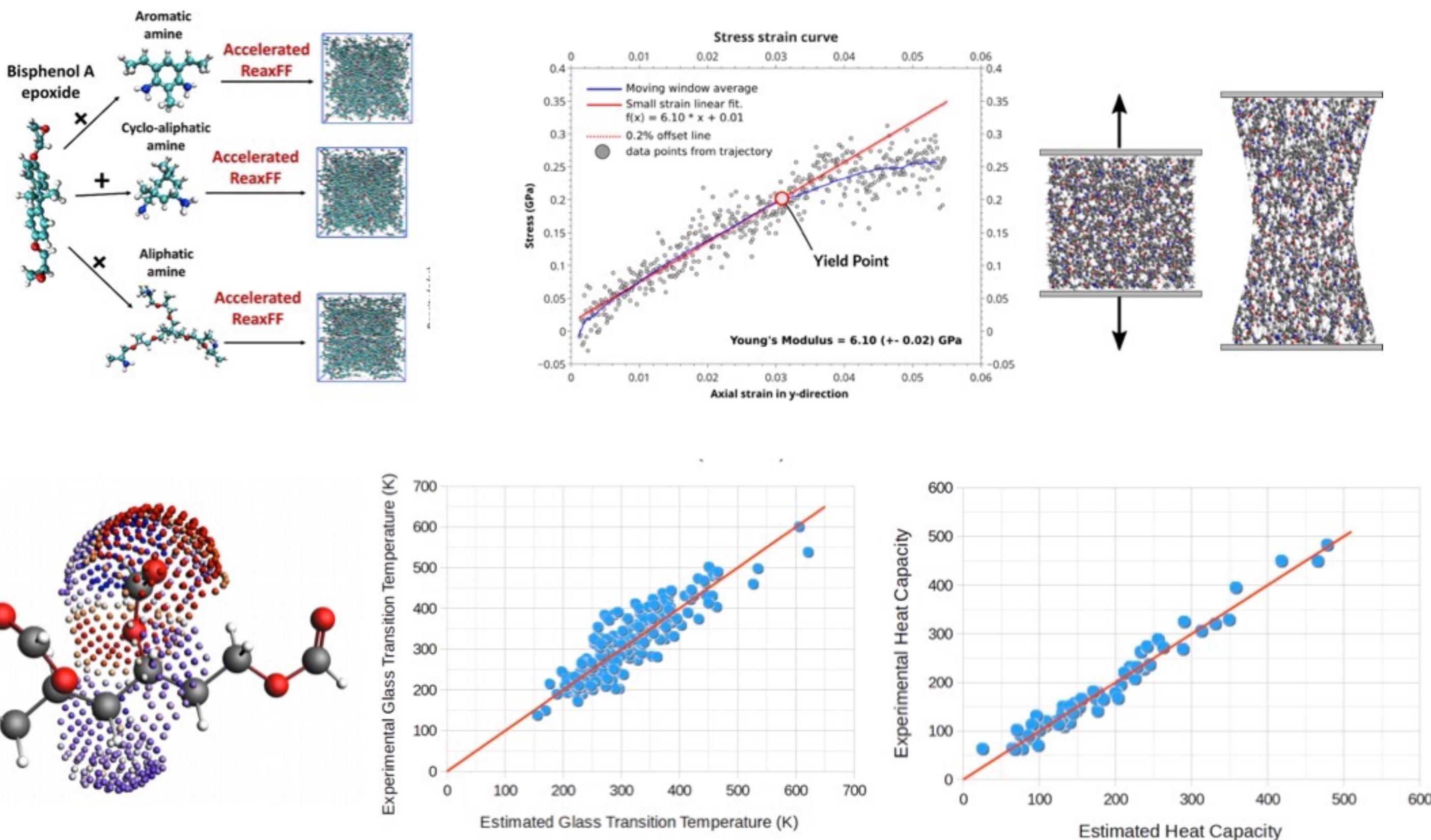


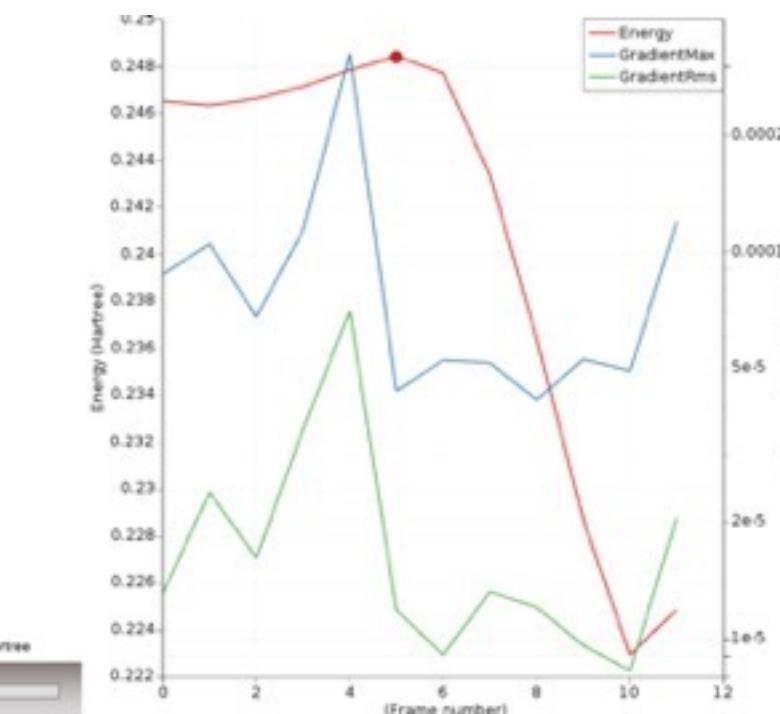
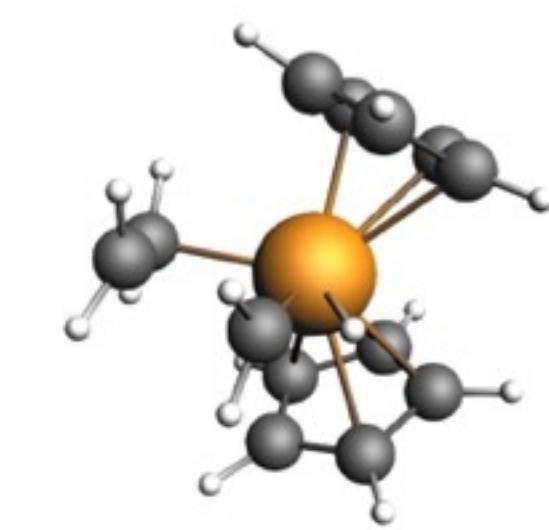
# Chemistry & Materials with the Amsterdam Modeling Suite: Polymers



# Simulating polymers: predict & understand

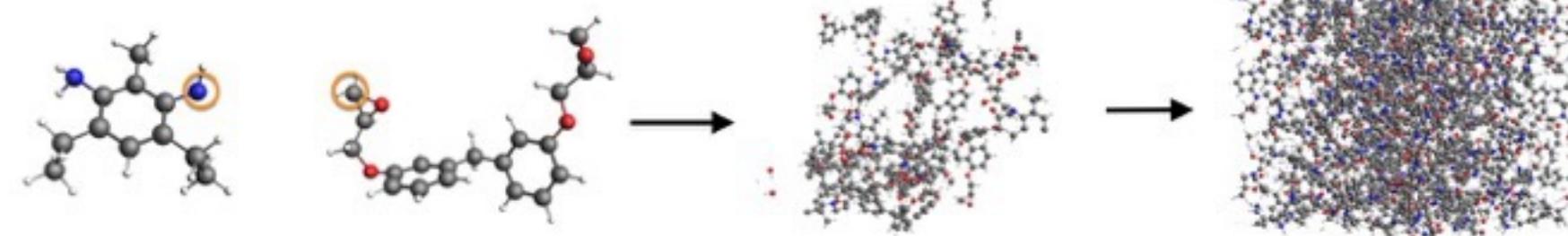
- Formation & curing

- Catalytic
- Thermally activated
- Free radical



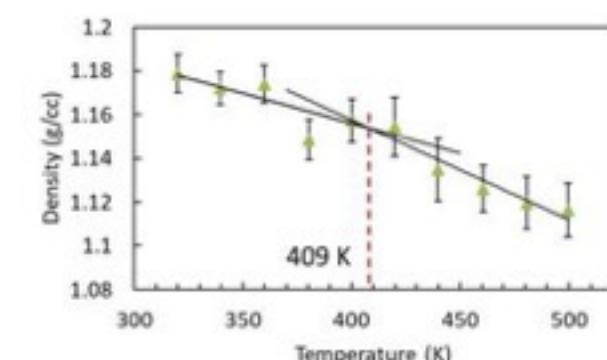
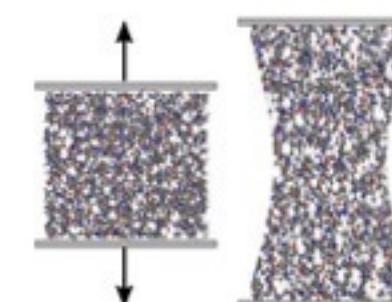
- Mechanical properties

- Moduli, stress-strain, CTE, Tg, yield point
- Degradation rates & mechanisms
- Heat transport (T-NEMD)



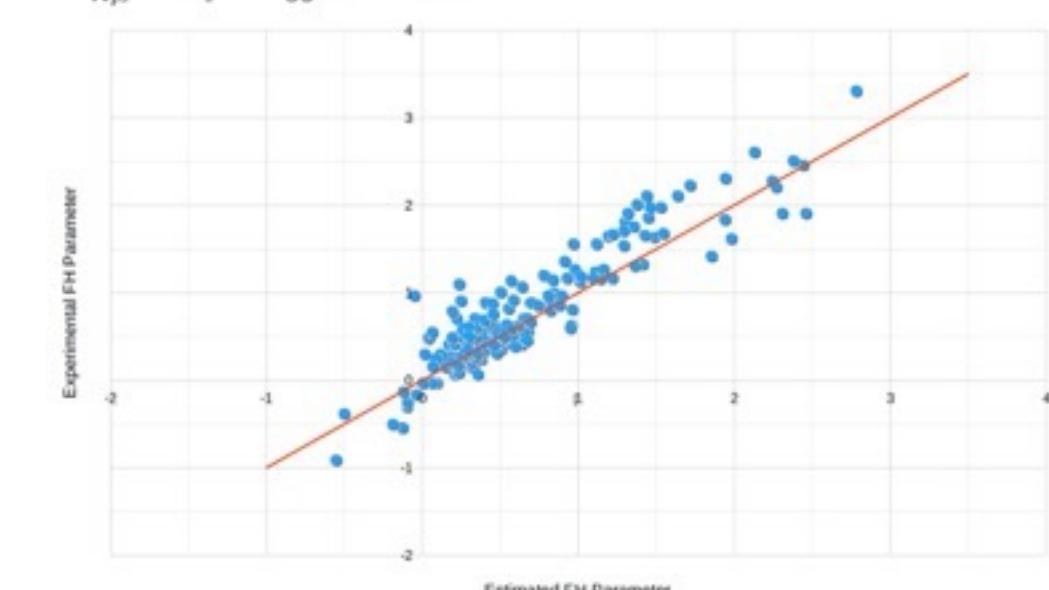
- Solubility, mixtures, sorption

- Recovery & extraction
- Blends & stability



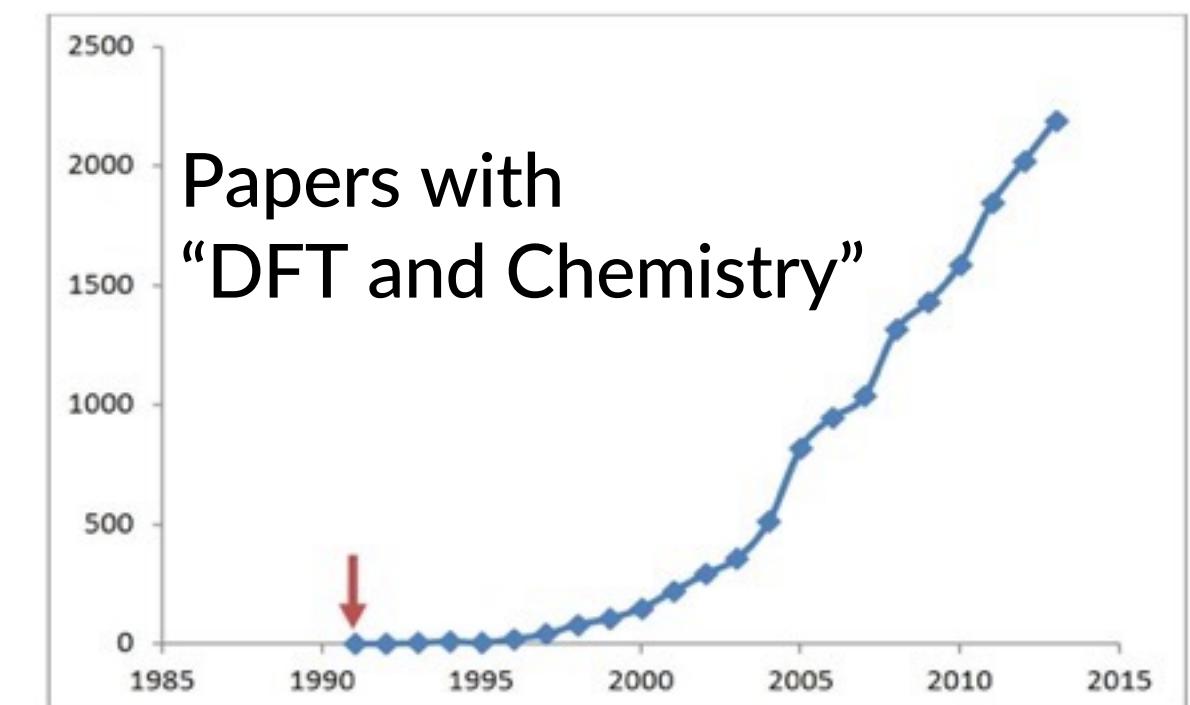
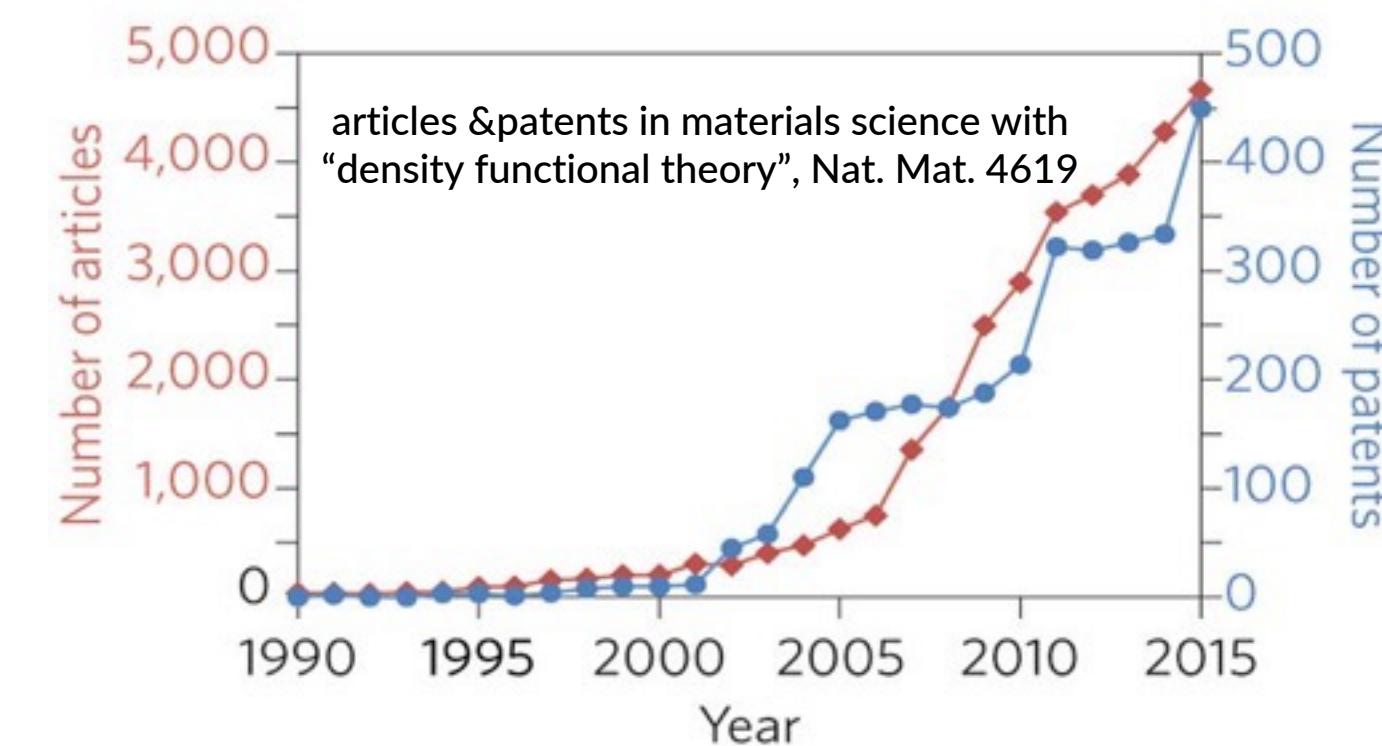
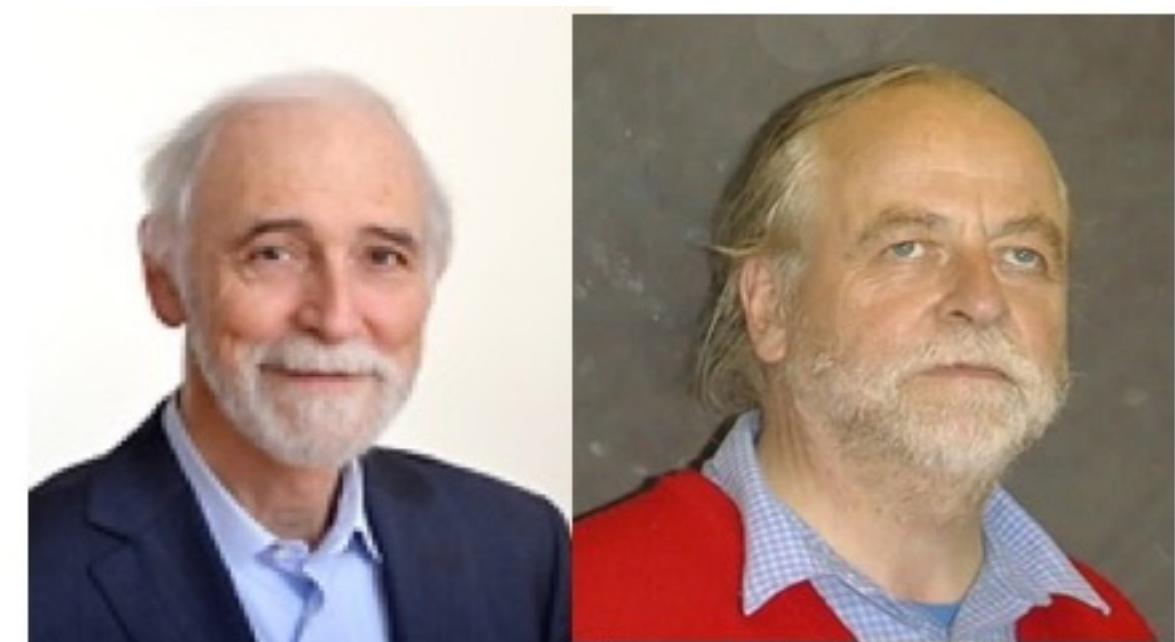
- (Optical & electronic properties)

- Dielectric function
- Electrode Potential, charge mobility



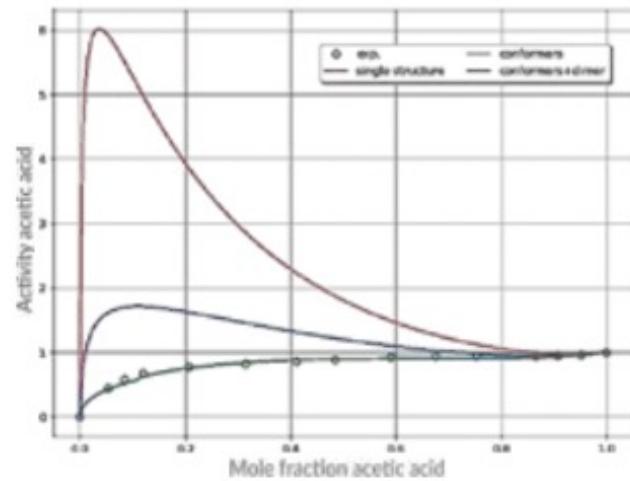
# Background: SCM, ADF & AMS

- ADF: first DFT code to understand chemistry (1970s)  
Baerends@VU (>'73), Ziegler@Calgary<sup>(+)</sup> (>'75)
- 1980s: Mitsui, Shell, Akzo, Unilever: training@Amsterd
  - Tom Ziegler => Ziegler-Natta catalysts, hydroformulation
  - BAND for periodic systems
- SCM: Spin-off company 1995
  - To keep supporting users
- 2010s: DFTB, ReaxFF, COSMO-RS (Albemarle, DSM)
- 2019: Multi-scale: ReaxPro (BASF, Dow, Shell, JM)
- 23 people (19 senior PhD's) + 5 EU fellows
- Many academic collaborators & EU networks
- SCM: development, debug, port, optimize, & support

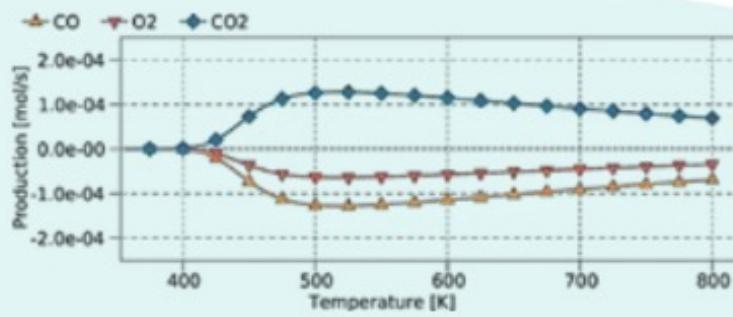


# Amsterdam Modeling Suite

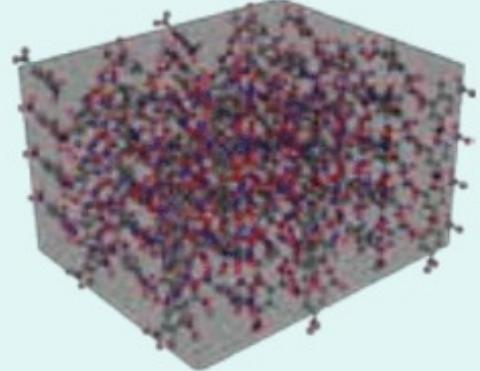
Continuum



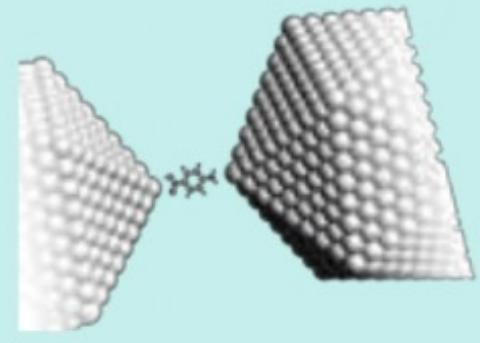
Mesoscale



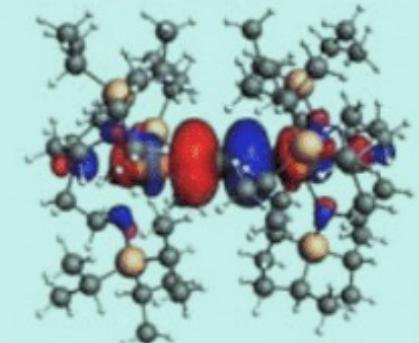
Materials



Nano



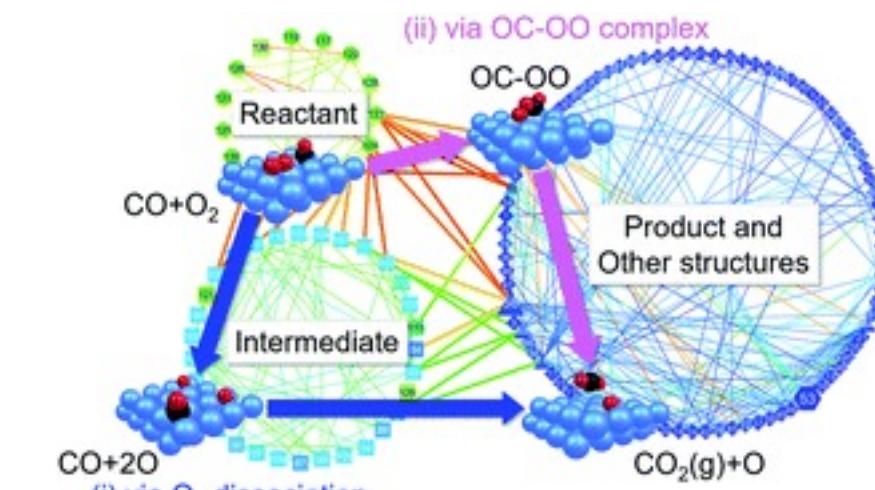
Atomistic



## Fluid Thermodynamics

COSMO-RS  
COSMO-SAC  
UNIFAC

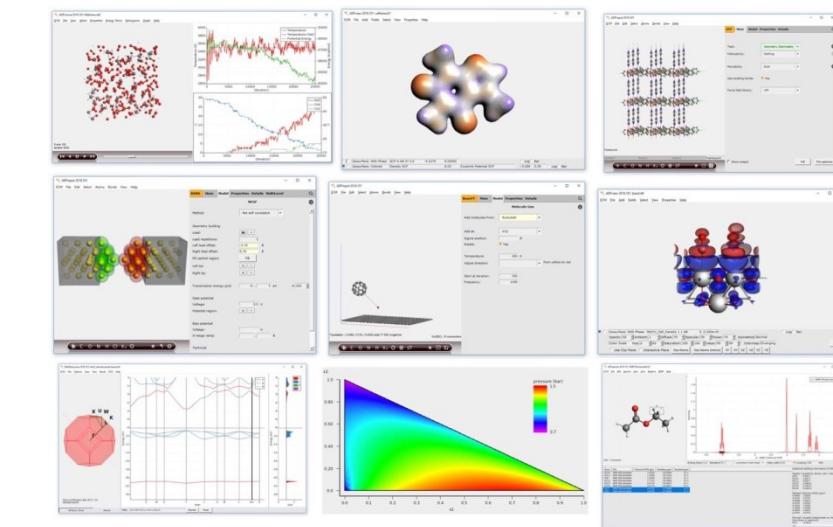
- MD, MC PES exploration



## Kinetics

Kinetic Monte Carlo  
Microkinetics

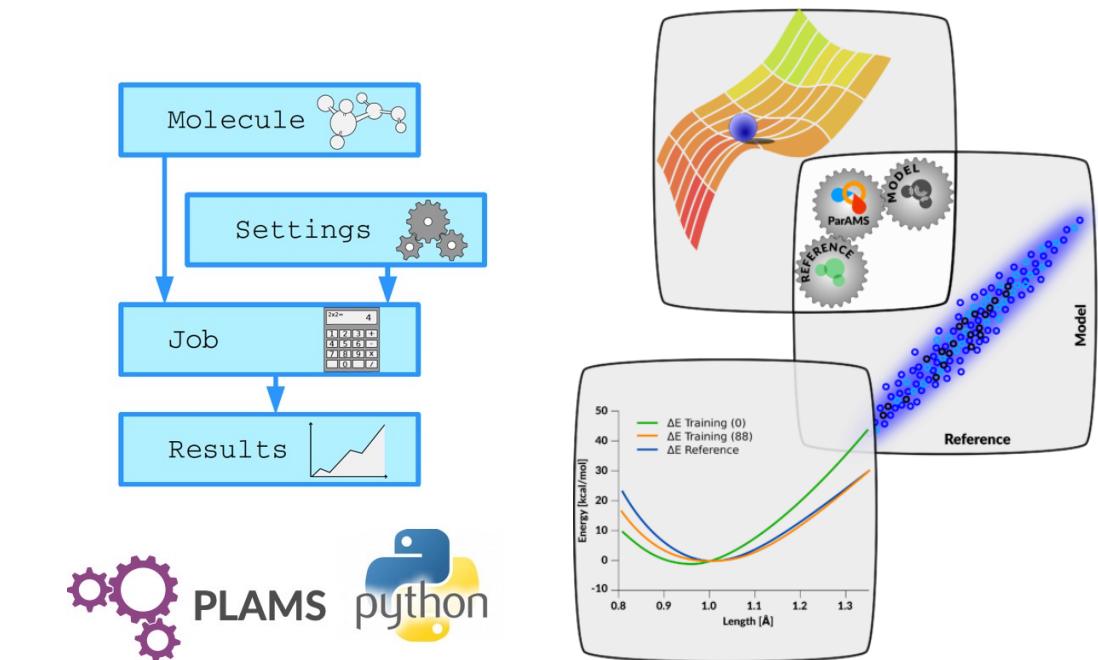
- Integrated GUI



## Force Fields

ReaxFF, GFN-FF  
Machine Learning Potentials  
Apple & P

- Python scripting (workflows)



