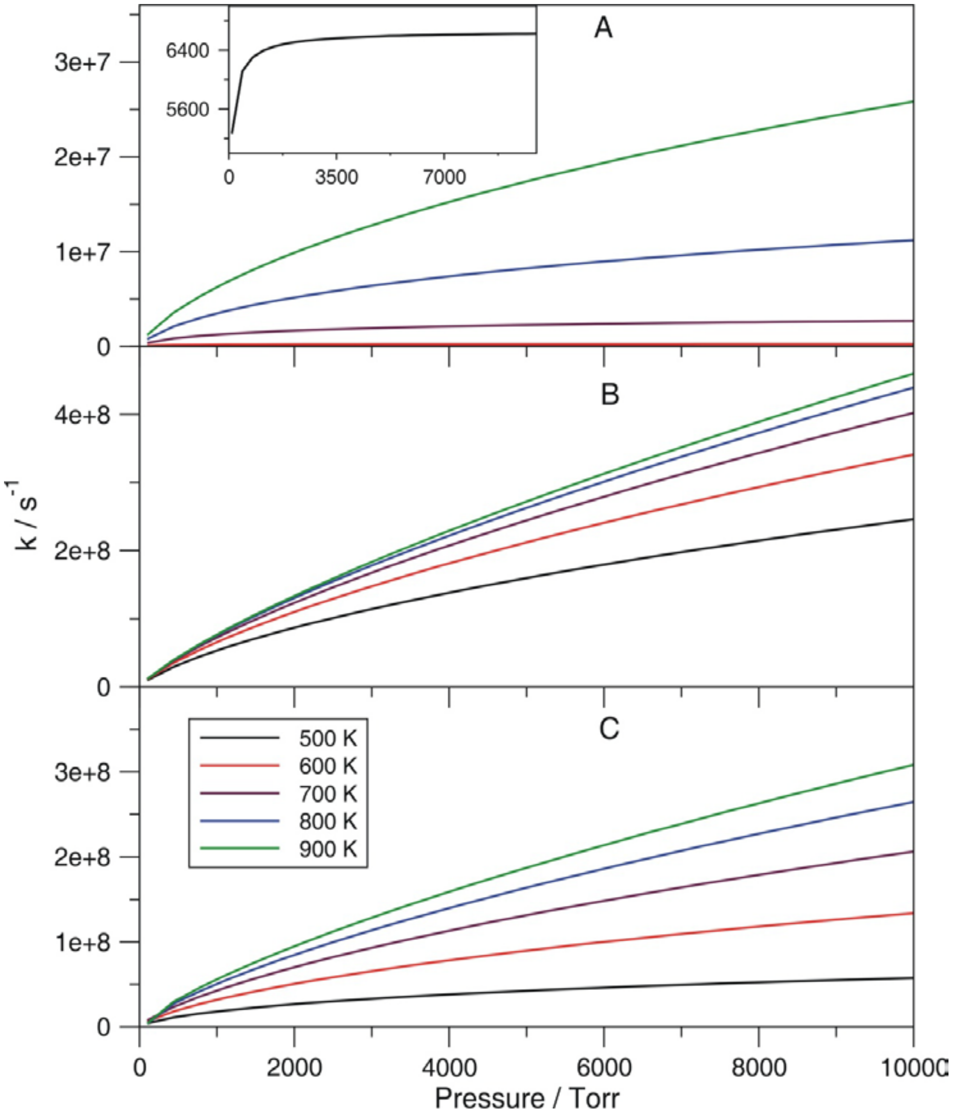
Step 1: Knowing the Reaction Channels



Quantum Chemical Calculation of Multistep Reactions

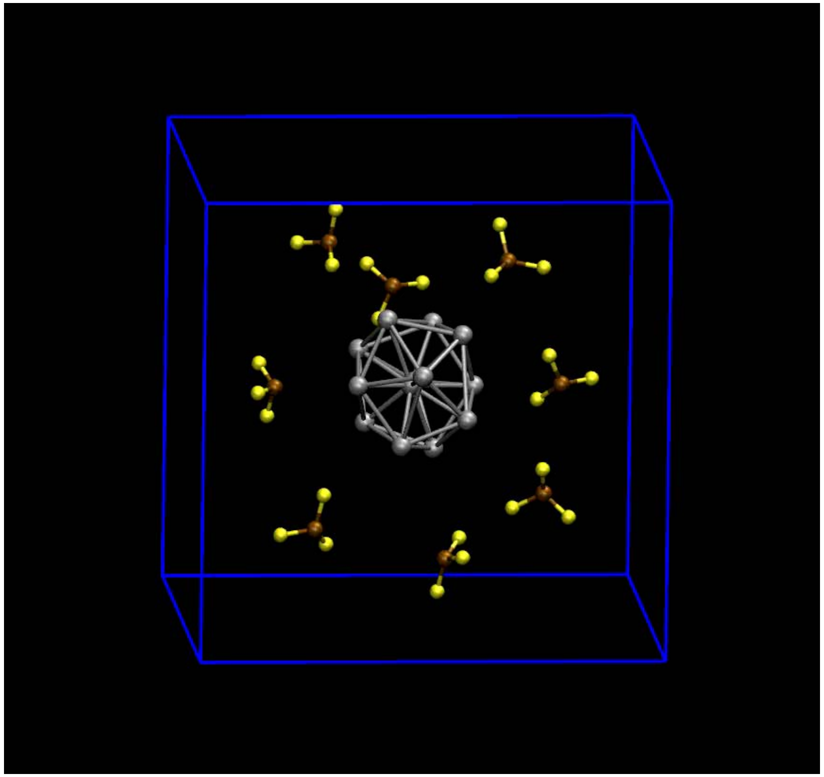
Ranking the Reaction Channels



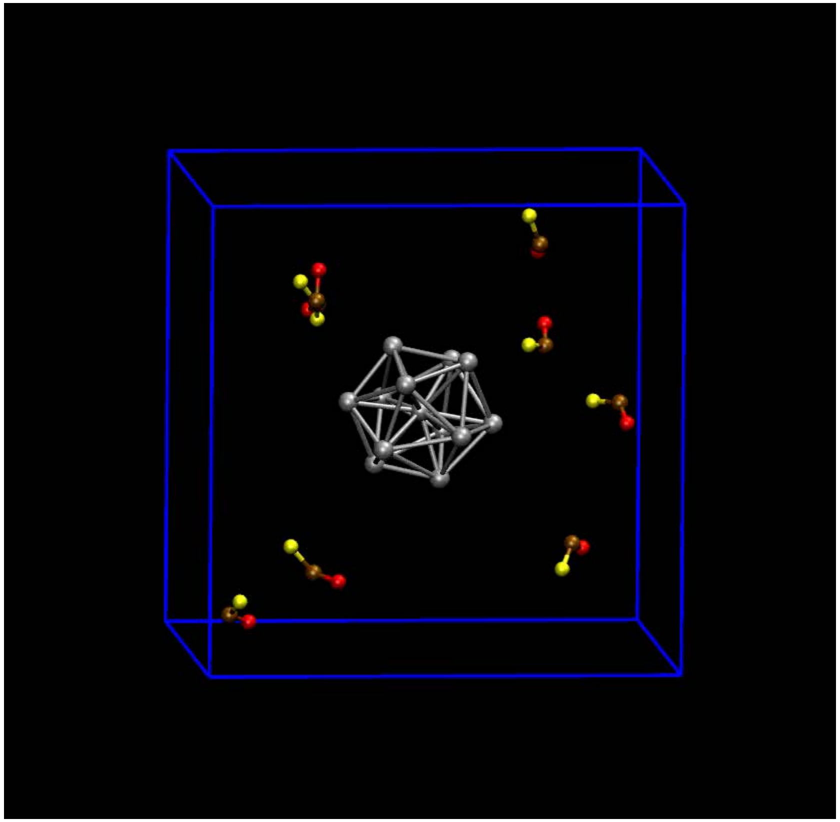


RRKM Theory Models for T and P Dependence of Gas Phase Reactions

Step 2: CPMD and Thermal Sampling

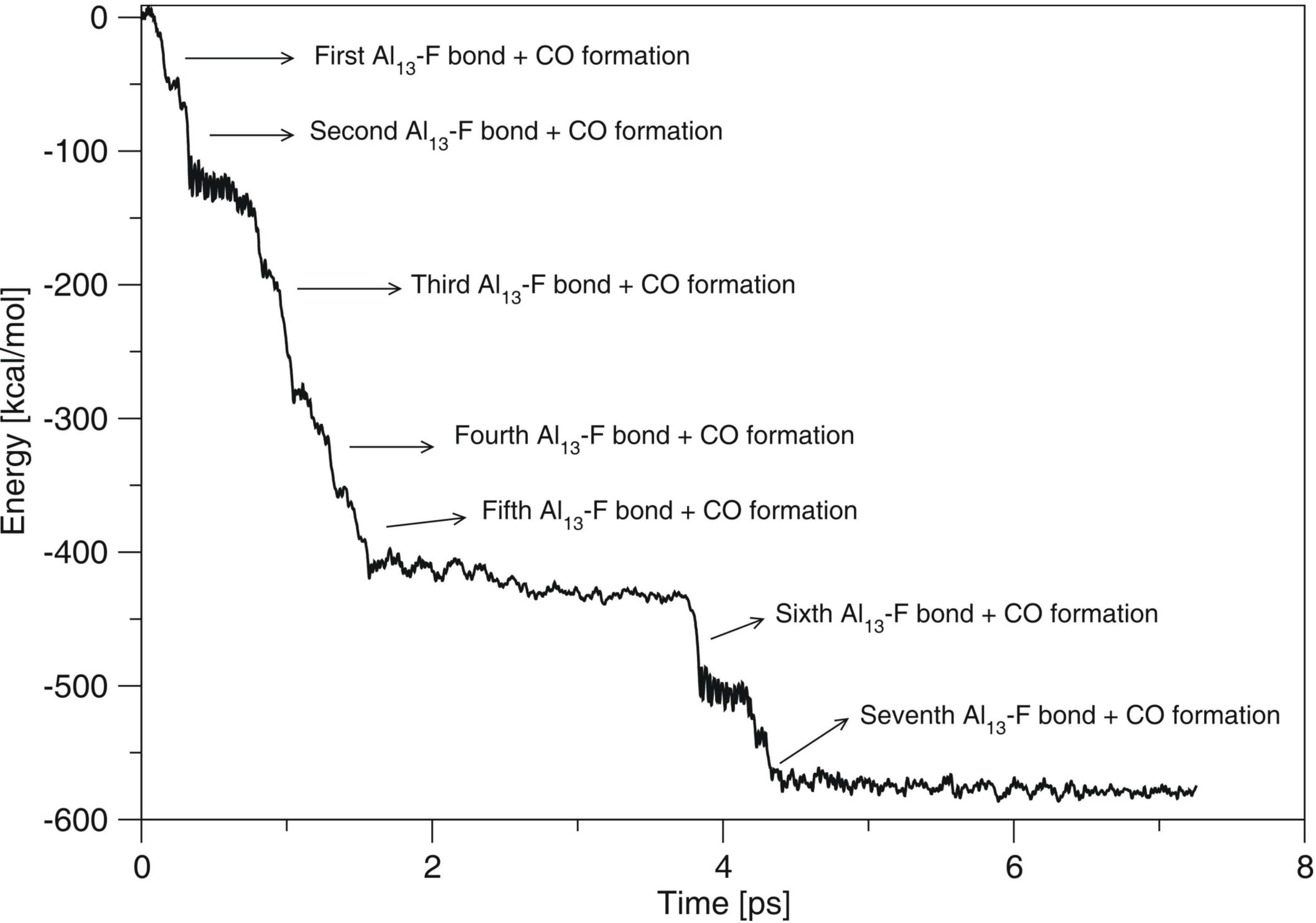


CF3 Reacting with Al

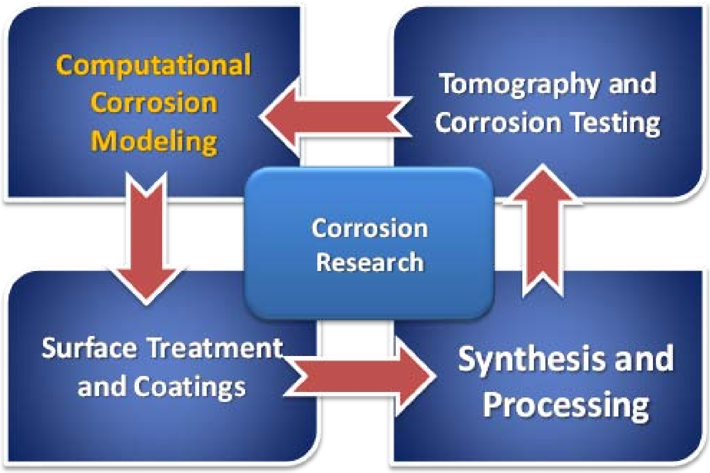


COF Reacting with Al

Step 3: QM/MD and Accounting



Example 3: Corrosion of Metals



