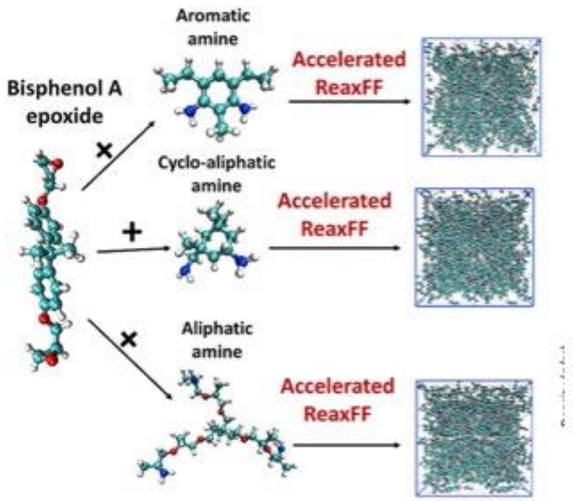
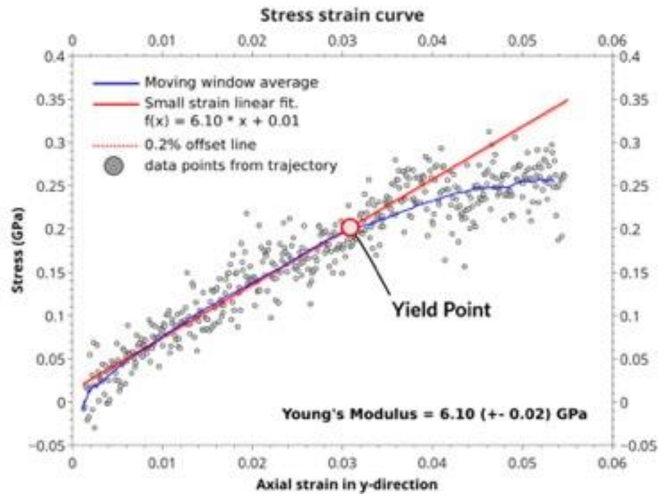
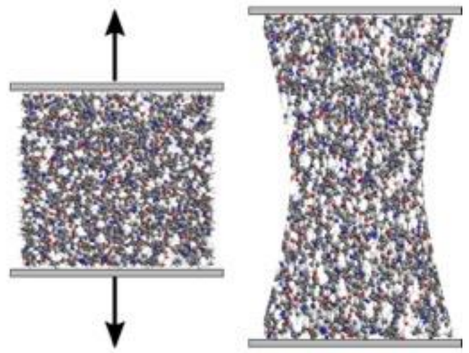
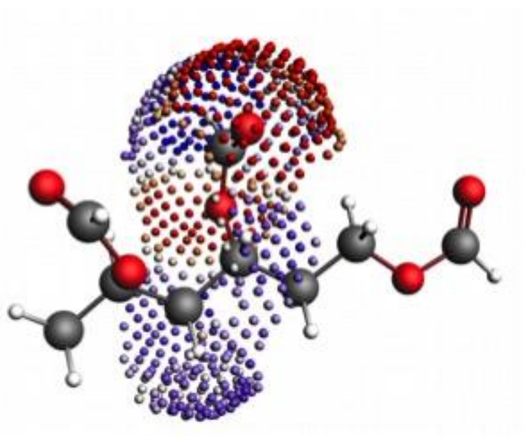
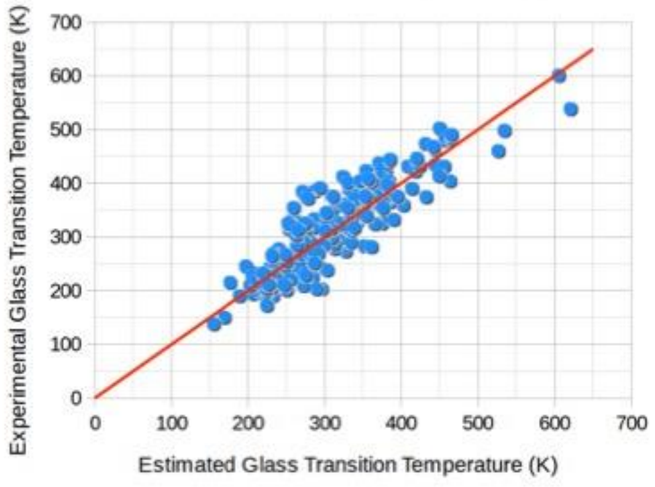
Chemistry & Materials with the Amsterdam Modeling Suite: Polymers

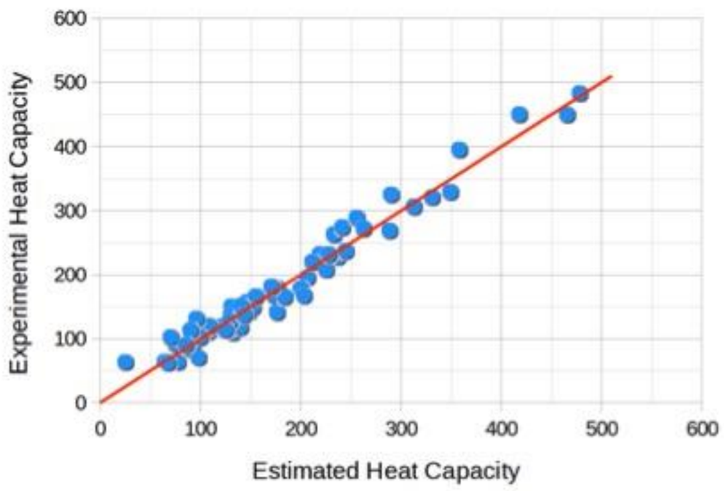












SCM
Software for Chemistry & Materials

Fedor Goumans, goumans@scm.com
SCM support: support@scm.com

Background: SCM, ADF & AMS

- AMOL/ADF: first DFT code for chemistry (1970s)
  Baerends@VU (>'73), Ziegler@Calgary(+) (>'75)

- 1980s: Mitsui, Shell, Akzo, Unilever: AMOL training
  - Tom Ziegler => Ziegler-Natta catalysts, hydroformulation
  - BAND for periodic systems

- SCM: Spin-off company 1995
  - To keep supporting (industrial) end users!

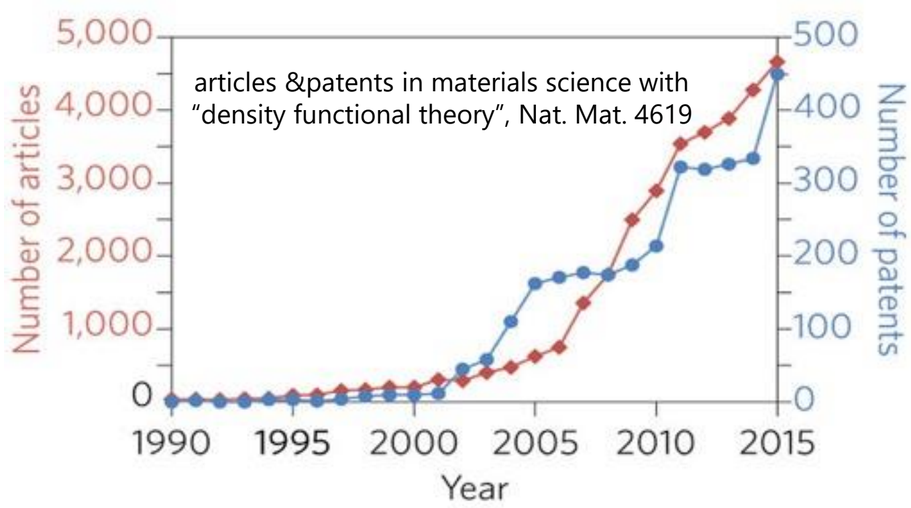
- 2010s: DFTB, ReaxFF, COSMO-RS (Albemarle, DSM)

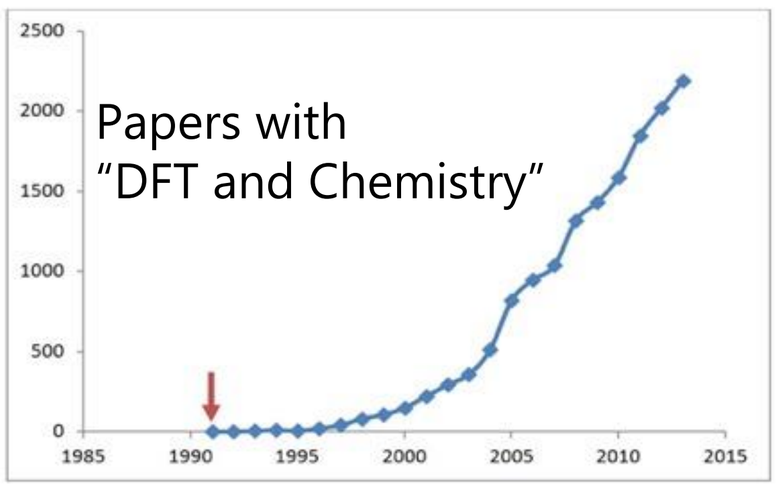
- 2019: Multi-scale: ReaxPro (BASF, Dow, Shell, JM)

- 21 people (16 senior PhD's) + 4 EU fellows

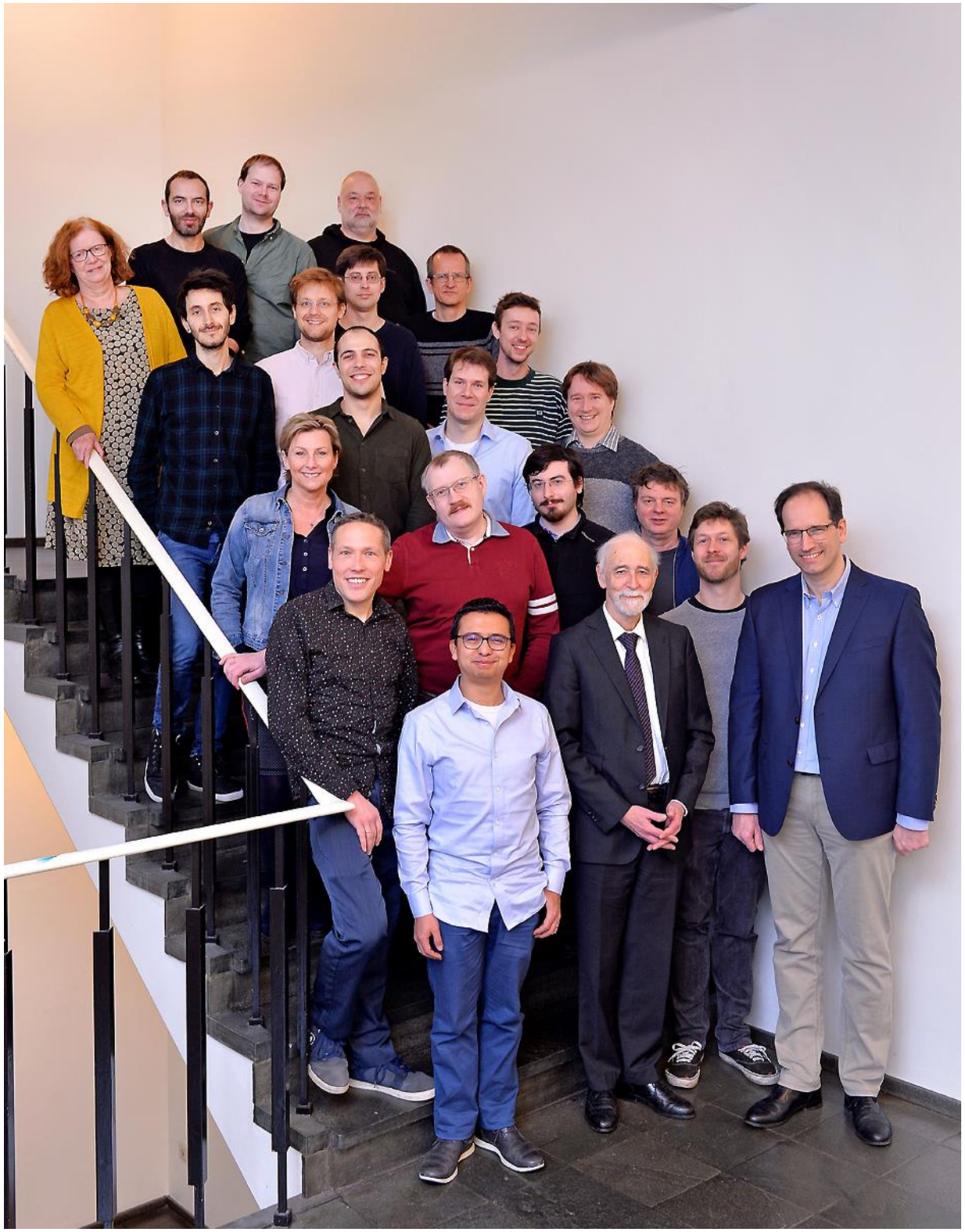
- Many academic collaborators & EU networks

- SCM: development, debug, port, optimize, & <u>support</u>





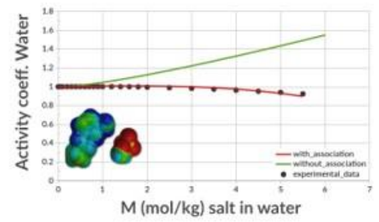
The SCM team in Amsterdam



- 2 office support
- 15 developers
- 3 support scientists
- 4 PhD students (EU)

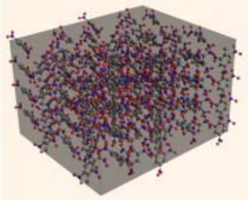
Amsterdam Modeling Suite

- ADF: powerful molecular DFT
  - Reactivity, spectroscopy
- BAND: periodic DFT, QE & VASP interface
  - (2D) Materials, spectroscopy, analysis
- DFTB & MOPAC: fast electronic structure
- ReaxFF: Reactive MD complex systems
- MLPotential
  - Backends SchNetPack, sGDML, PiNN, TorchANI
- COSMO-RS: fluid thermodynamics
  - VLE, LLE, logP, solubility
- AMSdriver: PES exploration, MD, MC
  - Hybrid: multi-layer, QM/MM, QM/QM'
- Integrated GUI, PLAMS: python scripting
- Interface with multi-scale and ML methods

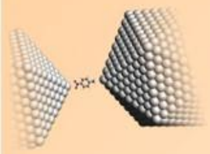


AMS driver GUI PLAMS

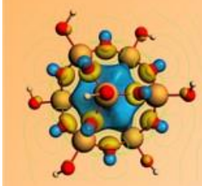
Continuum



Materials



Nano



Atomistic

COSMO-RS
Fluid Thermodynamics & Property Estimation

ReaxFF
Reactive Force Field

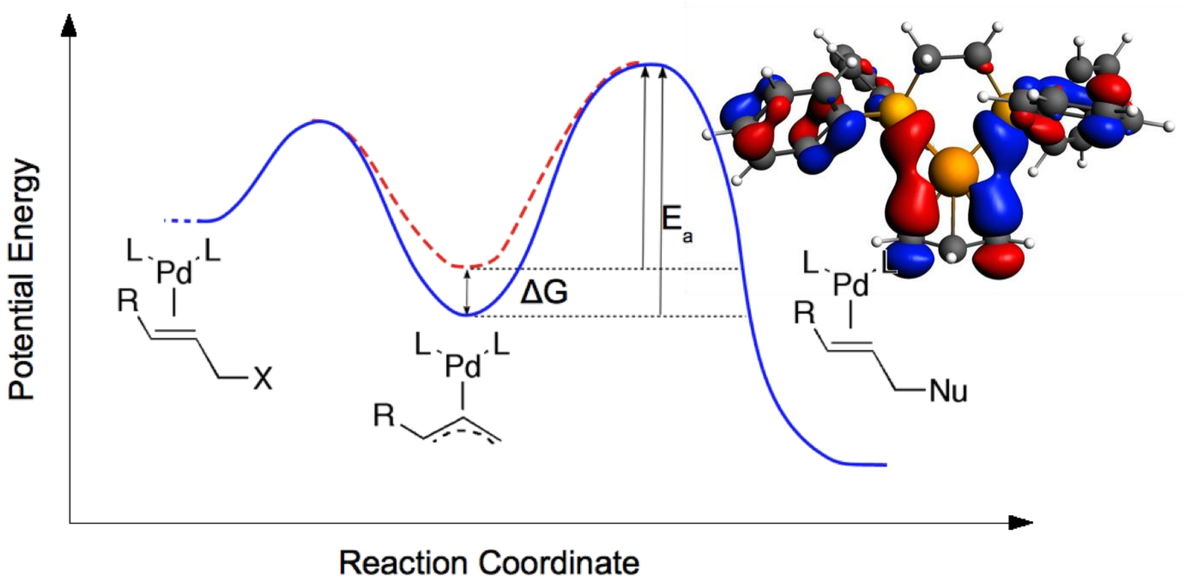
MLPotential
Machine Learning Potentials

DFTB & MOPAC
Fast approximate DFT Semiempirical

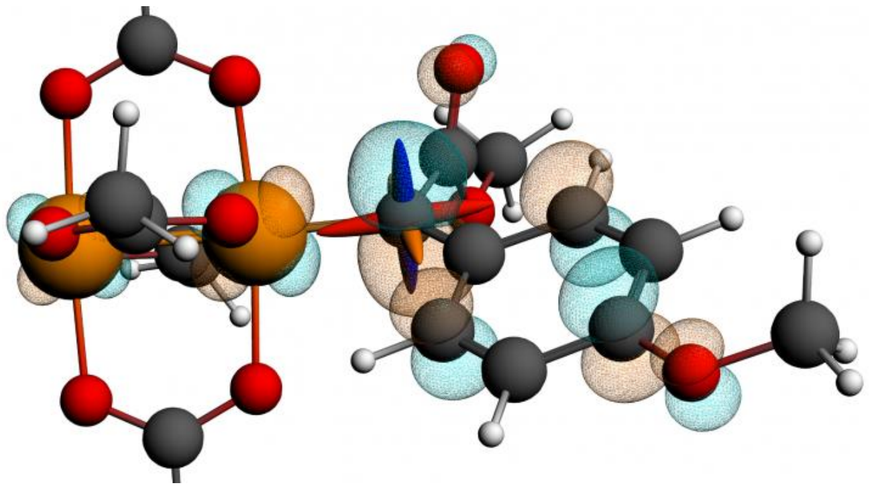
BAND
Periodic DFT

ADF
Molecular DFT

ADF: Molecular DFT



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



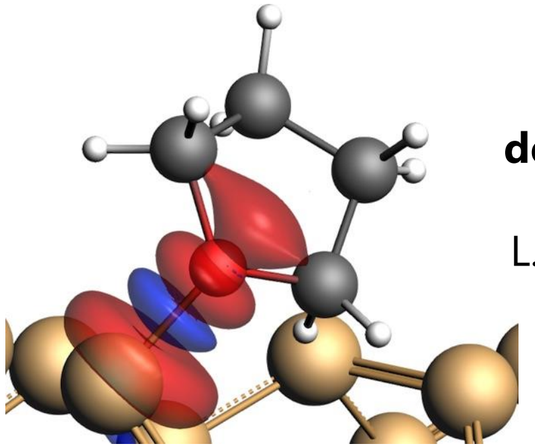
NMR calculations locate ^{13}C di-Rh carbene catalyst intermediate, Science, **342**, 351 (2013)