## QM/MM

FDE, Hybrid Engine

## Tight binding

GFN-xTB, DFTB

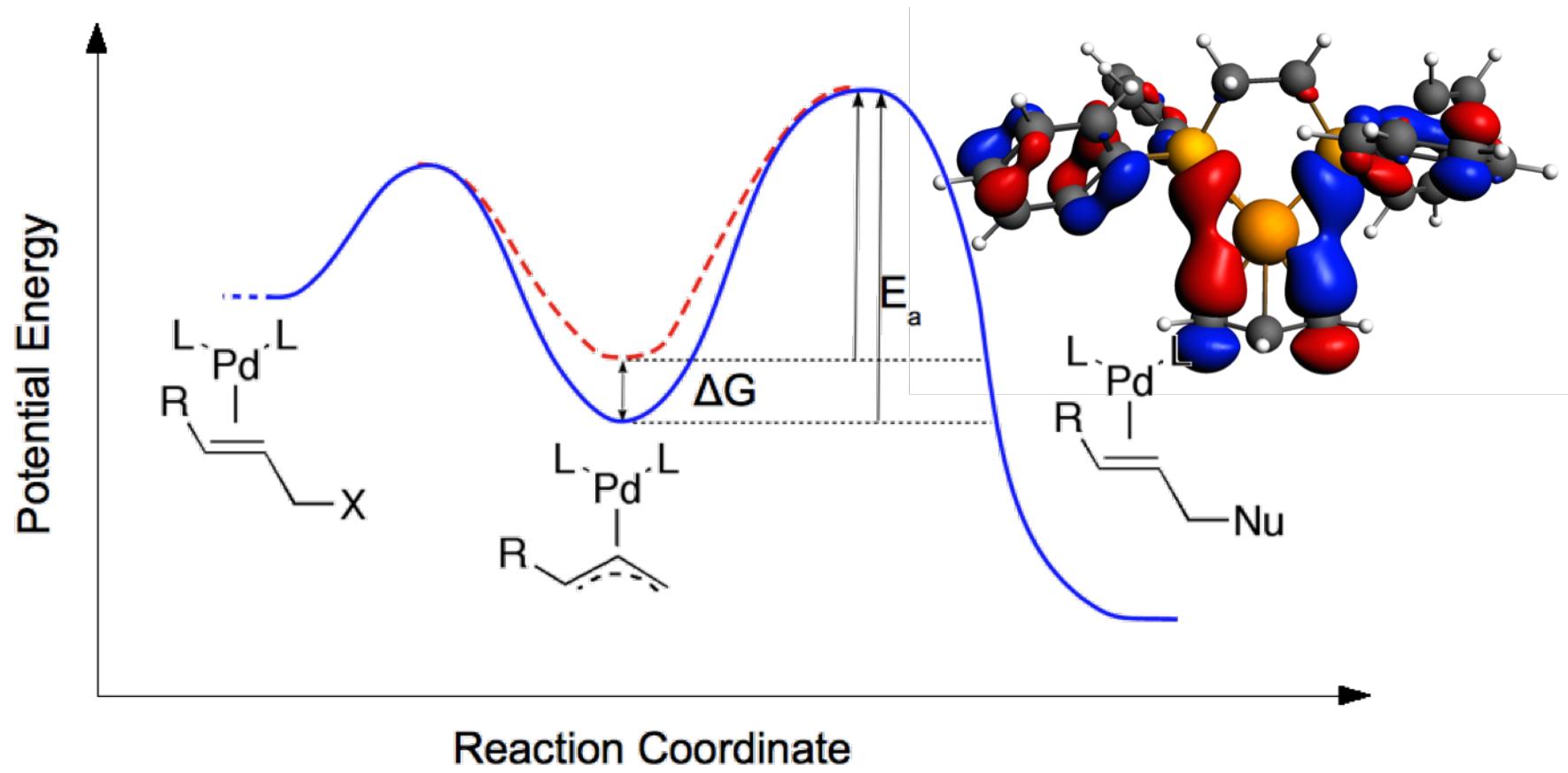
## Periodic DFT

BAND, Quantum Espresso

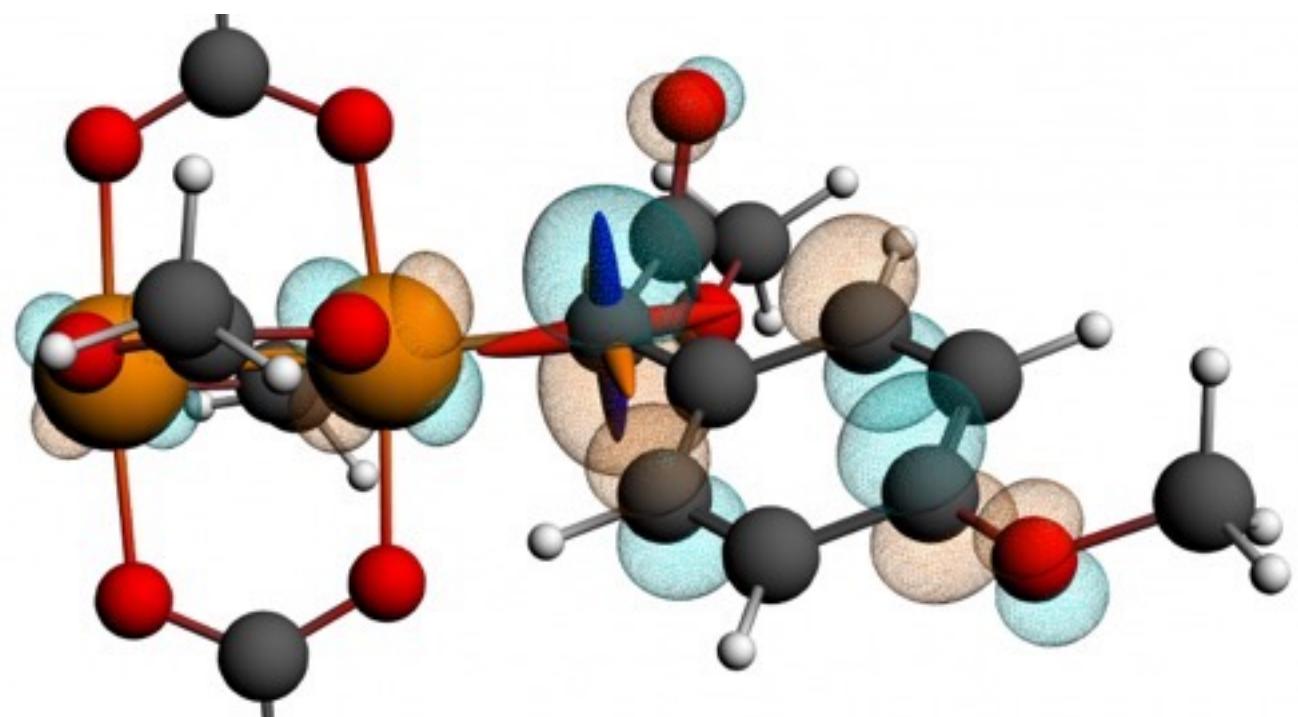
## Molecular DFT

ADF

# ADF: Molecular DFT



Bonding analysis: Understanding Catalyst-Substrate Interactions [Nature Chem. 2, 417 \(2010\)](#)



NMR calculations locate  $^{13}\text{C}$  di-Rh carbene catalyst intermediate, [Science, 342, 351 \(2013\)](#)

## Strong & unique points

- All-electron Slaters, H-Og
- Relativity: ZORA (SR, SOC)
- Spectroscopy
  - EPR, NMR, IR (VCD), UVVIS, XANES
- Fast double hybrids (energies)
- Bonding analysis
  - Fragment-based approach
  - ETS-NOCV, QTAIM, MO diagrams, NCI, Fukui function, dual descriptor
  - Transfer integrals
- Environments
  - Subsystem DFT (FDE), QM/MM, QM/QM', polarizable force fields
  - SM12, COSMO
  - 3D-RISM

# Analyzing reactivity

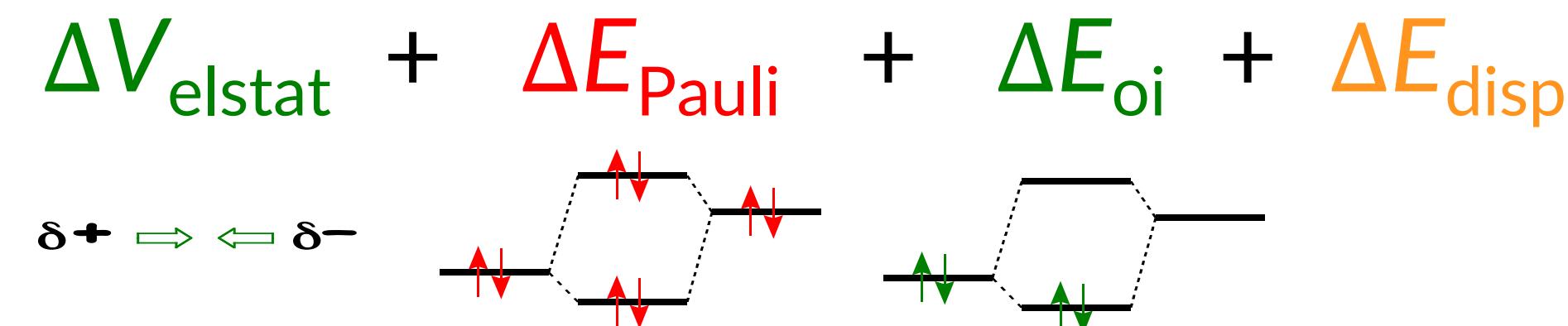
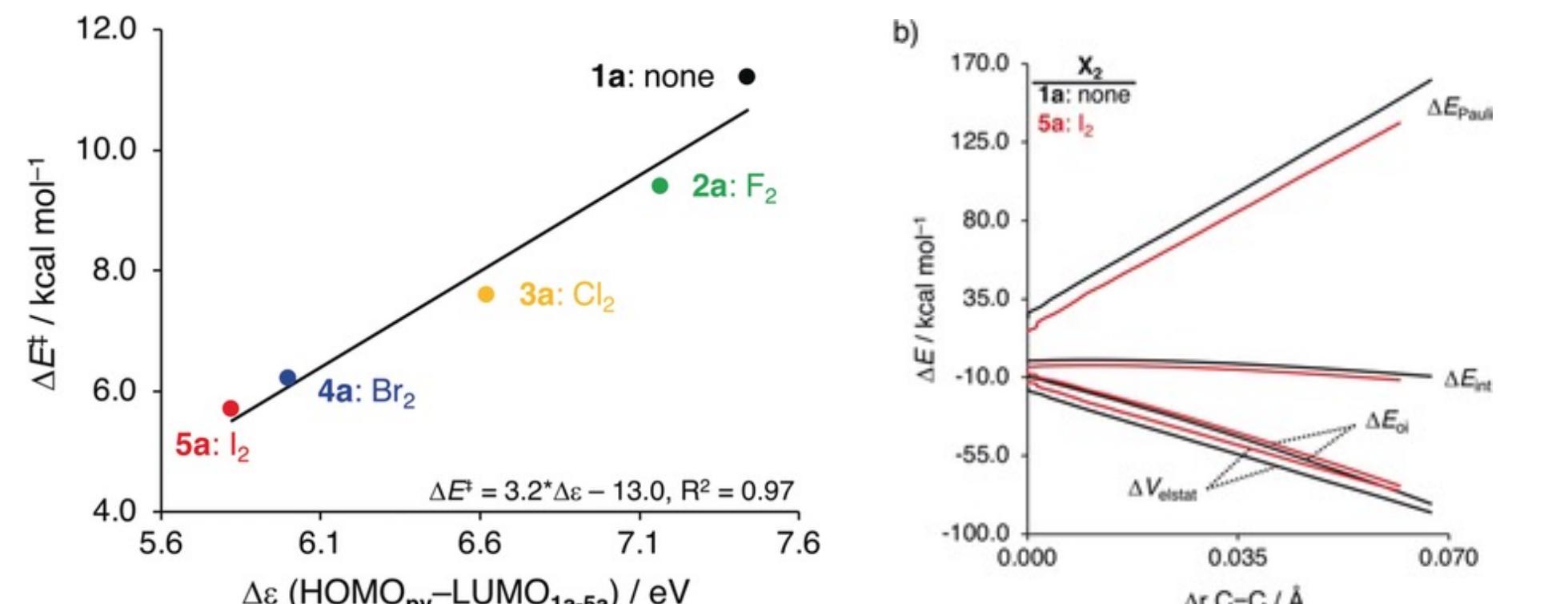
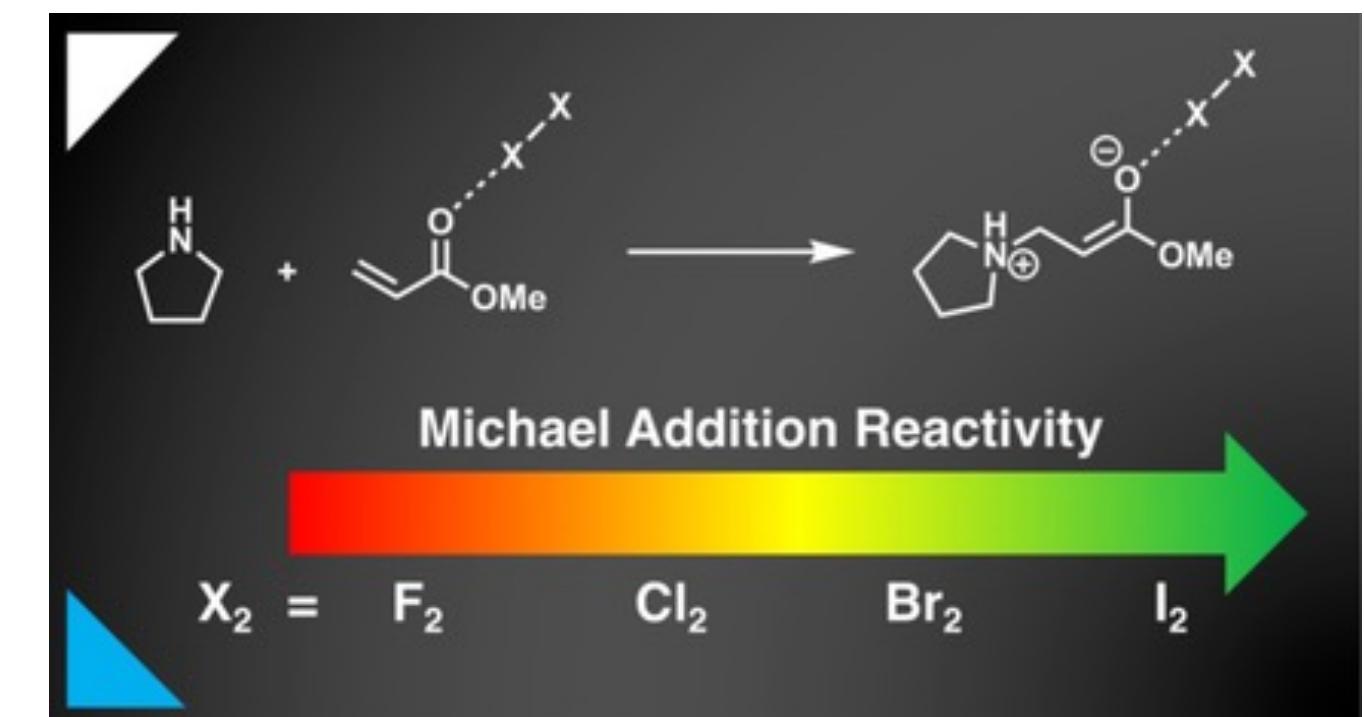
- Transition States -> rates
  - Harmonic TST
  - [microkinetics, kinetic Monte Carlo](#)
- Conceptual DFT
  - [Fukui function, dual descriptor](#)
- Bonding analysis
  - [Energy decomposition](#)
  - Activation strain analysis
  - => 'design' catalysis

Bickelhaupt, Hamlin, Vermeeren, ...

Chem. Soc. Rev. 2014, 43, 4953;

WIREs Comput. Mol. Sci. 2015, 5, 324

[Chem. Commun., 2021, 57, 5880](#)

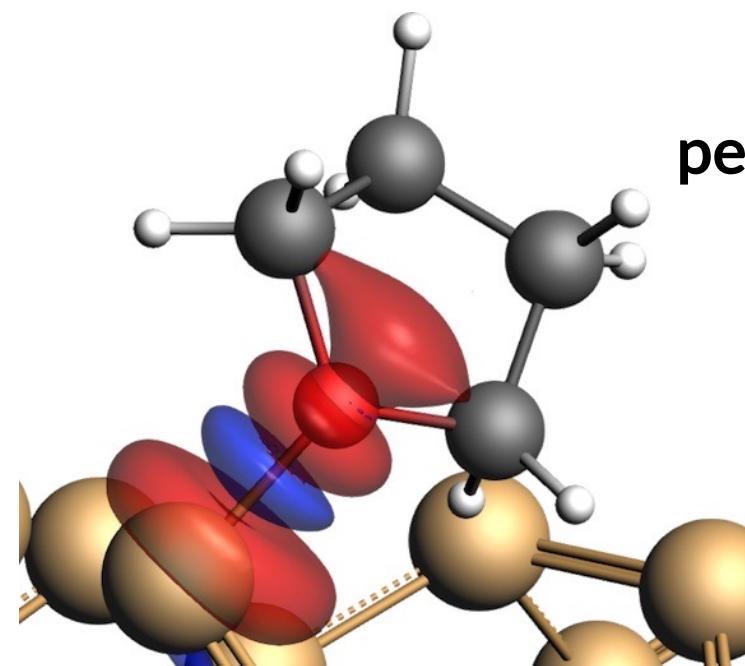


Heavier halogen reduces Pauli repulsion in aza-Michael TS,  
[Angew.Chem.Int.Ed. 58, 8922 \(2019\)](#)

# BAND vs. Plane Wave codes (QE)

- Atom centered basis functions, STO or NAO

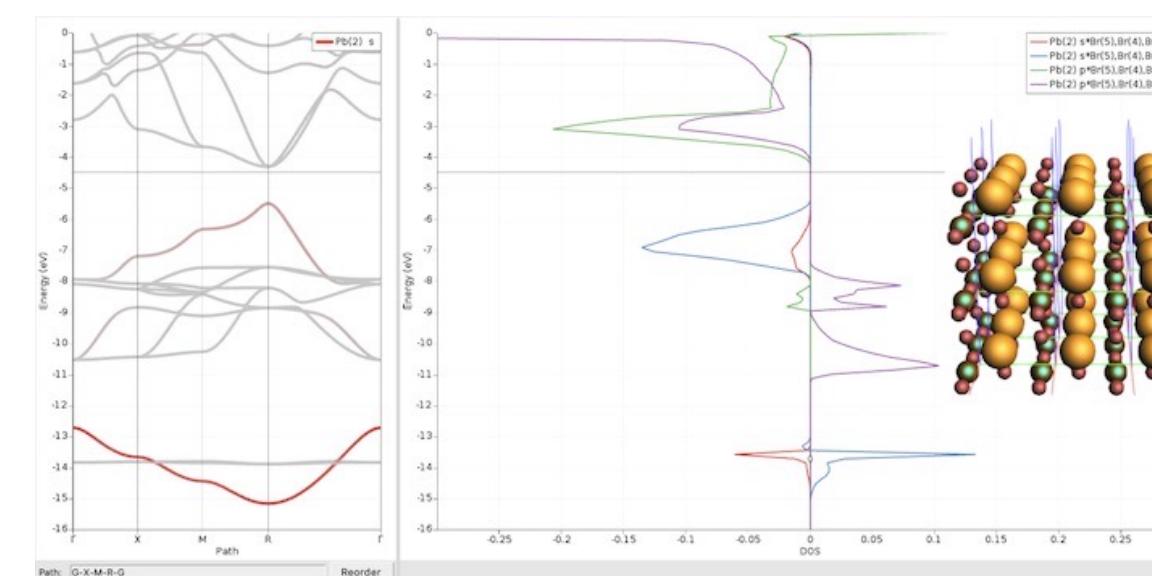
- Compare cluster with periodic
- No pseudopotentials, all elements
- Core spectroscopy (core holes)
- Easy orbital analysis: pDOS, COOP, EDA
- Fast for empty (1D, 2D, porous)
- xc: SCAN, MN15-L, HSE06, GLLB-sc, D3(BJ), DFT-1/2
- Self-consistent NEGF



periodic energy decomposition analysis ([tutorial](#))  
L. Pecher and R. Tonner  
[WIREs CMS, \(2018\)](#)

- True 2D surfaces, 1D polymers

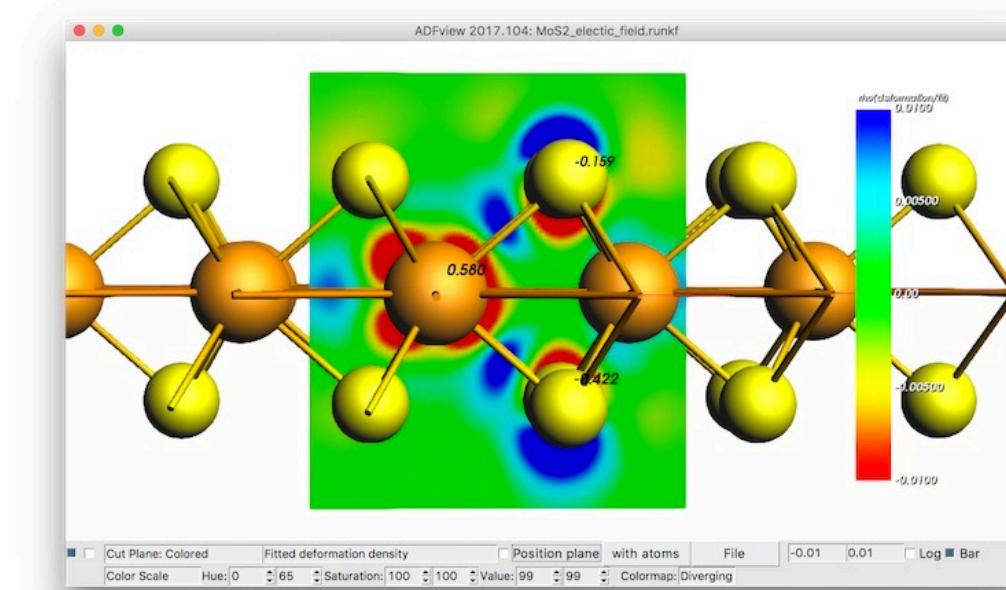
- Solvation: COSMO, SM12
- 1D, 2D electronics (homogeneous E field)
- Nanotubes



COOP in perovskites ([tutorial](#))  
Goesten & Hoffmann  
[JACS \(2018\)](#)

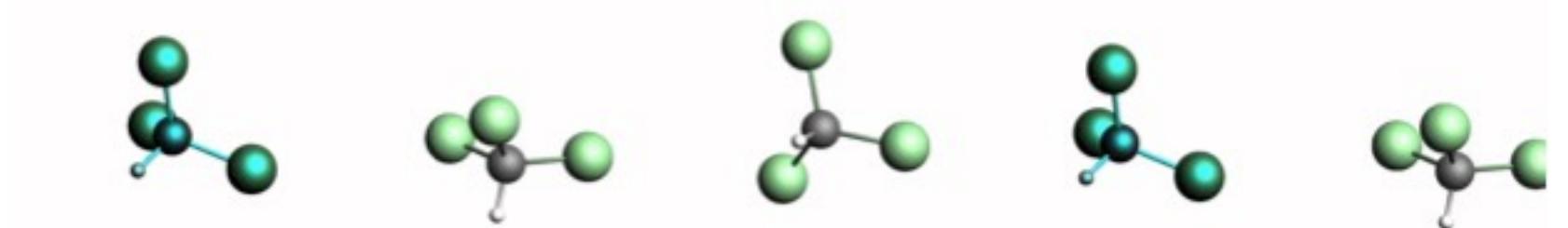
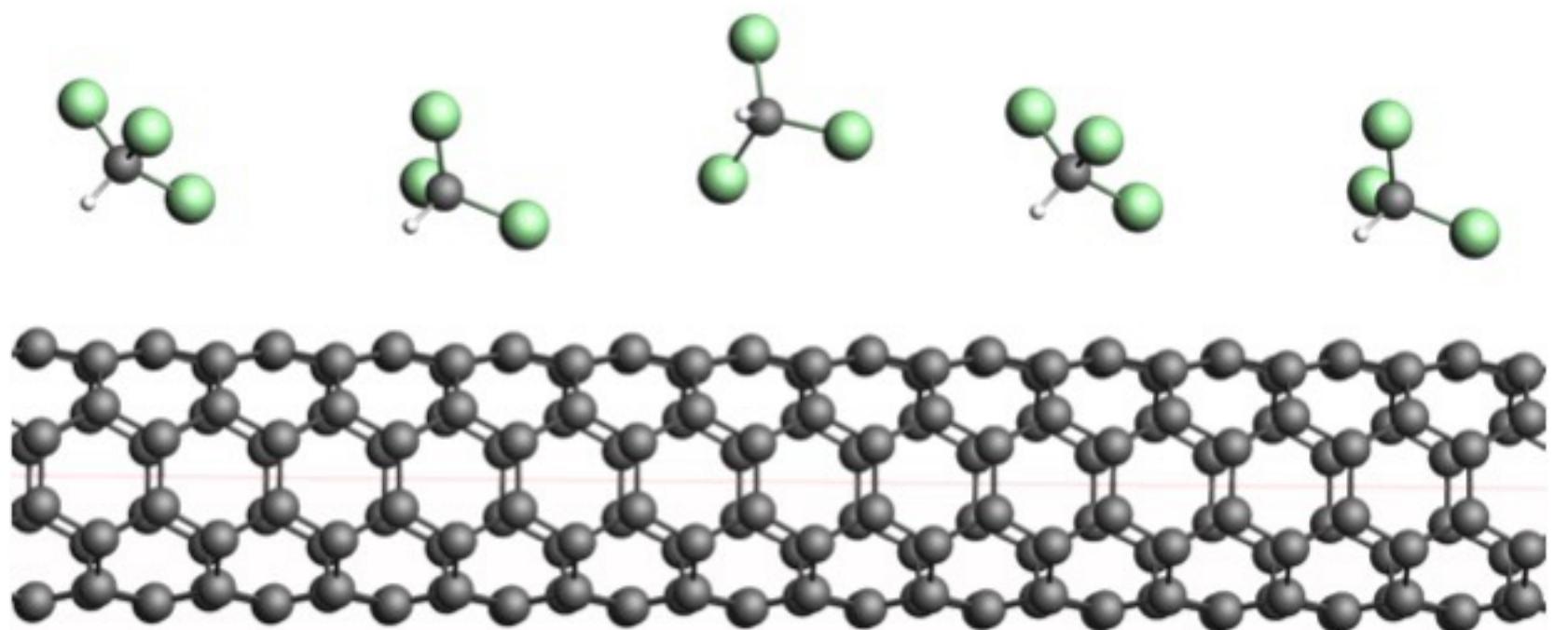
- Integrated Graphical Interface:

- Easy set up & analysis
- Switch: ADF, BAND & QE (VASP)

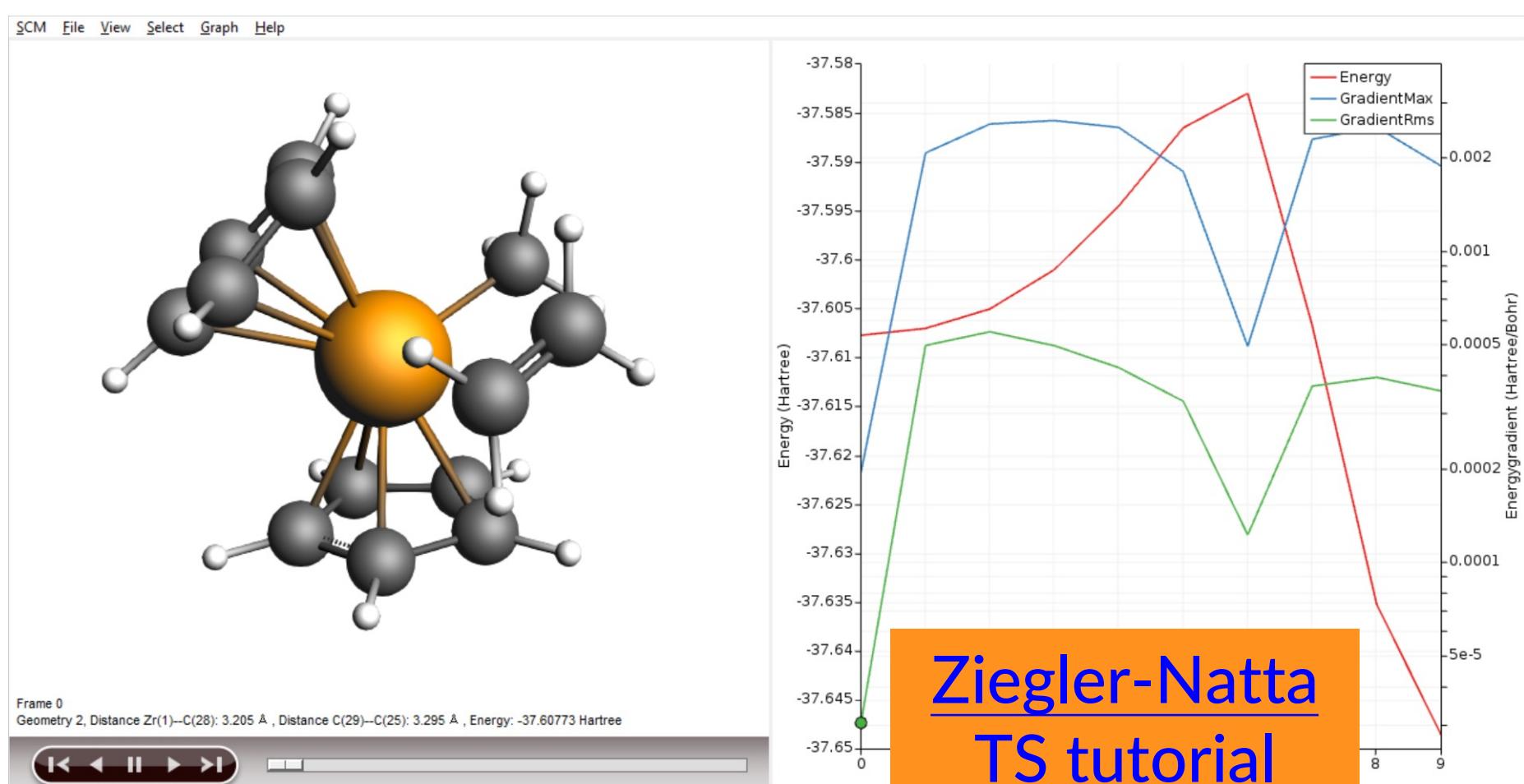


Polarizing 2D semiconductor ([tutorial](#))  
N. Zibouche et al.  
[PCCP \(2014\)](#)

# DFTB: 'fast DFT' for molecules & periodic



[Video: making DWCNT](#)



## Approximated DFT

- Nearest neighbor & minimal basis
- Tabulated elec & rep. parameters:
  - Grimme GFN-xTB ( $Z = 1-86$ )
    - GBSA solvation
  - QuasiNaNo & DFTB.org

## Capabilities & Features

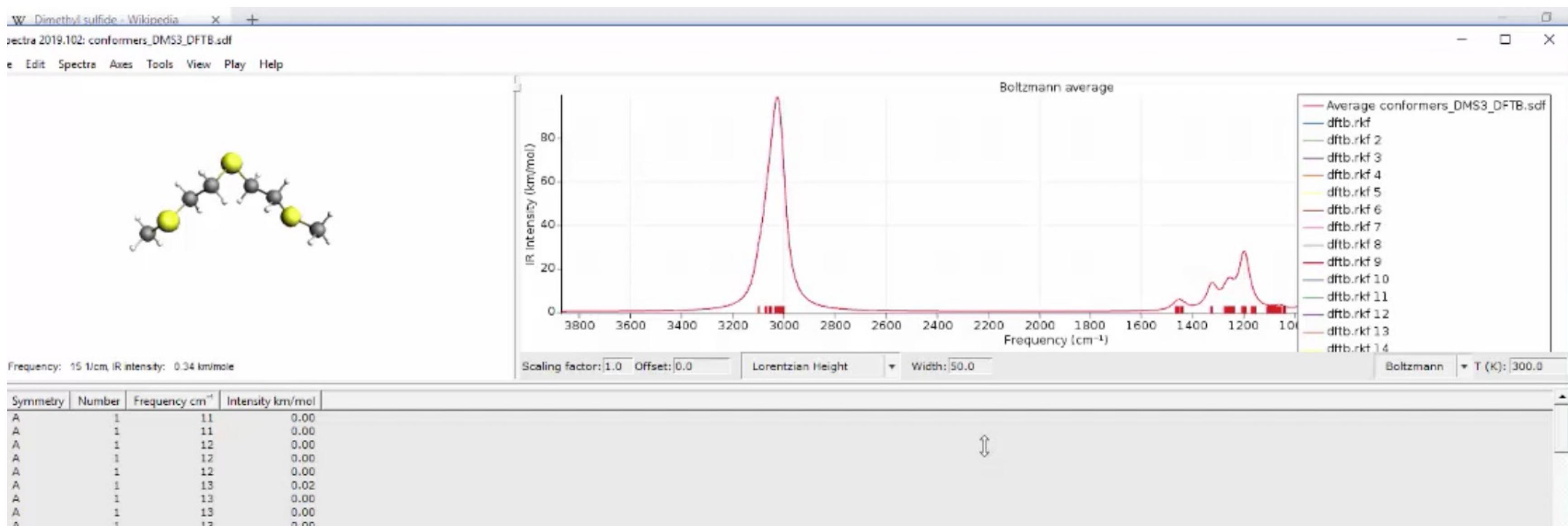
- UV/VIS for molecules (fast!)
- MOs, Band structures, DOS
- Molecules, 1D polymers, bulk