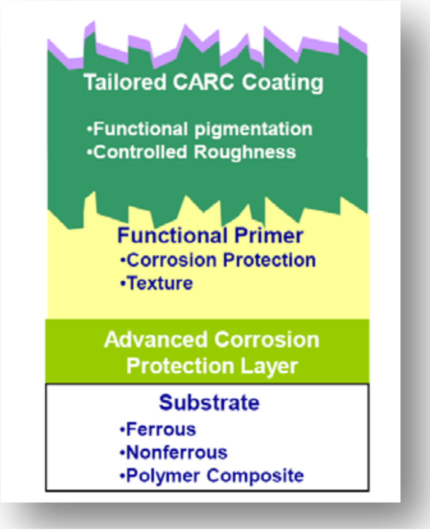
Computational Corrosion Modeling

Tomography and Corrosion Testing

Corrosion Research

Surface Treatment and Coatings

Synthesis and Processing



Tailored CARC Coating
- Functional pigmentation
- Controlled Roughness

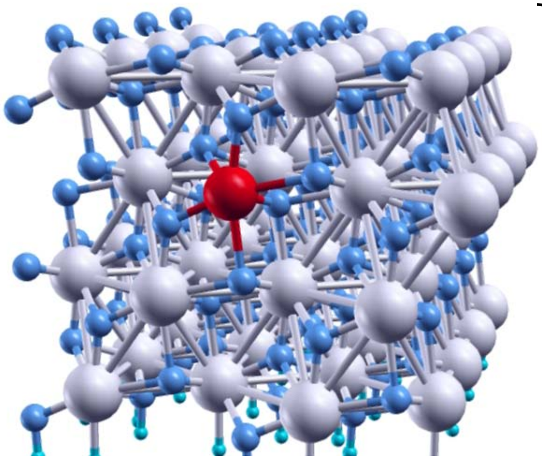
Functional Primer
- Corrosion Protection
- Texture

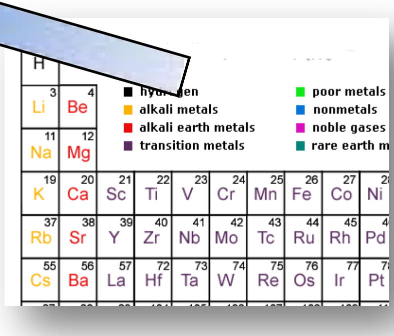
Advanced Corrosion Protection Layer

Substrate
- Ferrous
- Nonferrous
- Polymer Composite

Chem/Bio functionality by Design

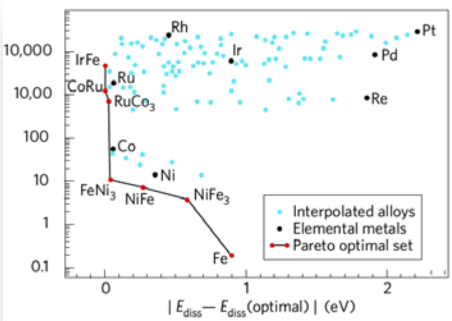
Barrier or Conversion Coatings





- ■ hydrogen
- 🟧 alkali metals
- 🟥 alkali earth metals
- ■ transition metals
- 🟩 poor metals
- 🟦 nonmetals
- ■ noble gases
- ■ rare earth m

H									
3 Li	4 Be								
11 Na	12 Mg								
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	2 Ni
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	4 Pd
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	7 Pt



Transport of Ions and Reactivity

Magnesium Alloys

Benefits and challenges

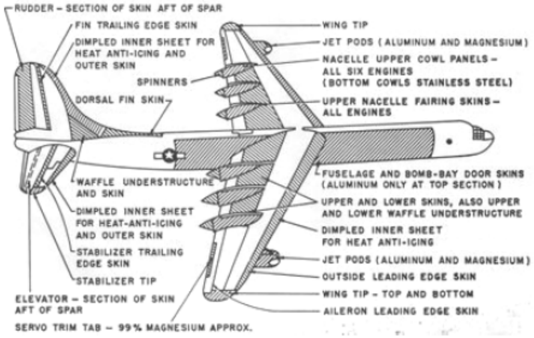
What makes Mg alloy so attractive to the industry?