Strong & unique points

- All-electron Slaters, H-Og
- Relativity: ZORA (SR, **SOC**)
- Modern xc functionals
- Spectroscopy
  - EPR, NMR, IR (VCD), UVVIS, XAS
- Bonding analysis:
  - Fragment-based approach
  - ETS-NOCV, QTAIM, MO diagrams, NCI, ...
  - Activation strain model
  - Transfer integrals
- Environments
  - Subsystem DFT, DRF, QM/MM

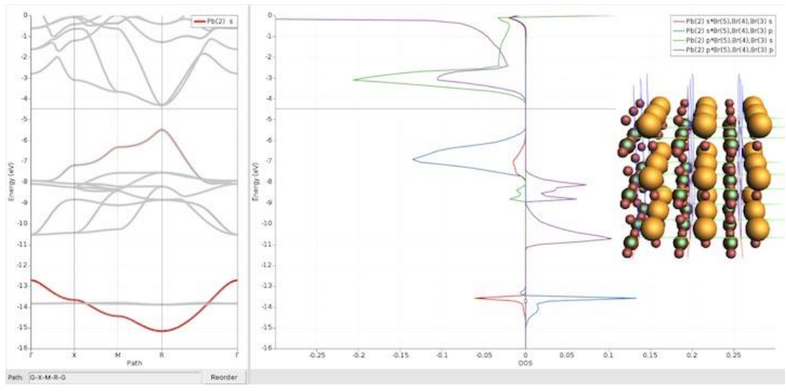
BAND vs. Plane Wave codes (QE)

- 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



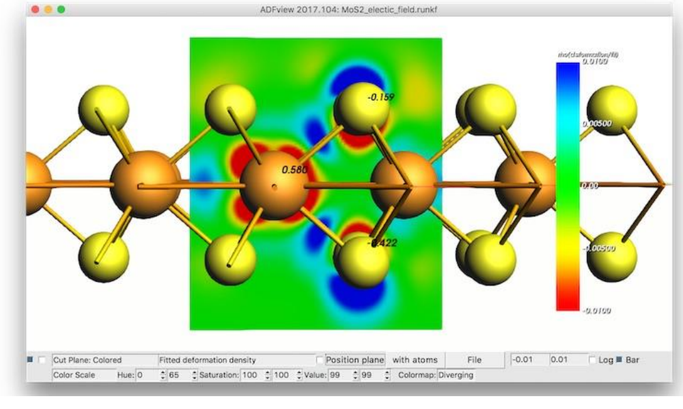
periodic energy decomposition analysis (tutorial)
L. Pecher and R. Tonner
WIREs CMS, (2018)

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



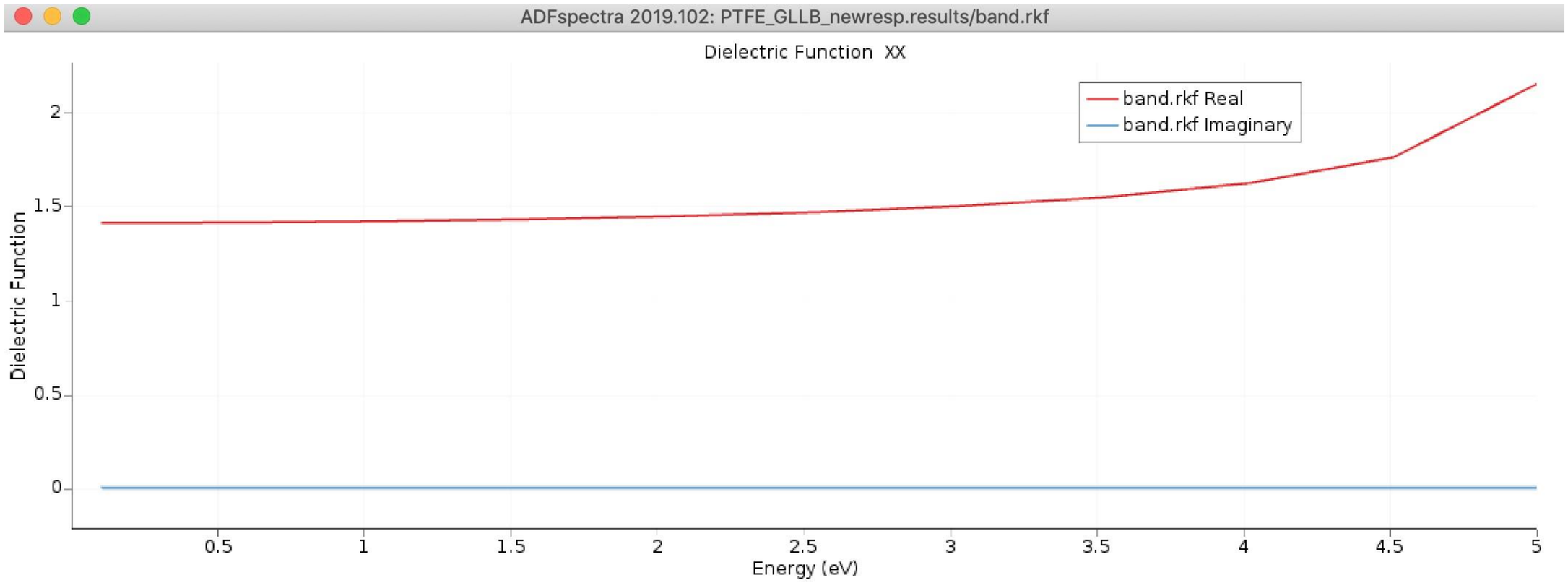
COOP in perovskites (tutorial)
Goesten & Hoffmann
JACS (2018)

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

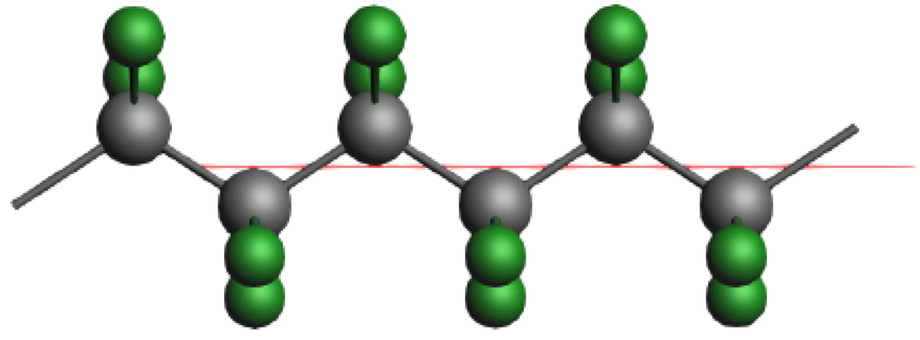


Polarizing 2D semiconductor (tutorial)
N. Zibouche et al.
PCCP (2014)

TDCDFT for polymers (proper 1D)



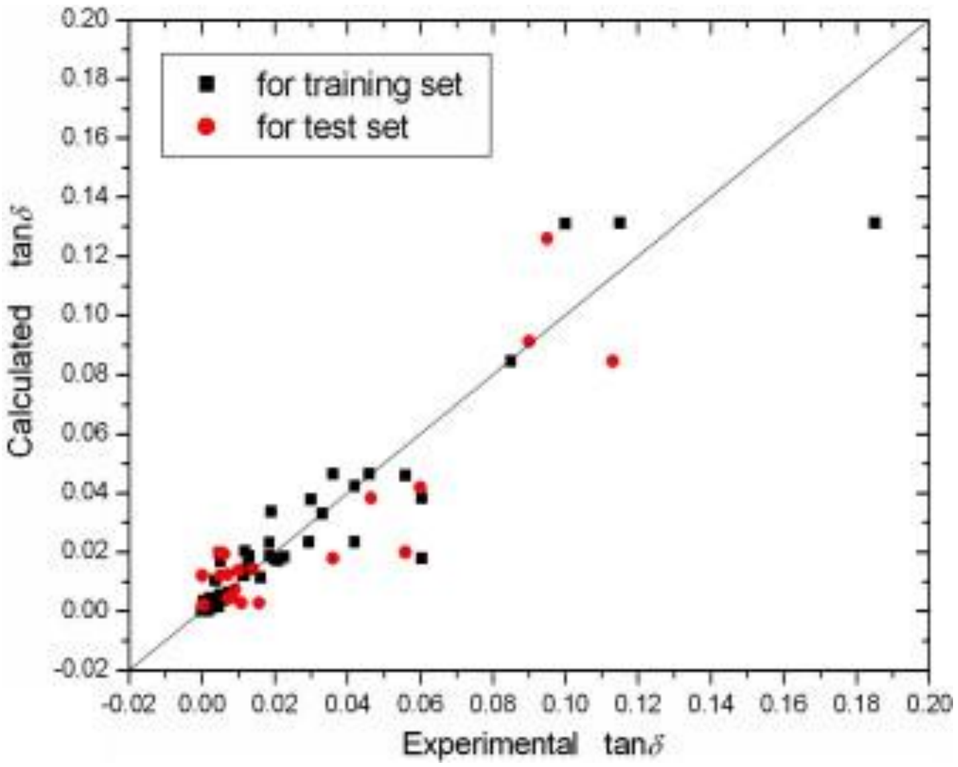
PTFE
tangent loss at 0.1 eV = 1e-05



Dielectric properties from QSPR or MD

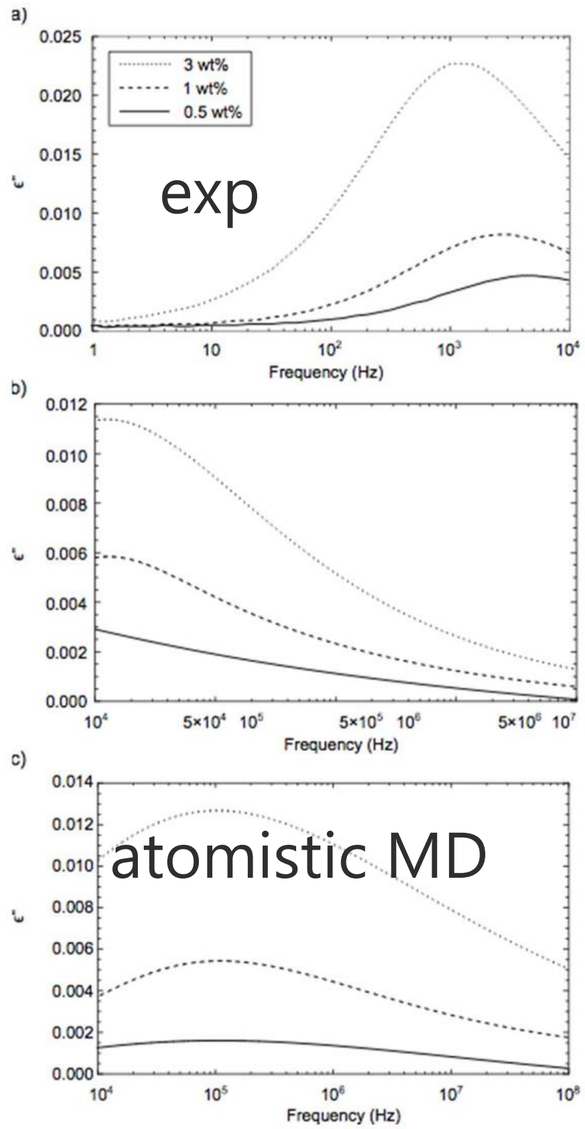
(to be implemented?)

$$\epsilon(0) = \epsilon_\infty + \frac{4\pi}{3}\frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{V k_\mathrm{B} T}$$



ANN: HOMO, LUMO, q+, q-

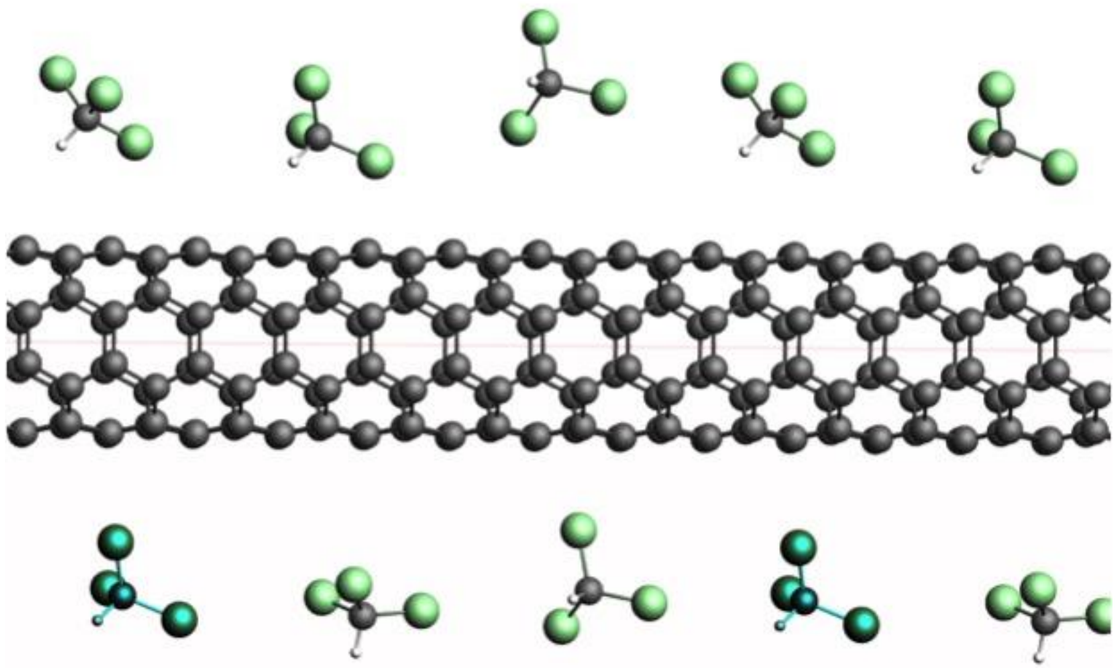
test set *rms* error 0.01463 (R = 0.902)