## DFTB & MOPAC + AMS driver

- Geometries, frequencies, phonons
- Stress tensors (optimize under p)
- Advanced MD, PES scans
- GCMC, molecule gun

# DFTB example: vibrations oligomer

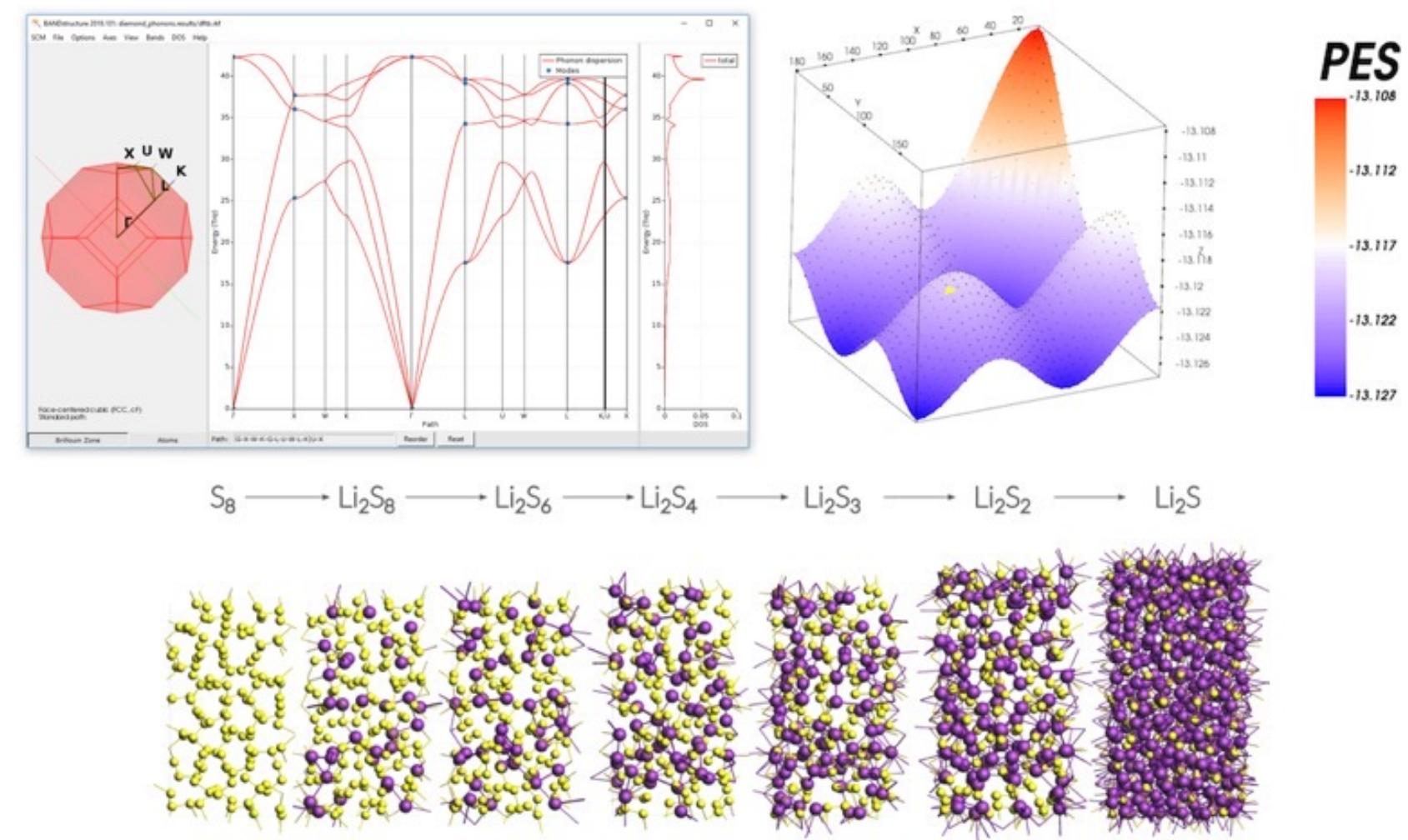
- Define new monomer
- Build oligomer
- Find lowest conformers
- Calculate IR (Boltzmann averaged) with DFTB



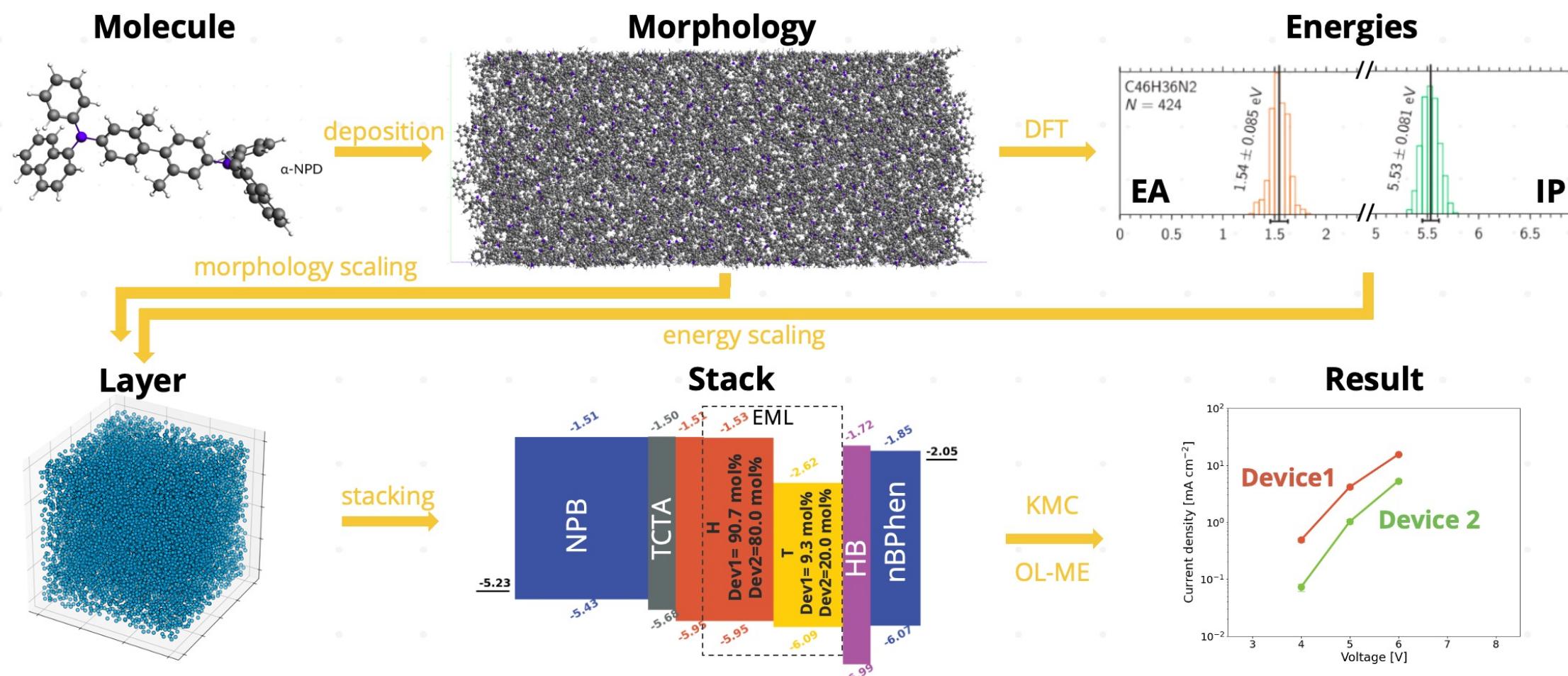
[Video IR spectrum polymer fragment](#)

# Machine learning in materials science

1. Direct Structure-Property prediction ‘QSPR’
2. Predict Potential Energy Surface (atomic coordinates)
  - Determine how atoms move in space & time
  - Predict various properties:
    - Chemical reactivity
    - Thermodynamics
    - Mechanical properties
    - Mobility rates
    - .....
3. Hybrid/other: e.g. predict reaction networks, interpolate kinetics (kMC) under different conditions

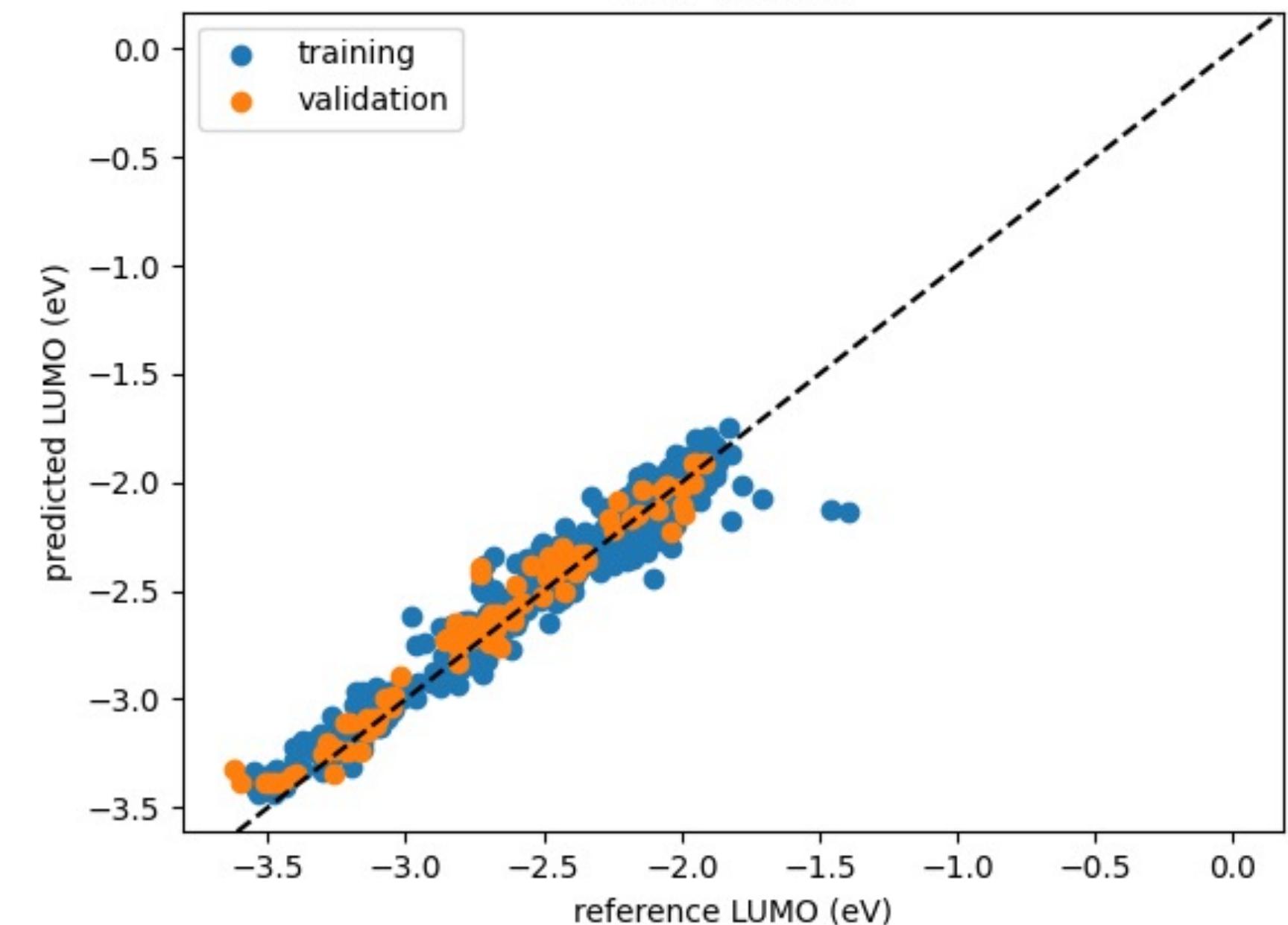


# ML predictions (for multi-scale OLED)

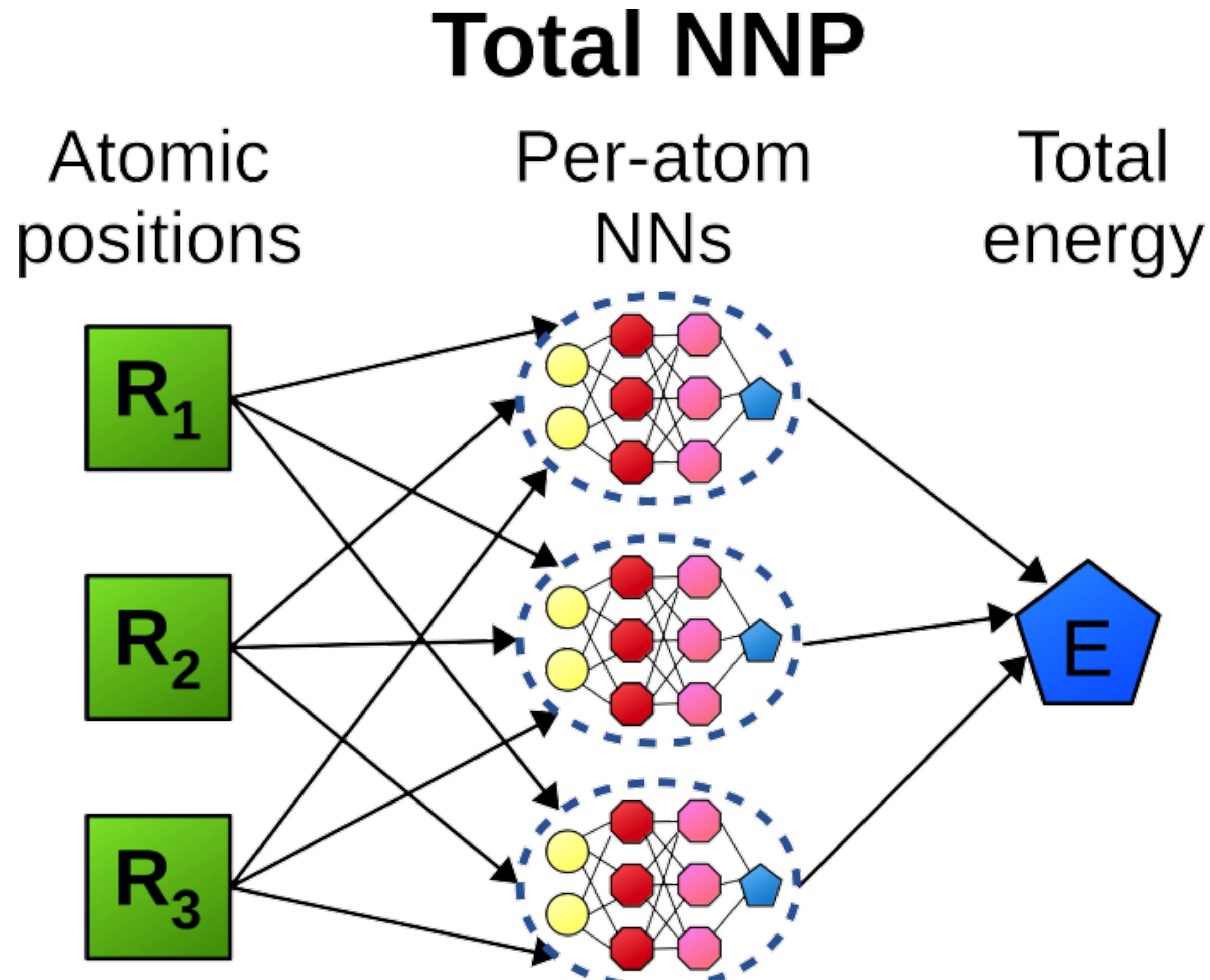


ECFP (1024)

- Environment effects important
- Fast GW (+BSE)
- IP, EA well trained with NN
- Bottleneck: deposition



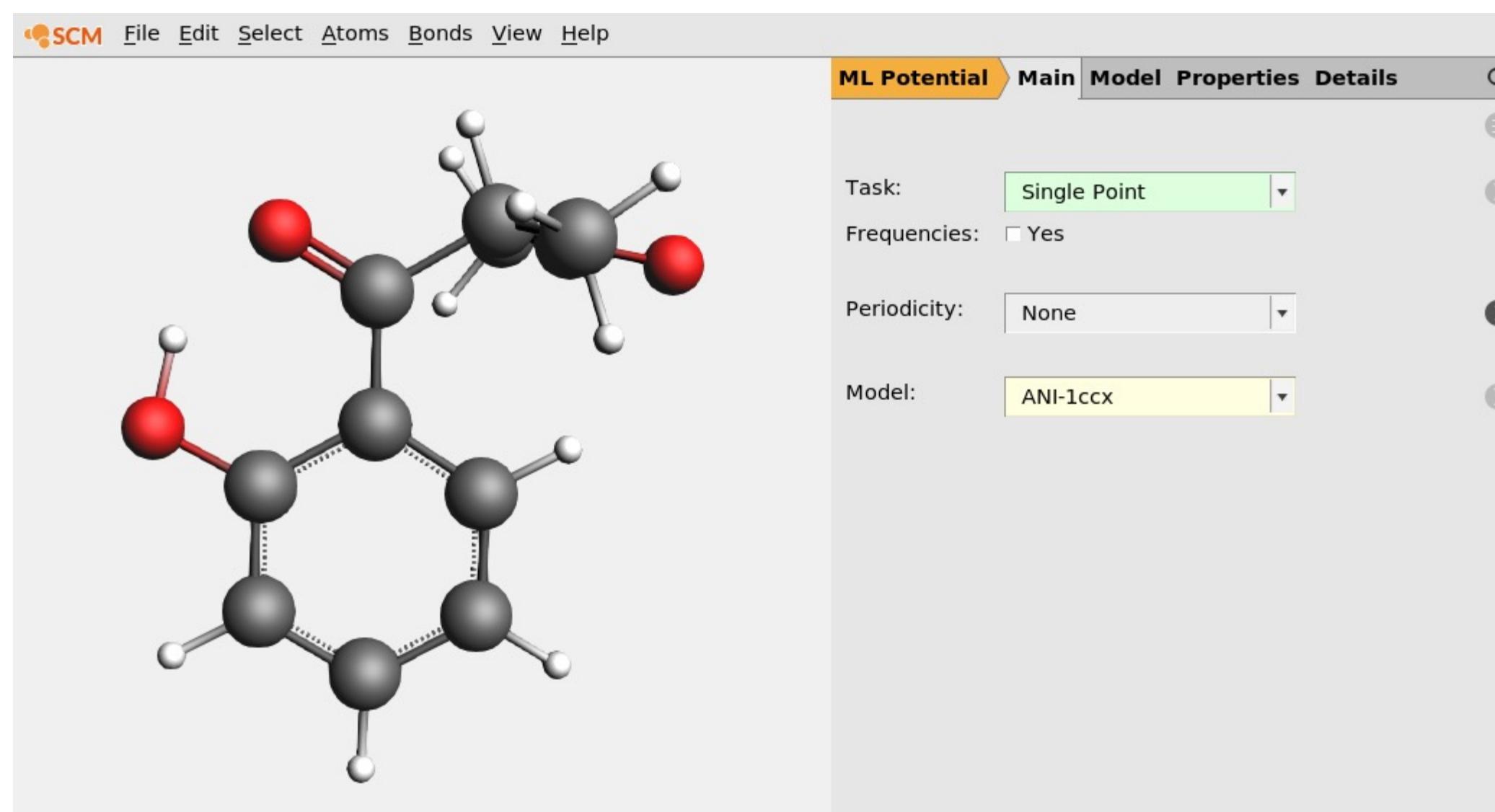
# High-dimensional neural network potentials



J. Behler, M. Parrinello, Phys. Rev. Lett. 98 146401 (2007); J. Behler, J. Chem. Phys. 134 074106 (2011)

# Machine Learning Potentials

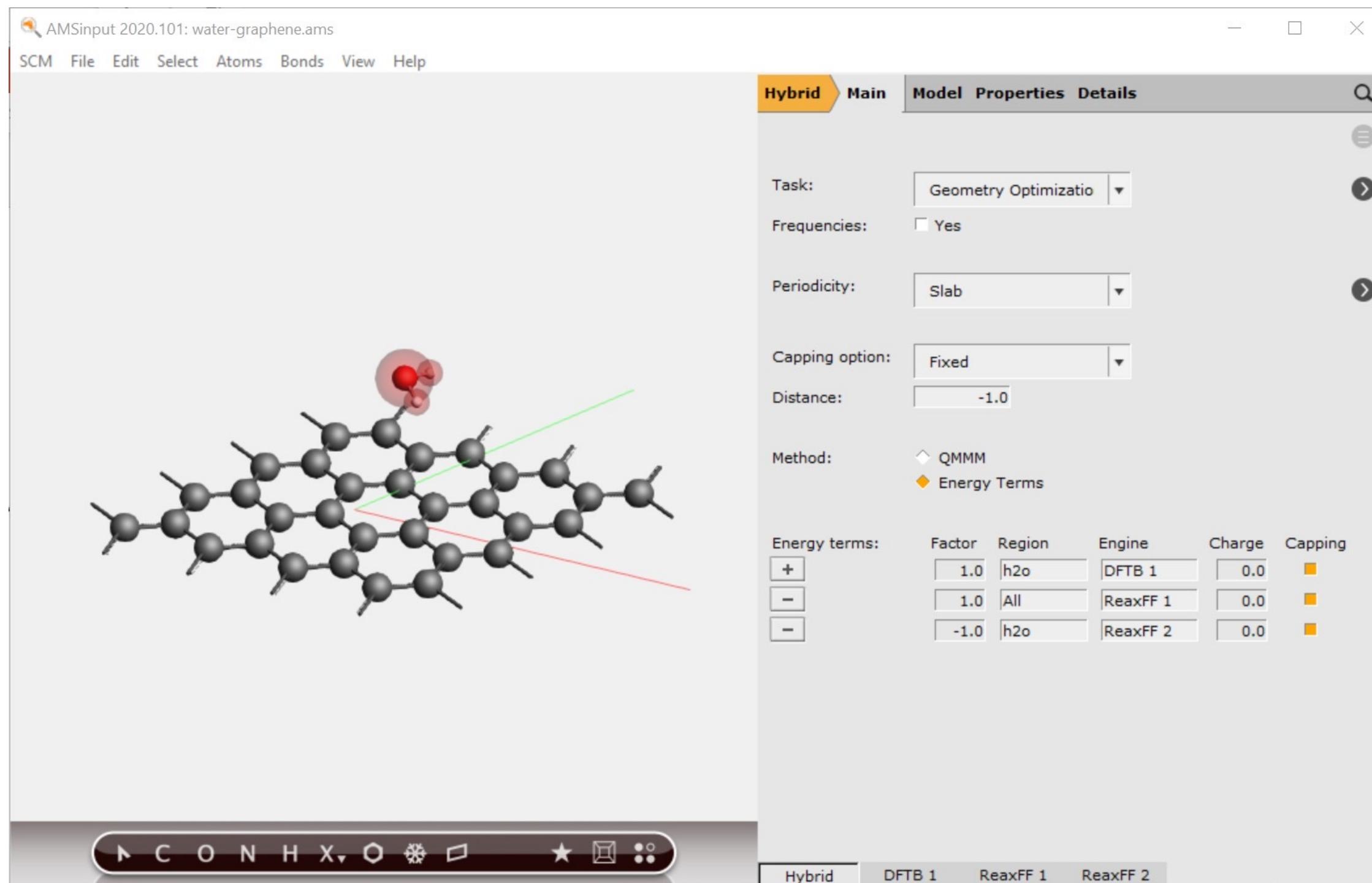
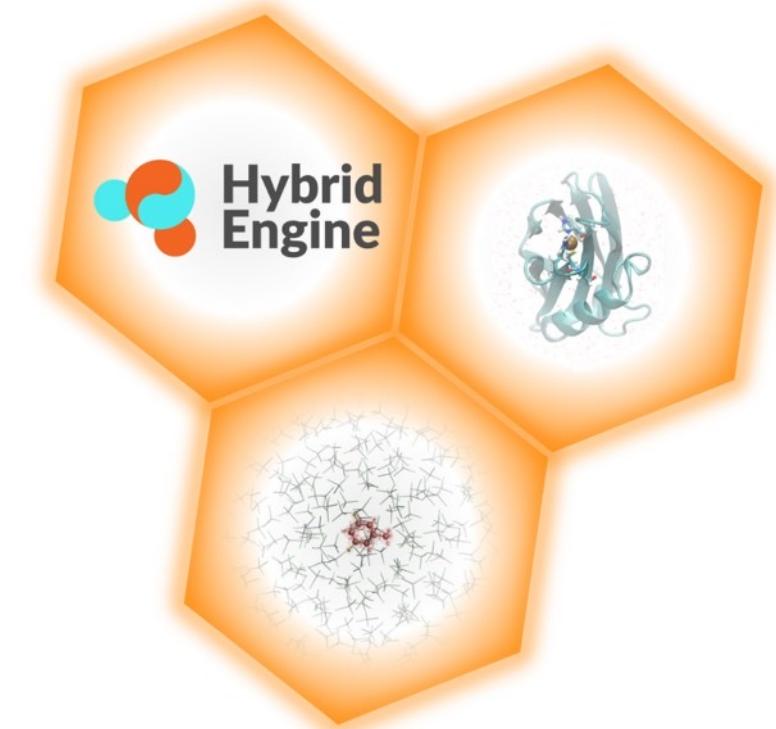
- Use machine learning potentials with AMS driver
  - PES scans, conformers, MD, reaction energies, ...
- Automatically install popular ML Backends
  - SchNetPack, sGDML, PiNN, TorchANI
  - Pre-parametrized neural network potentials ANI-1ccx, ANI-2x
  - CUDA-enabled PyTorch and Tensorflow can be used
  - Under development: on-the-fly ML force field (Flare)



[Demo video](#)

# Hybrid Engine: combine methods

- Multi-layer (subtractive, QUILD, ONIOM)
  - combine any periodicity, number of layers, and QM or MM methods
- 2-layer: (additive) QM/MM
  - any periodicity
  - QM: ADF, DFTB, BAND, MM: Force Field engine



[Demo video](#)

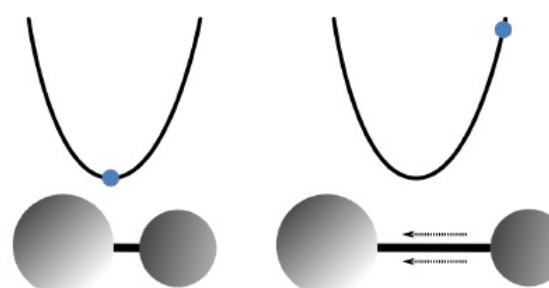
# ReaxFF: concept

- Simulate complex systems at realistic scales

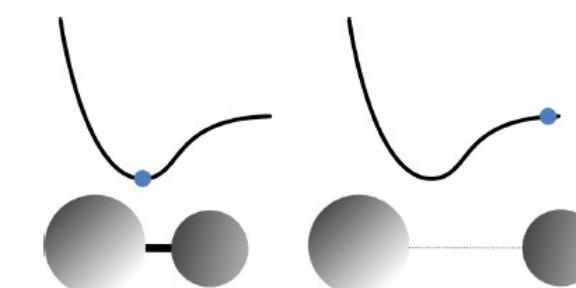
- Atomistic potentials – single atom type (reasonably transferable)
- Update charges and bond orders at every step

A.C.T. van Duin et al ,J. Phys. Chem. A 2001 , 105, 9396-9409.

Standard forcefields vs ReaxFF

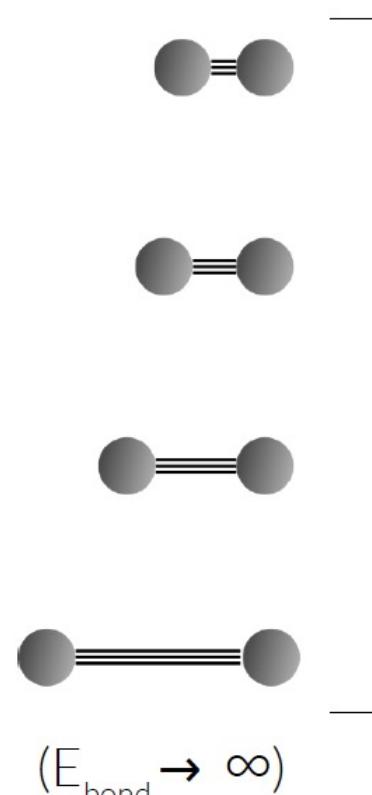


ReaxFF



Harmonic potentials based on atom distance,  
bond breaking impossible, e.g.

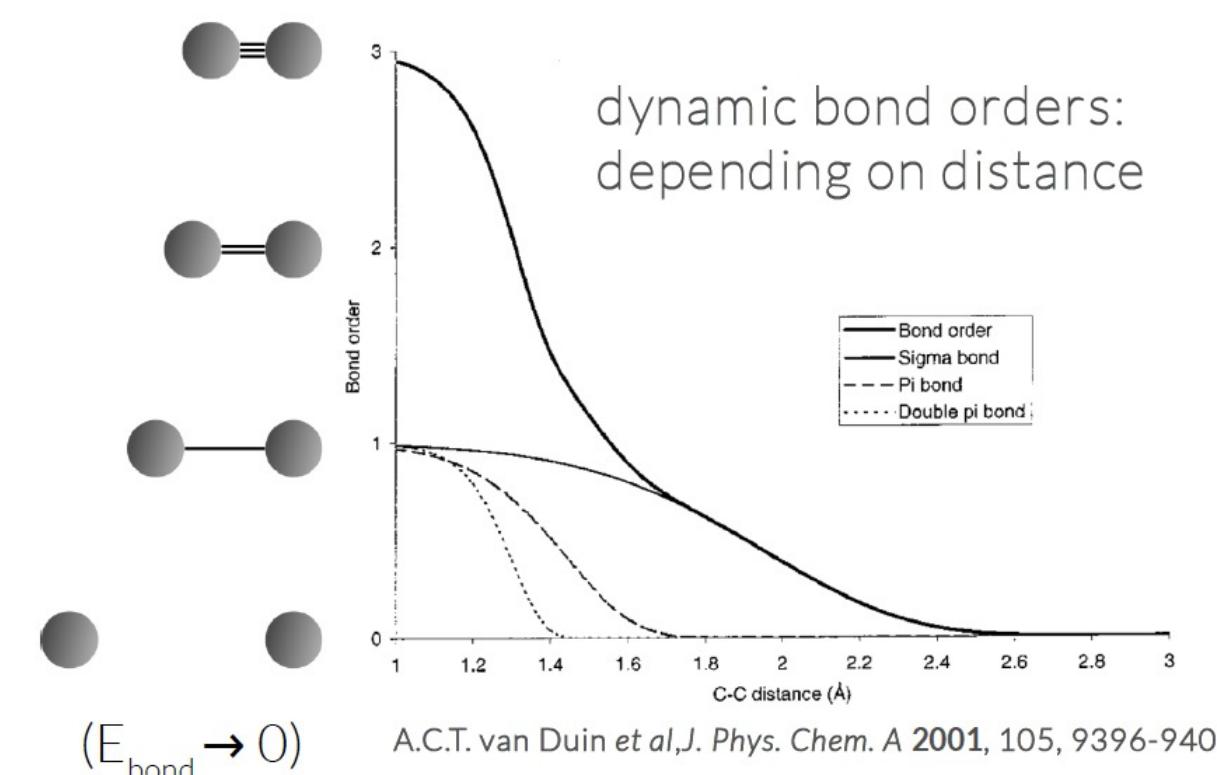
$$E_{\text{bond}} \propto (\text{distance})^2$$



a triple "bond" will always  
stay a triple "bond"...