- Abundance (8th on earth).
- Light weight with high strength-weight ratio.
- Reasonable processing capability.
- Good thermal conductivity, recyclability, and many more.

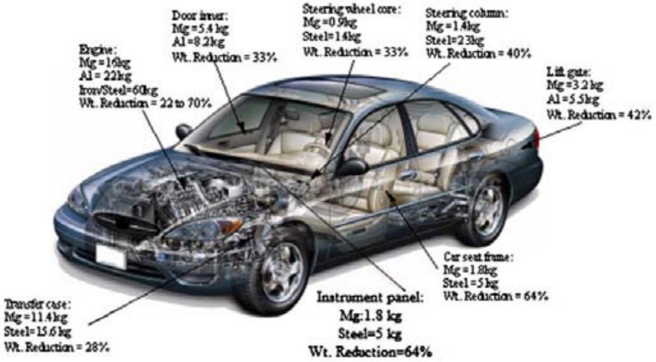
Current usage and potential applications in

- Automotive industry.
- Defense vehicle manufacturing and aerospace applications.
- Packaging solutions for IT devices.

The last B-36 built by Convair-Fort Worth was delivered to the Air Force August 14, 1954.



Schematic of Mg components used in the B-36 bomber.
Image courtesy of R. E. Brown. Magnesium Assistance Group, Inc.



Automotive components made of Mg alloy and the weight reduction.
M.K. Kulekci, Int. J. Adv. Manuf. Technol. (2008) 39:851.

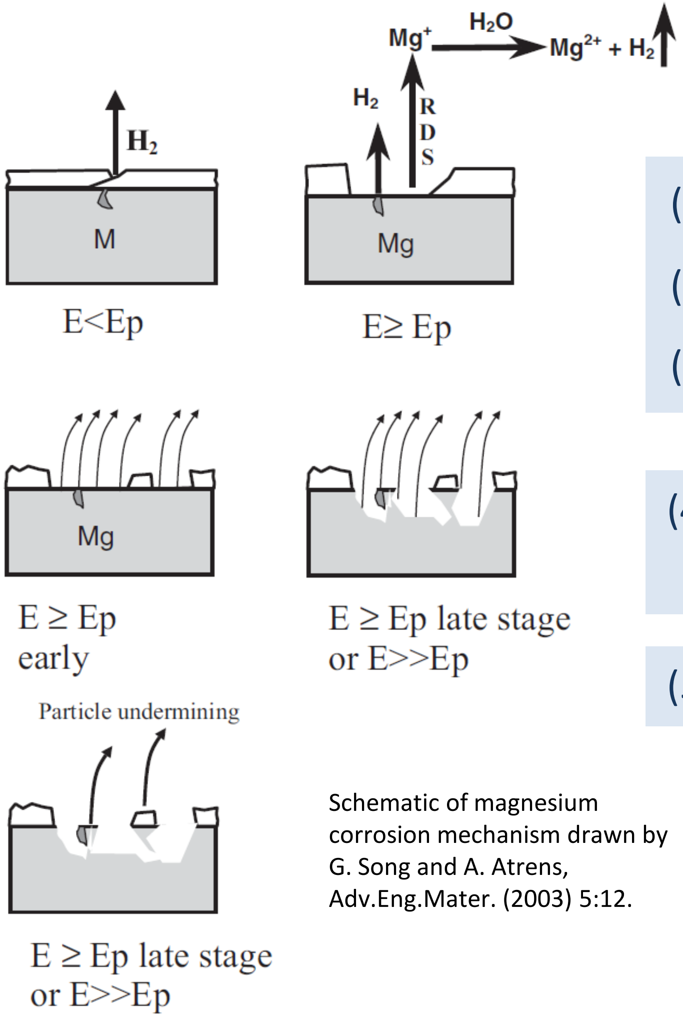
The biggest obstacle is its **poor corrosion and wear resistance** over regular exposure to harsh conditions which could result in:

- Atmospheric corrosion under severe condition.
- Corrosion in aqueous solutions via macro- and micro-galvanic corrosion.
- Environmentally assisted cracking from stress corrosion cracking and hydrogen embrittlement.

Surface Degradation of Magnesium

A simplified picture with the key electrochemical steps

[G. Song and A. Atrens, Adv. Eng. Mater. (2003) 5:12]



Schematic of magnesium corrosion mechanism drawn by G. Song and A. Atrens, Adv.Eng.Mater. (2003) 5:12.

(1) $2H^+ + 2e^- \rightarrow H_2$ (cathodic partial reaction)

(2) $Mg \rightarrow Mg^+ + e^-$ (anodic partial reaction)

(3) $2Mg^+ + 2H_2O \rightarrow 2Mg^{2+} + 2OH^- + H_2$ (chemical reaction)

(4) $2Mg^+ + 2H^+ + 2H_2O \rightarrow 2Mg_2+ + 2OH^- + 2H_2$
(overall reaction) *