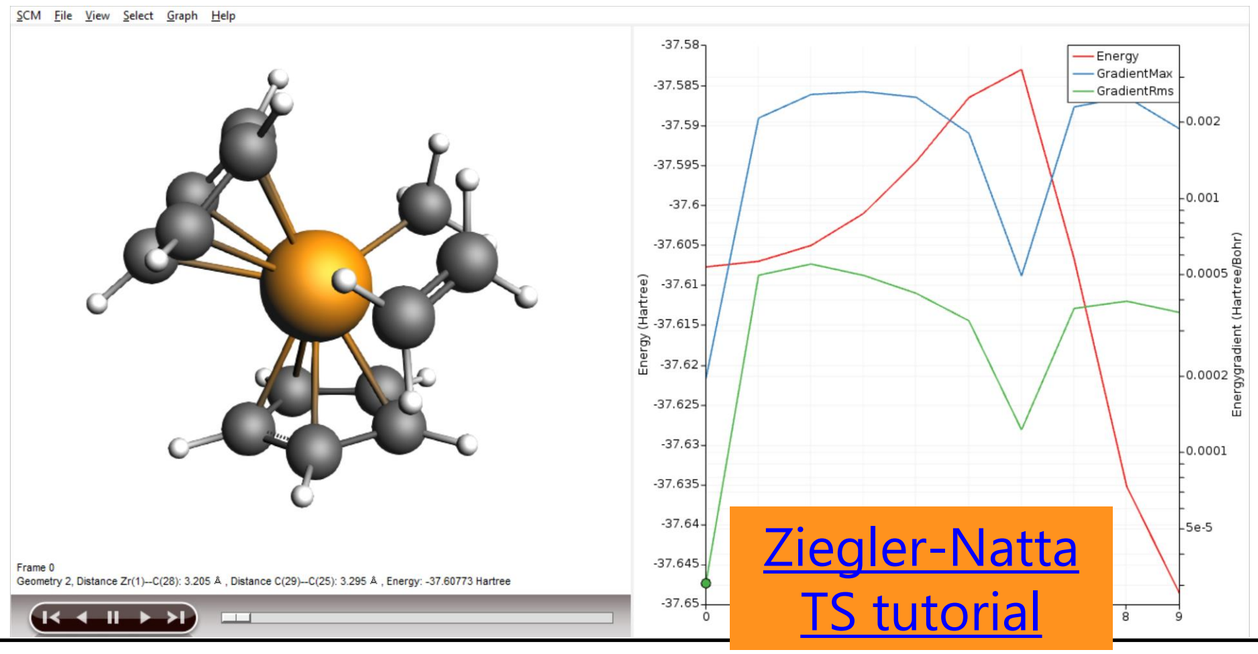
polypropylene w/ meso-erythritol

agreement OK from MD,
but tough to get below 10kHz

DFTB: 'fast DFT' for molecules & periodic



Video: making DWCNT



Ziegler-Natta TS tutorial

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

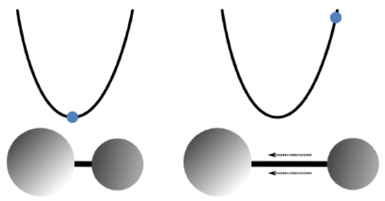
- Geometries, frequencies, phonons
- Stress tensors (optimize under p)
- Advanced MD, PES scans
- GCMC, molecule gun

ReaxFF: concept

- Simulate complex systems at realistic scales
  - Atomistic potentials – single atom type (reasonably transferable)
  - Update charges and bond orders at every step

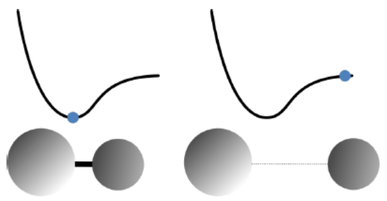
A.C.T. van Duin et al ,J. Phys. Chem. A 2001 , 105, 9396-9409.

Standard forcefields **vs** *ReaxFF*



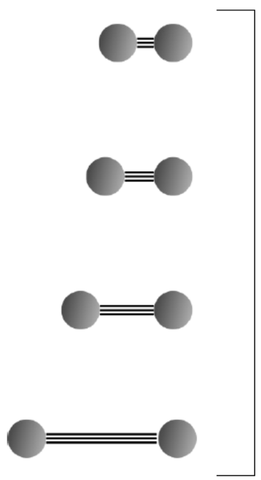
Harmonic potentials based on atom distance, bond breaking impossible, e.g.

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



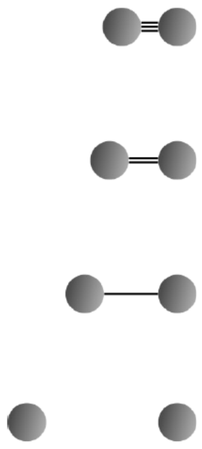
Non-harmonic potentials based on bond orders, bond breaking/forming possible, e.g.

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

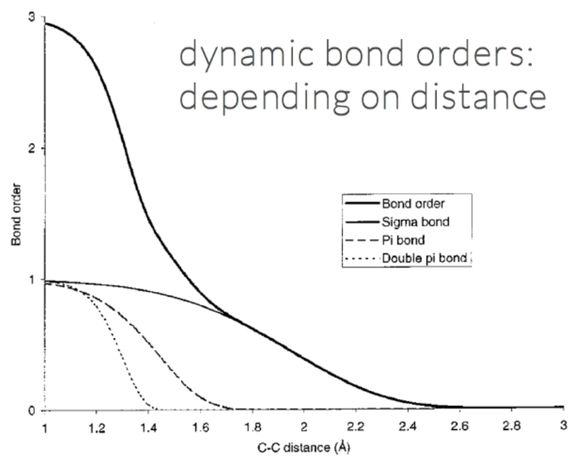


a triple "bond" will always stay a triple "bond"...

($E_{bond} \rightarrow \infty$)



dynamic bond orders: depending on distance

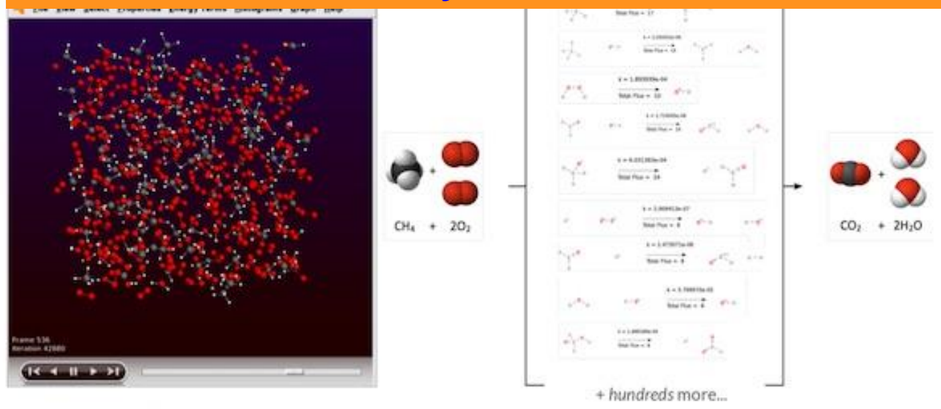


($E_{bond} \rightarrow 0$)

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

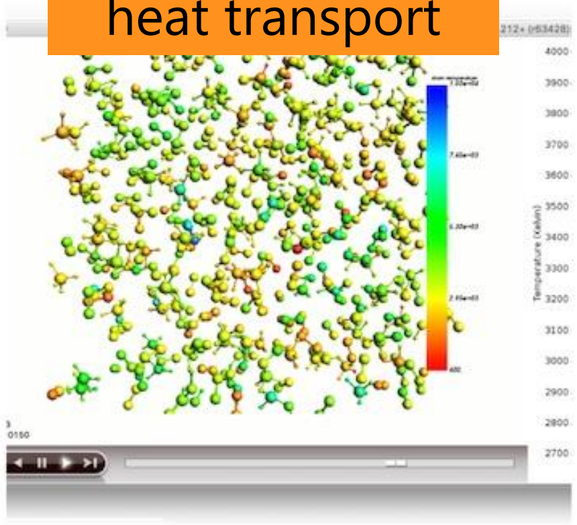
ReaxFF tools in Amsterdam Modeling Suite

ChemTraYzer: Automated rates & pathways
New: Analyze surface reactions

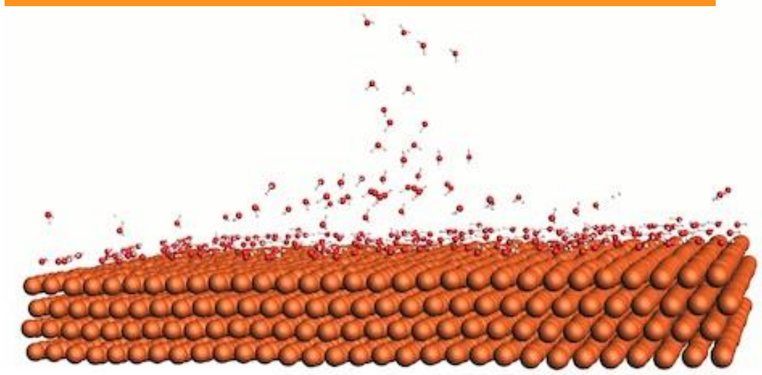


Tools += complete reaction networks
elementary reactions, rate constants, fluxes, timeline

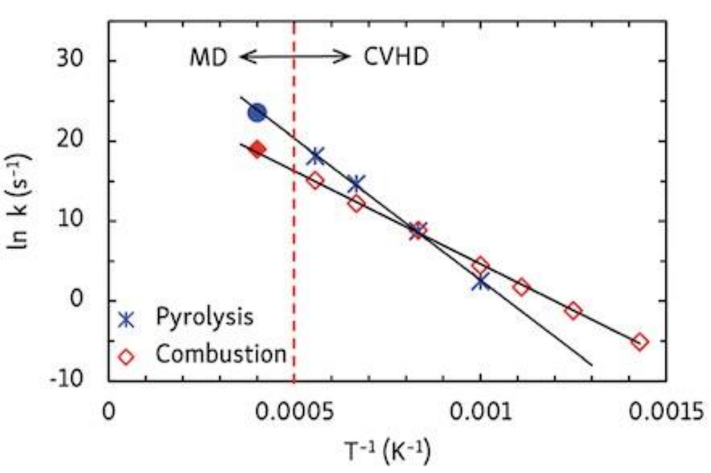
T-NEMD, local T:
heat transport

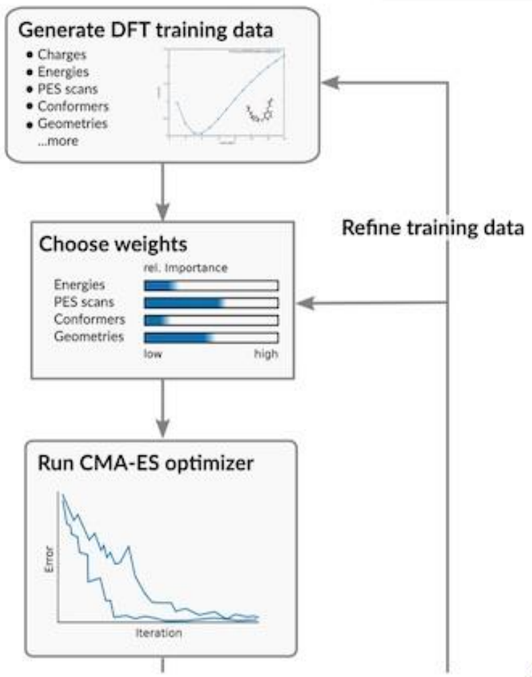


Molecule gun: depositing molecules on surfaces

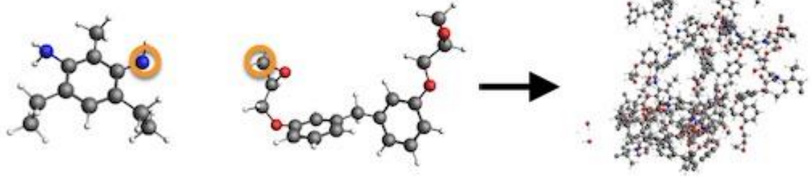


fbMC, CVHD, PRD?:
speed up kinetics

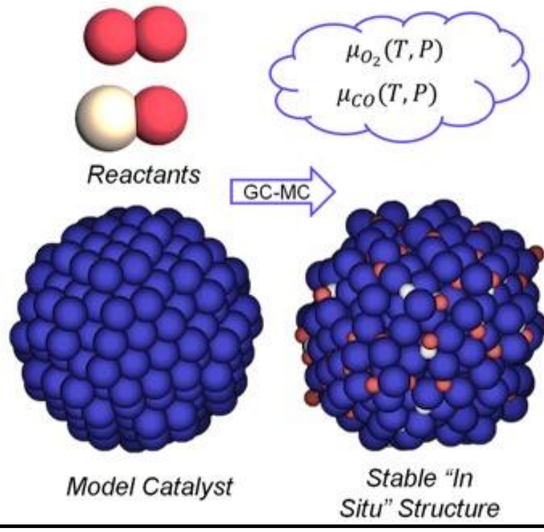


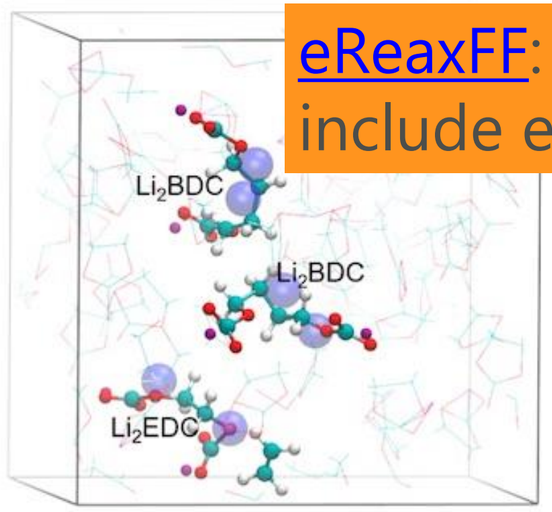


CMA-ES ReaxFF force field (re)parameterization

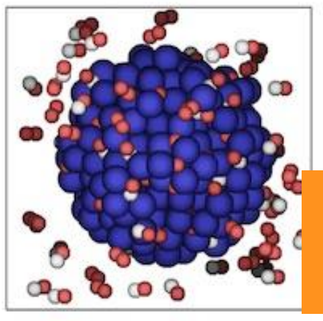


bond boost
build polymers





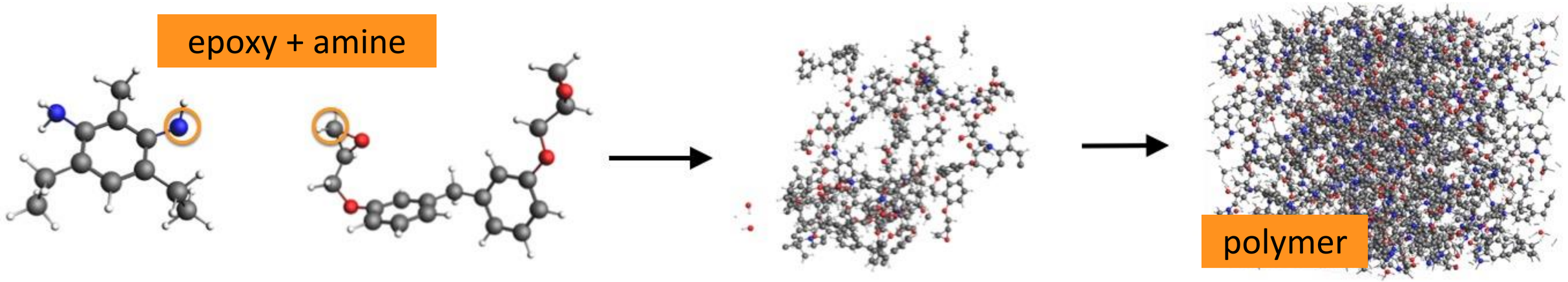
eReaxFF: include e-

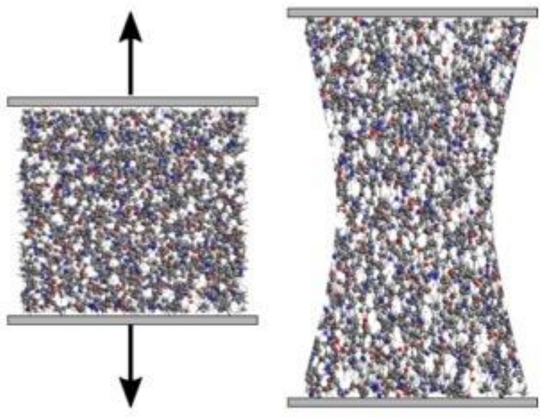


GCMC: speed up thermo

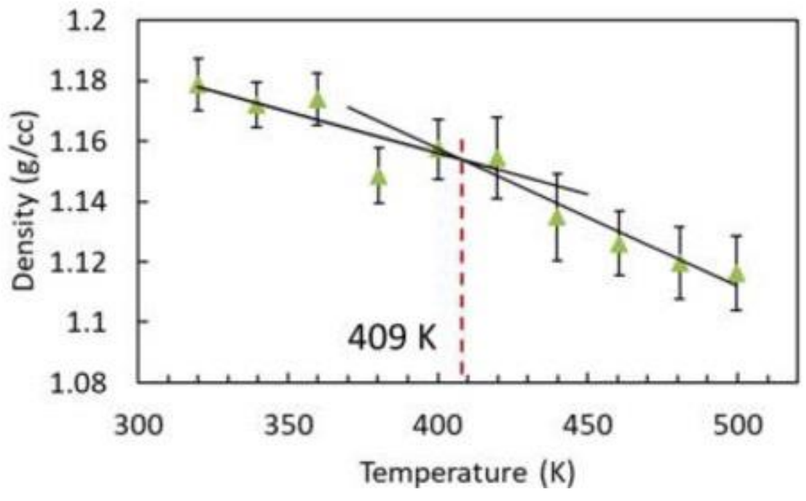
Epoxy polymers: structure & properties

- 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





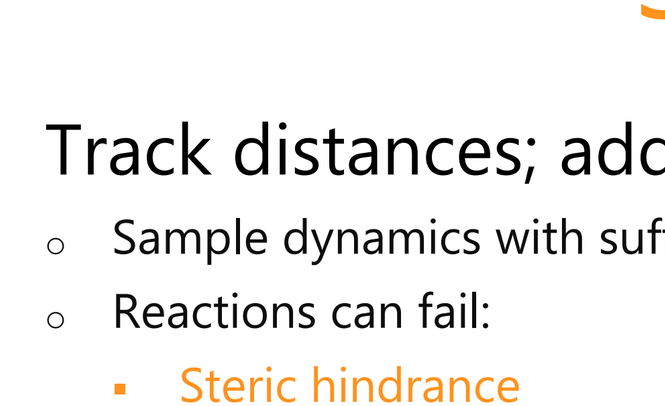
[Modulus, yield point](#)
J. Polym. Sci. B 2018, 56, 255