Non-harmonic potentials based on bond orders,  
bond breaking/forming possible, e.g.

$$E_{\text{bond}} \propto -( \text{bond order} ) \times \exp[ (1 - \text{bond order}) ]$$

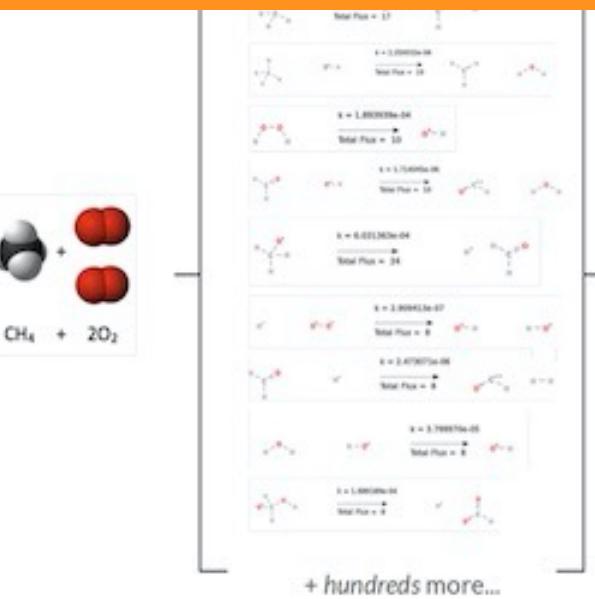
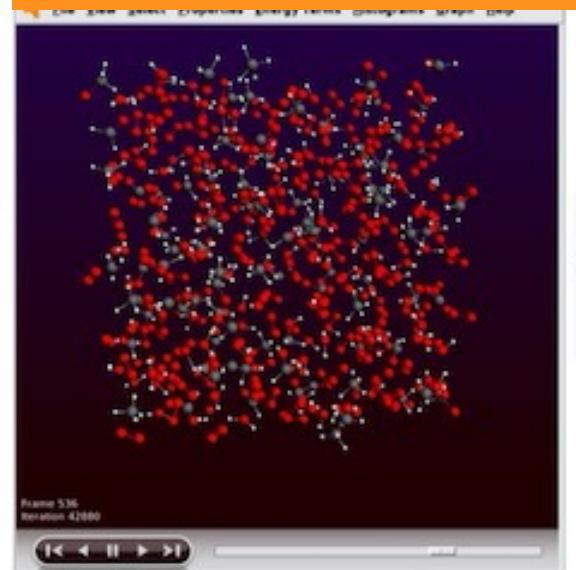


$$(E_{\text{bond}} \rightarrow 0)$$

A.C.T. van Duin et al,J. Phys. Chem. A 2001, 105, 9396-9409.

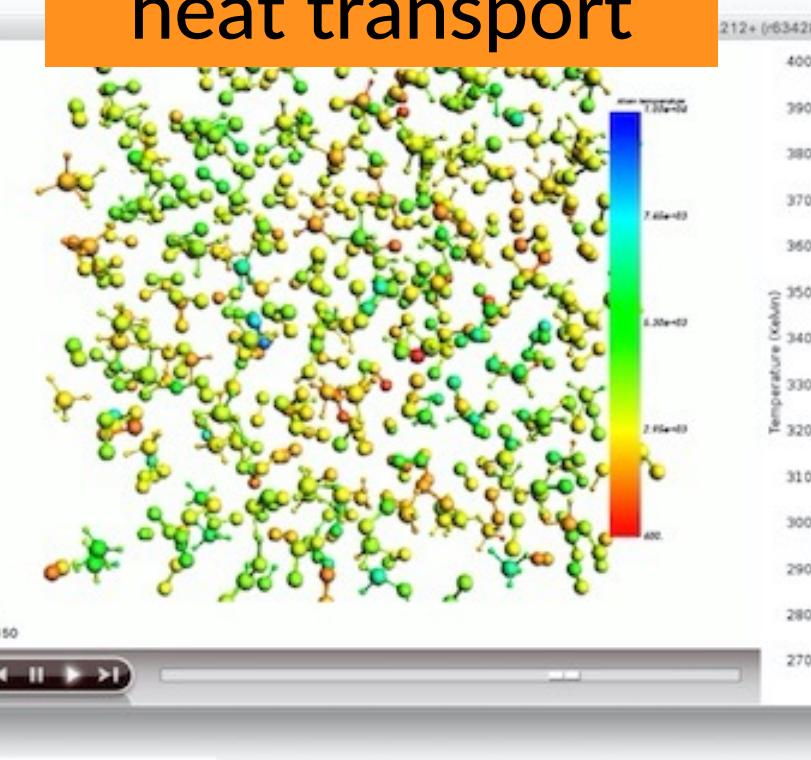
# Reactive MD tools Amsterdam Modeling Suite

ChemTraYzer: [Automated rates & pathways](#)  
New: [Analyze surface reactions](#)

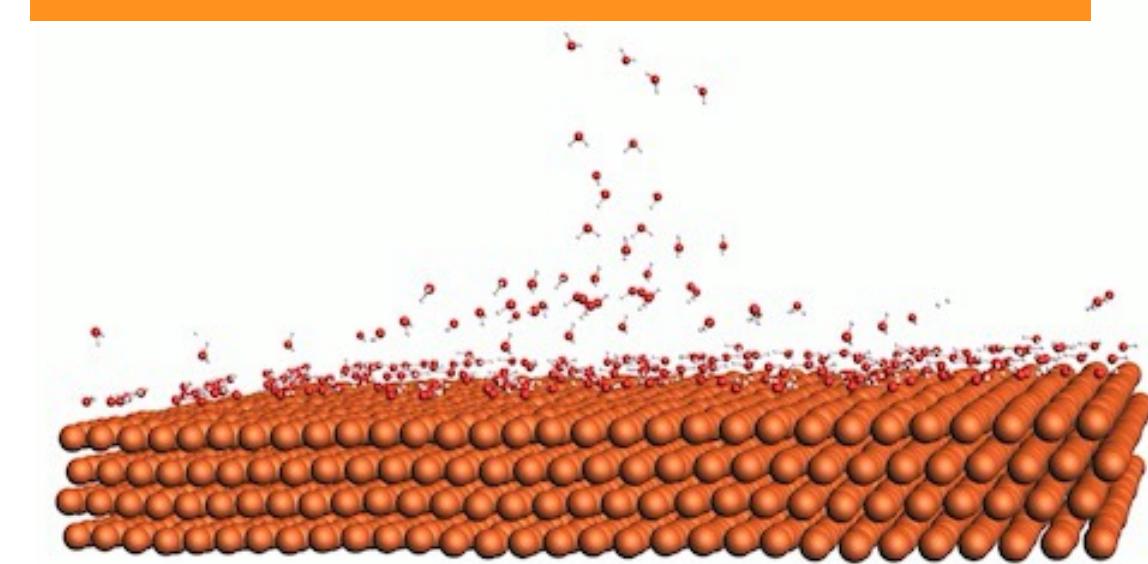


Tools += complete reaction networks  
elementary reactions, rate constants, fluxes, timeline

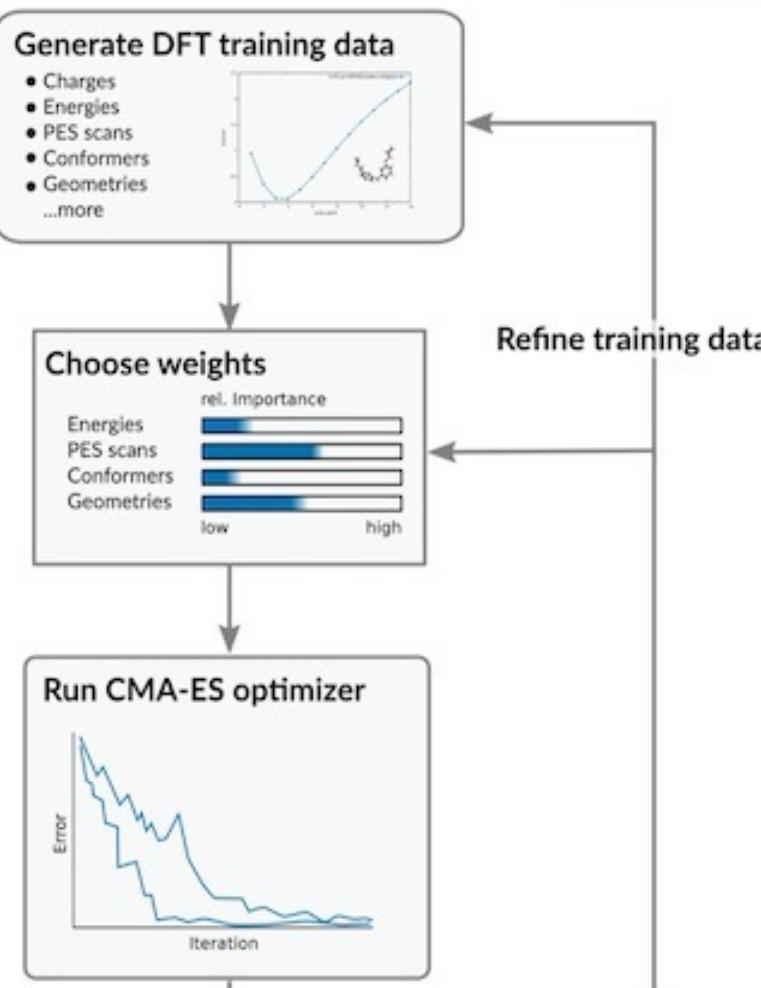
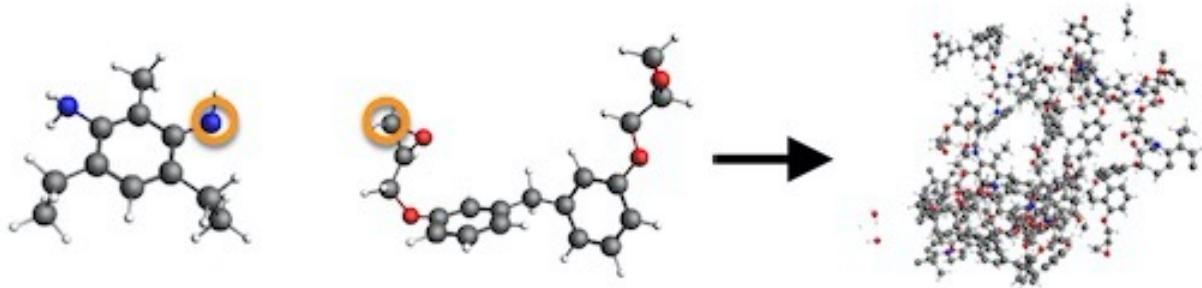
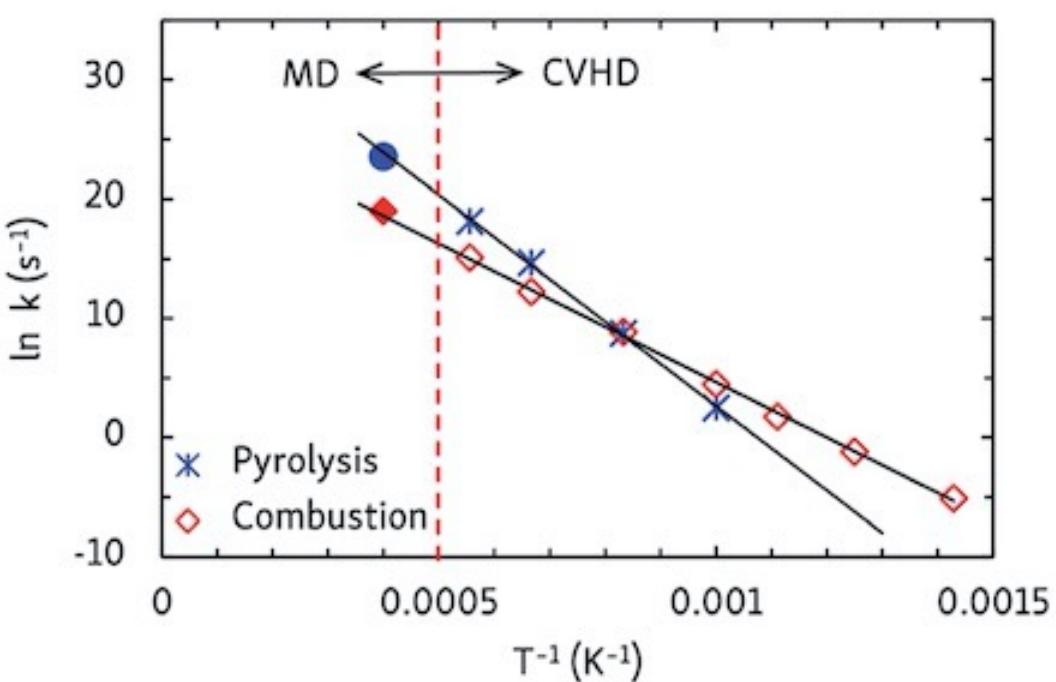
T-NEMD, local T:  
heat transport



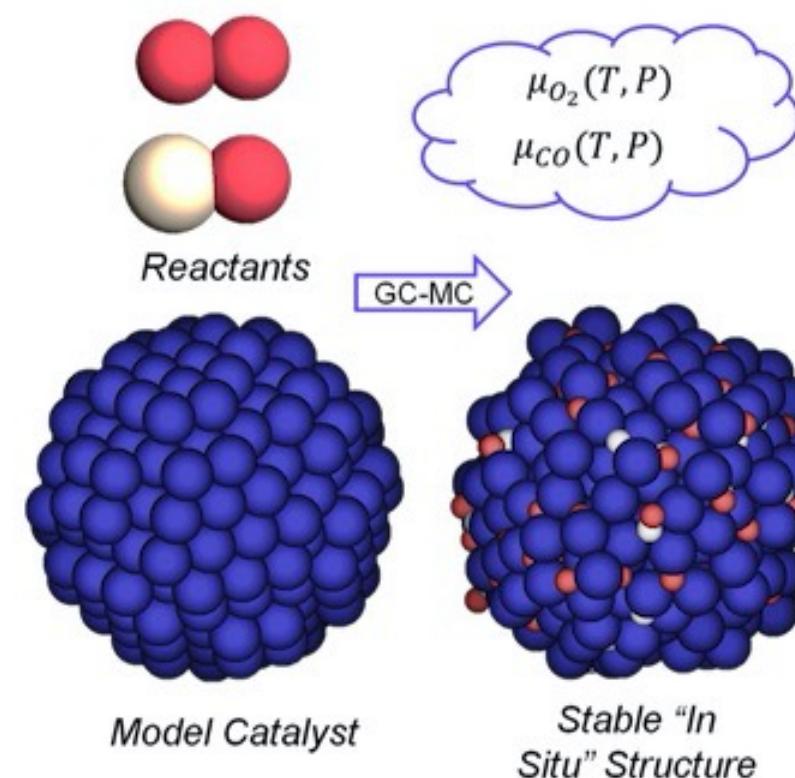
Molecule gun: depositing  
molecules on surfaces



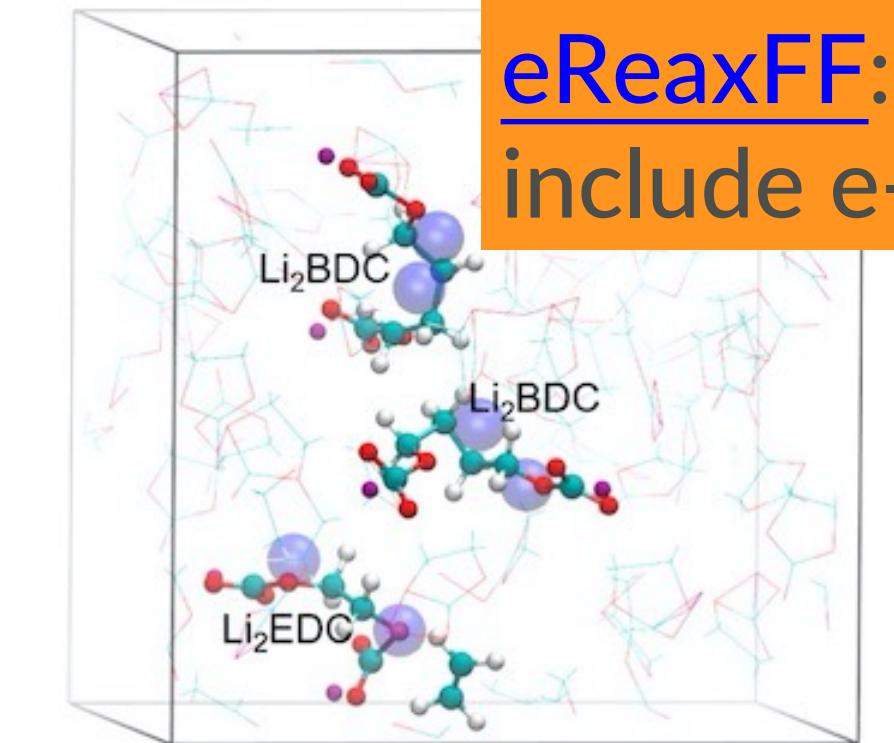
[fbMC](#), [CVHD](#), PRD?:  
speed up kinetics



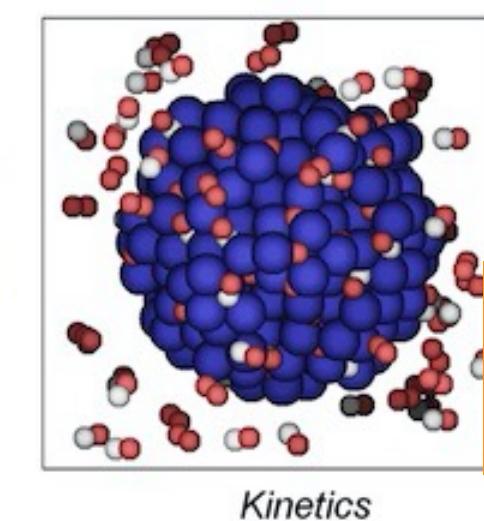
[ParAMS](#) - easy  
ReaxFF& DFTB  
(re)parameterization



[bond boost](#)  
build polymers



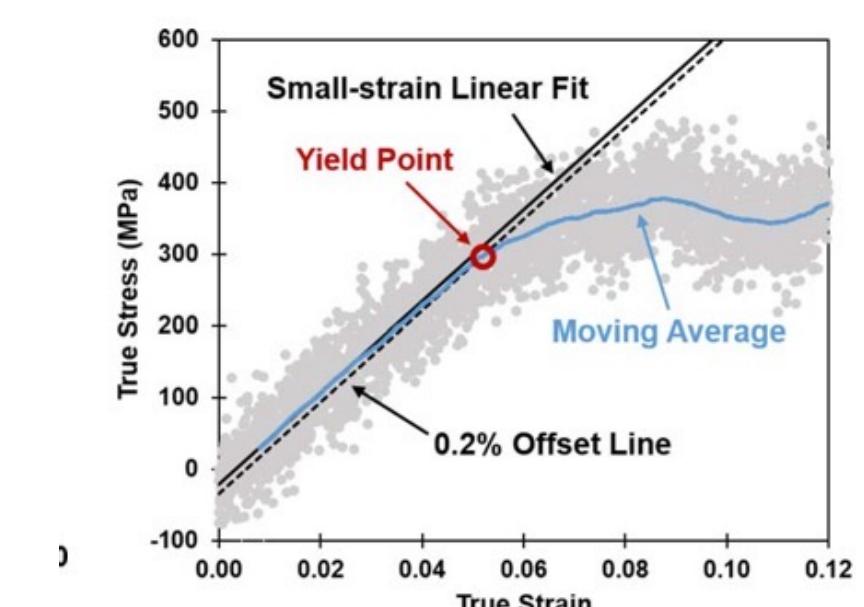
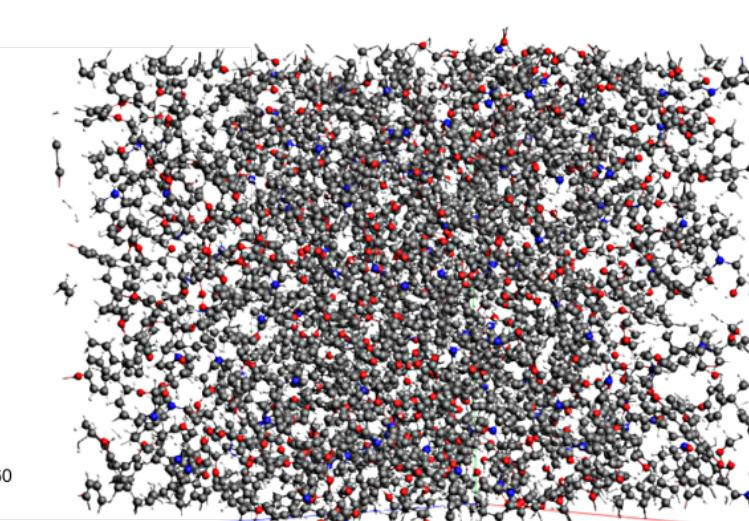
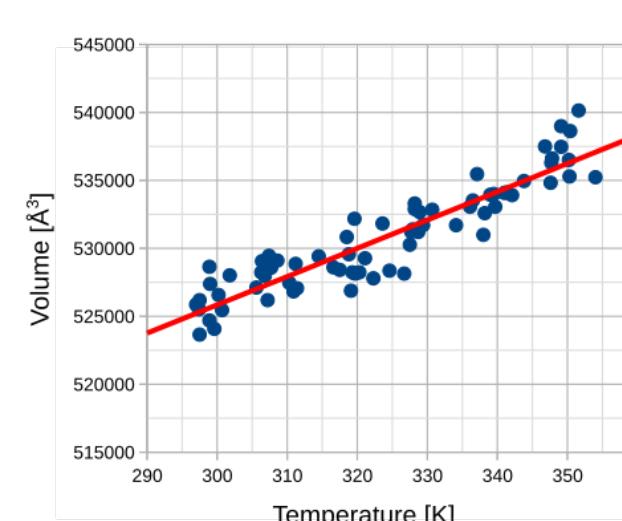
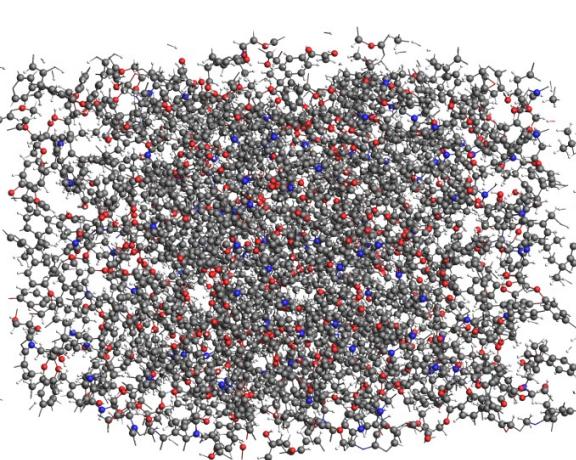
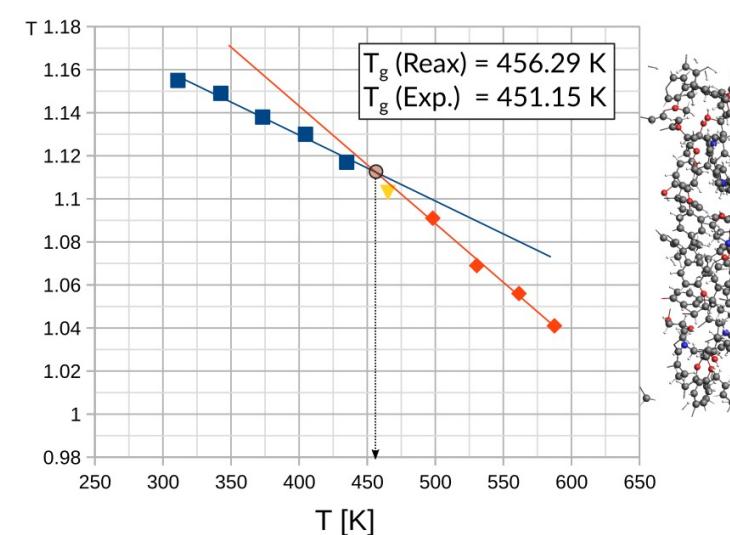
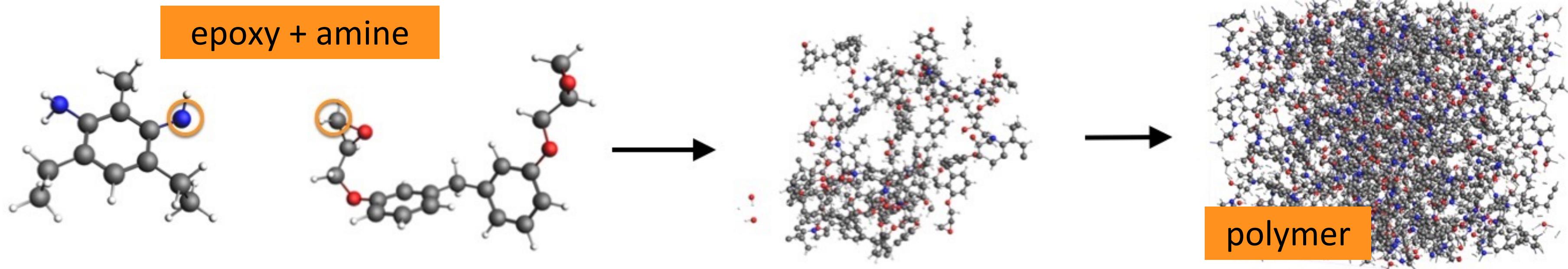
[eReaxFF](#):  
include e-



[GCMC](#): speed  
up thermo

# Epoxy polymers: structure & properties

- Understand & predict how cross-linking effects mechanical properties
  - Exp = slow: minutes to hours to reach ~80% cross-linking
  - ReaxFF: simulate few ns => accelerate kinetics to get highly xlinked structures



density( $T$ ) using npT  
glass transition  $T_g$

volume( $T$ ) npT  
CTE

Stress-strain:  
yield point, Poisson ratio

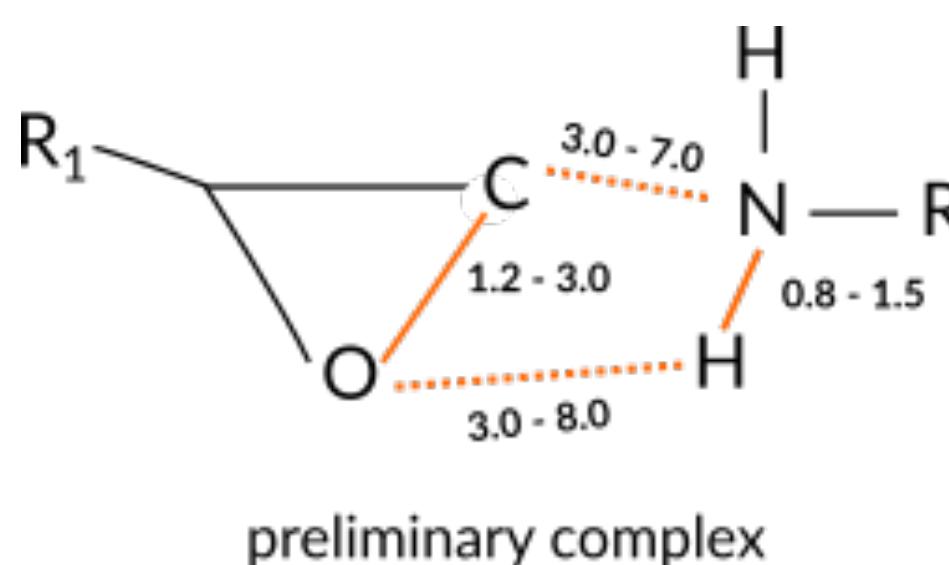
# Accelerating dynamics with Bond Boost

- Track distances; add ‘boost’ potential if within mask

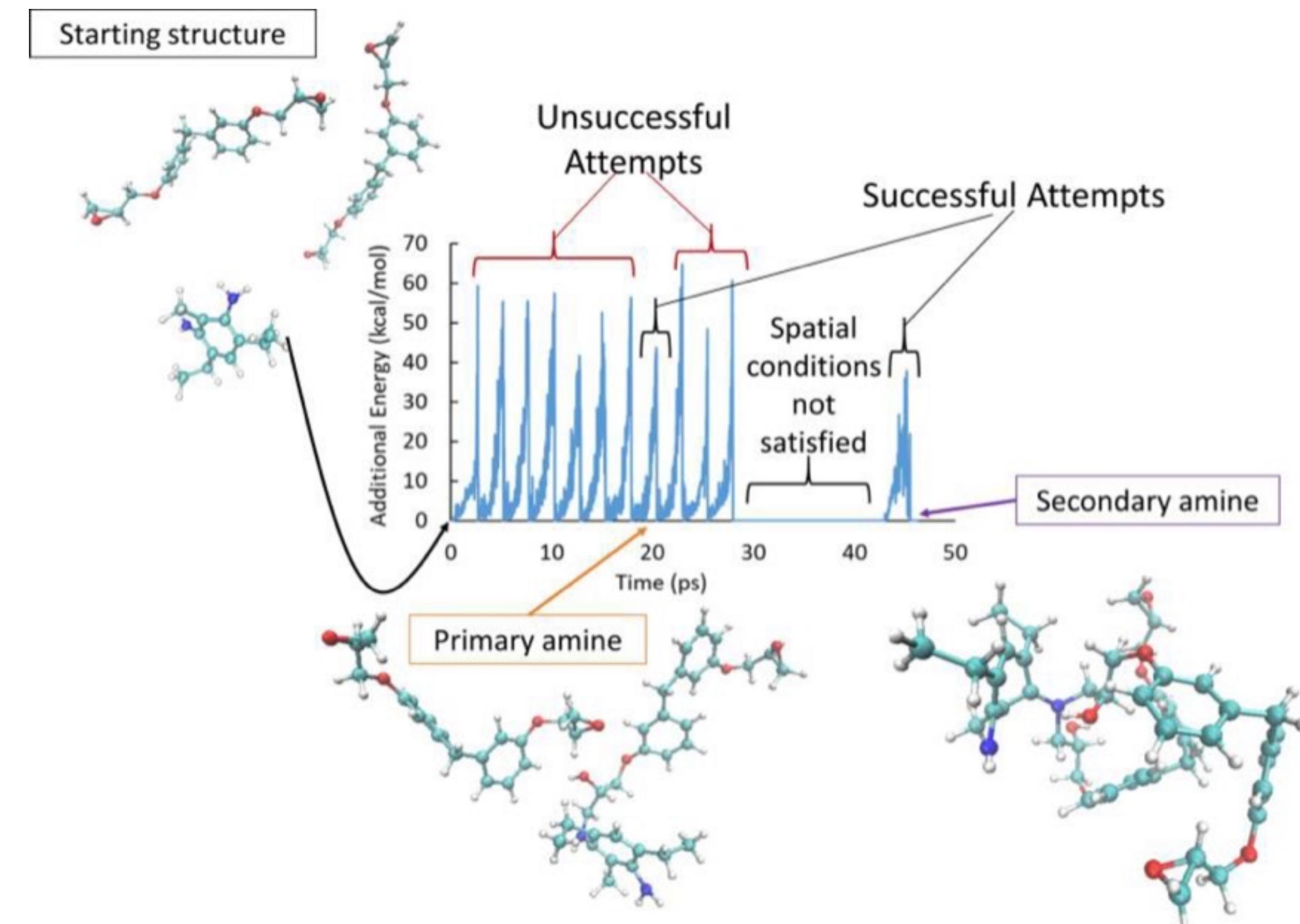
- Sample dynamics with sufficient energy to surmount barriers
- Reactions can fail:
  - Steric hindrance
  - Unfavorable approach path