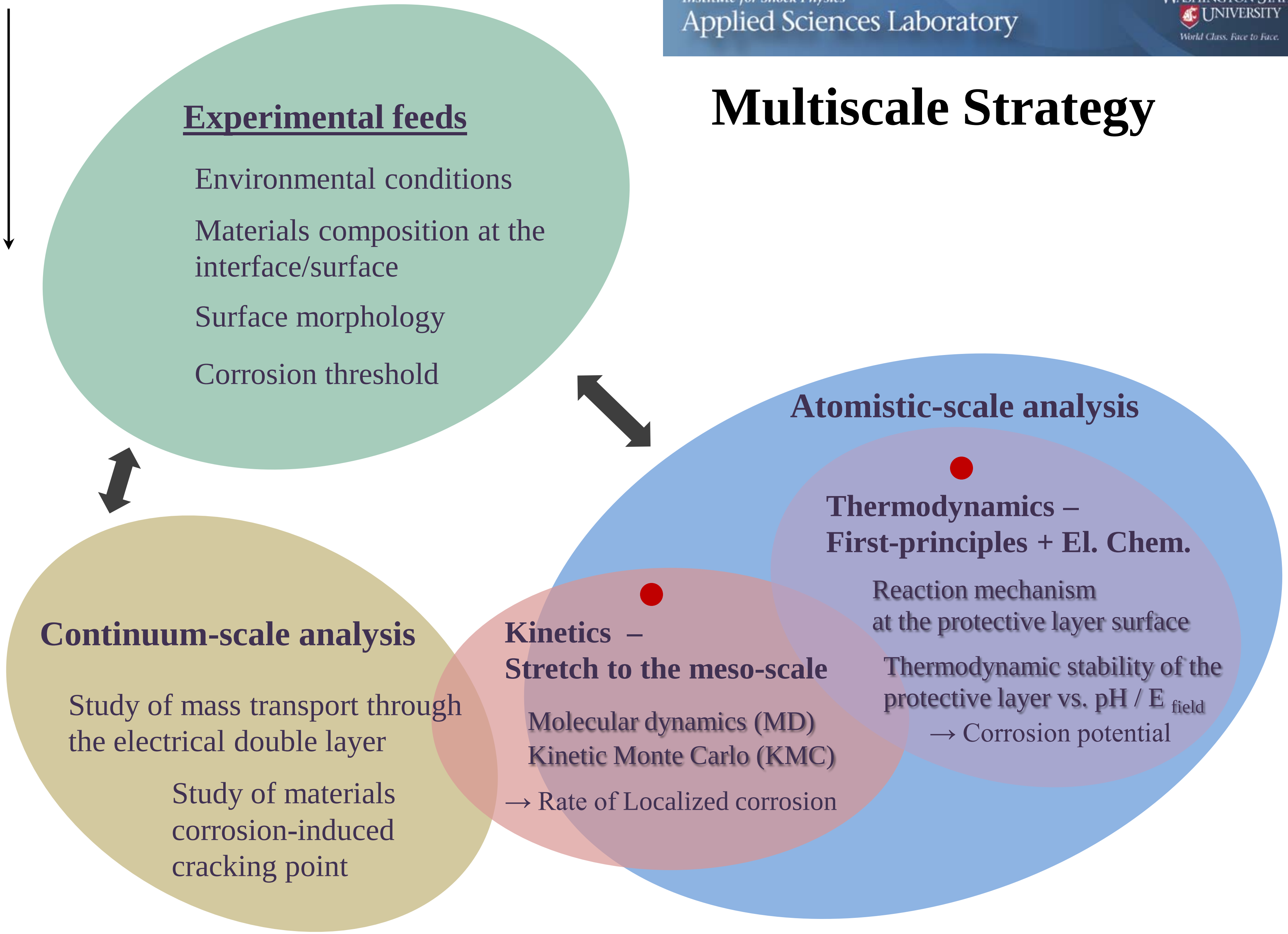
(5) $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ (product formation)**

*** (4) increases pH to favor (5); protective layer formation.**

**** $Mg(OH)_2$ protective layer plays a key role to the corrosion mechanism, e.g. negative difference effect (NDE).**

Multiscale Strategy

Numerical aspect



Experimental feeds

Environmental conditions

Materials composition at the interface/surface

Surface morphology

Corrosion threshold

Atomistic-scale analysis

Thermodynamics –
First-principles + El. Chem.

Reaction mechanism at the protective layer surface

Thermodynamic stability of the protective layer vs. pH / E_{field}
→ Corrosion potential

Continuum-scale analysis

Study of mass transport through the electrical double layer

Study of materials corrosion-induced cracking point

Kinetics –
Stretch to the meso-scale

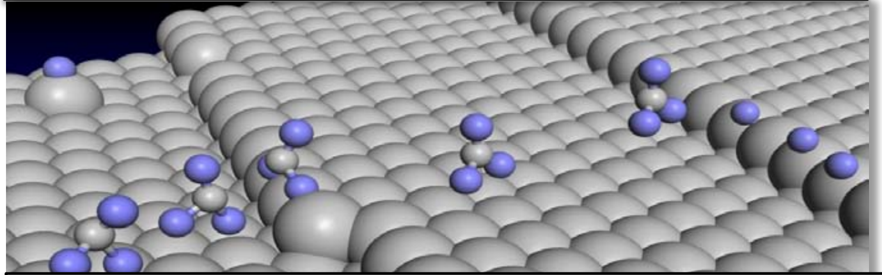
Molecular dynamics (MD)
Kinetic Monte Carlo (KMC)