glass transition T_g

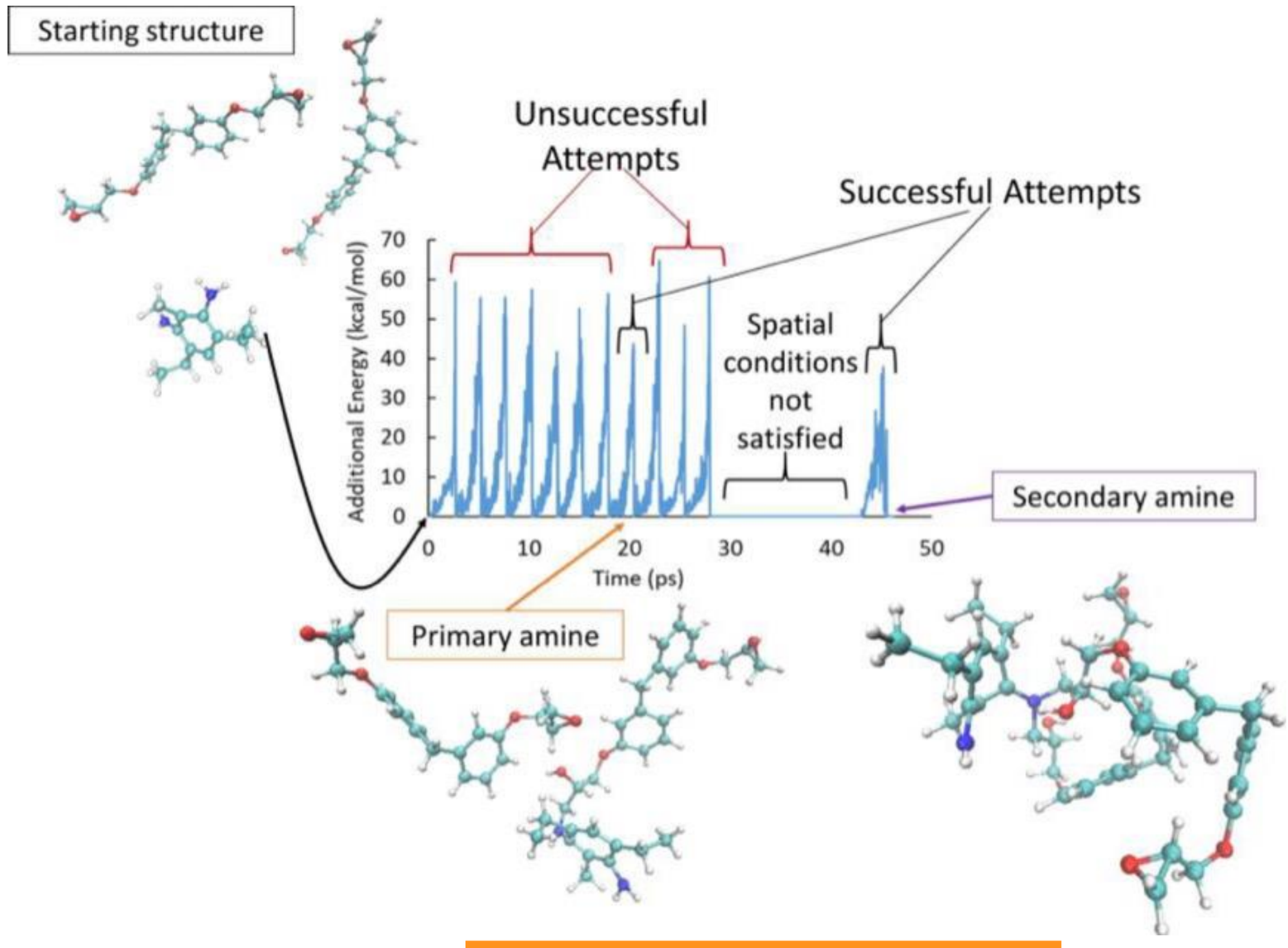
Accelerating dynamics with Bond Boost

- 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



preliminary complex

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



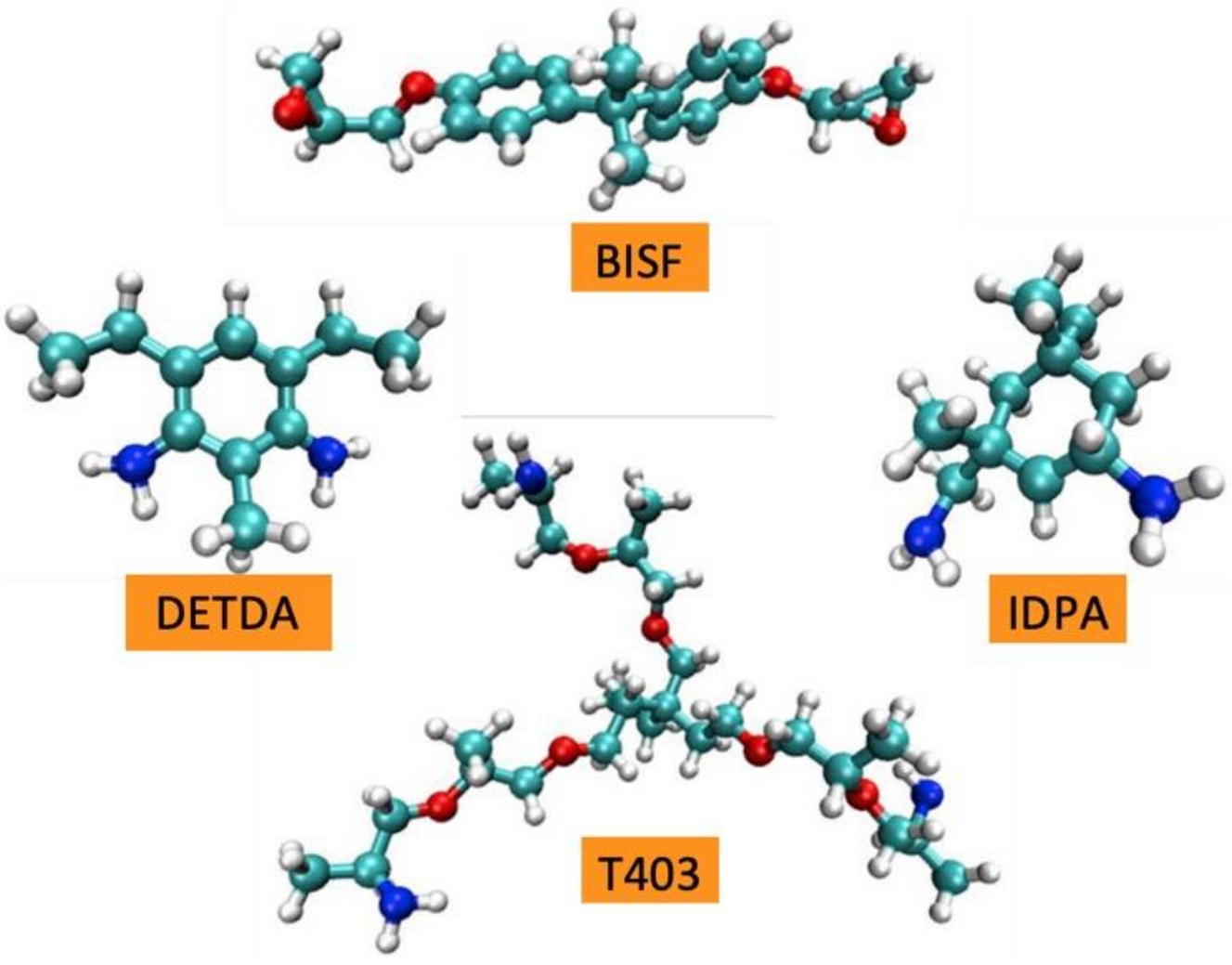
van Duin et al. J. Phys. Chem. A, **122**, 6633 (2018),
cf. Miron & Fichthorn JCP 119, 66210 (2003)

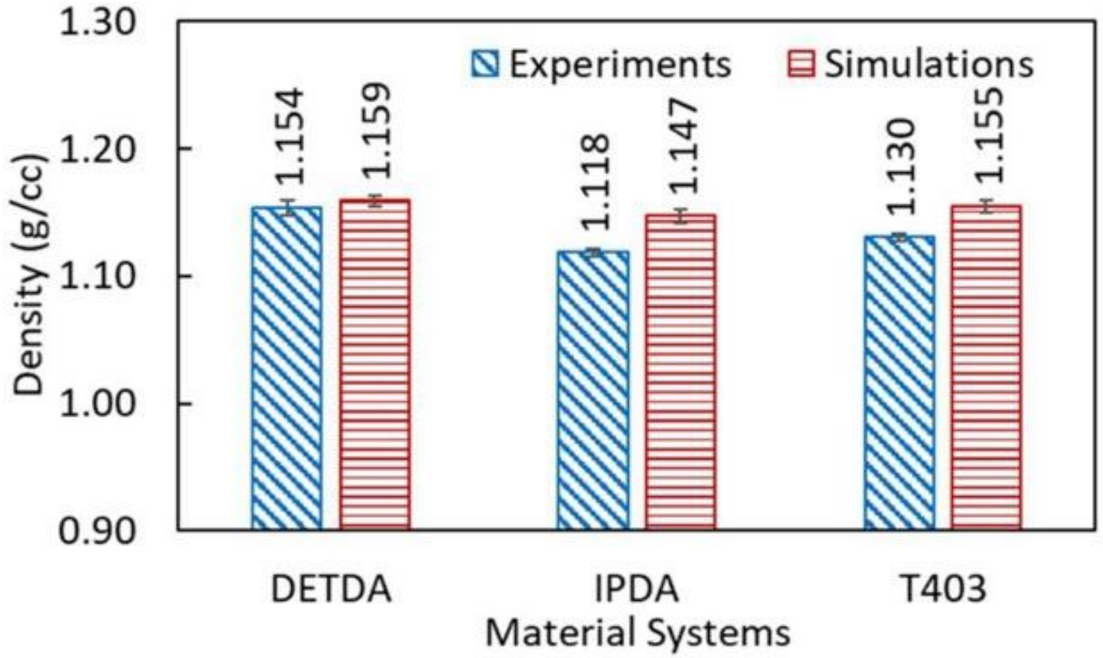
Video: realistic cross-linking

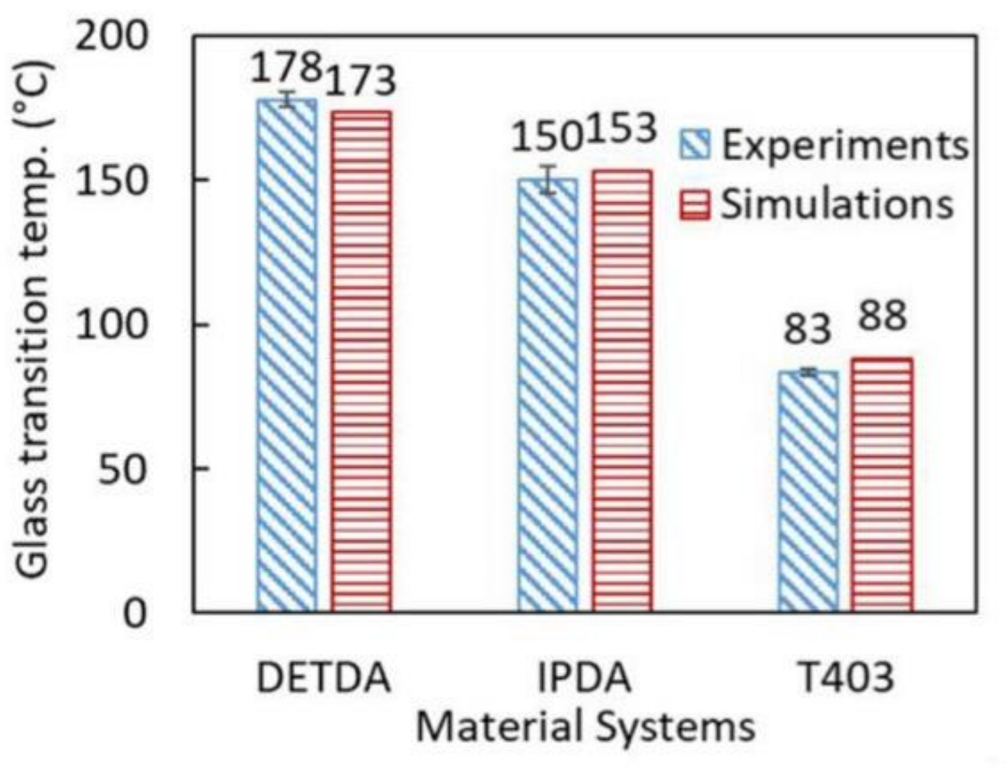
Tutorial: cross-linking

Properties of cross-linked epoxy polymers

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





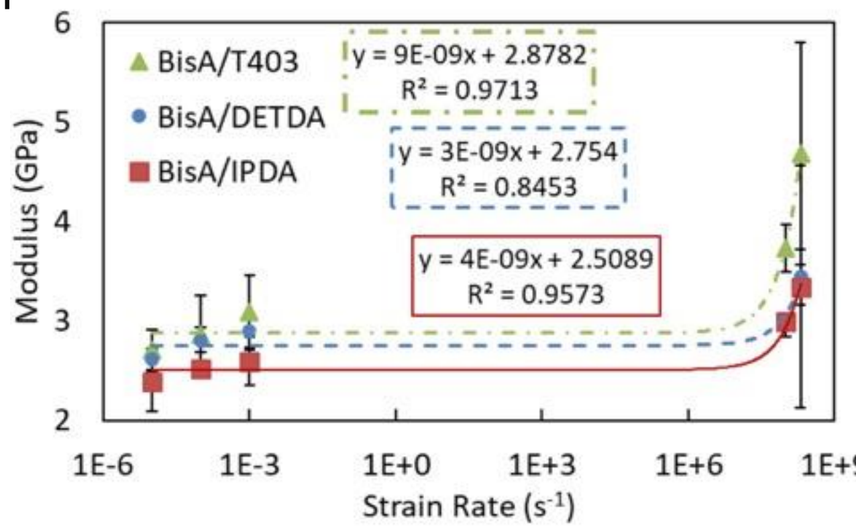


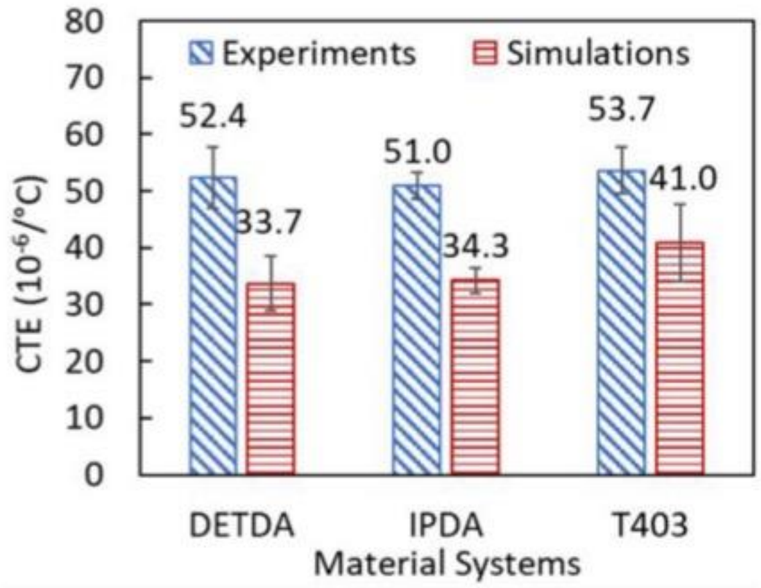
[Polymer 158, 354 (2018)]

[Tutorial Tg]

Properties of cross-linked epoxy polymers

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





Polymer 158, 354 (2018)