- Overcome slow kinetics

- Get to end result
- No mapping to real time



$$E_{rest} = F_1 \{1 - e^{-F_2(R_{ij}-R_{12})^2}\}$$



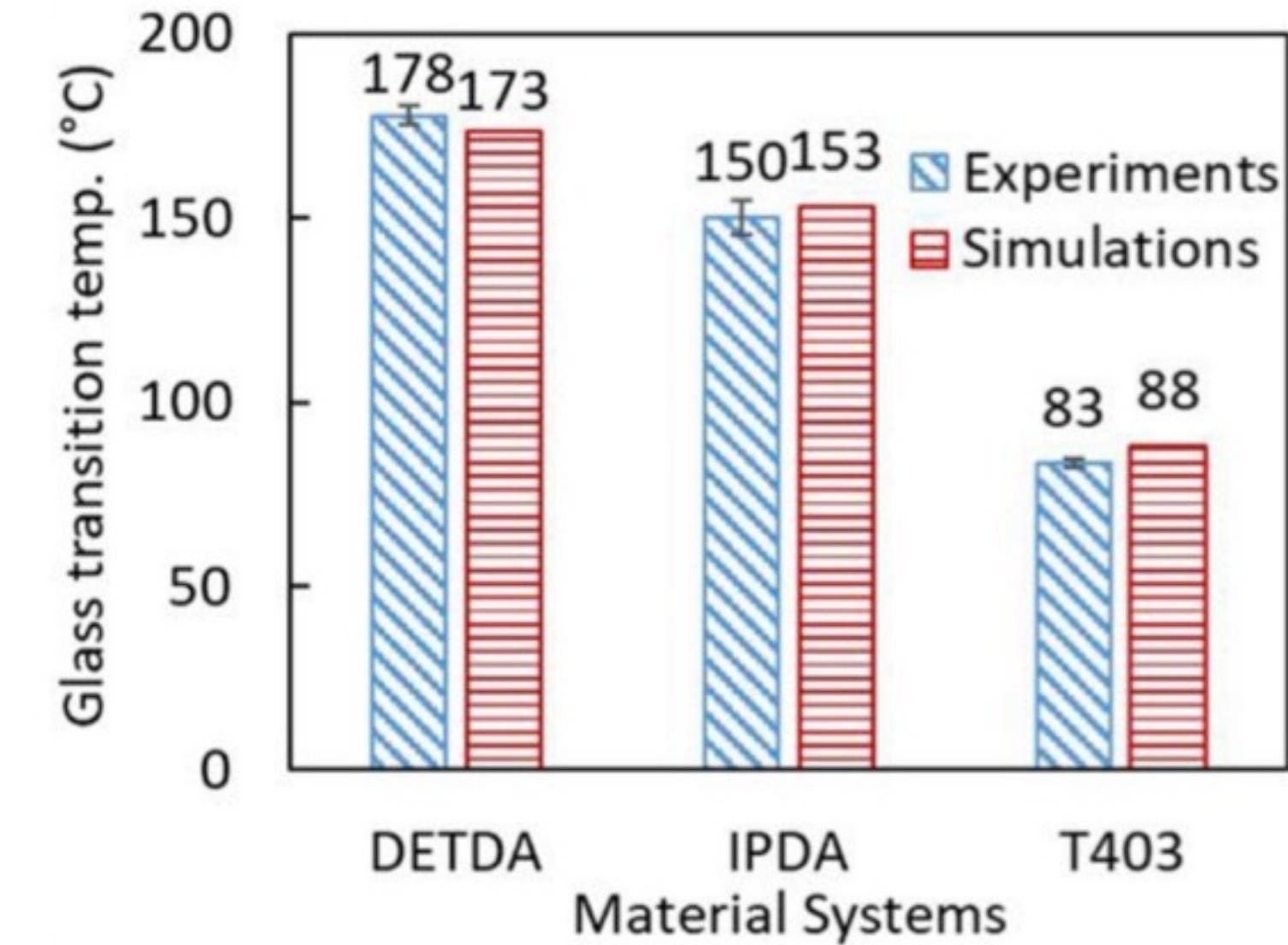
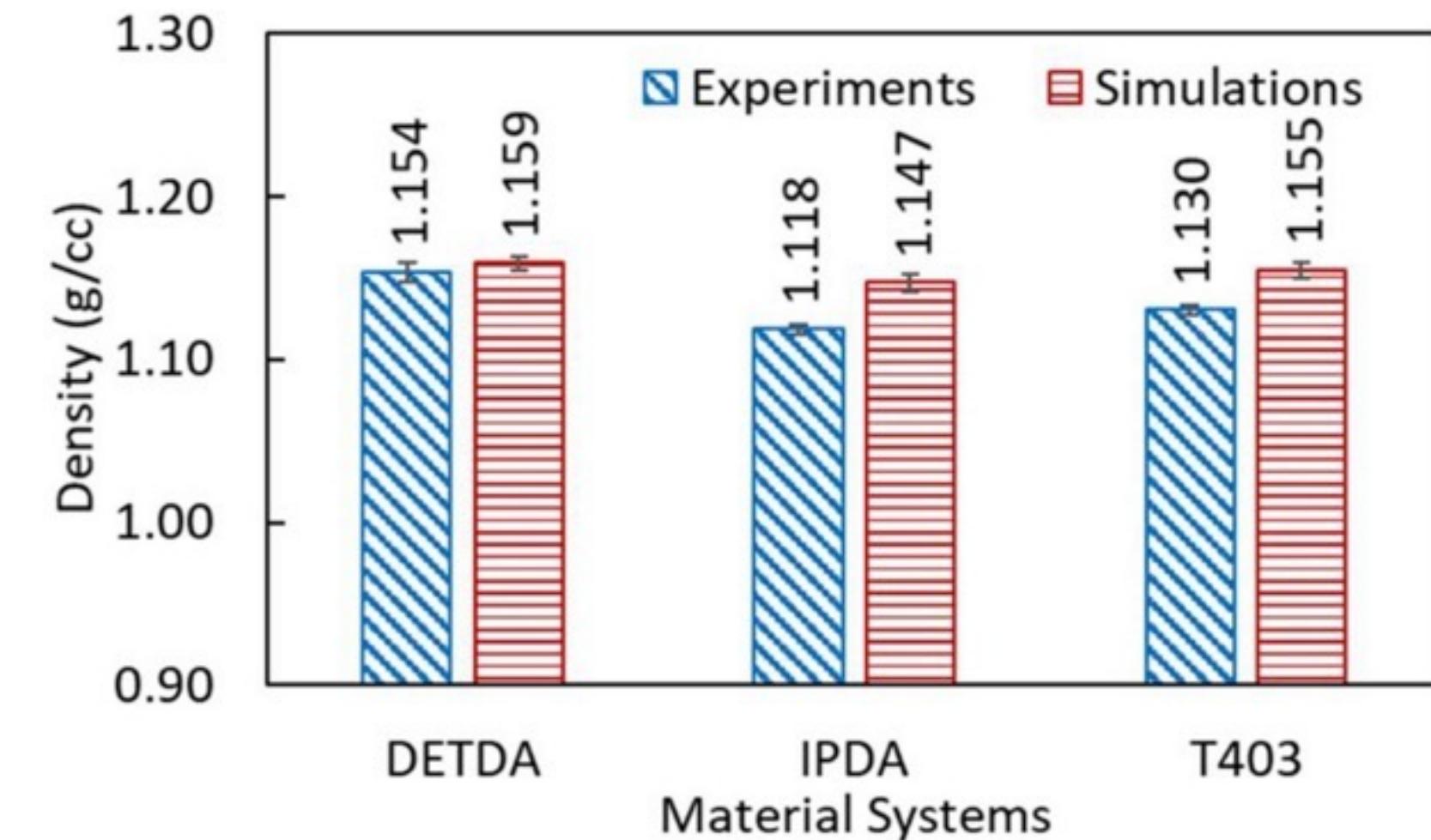
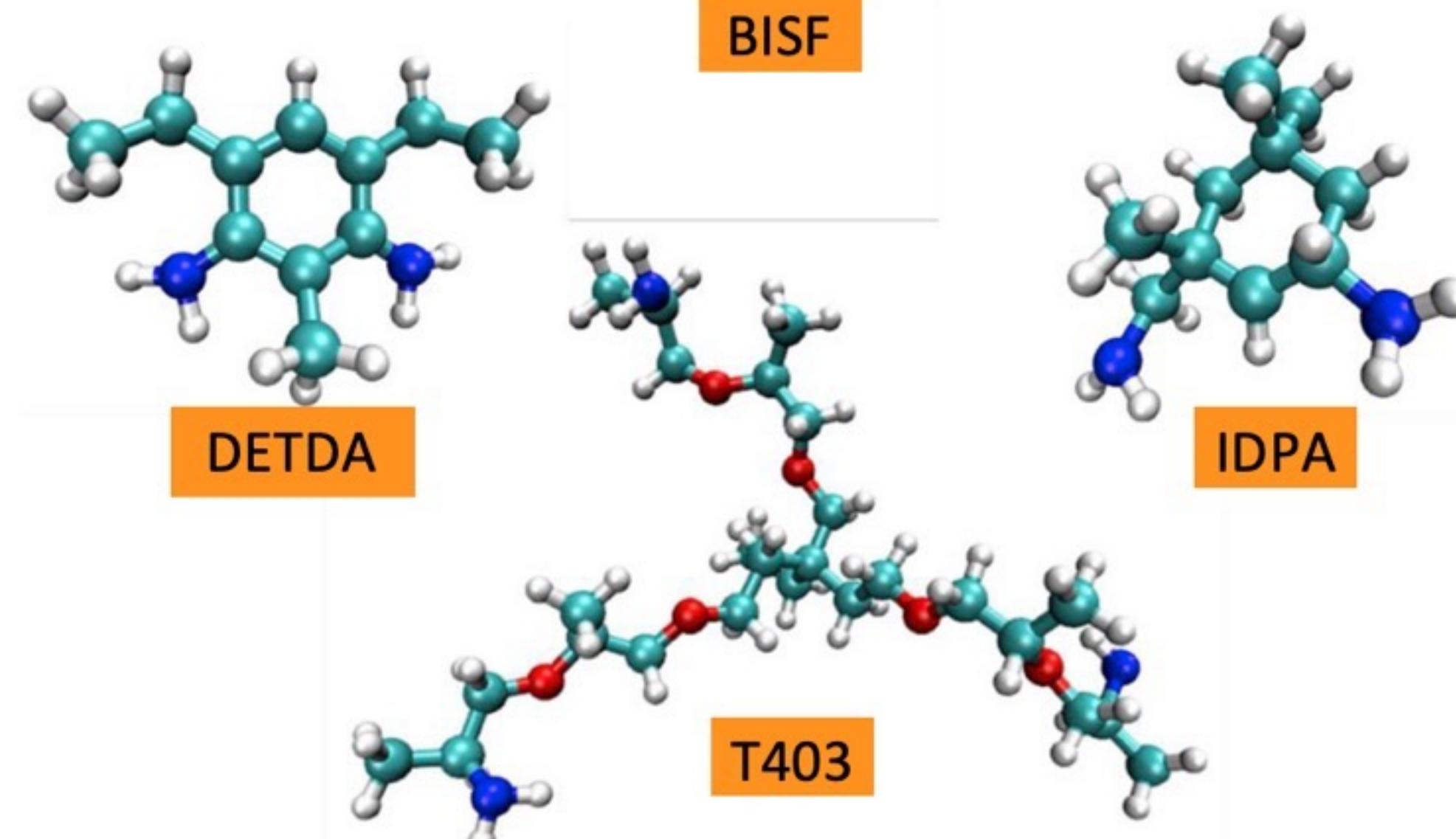
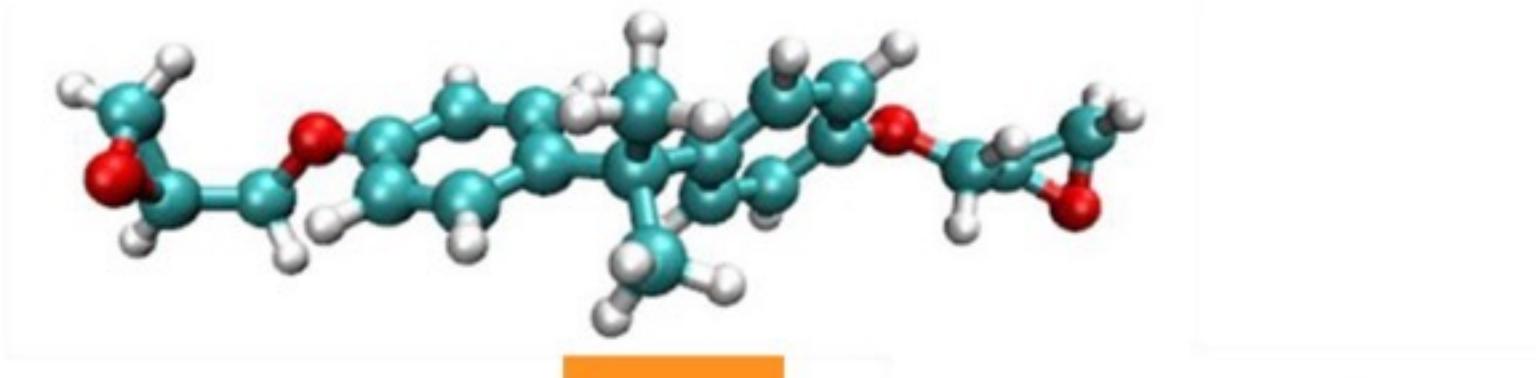
van Duin et al. *J. Phys. Chem. A*, **122**, 6633 (2018),  
cf. Miron & Fichthorn *JCP* **119**, 66210 (2003)

[Video: realistic cross-linking](#)

[Tutorial: cross-linking](#)

# Properties of cross-linked epoxy polymers

- Good predictions: densities &  $T_g$
- Aliphatic amine => lower  $T_g$

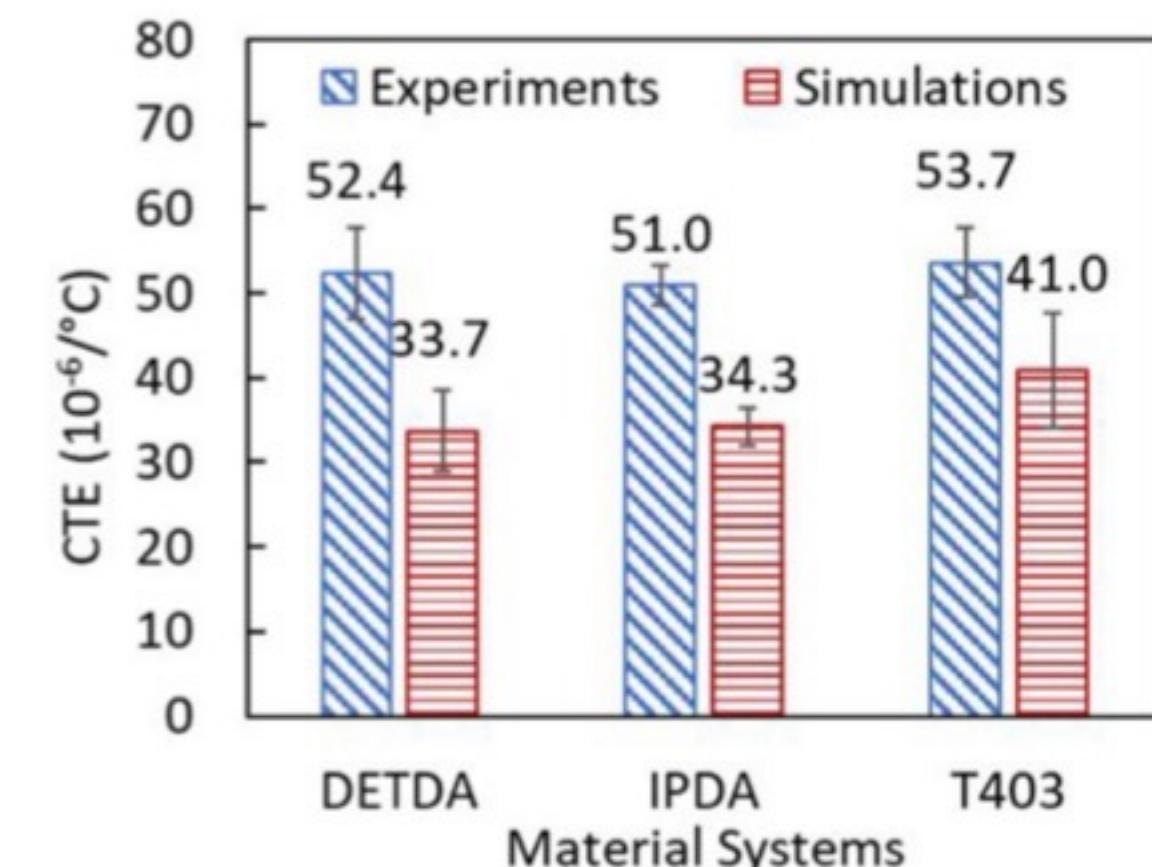
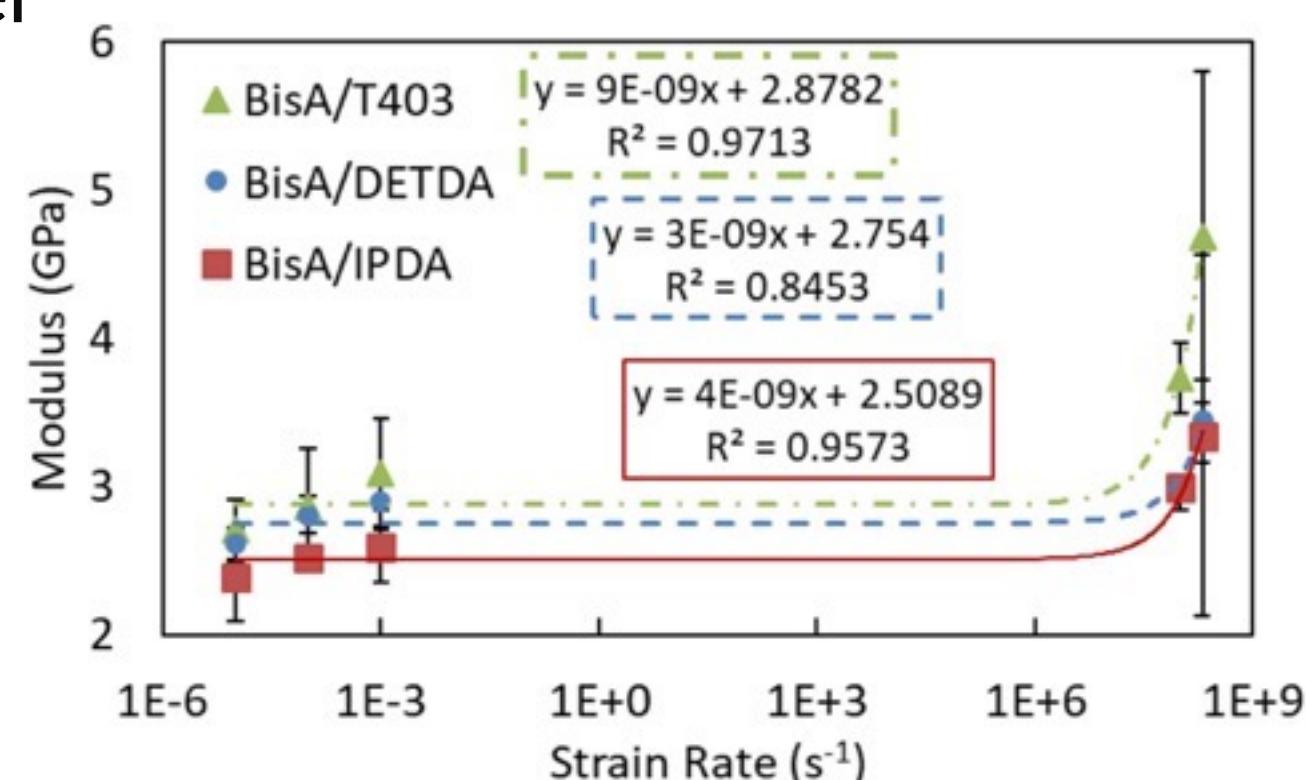


Polymer 158, 354 (2018)

Tutorial Tg

# Properties of cross-linked epoxy polymers

- Coefficients thermal expansion ([tutorial](#))
  - Predictions: too low -> Reparameterize ReaxFF? Other FF?
- Modulus: good linear fit (calc = high strain)
  - bulk stress tensors = faster
    - ReaxFF, DFTB

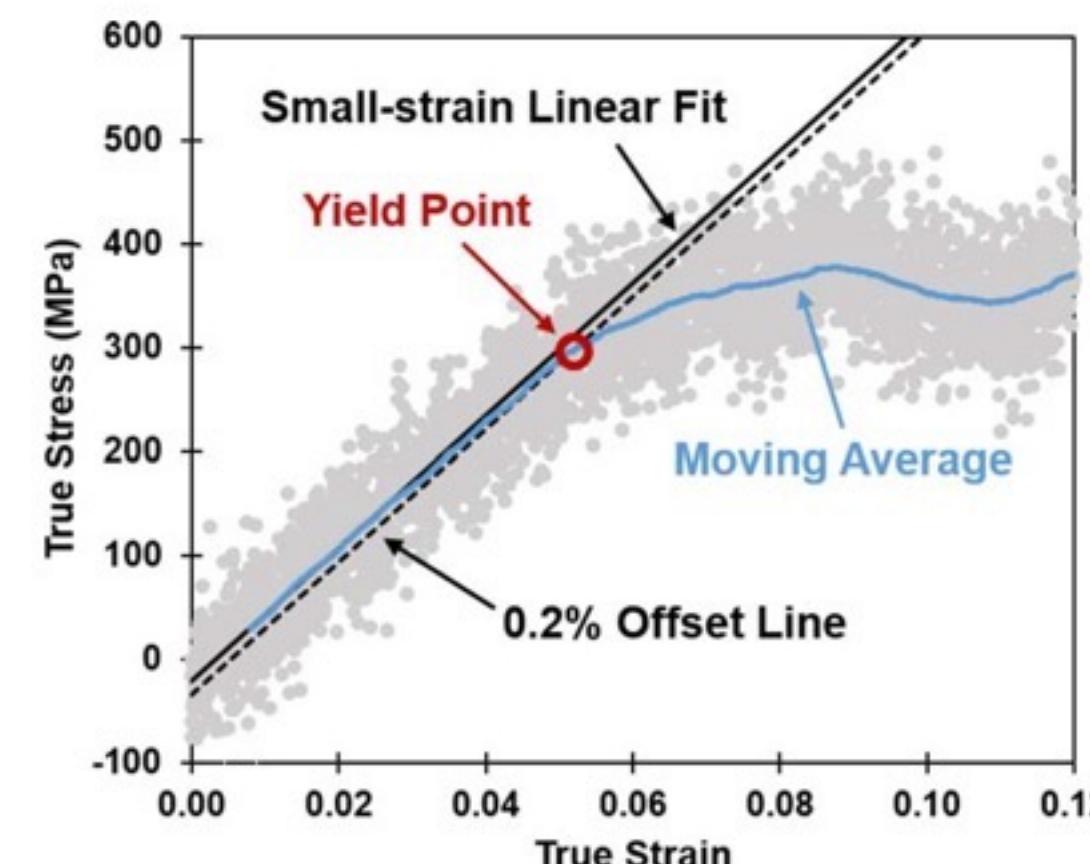
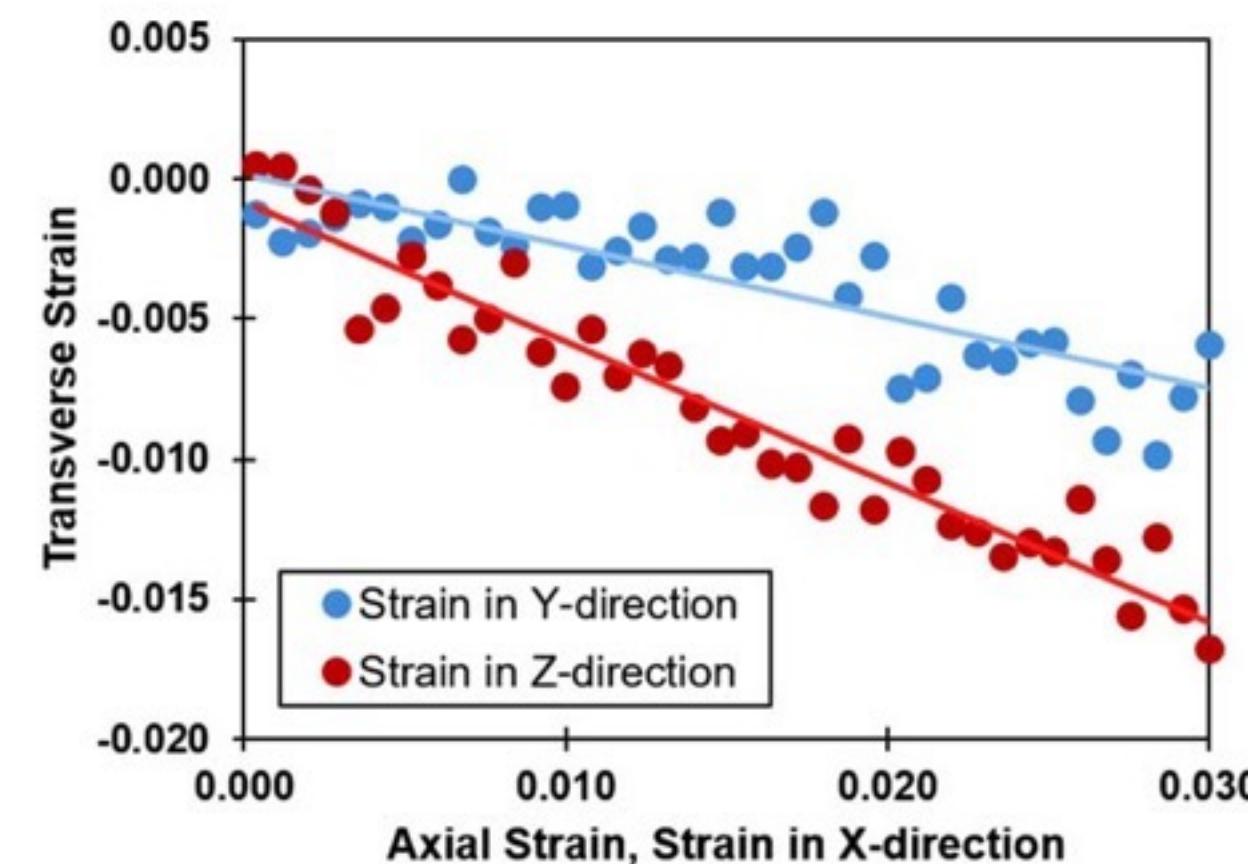


[Polymer 158, 354 \(2018\)](#)

From Stress-Strain:

- Yield point(s)
- Strain ratios

[J. Polym. Sci. B, 56, 255-264 \(2018\)](#)

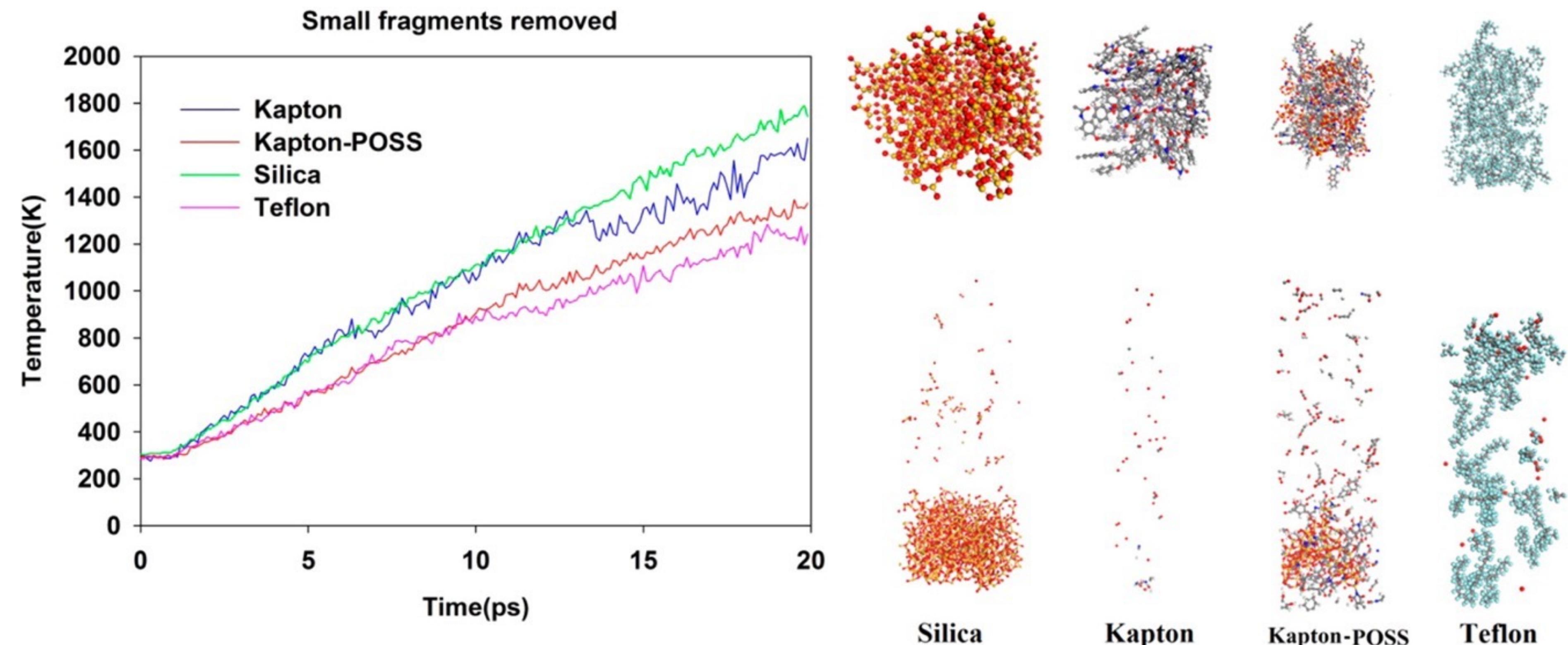


[Video: mechanical properties](#)

[Tutorial: stress-strain](#)

# Degradation of polymers in space

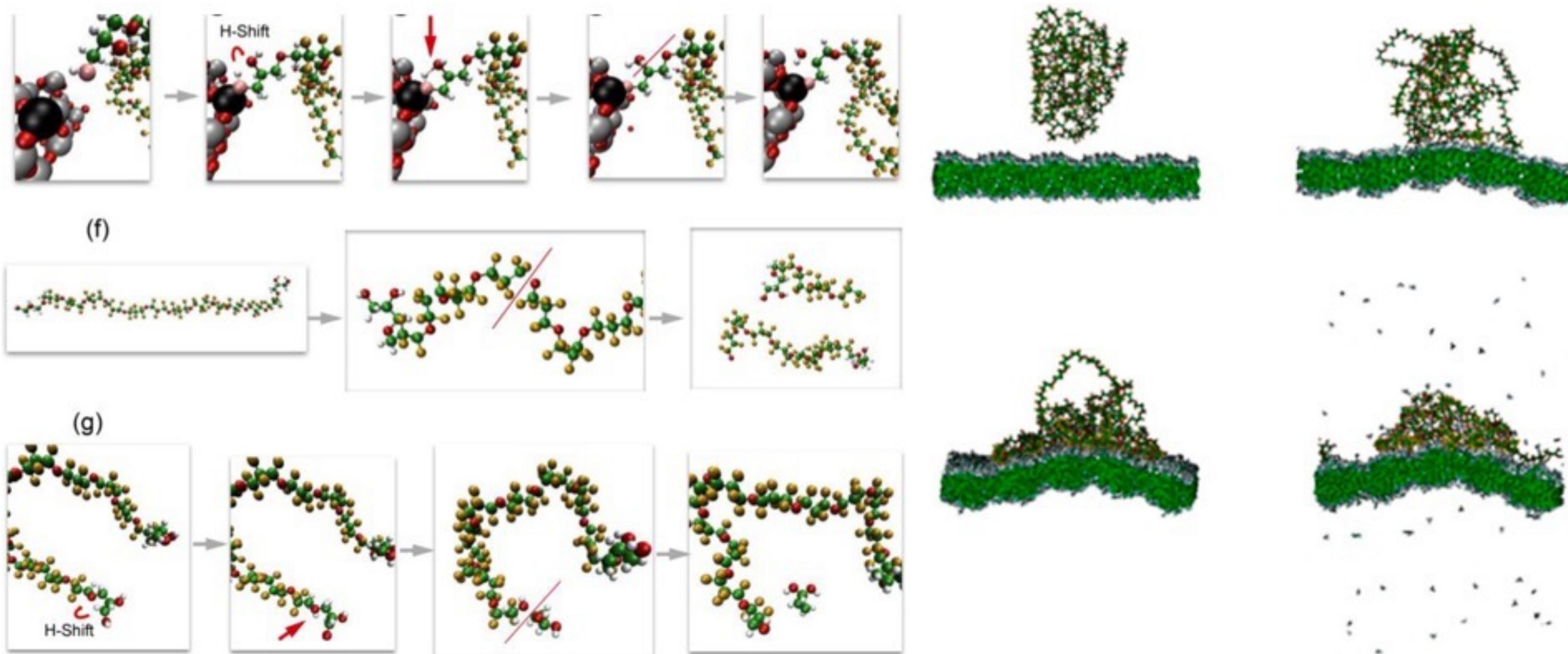
- Atomic Oxygen bombardment studying low earth orbit conditions
- Silica is high initial resilience, Teflon lowest erosion rate
  - Good heat transfer properties can help; Kapton can be stabilized with silica.