→ Rate of Localized corrosion

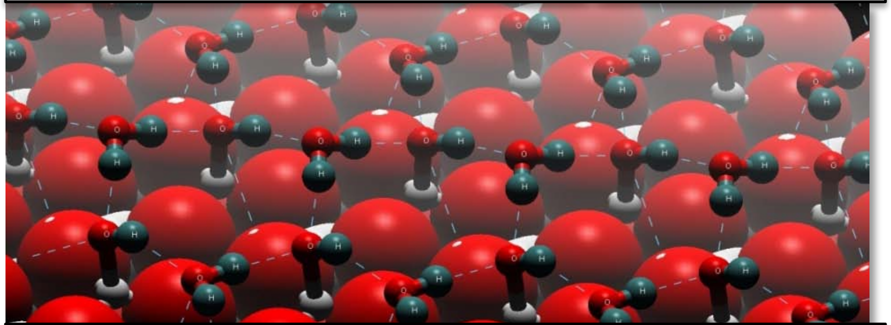
Theoretical frameworks

Length-scale

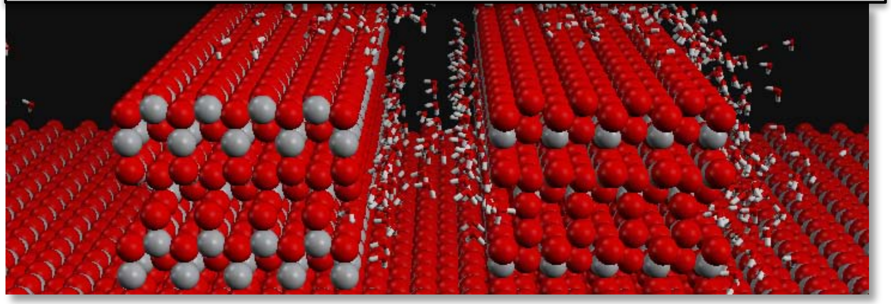
Step 1: Screening of Corrosion Reactions on Metal Surfaces and Doping Strategy to Counter Degradation

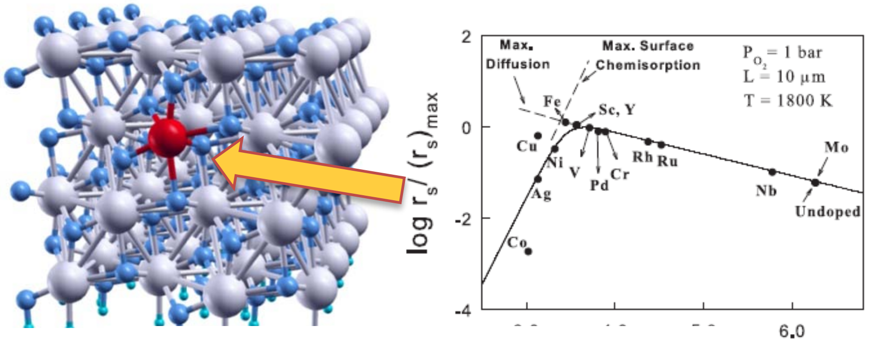


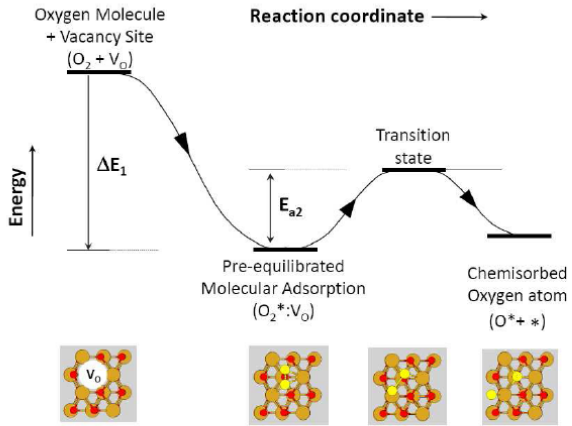
Step 2: Screening of Reactions on Oxide/hydroxide Surfaces with Ionic Species (H_2O, OH, H, Cl, SO_4 etc.)



Step 3: Transport and Solution Dynamics Calculations on Coatings for Slowing Down Corrosion







Task 1: Identify multi-dopant schemes for aiding surface stability using first-principles

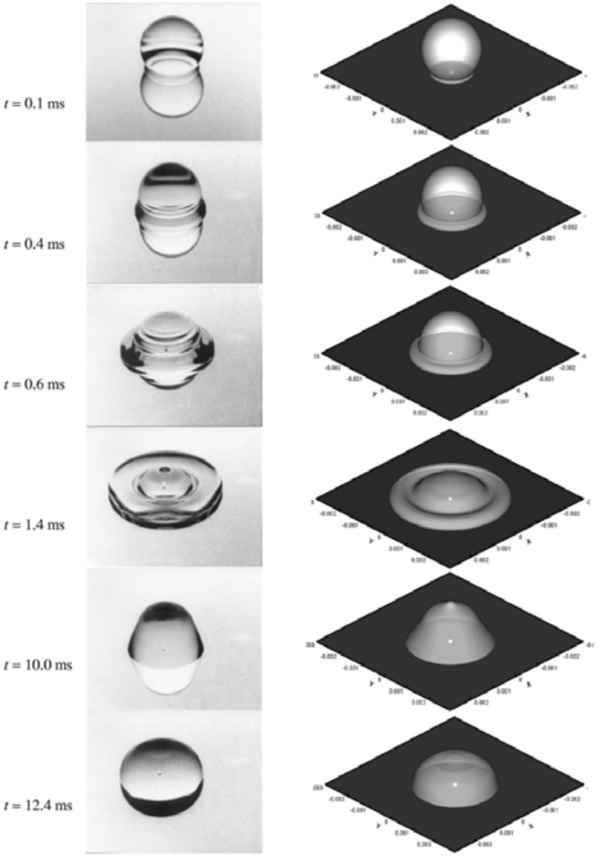
Task 2: Surface and bulk transport property calculations using MD/KMC in rough surfaces