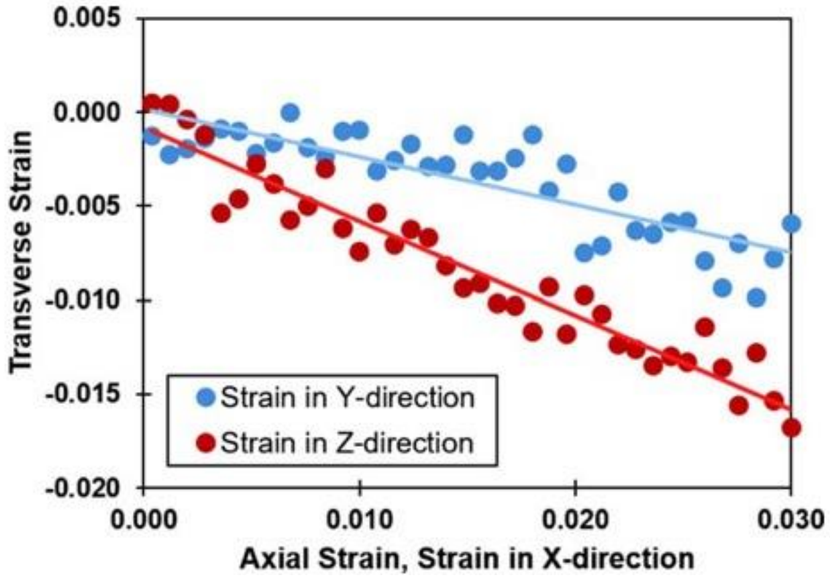
From Stress-Strain:

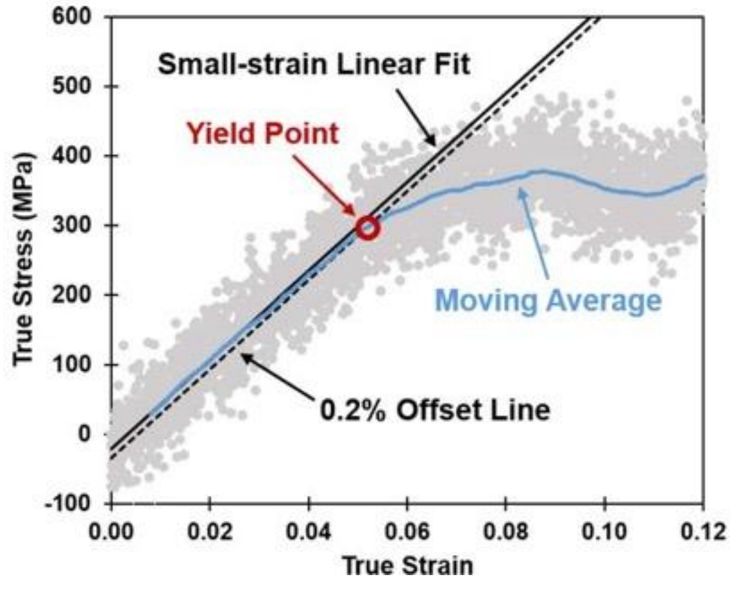
- Yield point(s)
- Strain ratios

J. Polym. Sci. B, 56, 255-264 (2018)

Video: mechanical properties

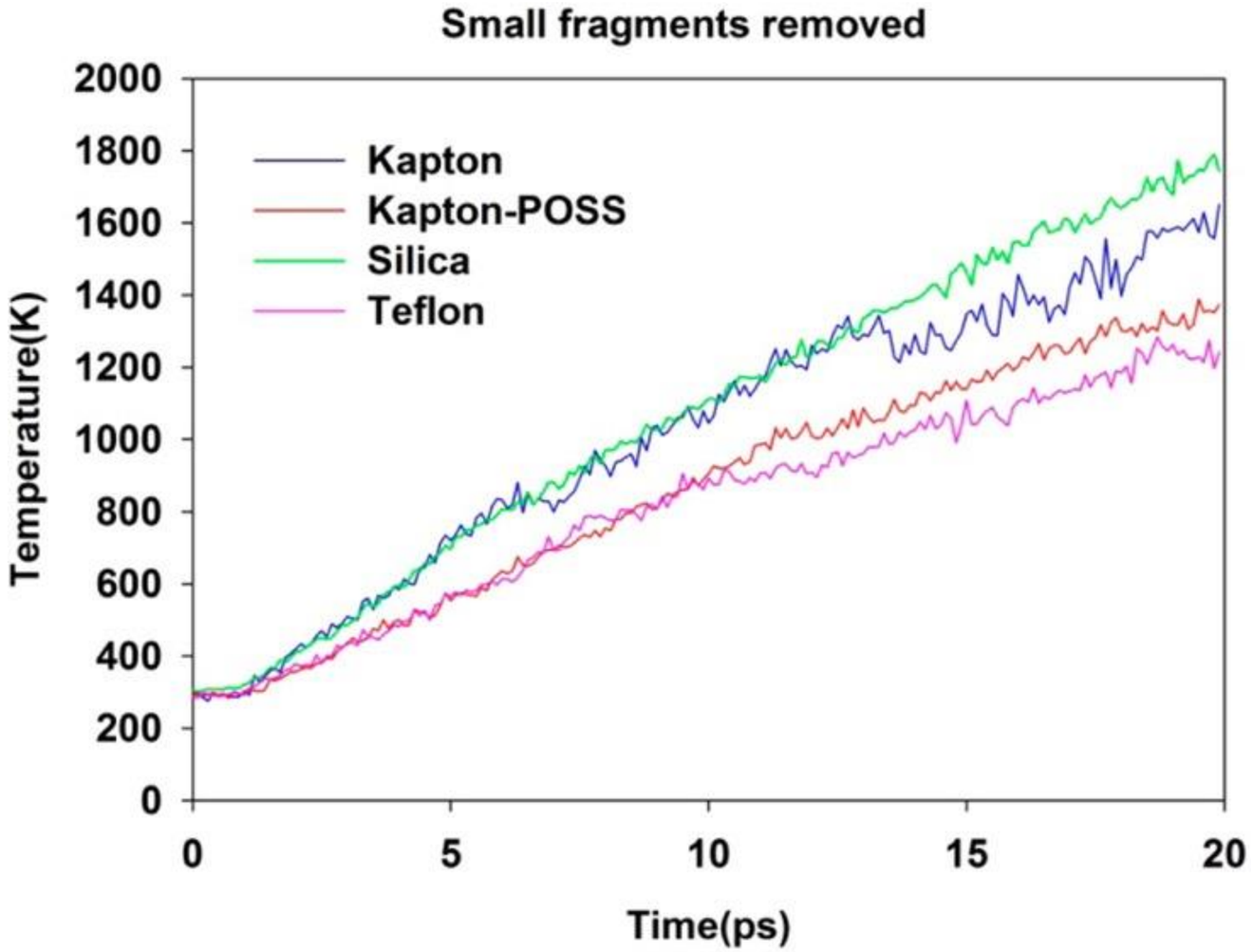
Tutorial: stress-strain

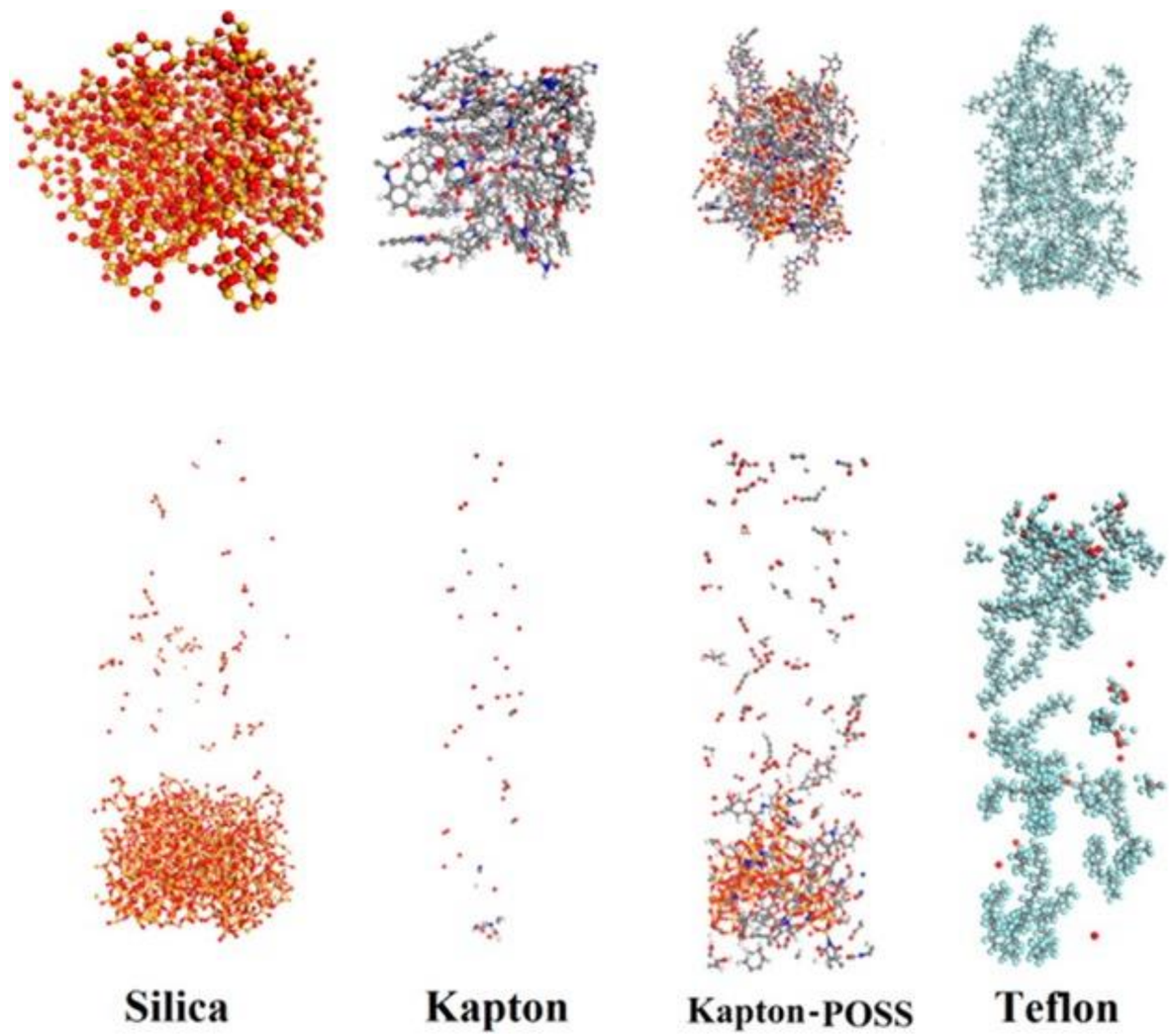




Degradation of polymers in space

- 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.

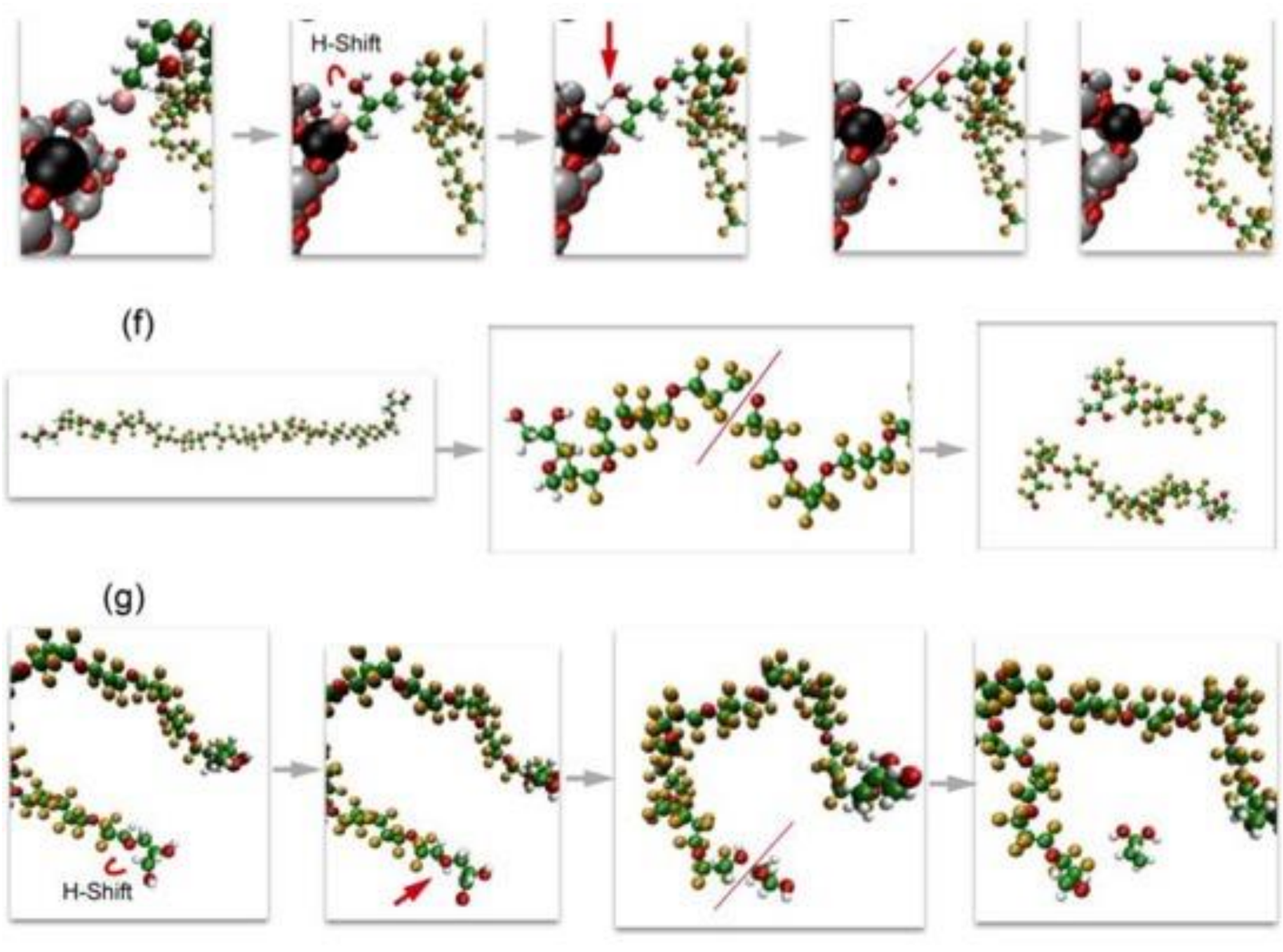


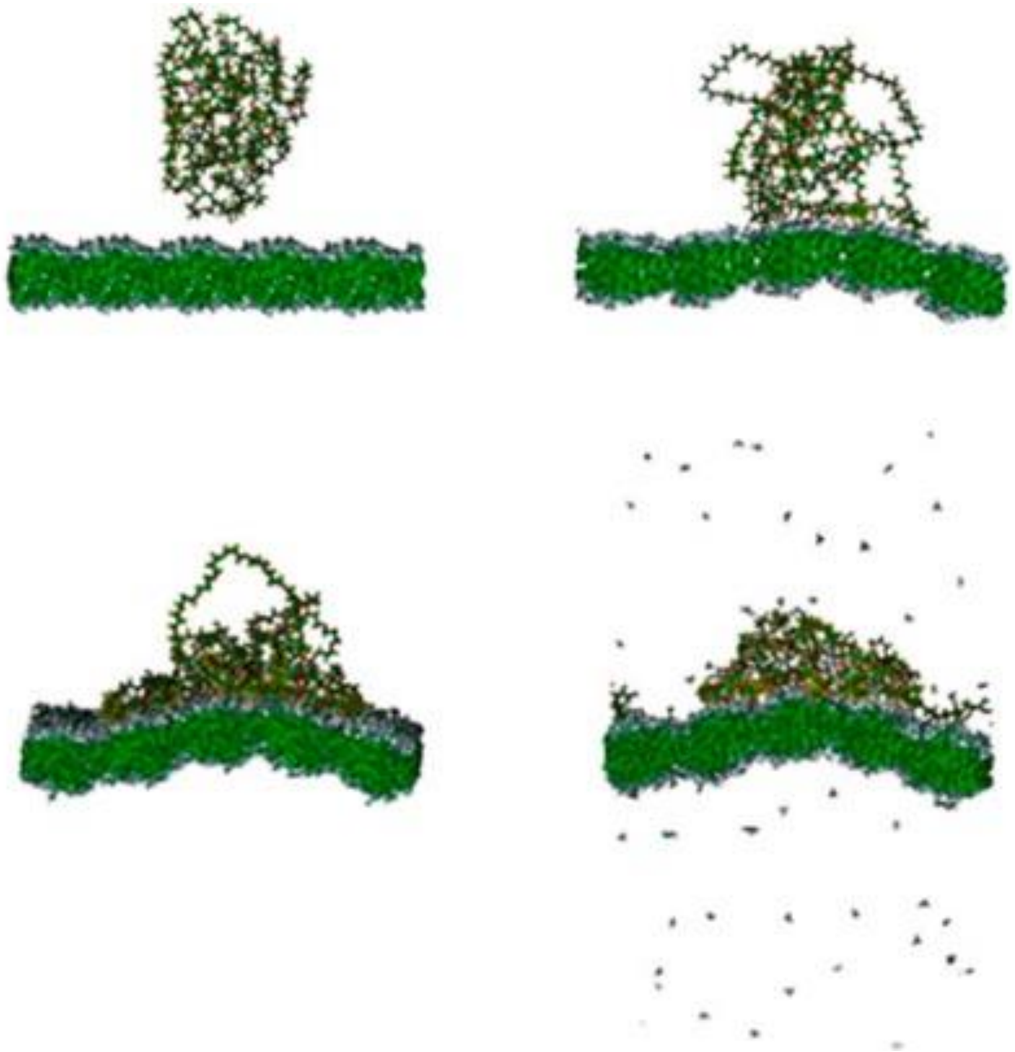


[J. Phys. Chem. A, 2014, (118), 2780]