[J. Phys. Chem. A, 2014, \(118\), 2780](#)

Tutorial coming

# ReaxFF simulations: degradation

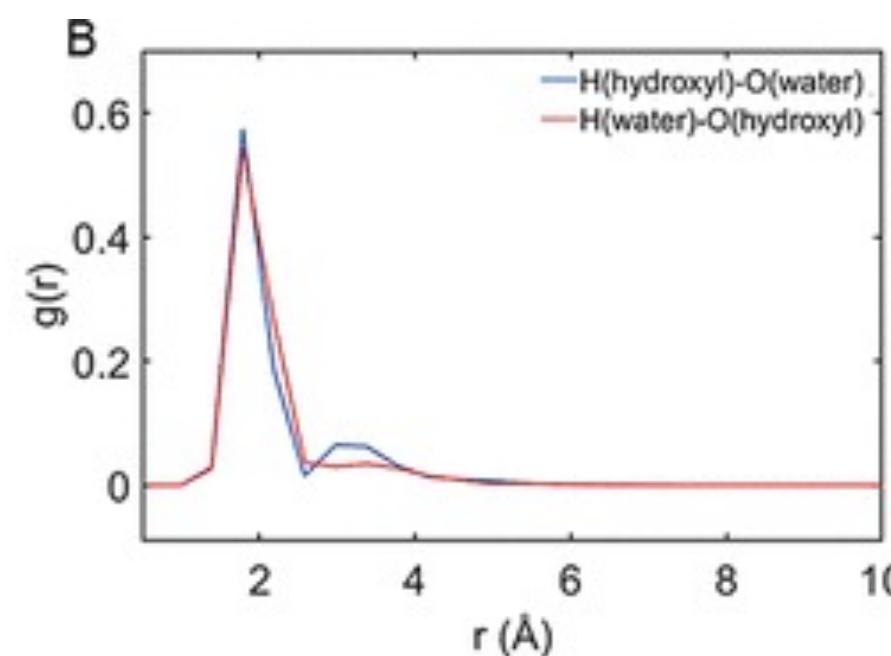
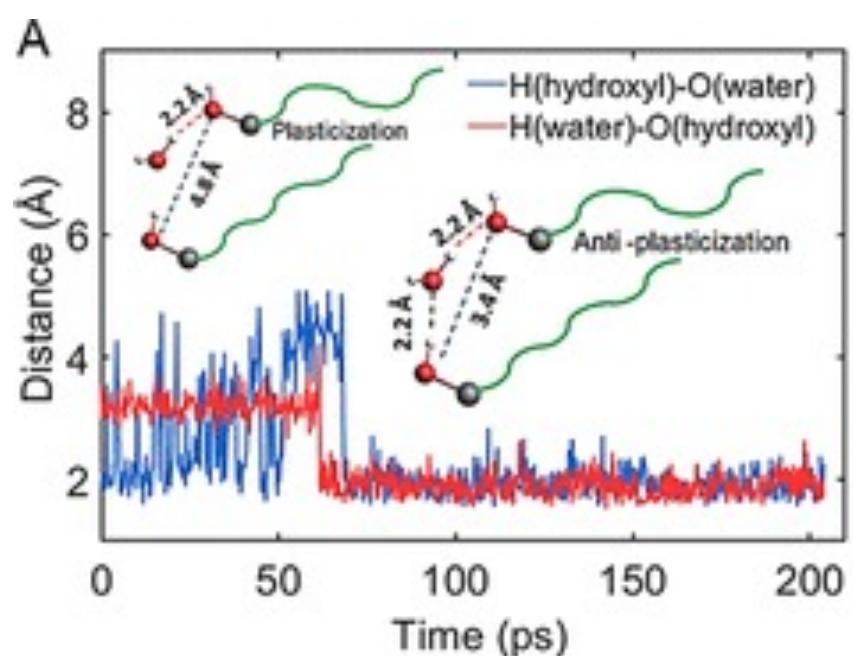


Degradation mechanisms perfluoropolyether lubricant on  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  nanoparticles & DLC, effect of oxygen and water. Work by van Duin (Penn State/RxFFconsulting) with Western Digital

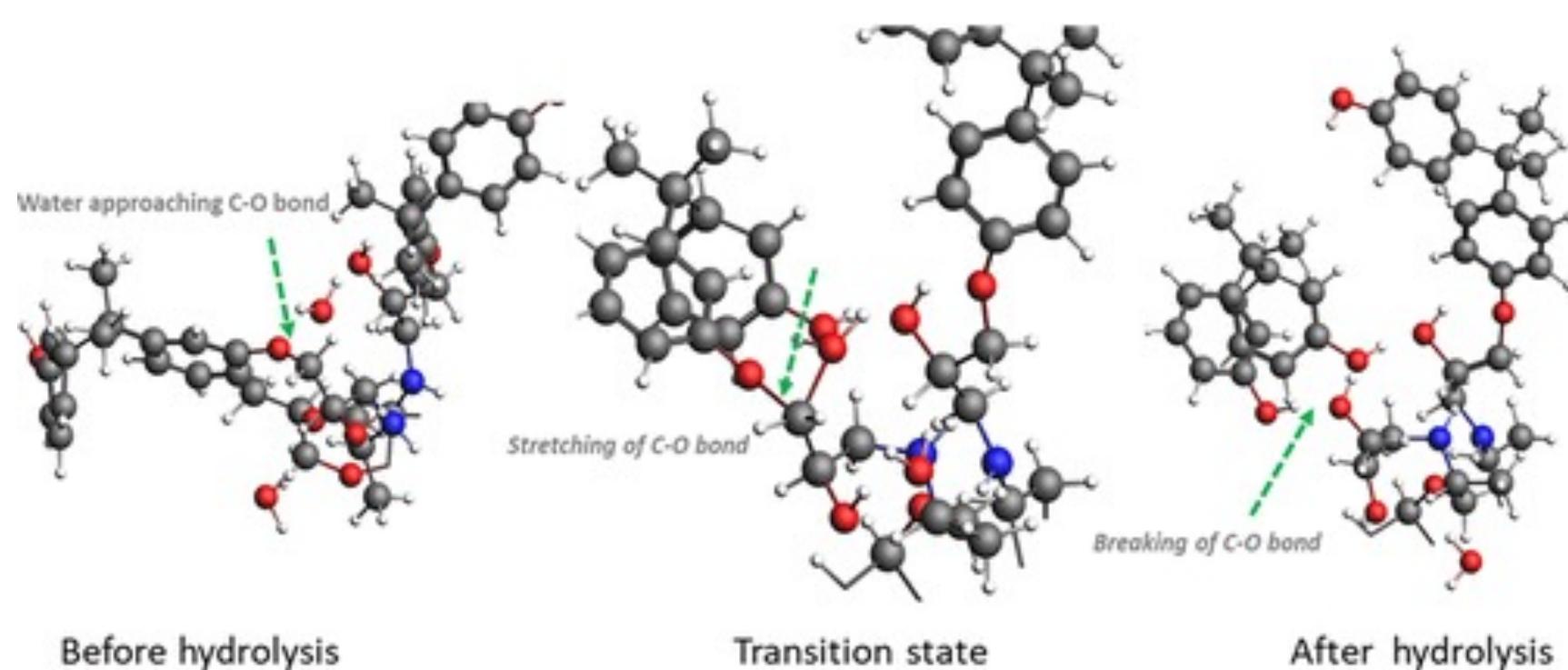
[J. Phys. Chem. C, 120, 27433 \(2016\)](#)

[J. Phys. Chem. C, 122, 2684 \(2018\)](#)

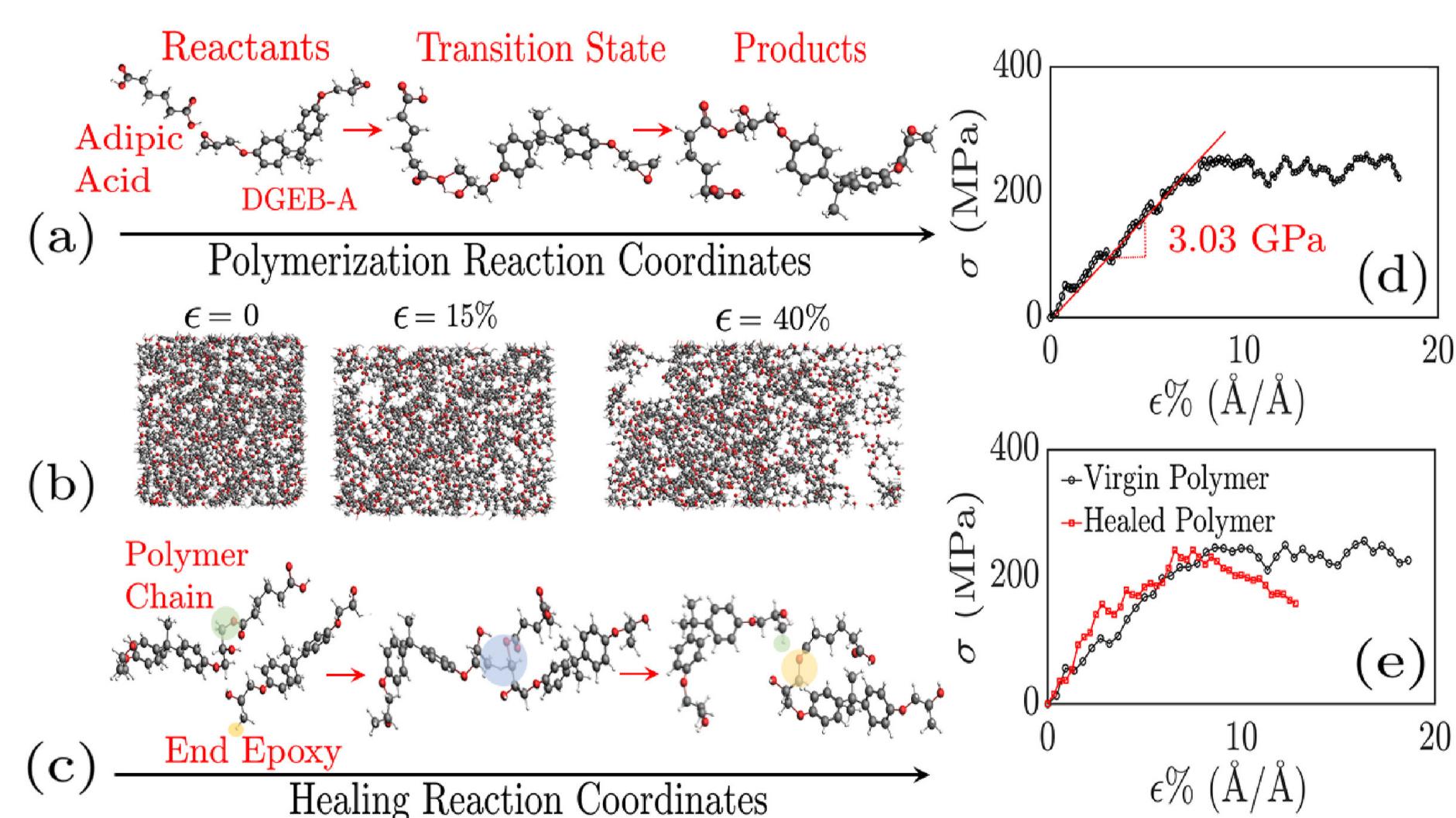
# Hygrothermal degradation, healing



Physical (top) and chemical (below)  
degradation depends on V, polarity



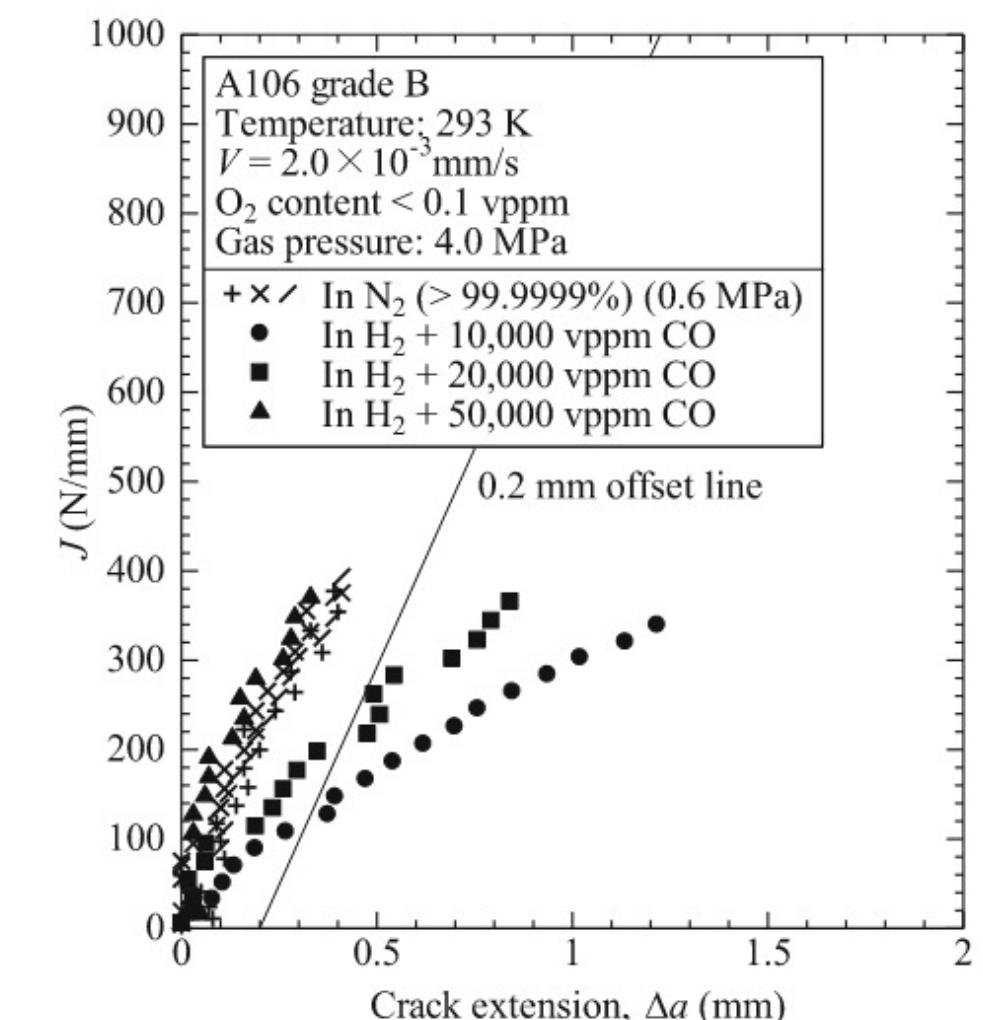
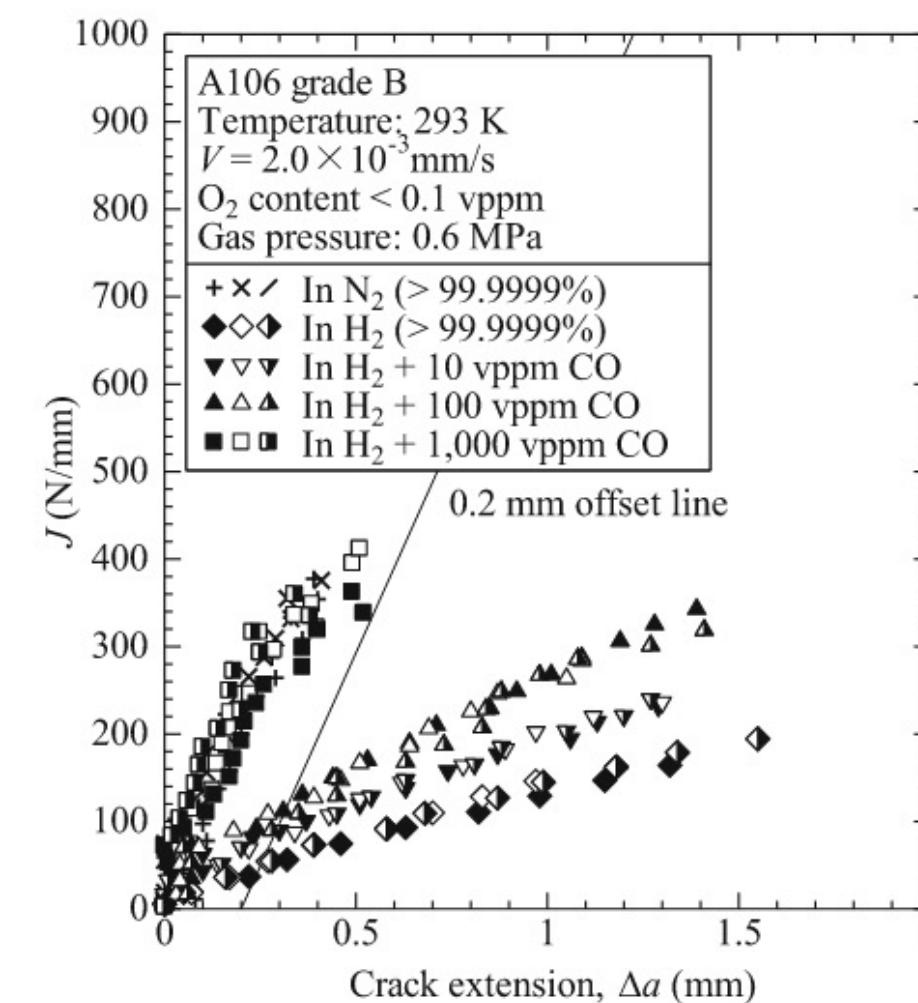
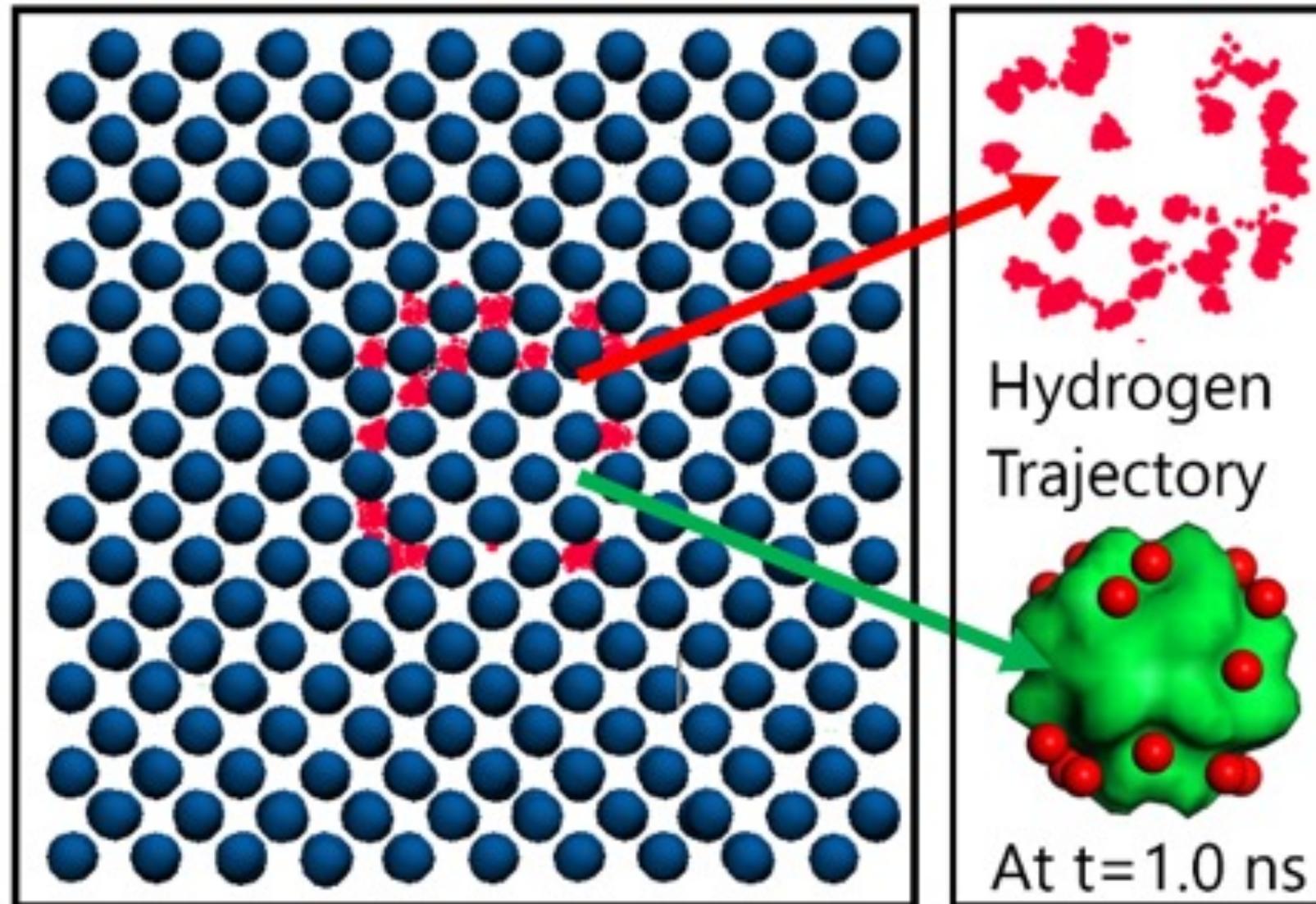
A. Karuth, A. Alesadi, A. Vashisth, W. Xia, and B. Rasulev, Reactive Molecular Dynamics Study of Hygrothermal Degradation of Crosslinked Epoxy Polymers, [ACS Applied Polymer Materials 4, 4411 \(2022\)](#)



Vitrimer polymers heal via transesterification

M. Kamble, A. Vashisth, H. Yang, S. Pranompont, C. R. Picu, D. Wang, N. Koratkara, Reversing fatigue in carbon-fiber reinforced vitrimer composites, [Carbon 187, 108 \(2022\)](#)

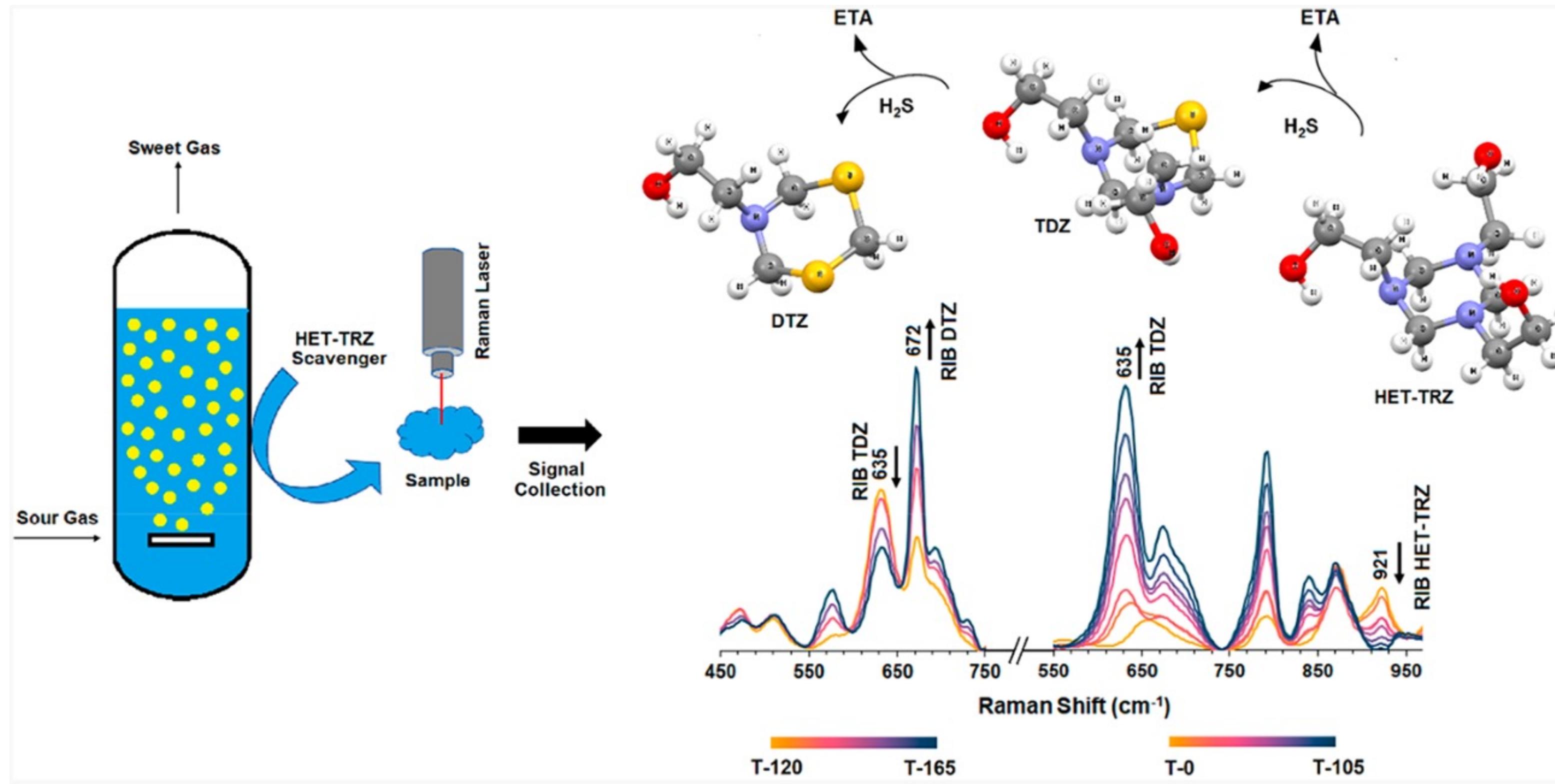
# ReaxFF: steel embrittlement



Steel hydrogen embrittlement processes with ReaxFF -> reduced by CO  
PCCP 761 (2016); [Metall. Mater. Trans. A 2021](#)