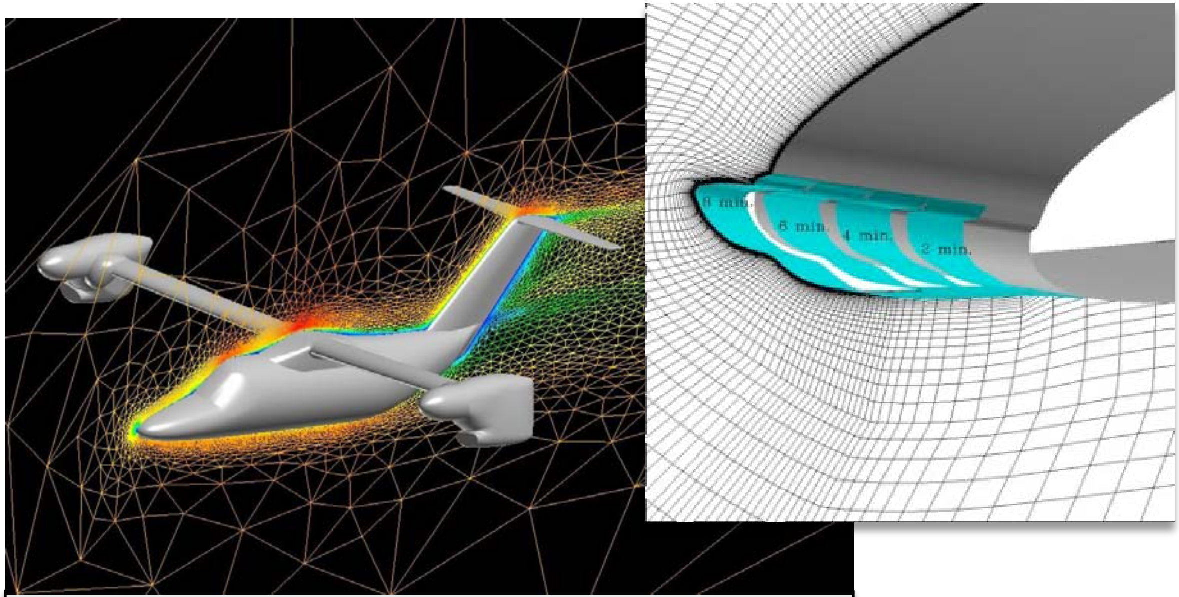
Challenge 1: Droplet Impact and Icing

Linking Atomistic Simulation and Fluid Dynamics to Design Anti-Icing Coatings

Santanu Chaudhuri, *Katie Mackie*, *Martin Losada*
Materials Modeling and Simulations Group