Tutorial coming

ReaxFF simulations: degradation





Degradation mechanisms perfluoropolyether lubricant on SiO_2, Fe_2O_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)

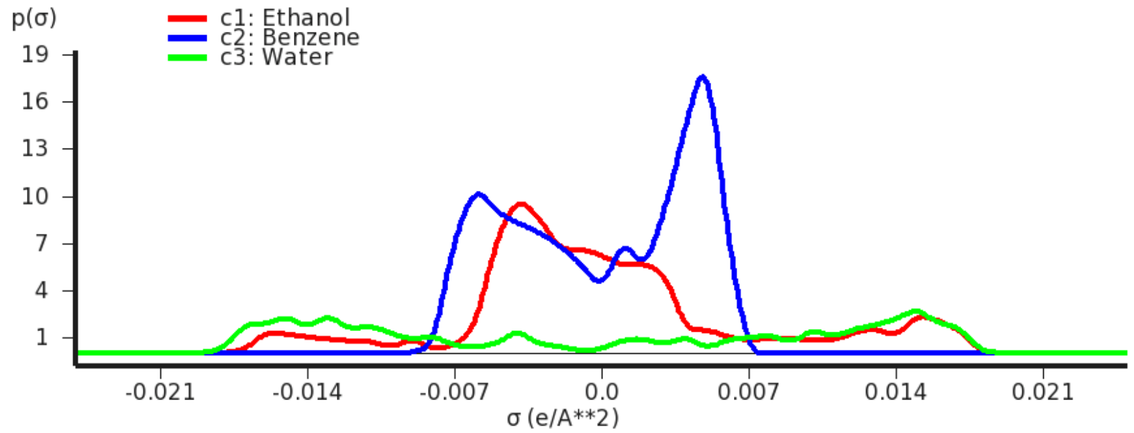
J. Phys. Chem. C, **122**, 2684 (2018)

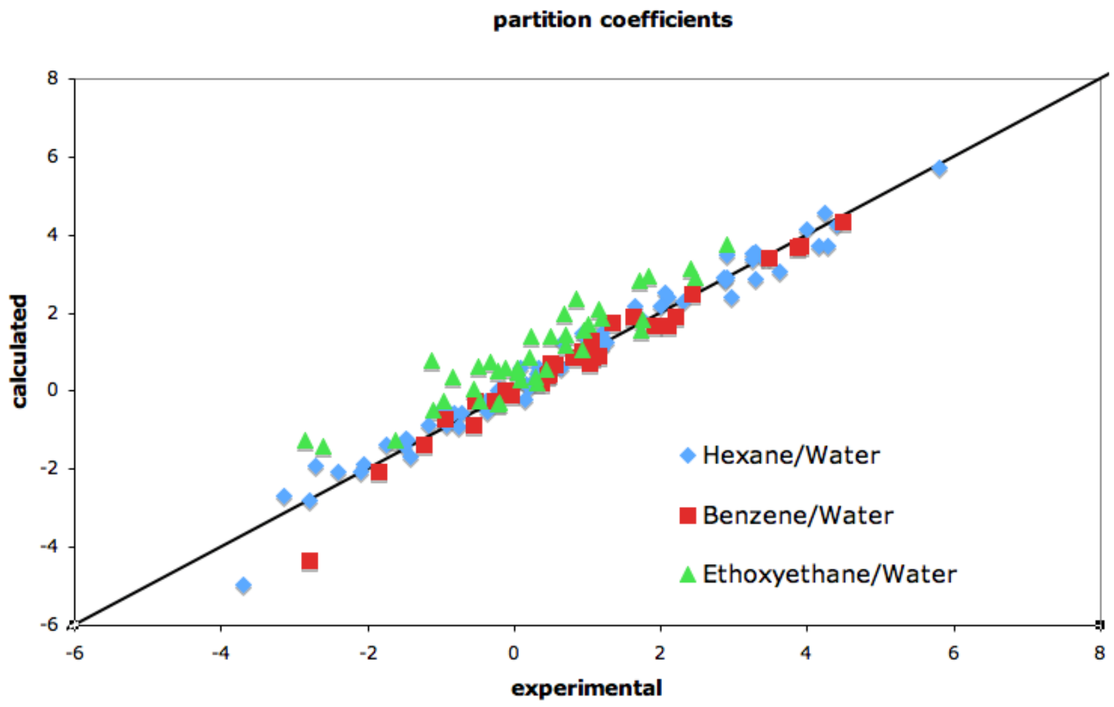
COSMO-RS/SAC: thermodynamic properties of fluids

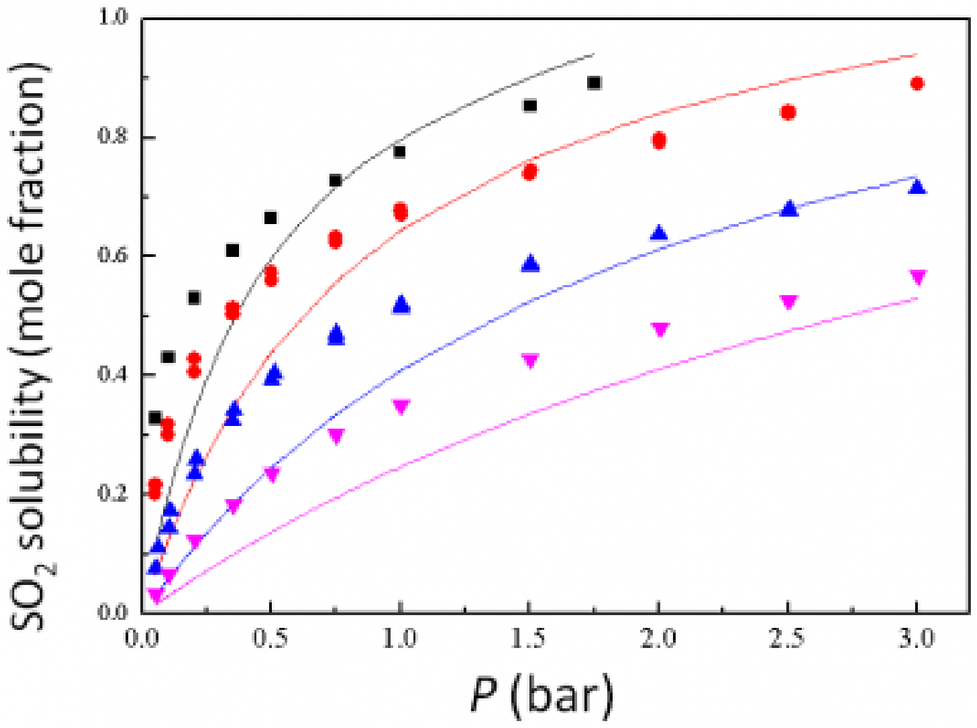
Quantum Chemistry & QSPR for quick property predictions

COntinuum Solvation MOdel + RS (Klamt), SAC (Sandler)
chemical potential => activity coefficients => instantaneous properties

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

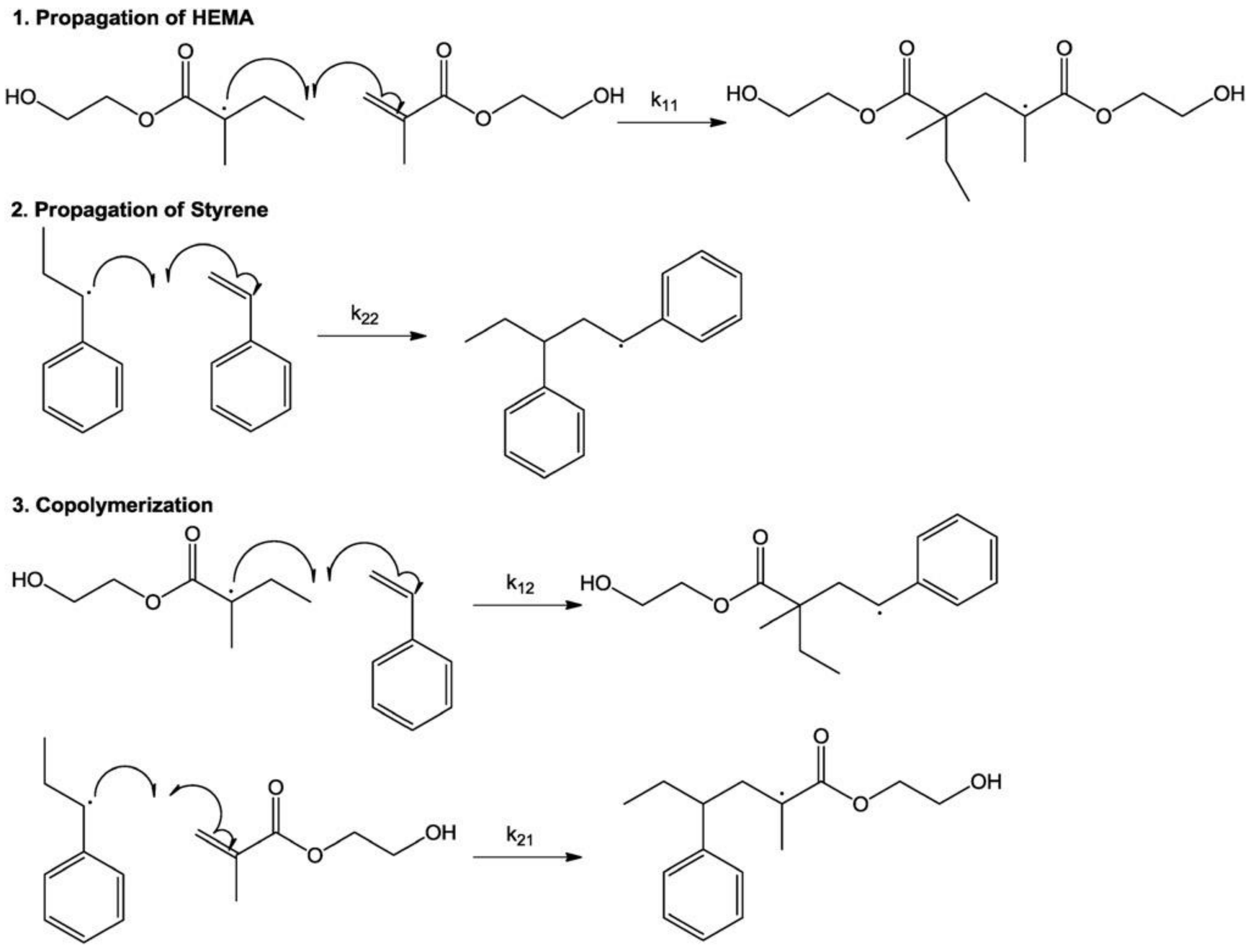






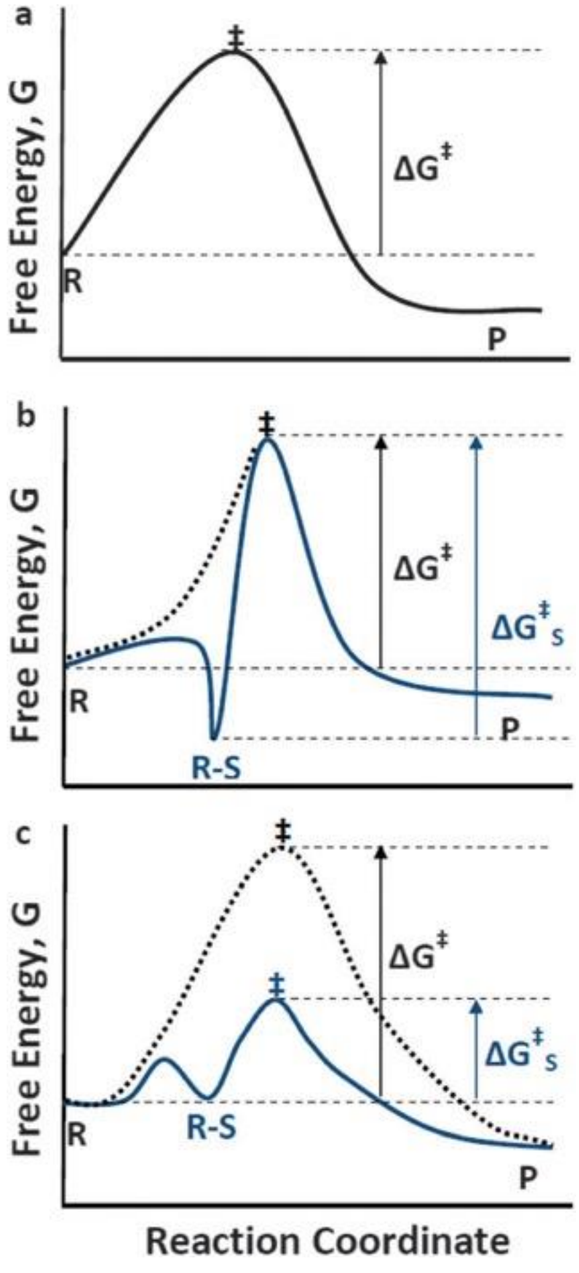
COSMO-RS reaction rates

Copolymer composition is solvent-dependent



COSMO-RS reaction rates

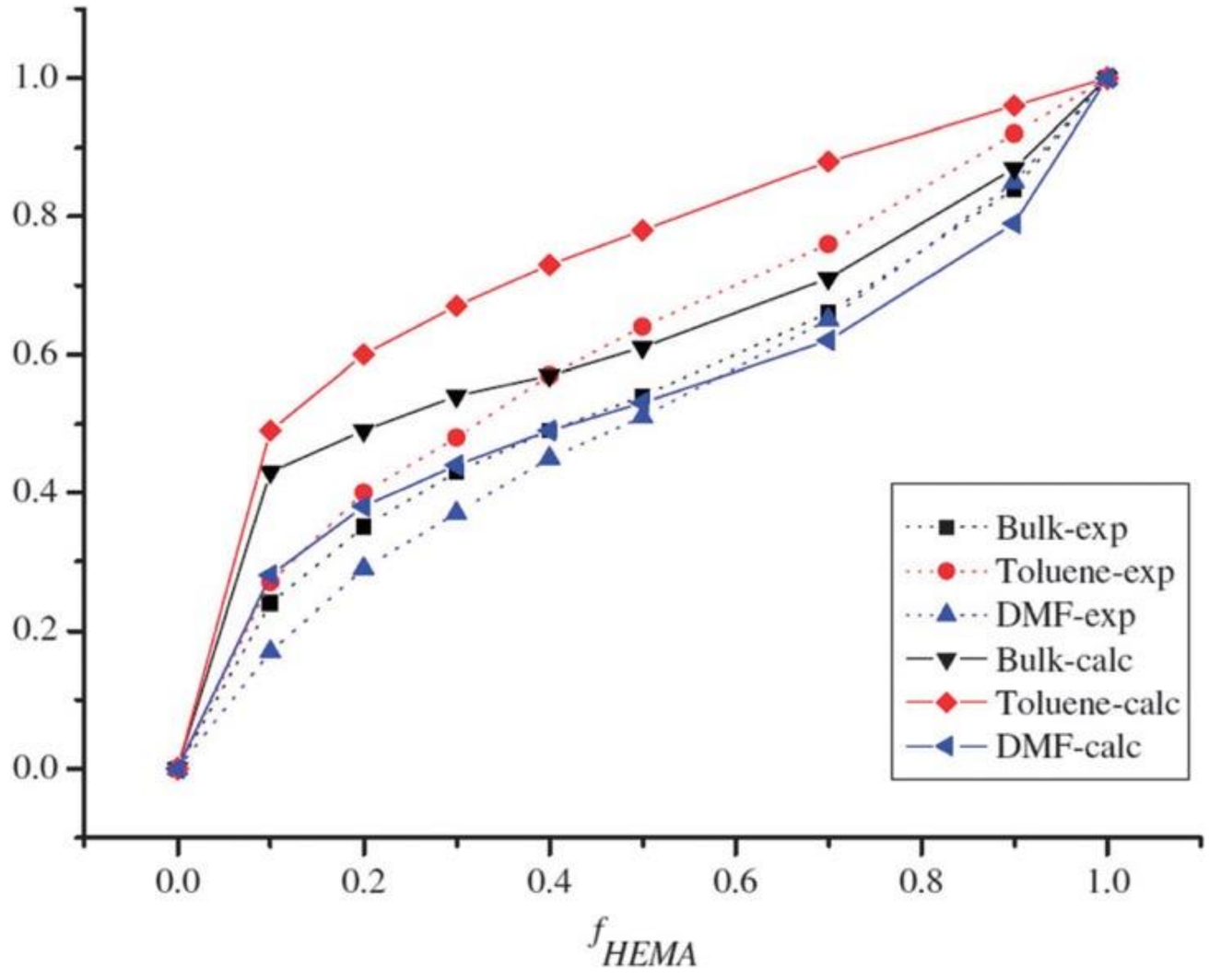
Copolymer composition is solvent-dependent



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

Organic electronics

- Phase stability
- Polymeric batteries

Drug Solubility

- Poorly water-soluble drugs
- Bioavailability

Polymer/Solvent-Polymer interactions

- Flory-Huggins parameters
- Swelling, solubility of polymer blends, etc.