# $\text{H}_2\text{S}$ scavenging: exp + calc

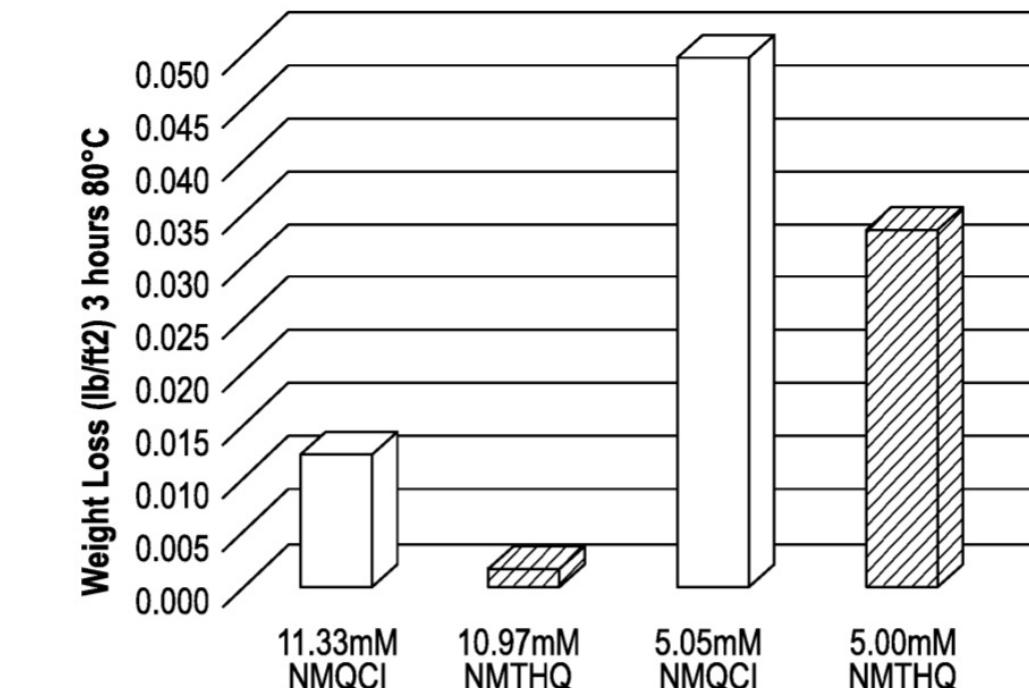
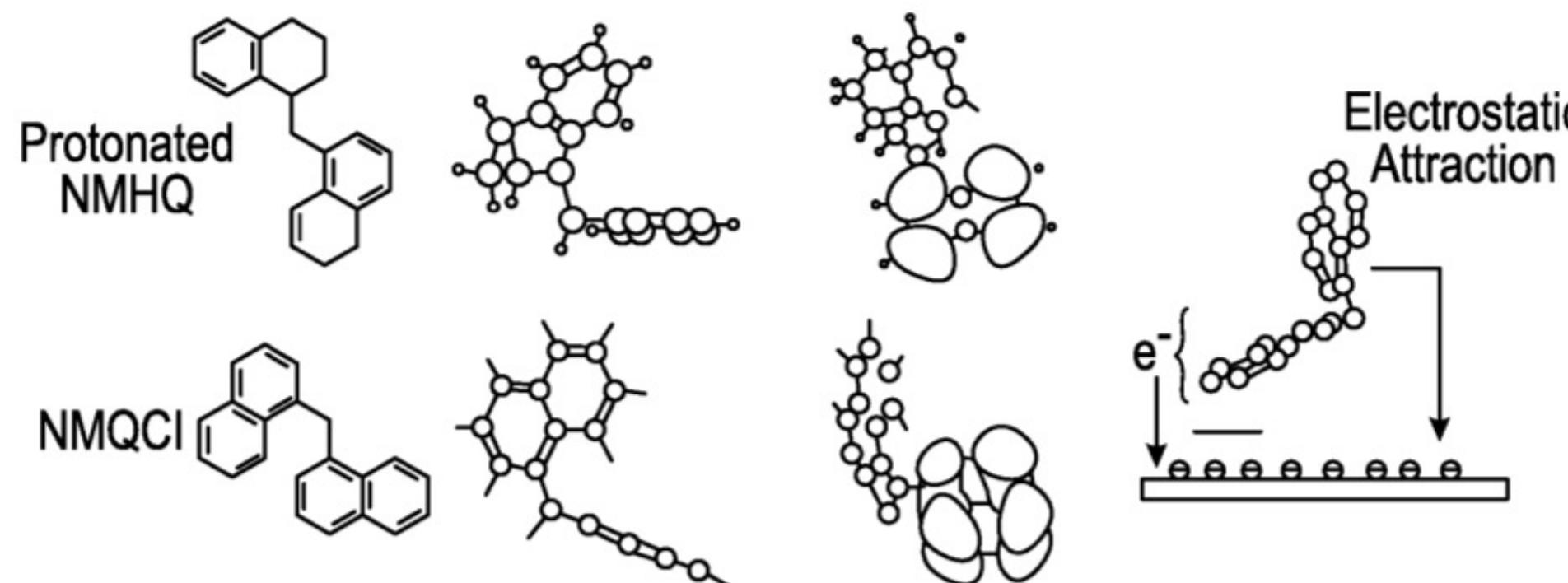
- Insight in mechanism contactor tower
- DFT + Raman to follow scavenging process



Schlumberger + Alberta [Ind. Eng. Chem. Res. 16, 5394 \(2021\)](#)

# Oxidation potentials / corrosion inhibition

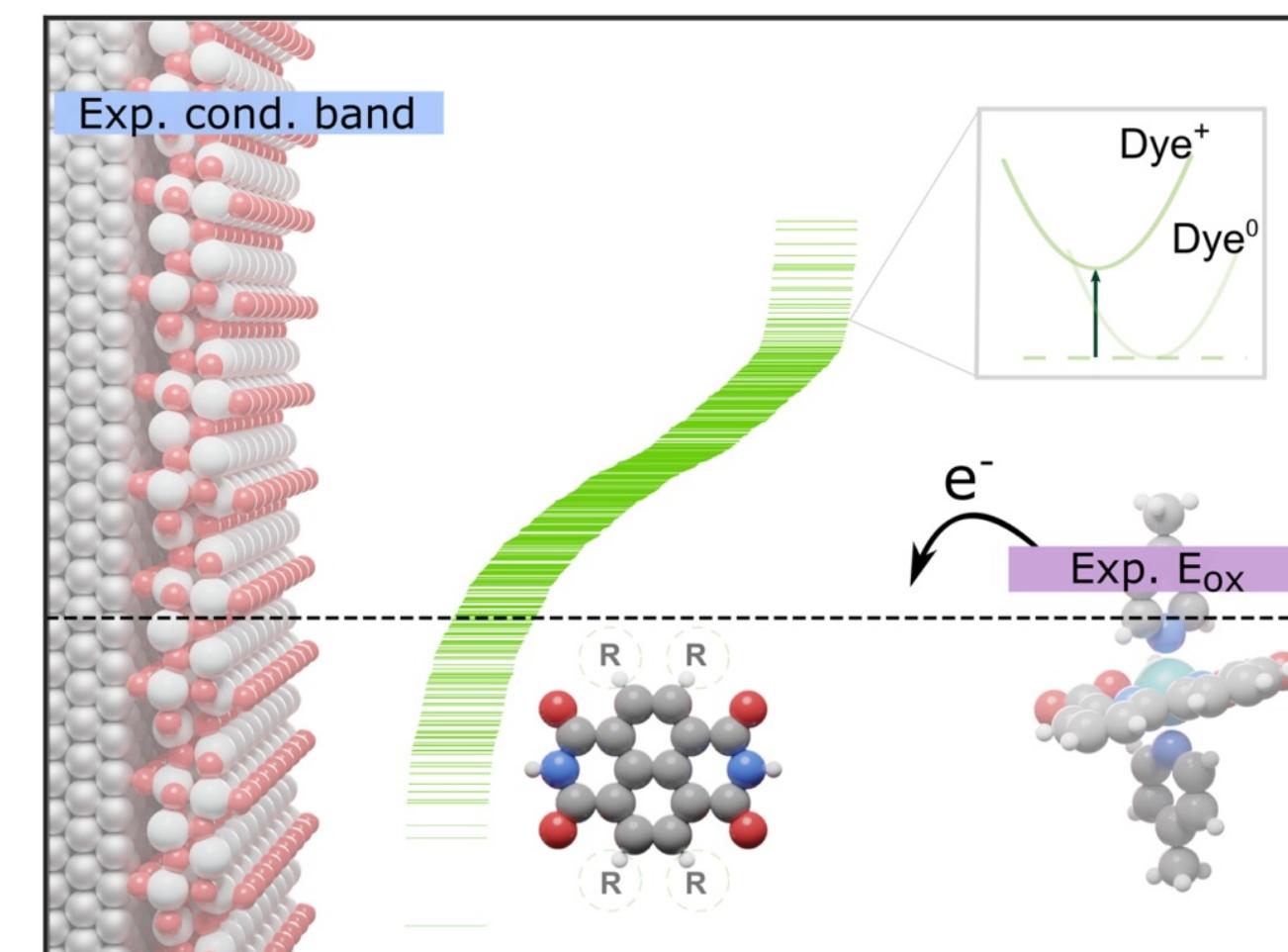
- Simple proxies: HOMO/LUMO energies, band gaps, solubility



[Schlumberger Patent](#): A corrosion inhibitor for protecting metal under acidizing conditions

- More advanced workflows:  
screen redox potentials

Automated assessment of redox potentials for dyes in dye-sensitized photoelectrochemical cells, [Phys. Chem. Chem. Phys.](#) 24, 197-210 (2022) see: [scripts](#)



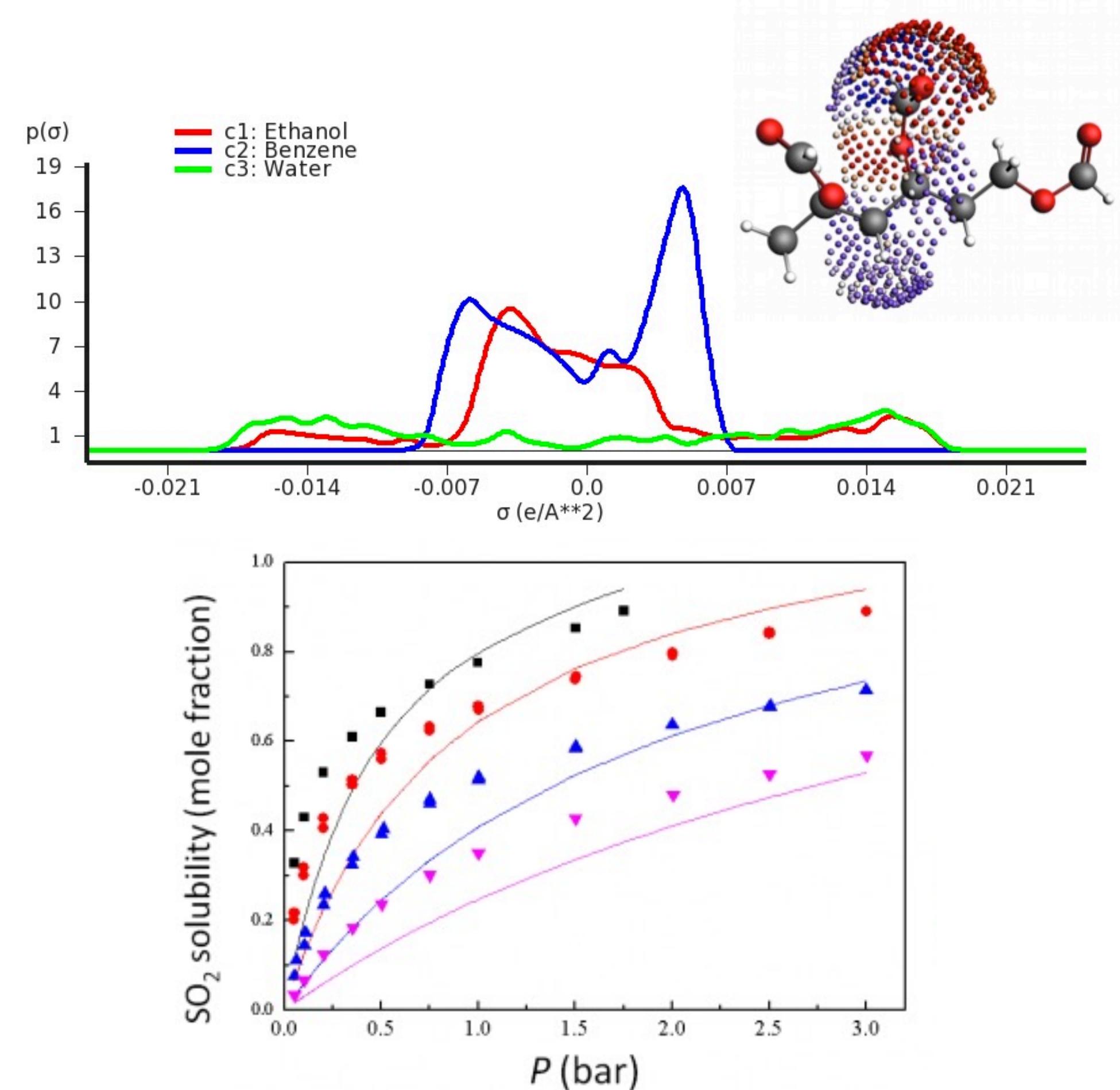
# COSMO-RS/SAC: thermodynamic properties of fluids

## Quantum Chemistry & QSPR for quick property predictions

COntinuum Solvation MOdel + RS (Klamt), SAC (Sandler)

DFT (or SMILES): chemical potential => activity coefficients => properties

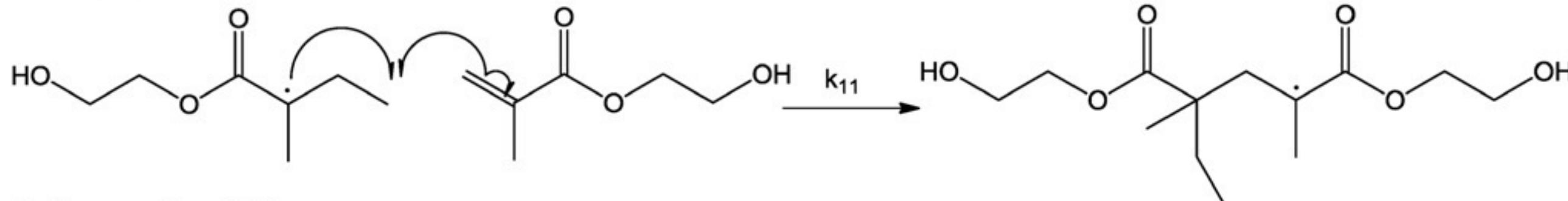
- Solvation & excess energies, pKa
- Solubilities, LLE, VLE, boiling points
- Optimize mixtures: solubility, LLE
- Polymers: Flory-Huggins X



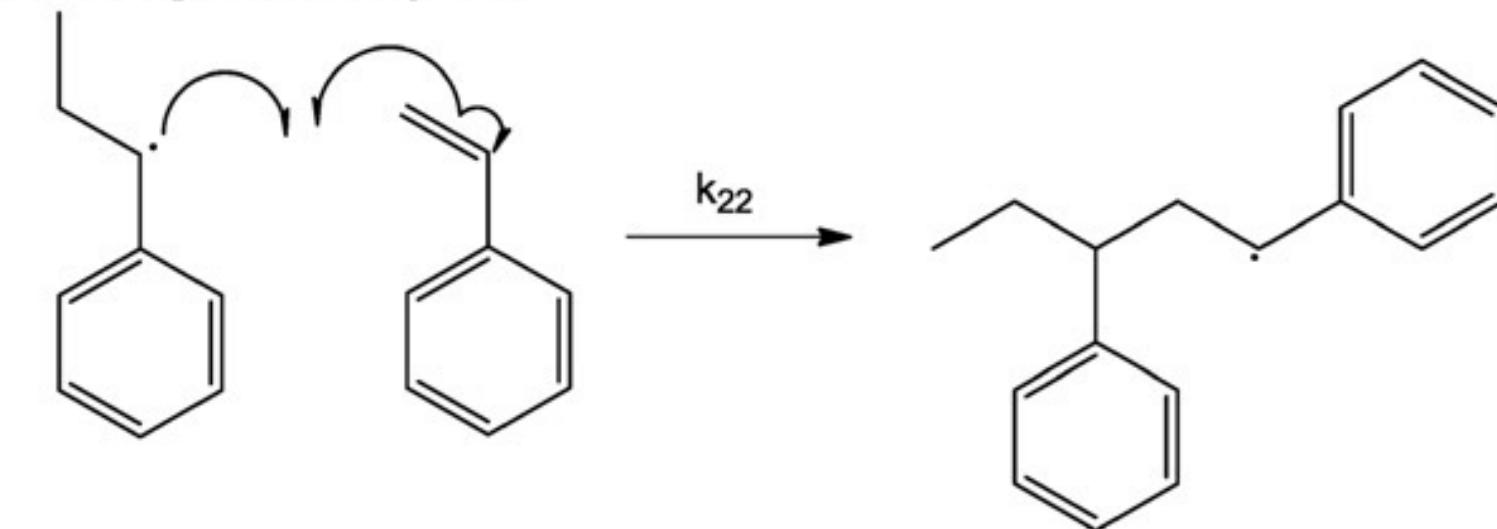
# COSMO-RS reaction rates

Copolymer composition is solvent-dependent

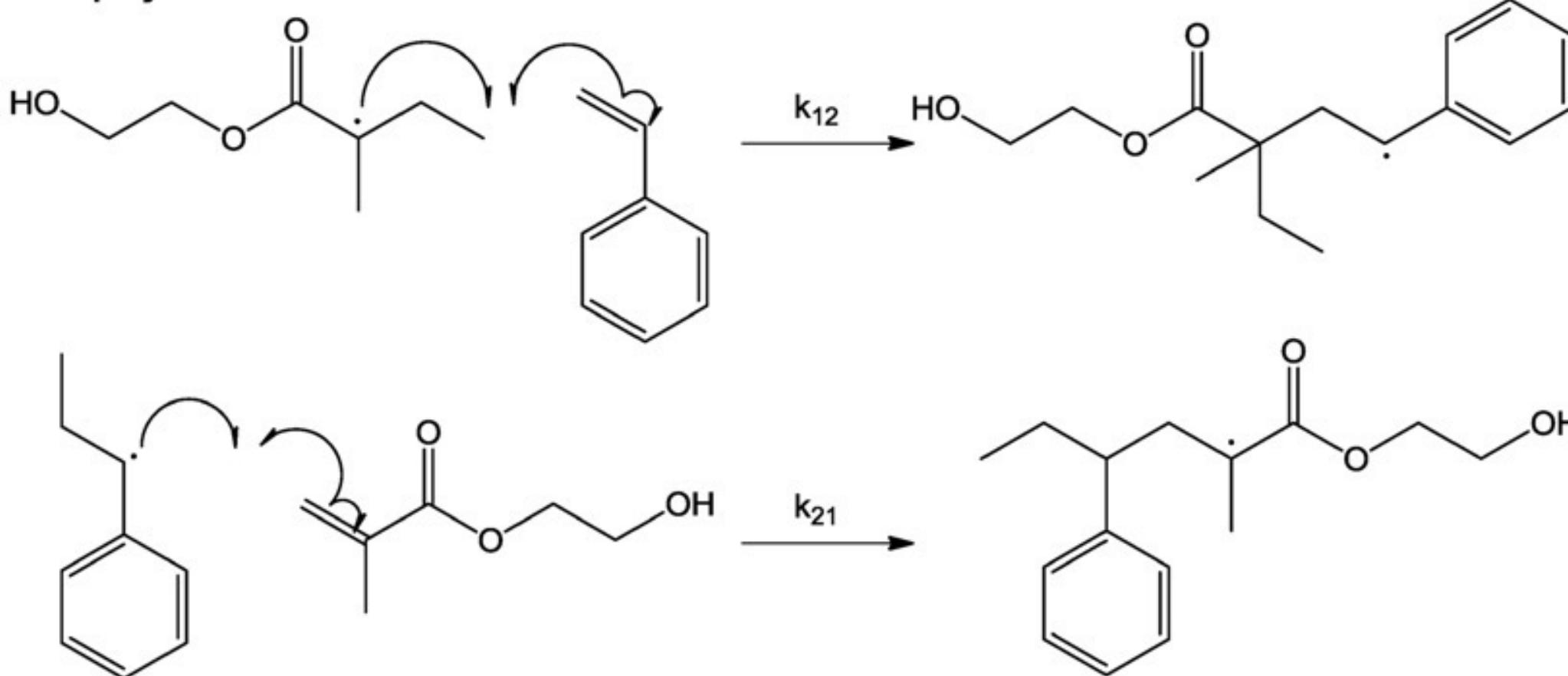
## 1. Propagation of HEMA



## 2. Propagation of Styrene

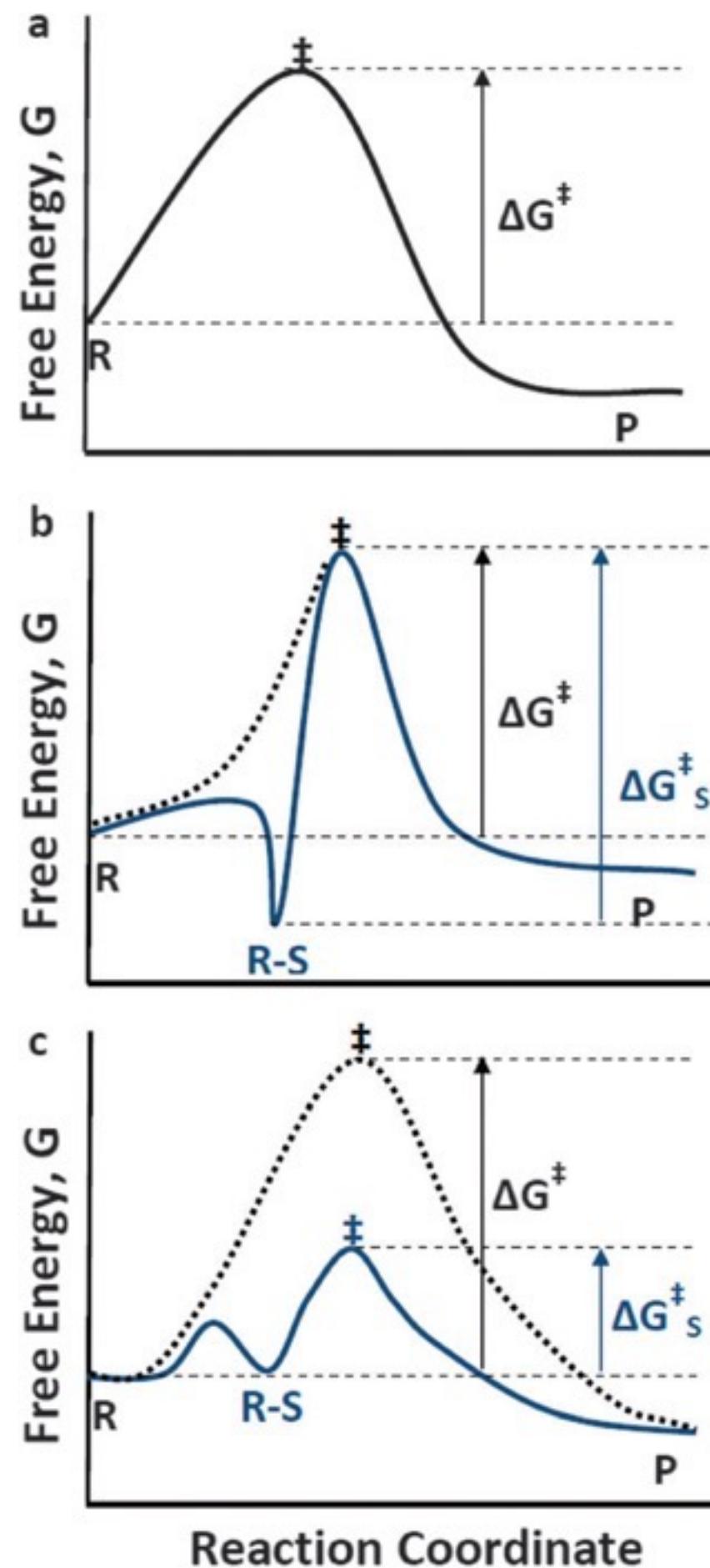


## 3. Copolymerization



# COSMO-RS reaction rates

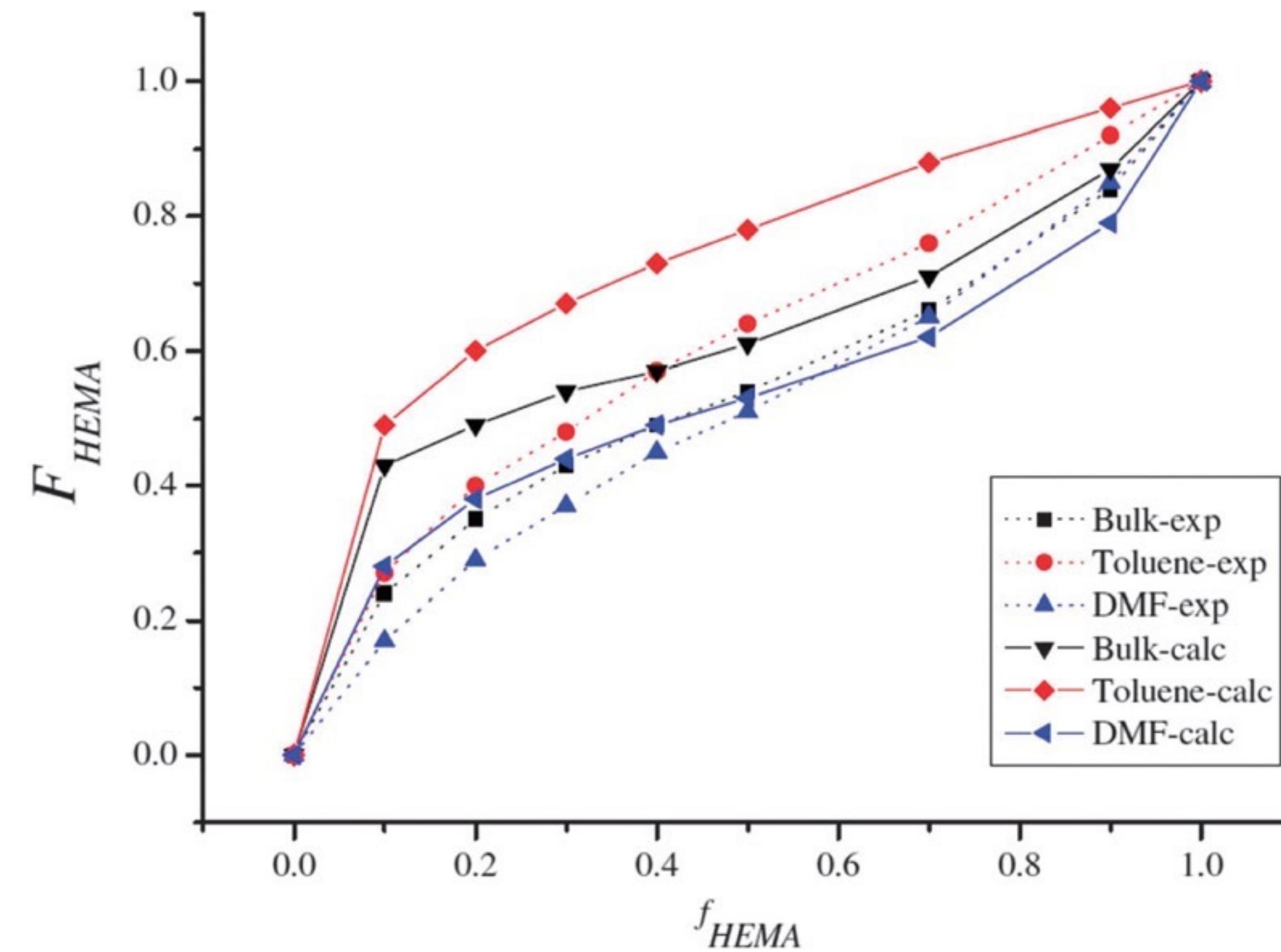
Copolymer composition is solvent-dependent