Icing: Atomistic to CFD Scale





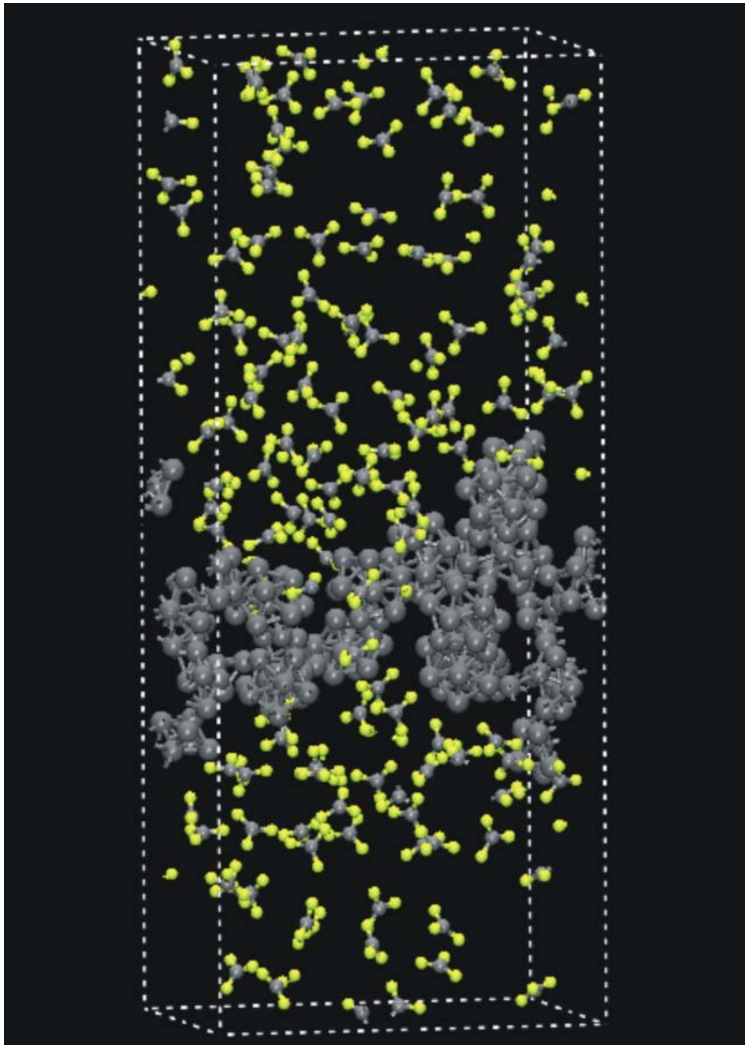
FENSAP-ICE – 3D Icing Model

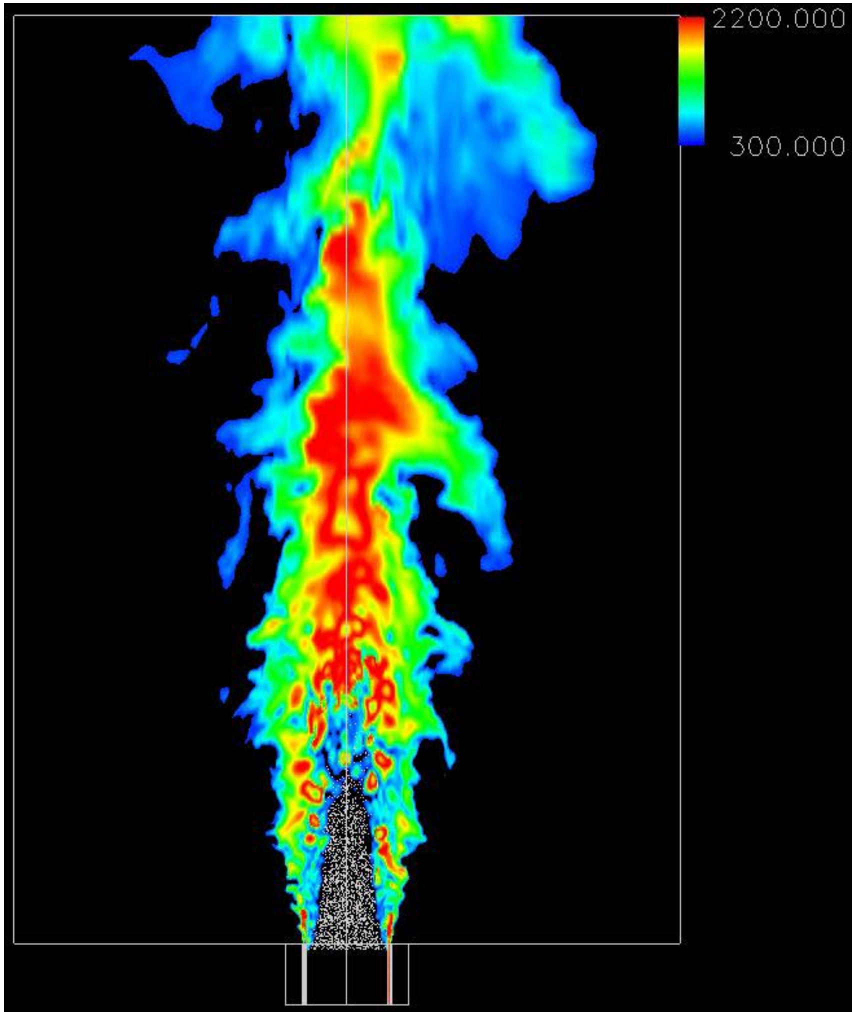
Structure and Aerodynamics Scale: Constant volume methods connecting suspended droplets stream at different air temperatures to ice accretion rates

Intermediate Scale: Droplet impact model – using LAMMPS for droplet impact on surfaces

Can nanoscale water droplet simulation be extended to micro/macroscale icing under flow of suspended droplets?

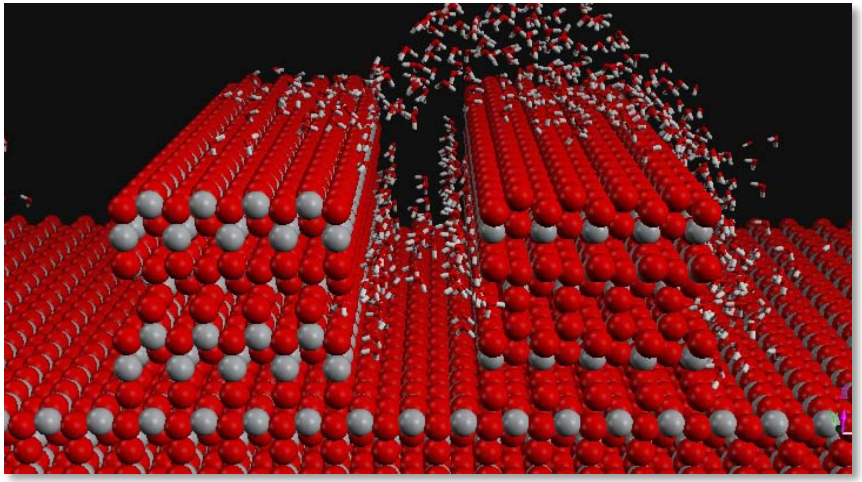
Challenge 2: Reactive Flow

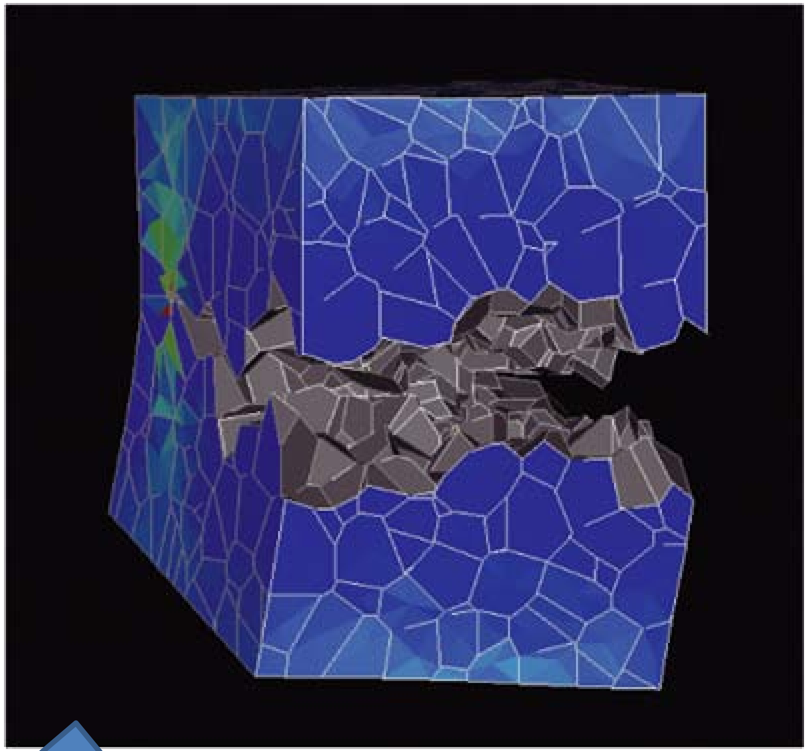




Large Eddy Simulation and Reactive Flow Dynamics for quantifying changes in first-principles predicted results

Challenge 3: Multiscale Corrosion





JAEA R&D Review

Connecting atomistic MD and KMC routines to macroscale corrosion rates and failure mechanisms

Summary

- We are at a crossroads where many exciting problems are open to new solutions

- Multiscale simulations provide platform for multidisciplinary science

- LAMMPS can spur growth as a collaborative platform for solving high-impact problems