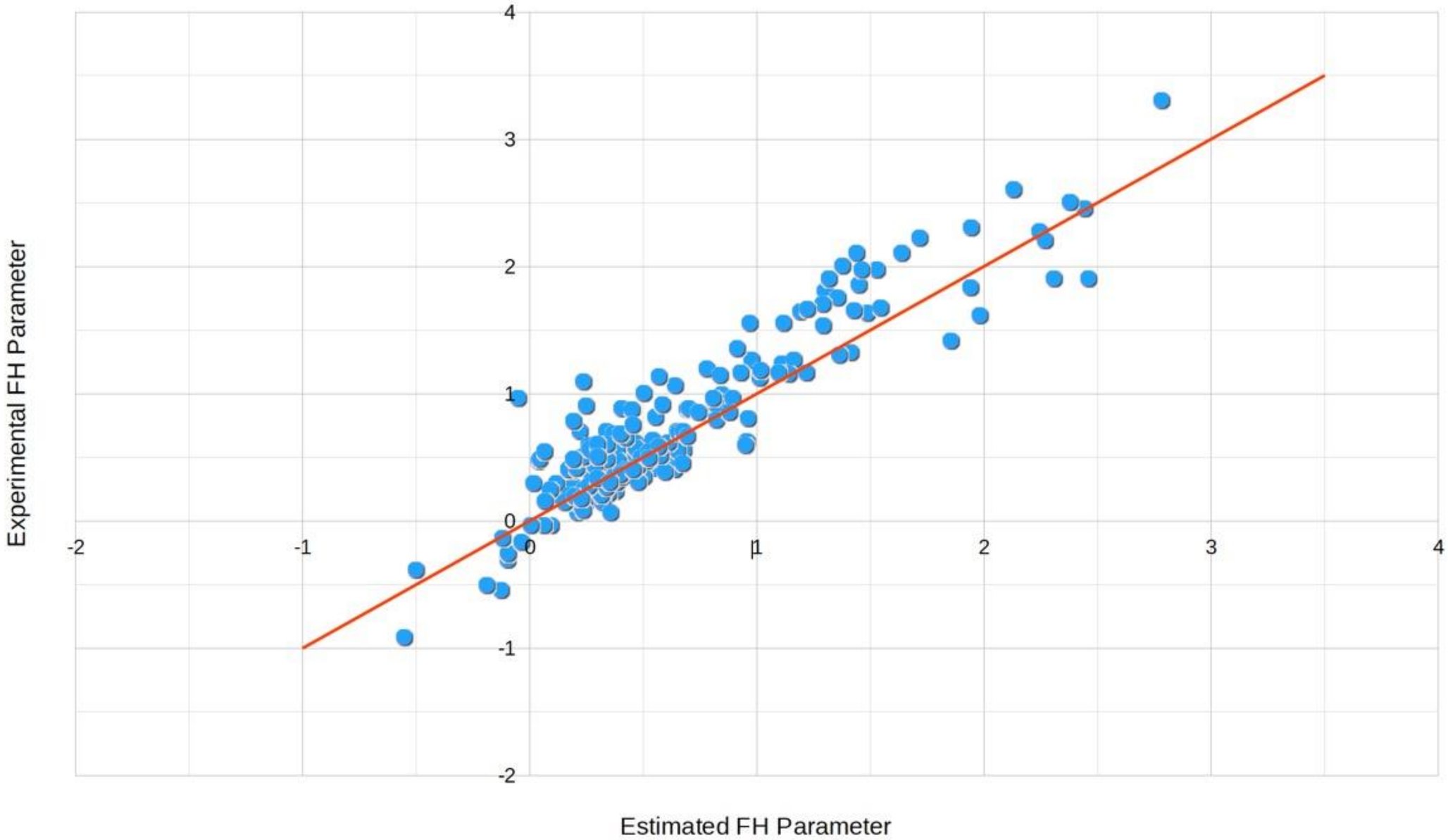
Flory-Huggins from COSMO-RS

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

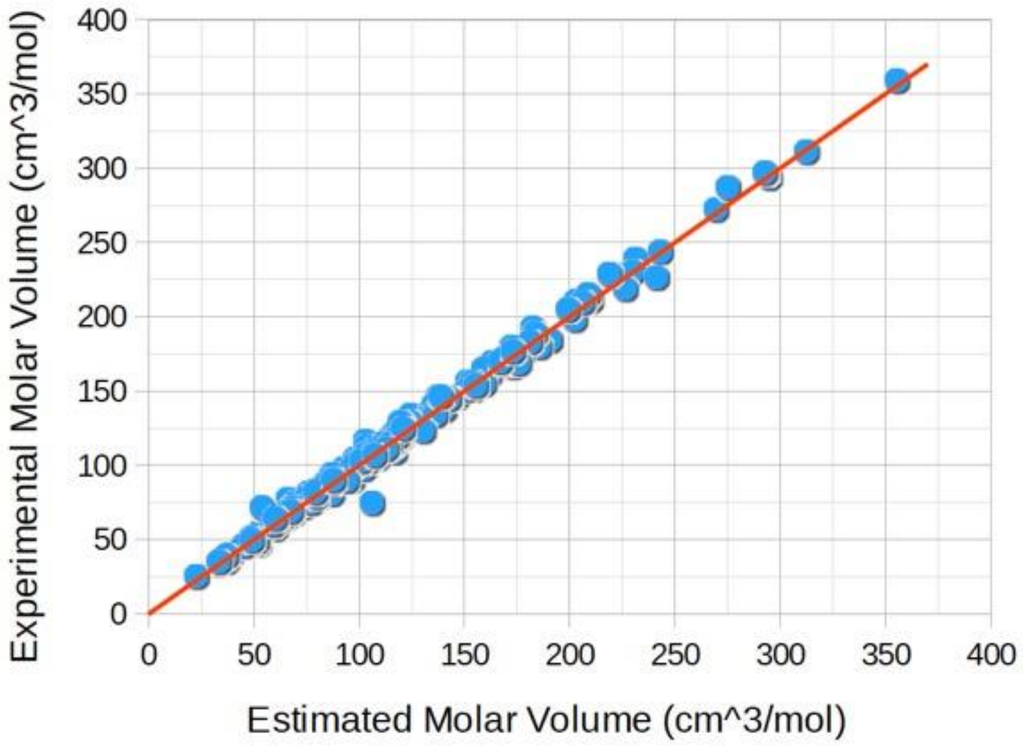
$\phi_{p/s}$ – *Volume fraction of polymer / solvent*

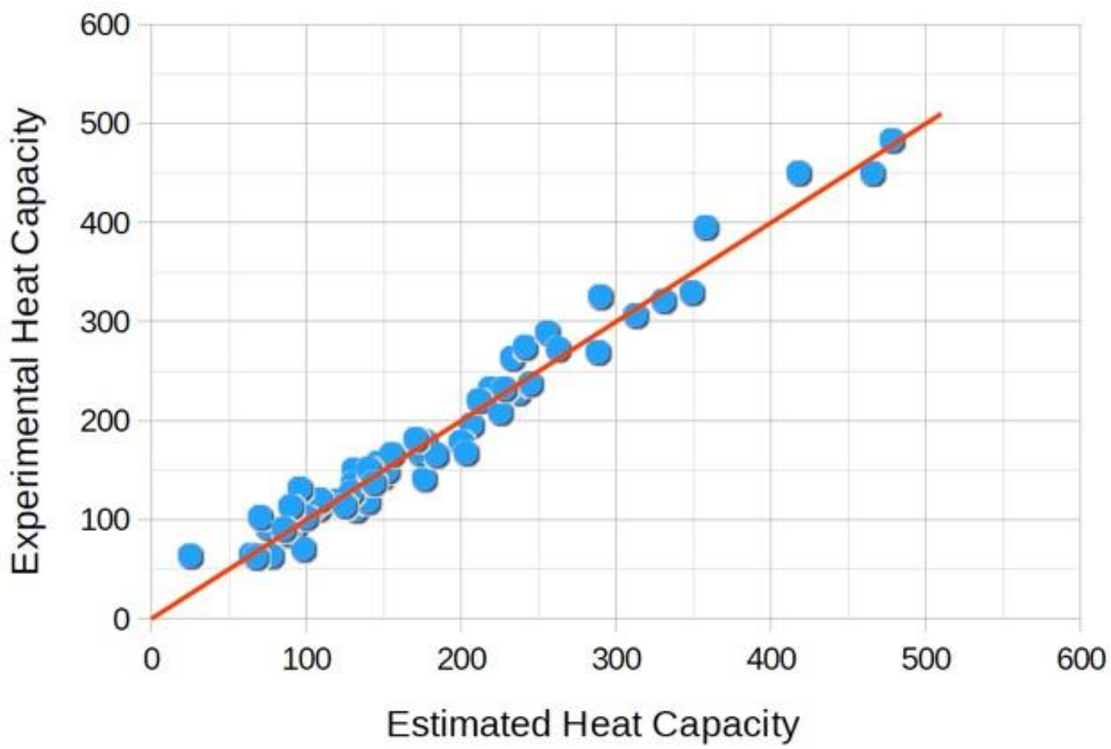
χ_{ps} – *Flory – Huggins Parameter*

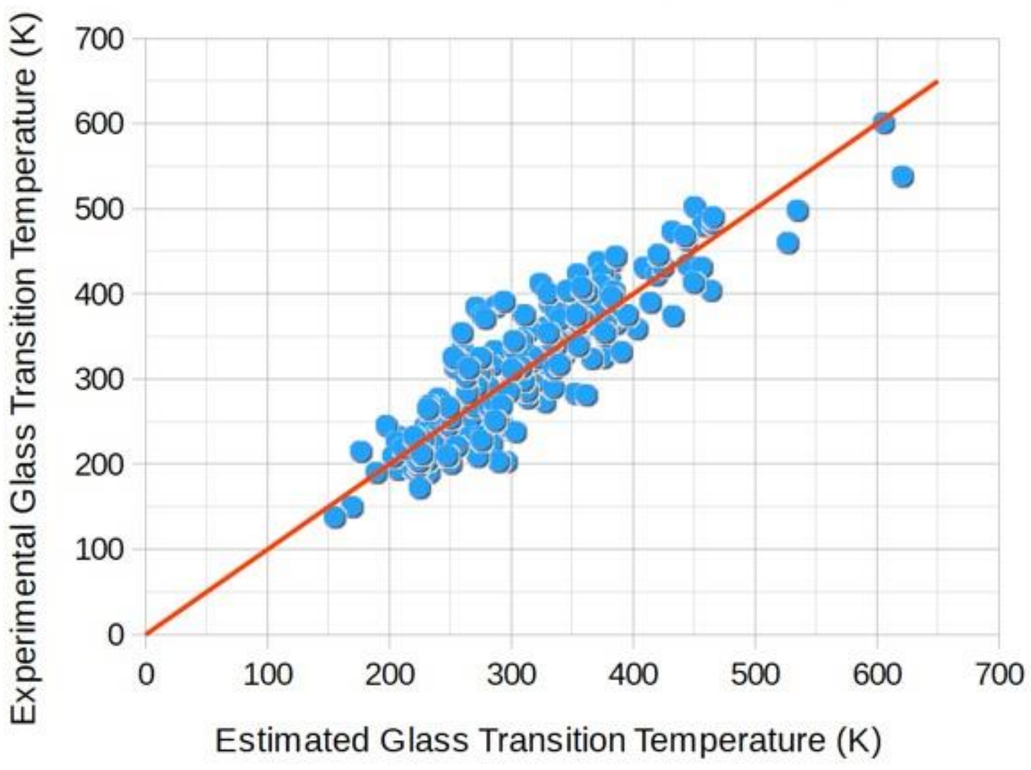
$$\frac{\Delta G_{mix}}{RT} = N_p \ln(\phi_p) + N_s \ln(\phi_s) + N_s \phi_p \chi_{ps}$$



QSPR predictions with sigma-moments







Basic statistics

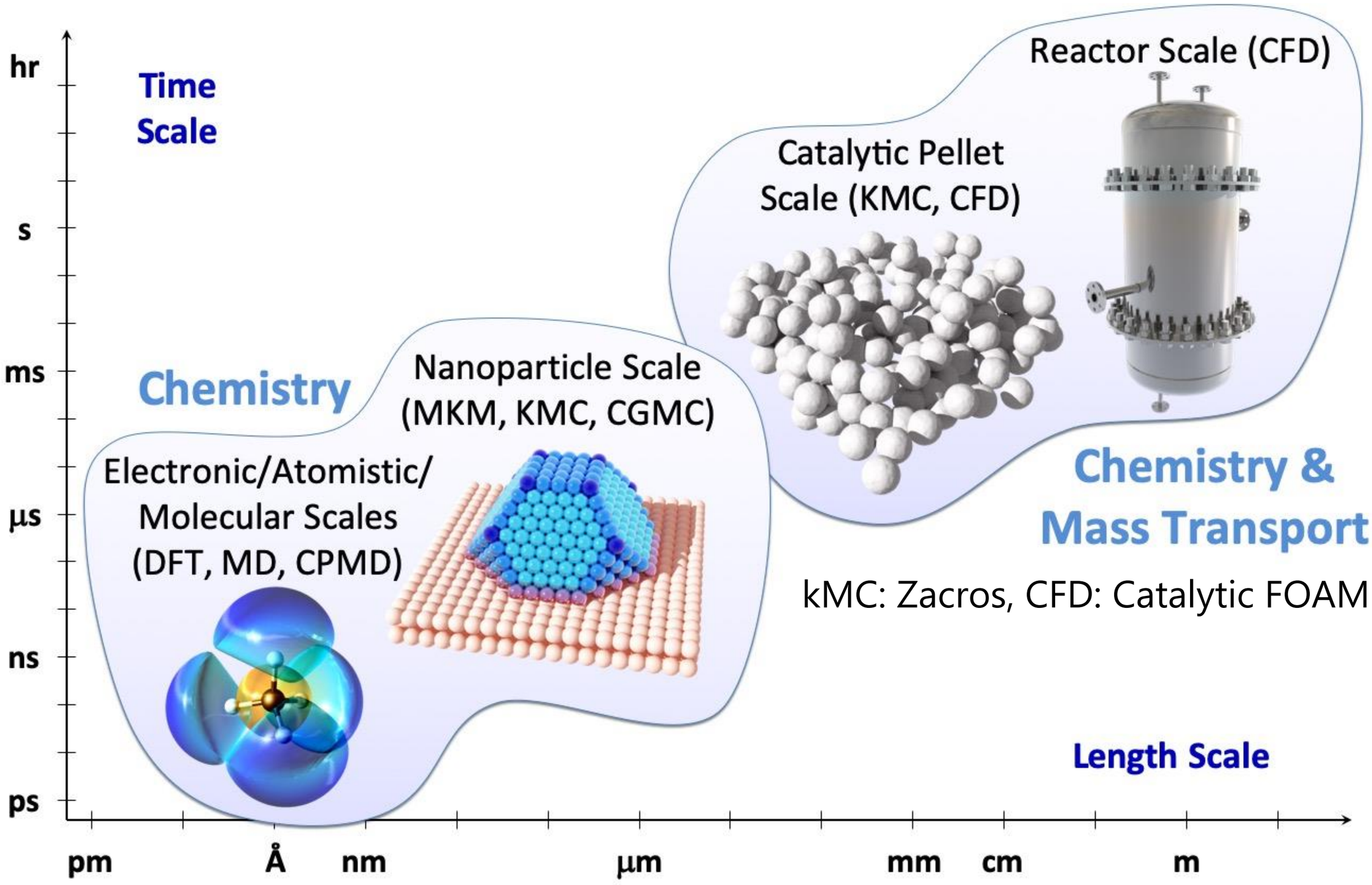
r^2:

- Molar volume: > 0.99
- Heat Capacity: 0.96
- Glass Transition Temp. : 0.81

Average absolute error:

- Molar volume: 3.1 cm^3/mol
- Heat Capacity: 13.8 J/(mol K)
- Glass Transition Temp. : 45 K