Gas phase

Reactants  
stabilized by  
solvation

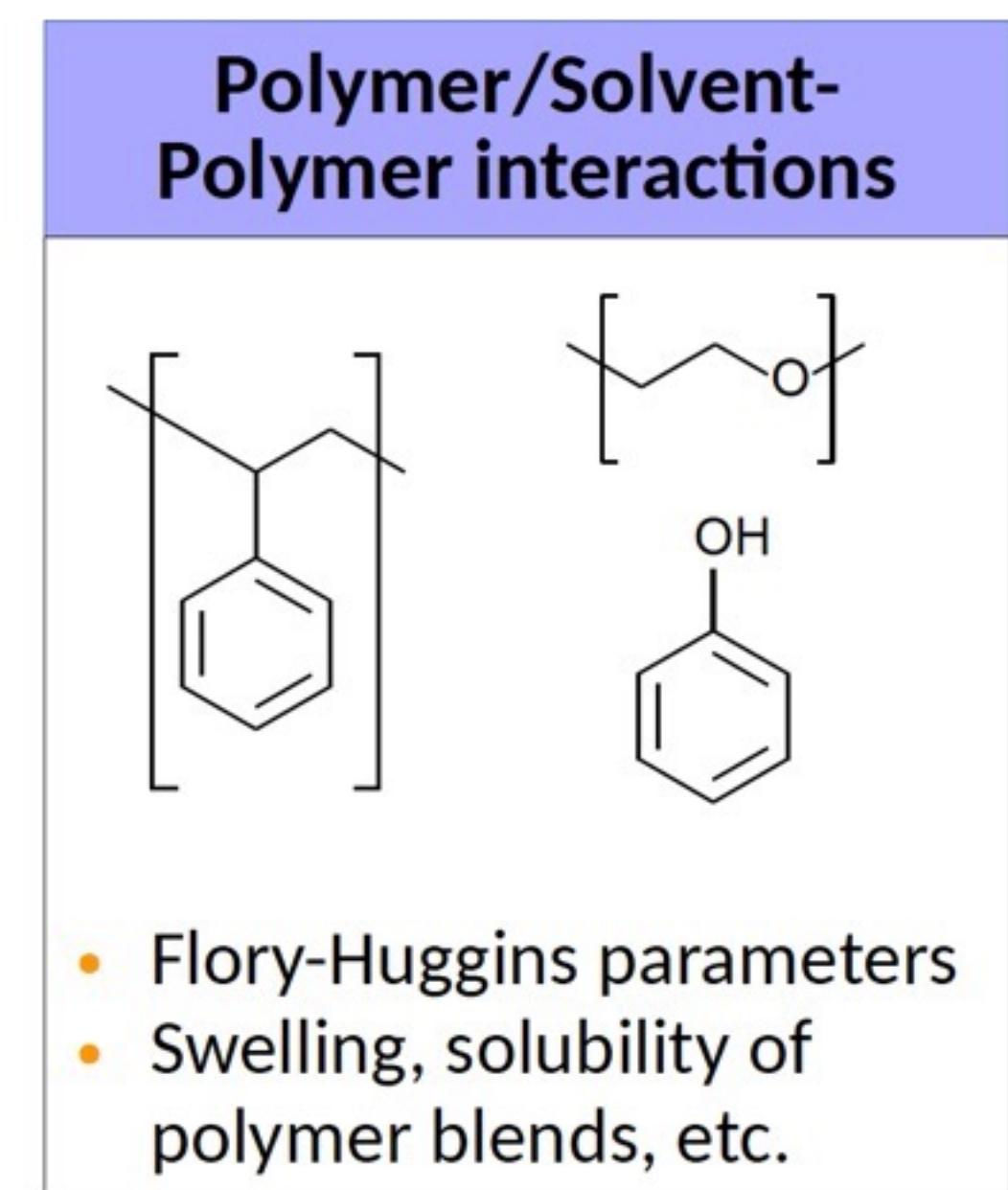
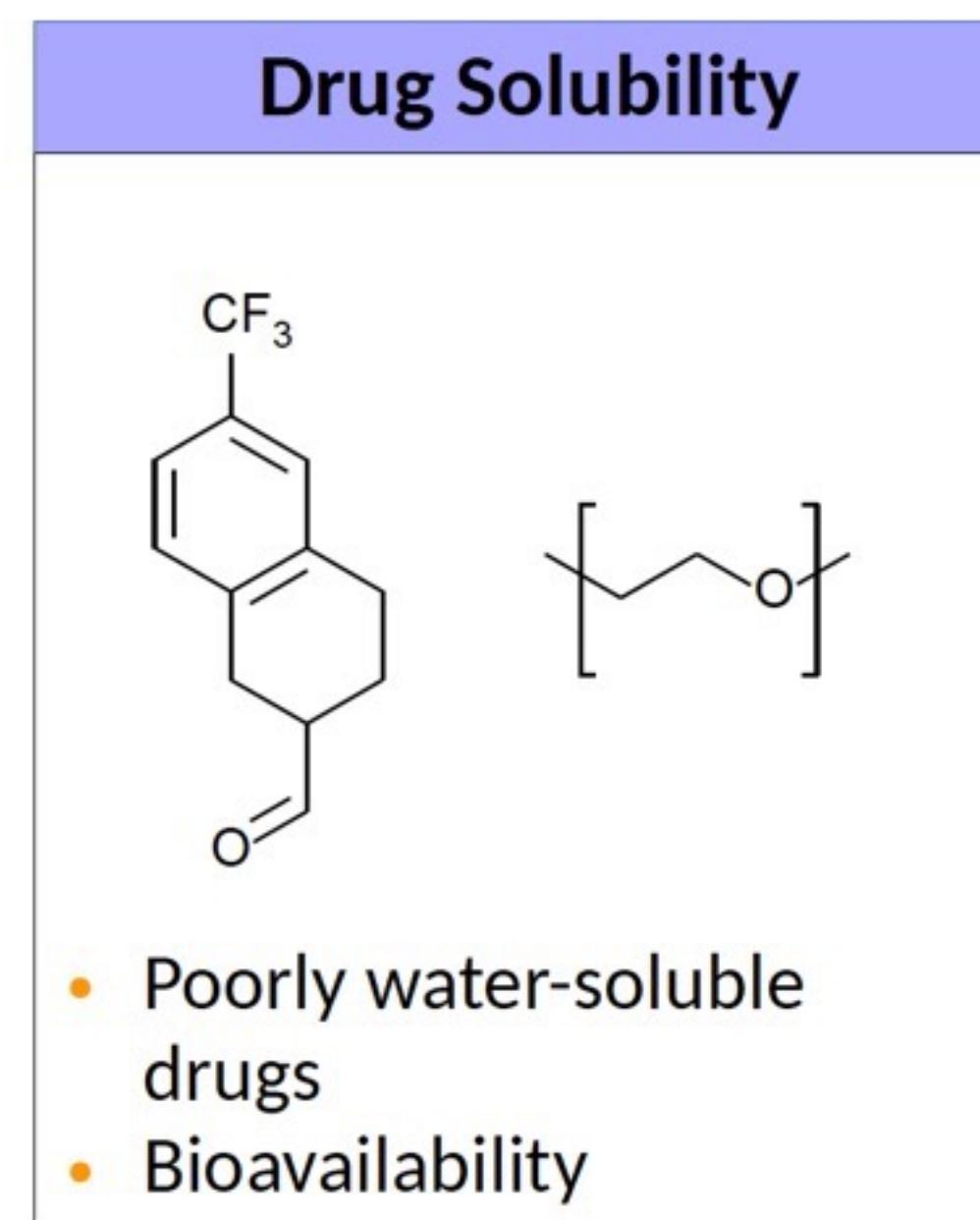
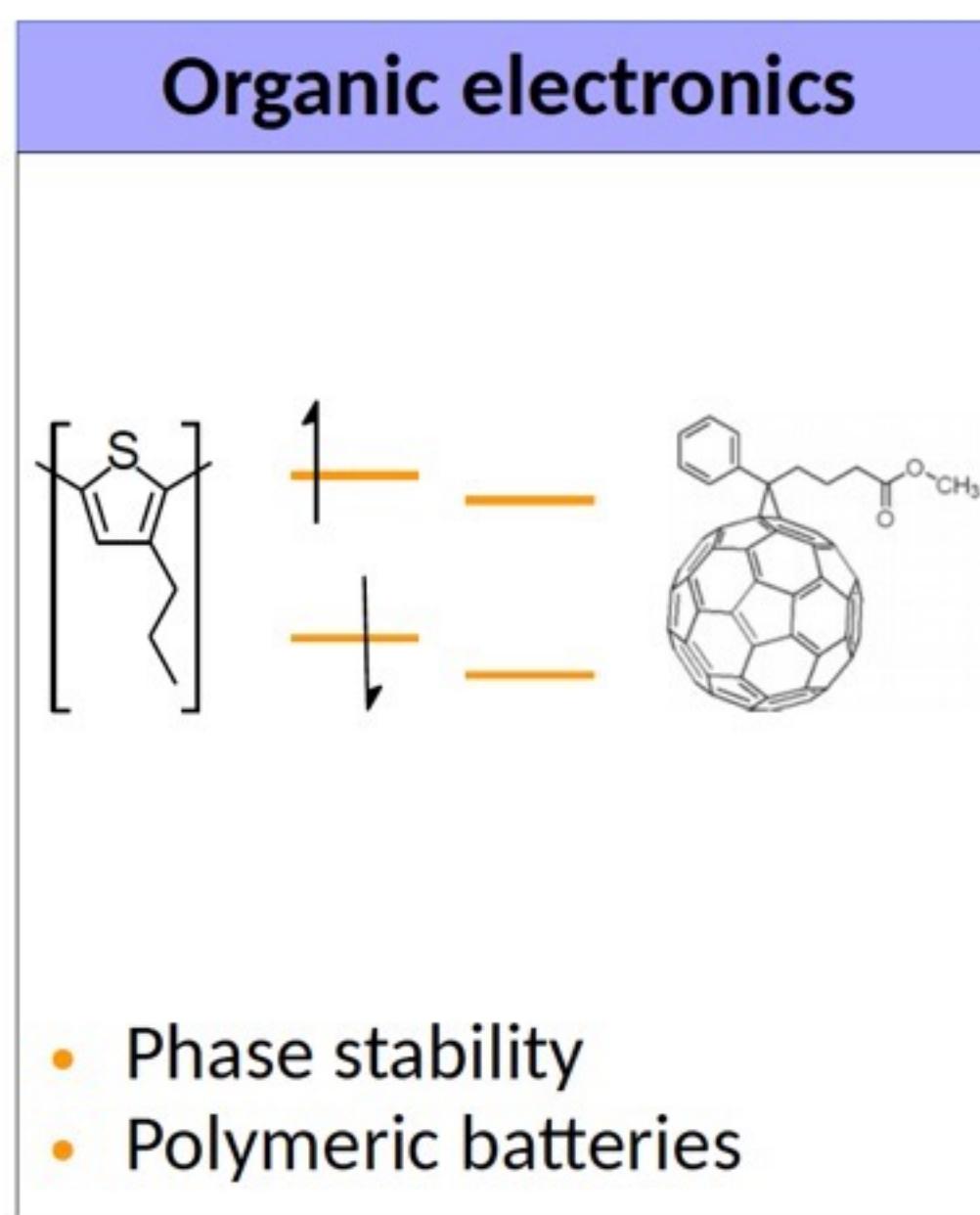
TS stabilized  
by solvation



[New J.Chem., 38, \(2014\) 170](#)

# Polymer mixture design with COSMO-RS

- COSMO-RS: mixture thermodynamics ([video demo](#))
  - Liquid-activity coefficient
  - Fit to experimental data (predictability outside fit)
  - Pseudo-chemical potential from quantum mechanics (surface charges)
- Existing design approaches focus on property targeting (QSPR)
- Mixing => requires free energies, activities



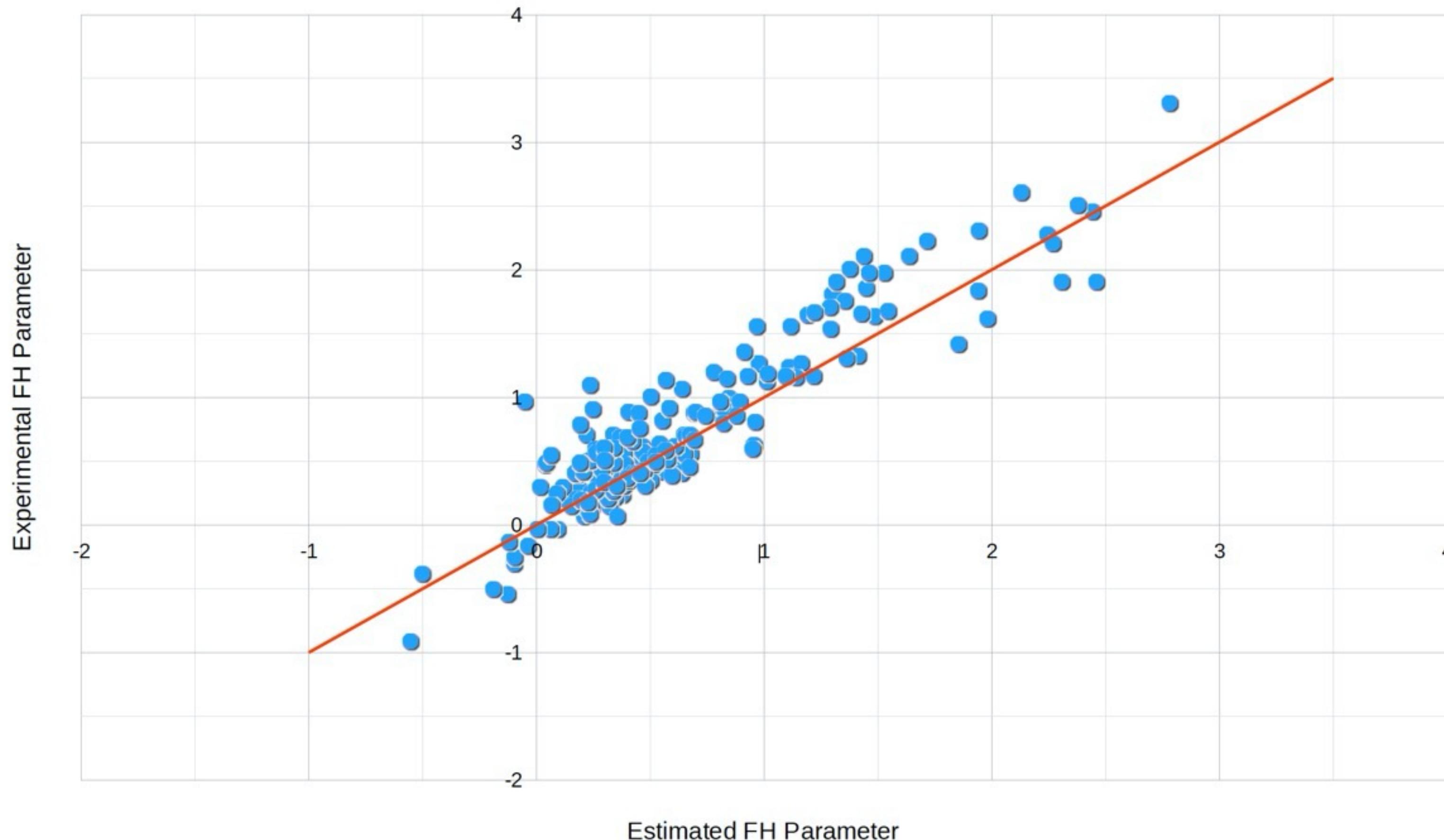
# Flory-Huggins from COSMO-RS

$N_{p/s}$  – Number of moles of polymer / solvent

$\phi_{p/s}$  – Volume fraction of polymer / solvent

$\chi_{ps}$  – Flory – Huggins Parameter

$$\frac{\Delta G_{mix}}{RT} = N_p \ln(\phi_p) + N_s \ln(\phi_s) + N_s \phi_p \chi_{ps}$$



# Optimize solvent mixtures: extraction

- Remove impurities or extract (natural) products

## Specify solvents

Water  
Methanol  
Ethanol  
1-Hexanol  
Diethyl ether  
Benzene  
Toluene  
Acetic acid  
2-Hexanone  
DMF  
THF  
Dioxane  
...

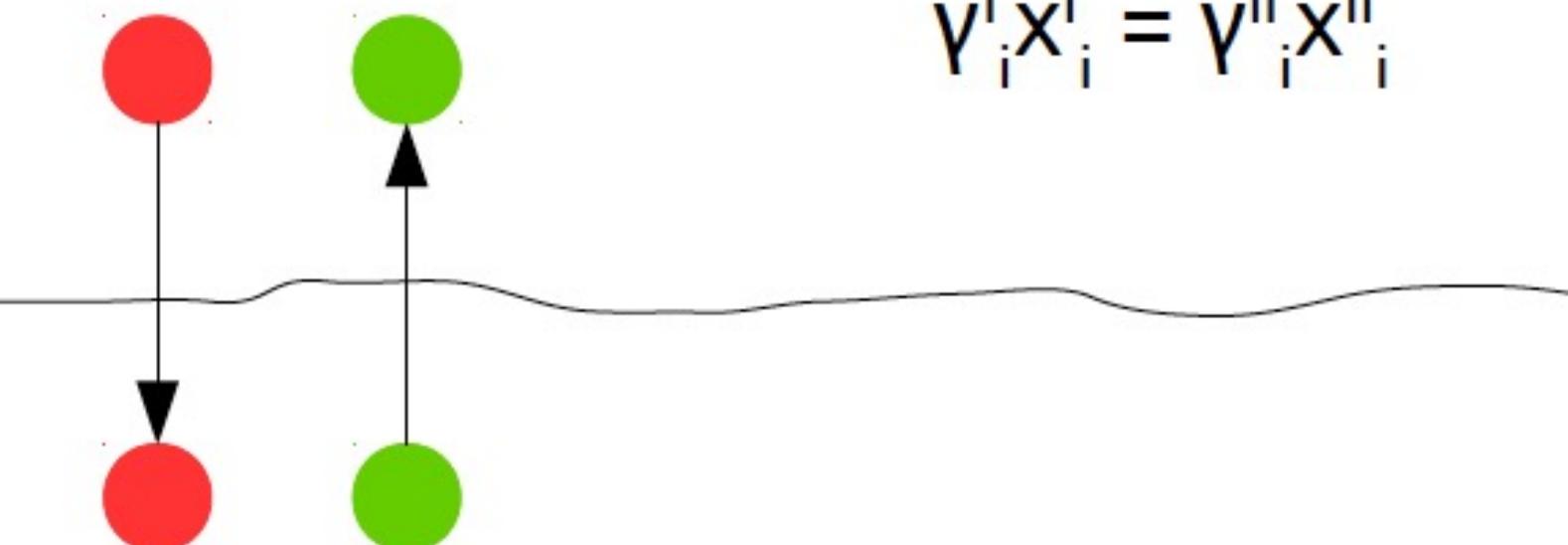
## Specify problem conditions

Optimization direction: maximize  
Maximum number of solvents: 3  
Temperature: 298.15K (or range)  
...

## Specify solutes

Acetic acid   
Water 

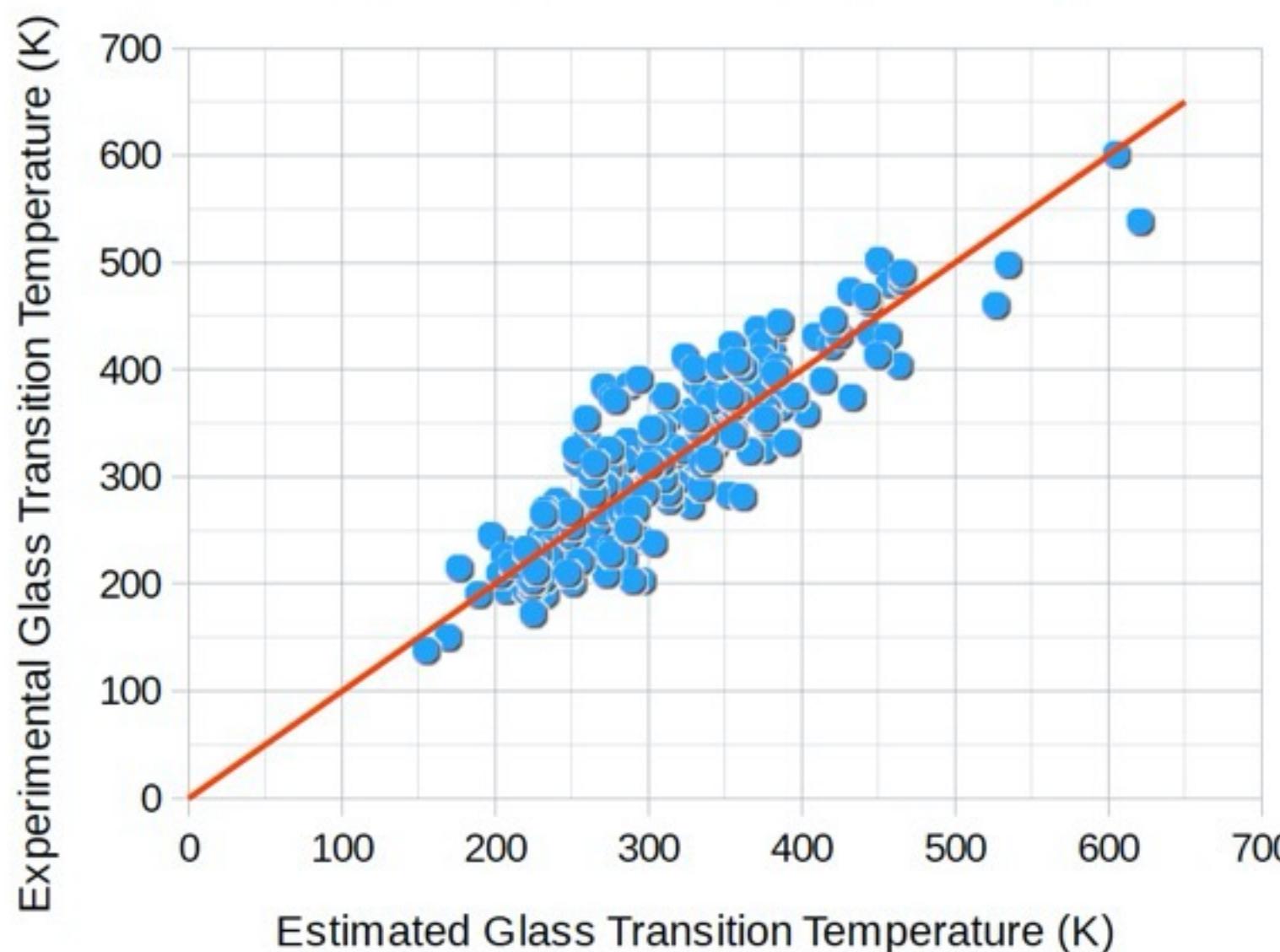
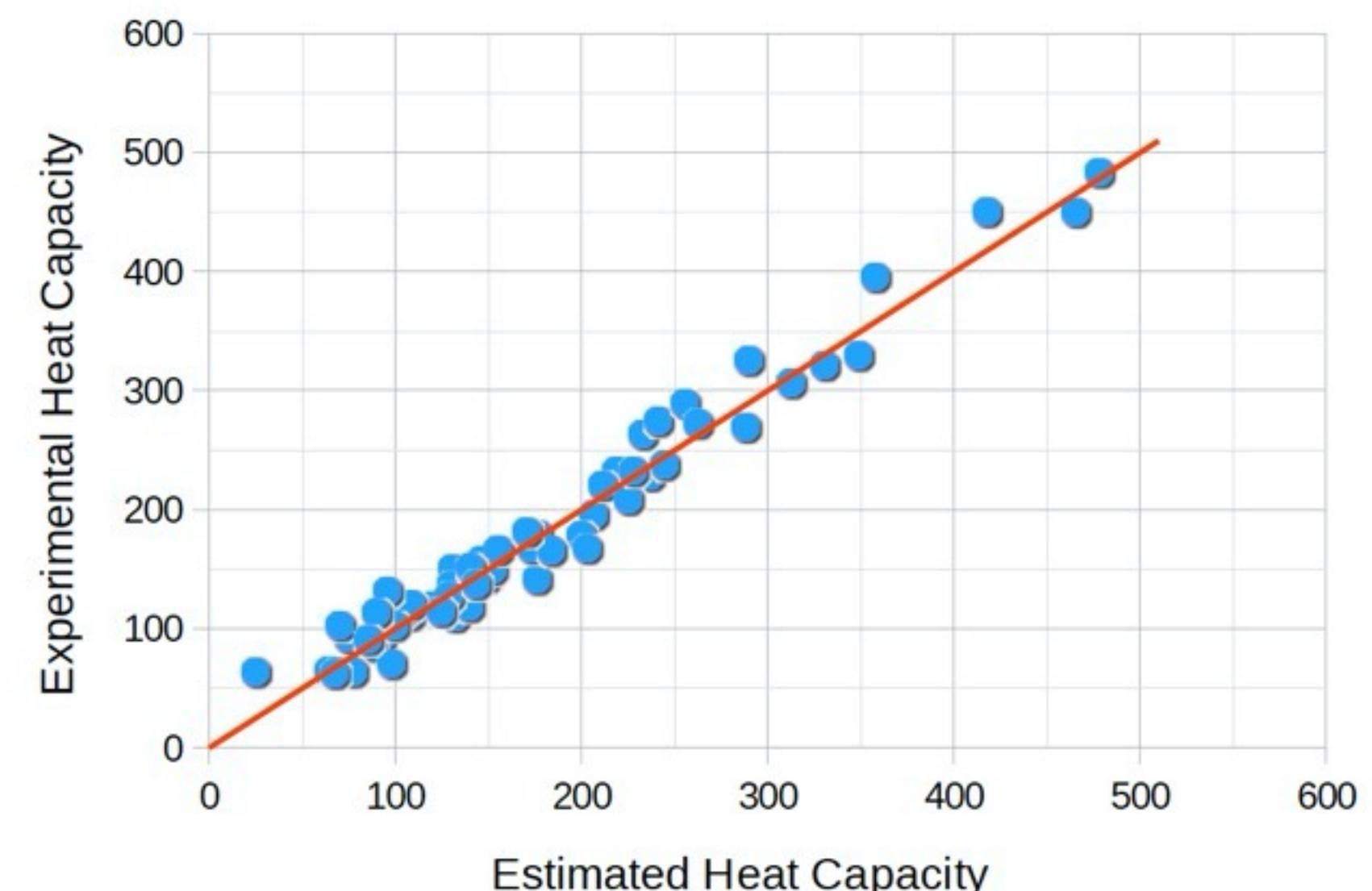
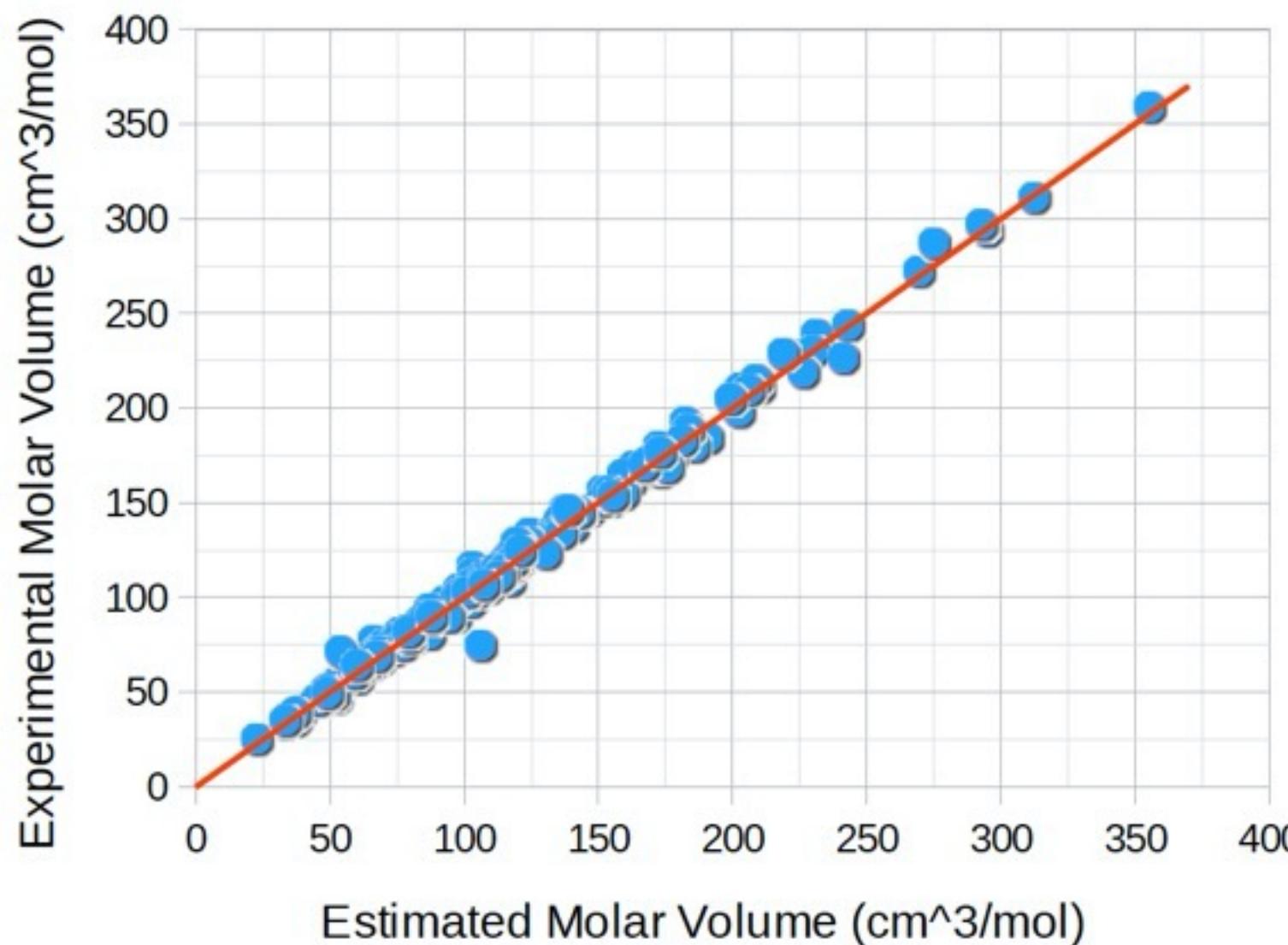
## Liquid phase I



## Liquid phase II

Maximize  
the partition  
coefficient

# QSPR predictions with sigma-moments



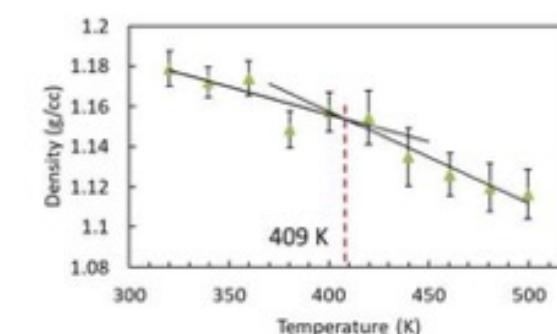
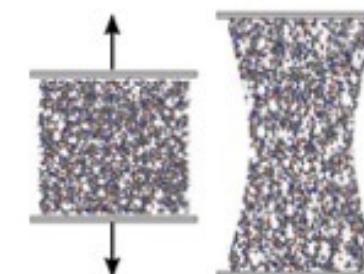
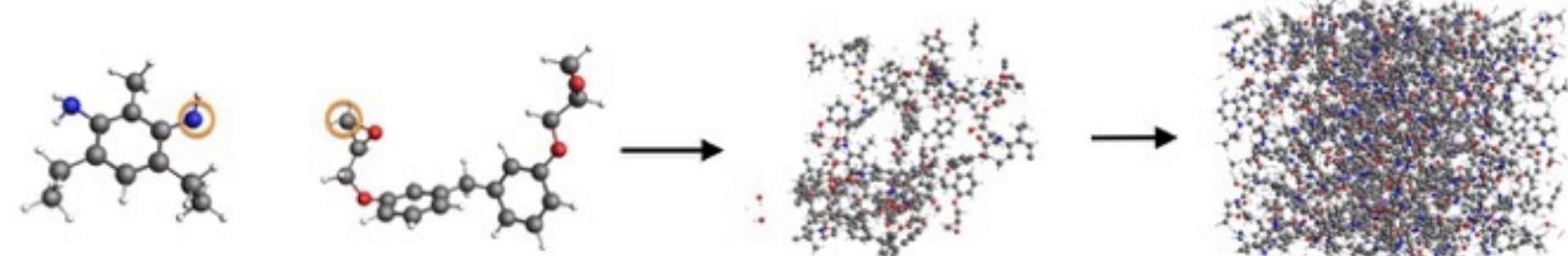
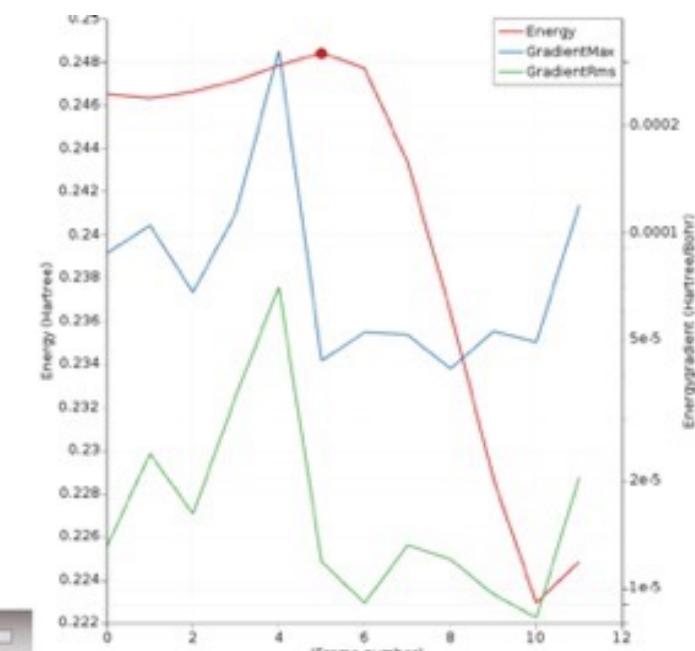
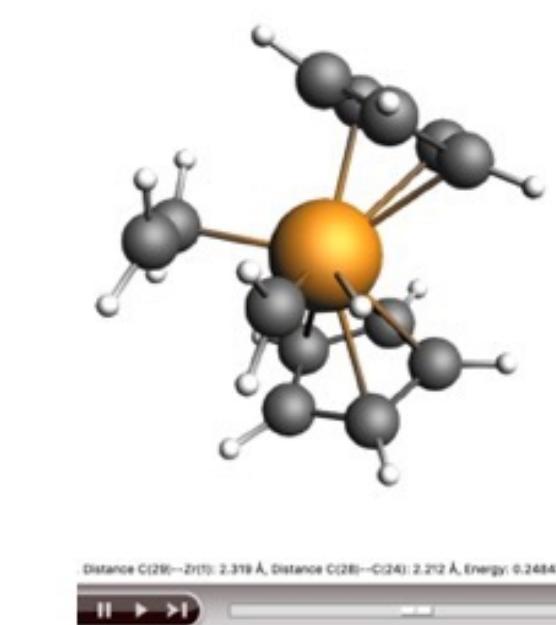
Basic statistics	
r <sup>2</sup> :	
• Molar volume:	> 0.99
• Heat Capacity:	0.96
• Glass Transition Temp. :	0.81
Average absolute error:	
• Molar volume:	3.1 cm <sup>3</sup> /mol
• Heat Capacity:	13.8 J/(mol K)
• Glass Transition Temp. :	45 K

# Let's help you accelerate your R&D!

What can be improved?  
Need help setting up?  
Errors?

[support@scm.com](mailto:support@scm.com)

[goumans@scm.com](mailto:goumans@scm.com)



$N_{ps}$  – Number of moles of polymer / solvent  
 $\phi_{ps}$  – Volume fraction of polymer / solvent  
 $\chi_{ps}$  – Flory – Huggins Parameter

$$\frac{\Delta G_{mix}}{RT} = N_p \ln(\phi_p) + N_s \ln(\phi_s) + N_s \phi_p \chi_{ps}$$