ReaxPro: Reactive Process Design as a Multi-scale / Multi-equation Problem

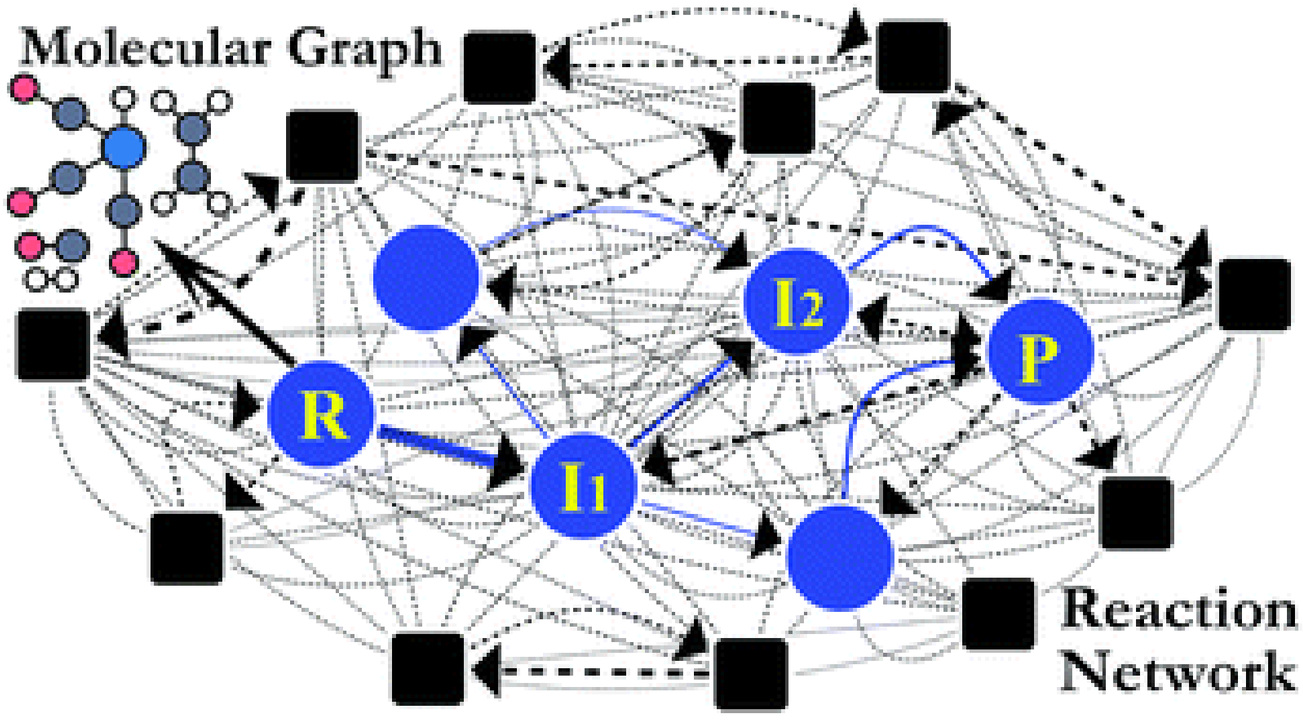


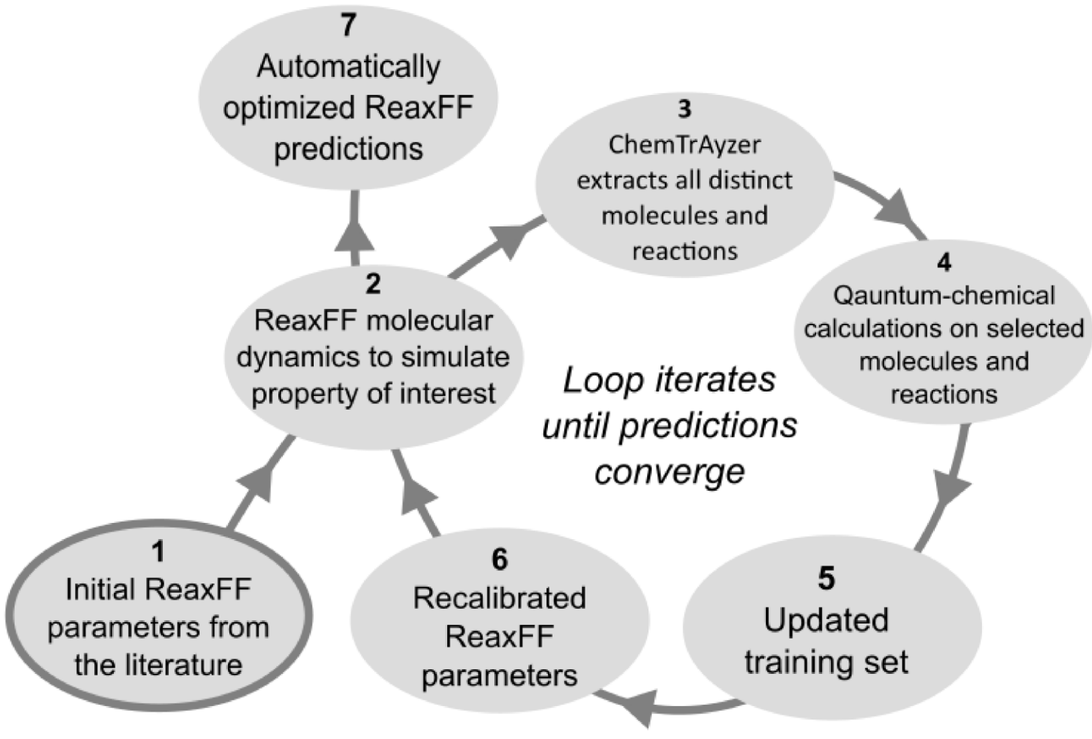
EU project 2019-2023 **Industrial partners**: BASF, JM, DowDuPont, Shell

AutoCheMo: Automatic generation of Chemical Models

4 PhD projects, in collaboration with Universities of Gent and Aachen:

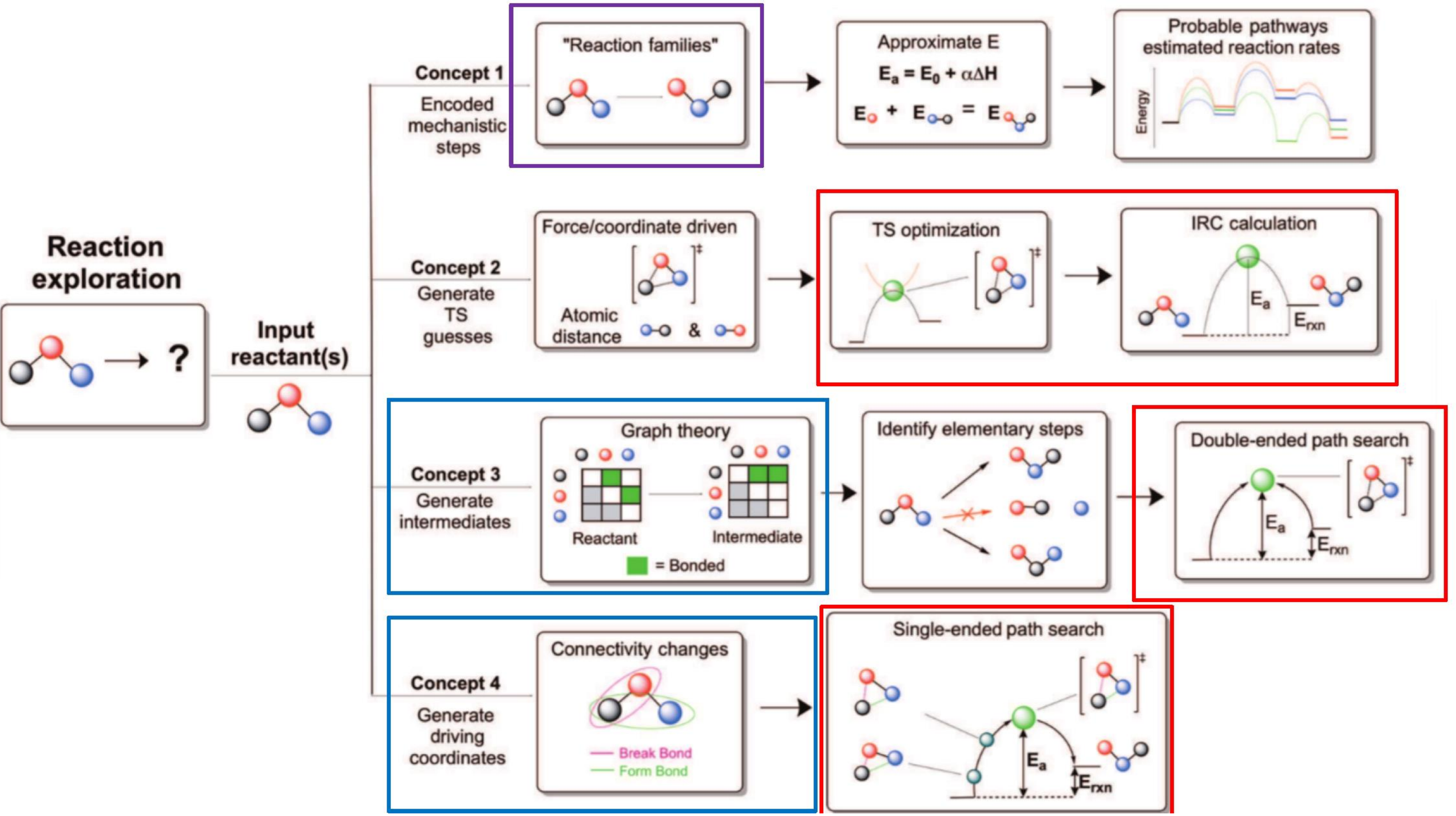
- Complex reaction networks
- Application-driven automated ReaxFF force field parameterization
- Efficient (Bayesian) methods to estimate ReaxFF parameters
- Large amplitude motions





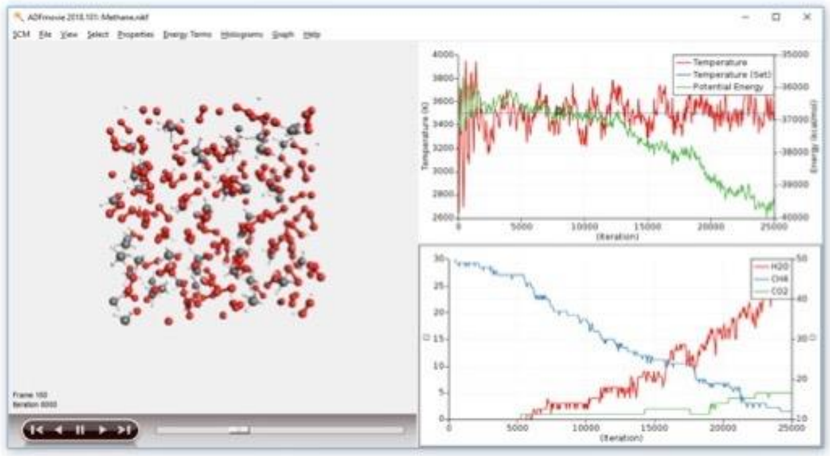
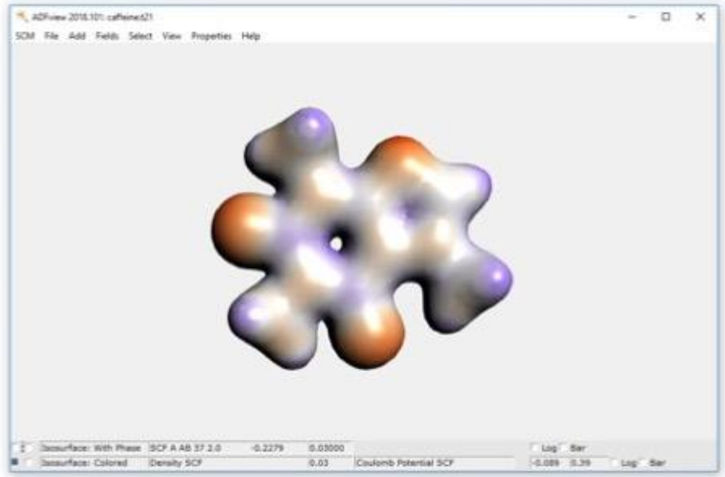
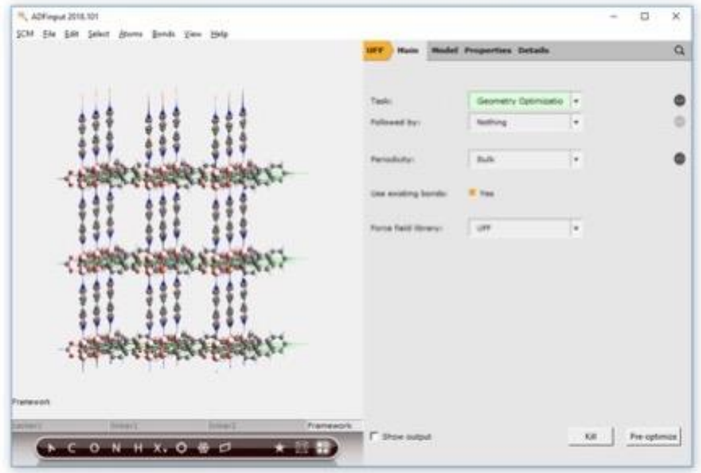
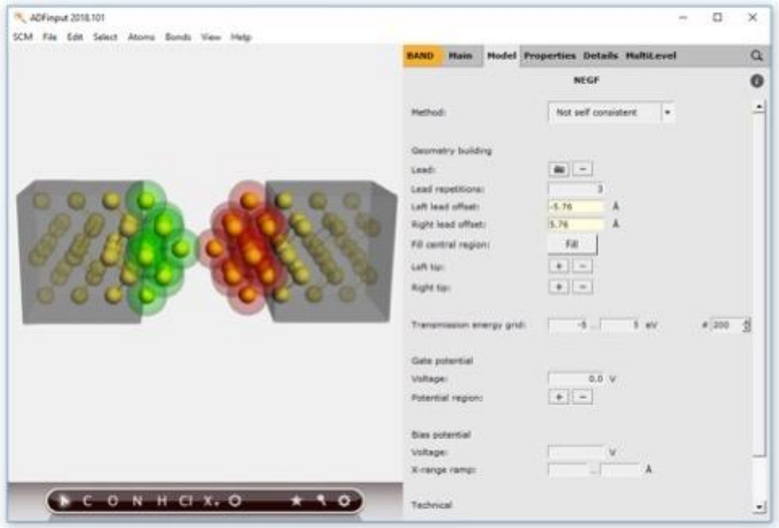
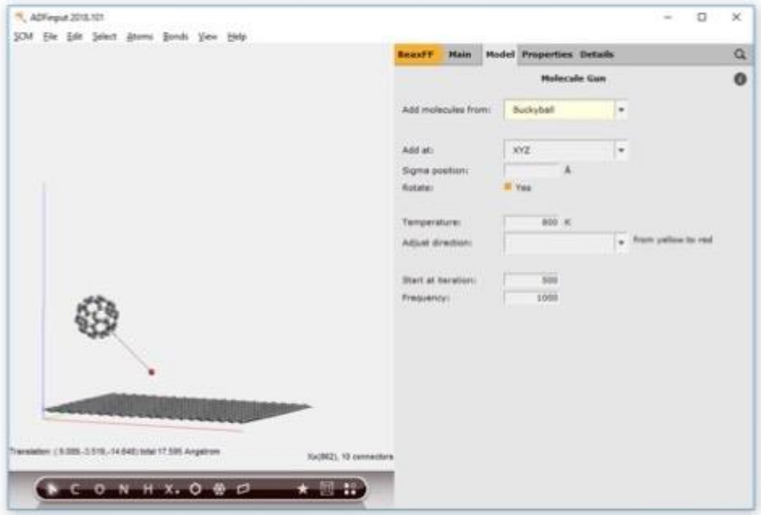
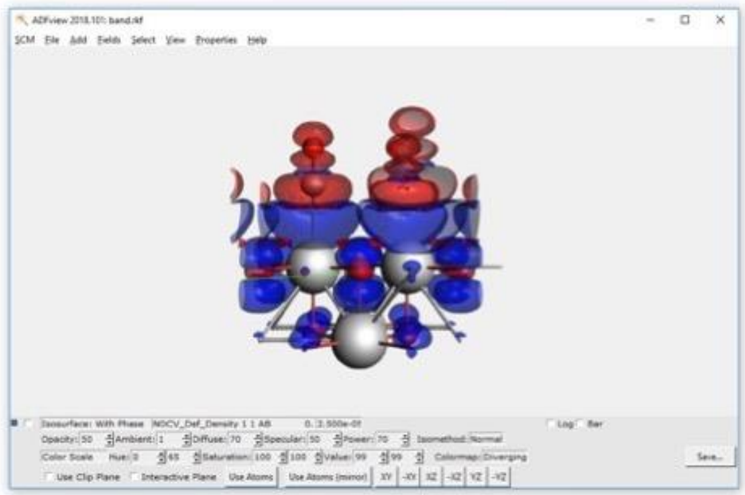
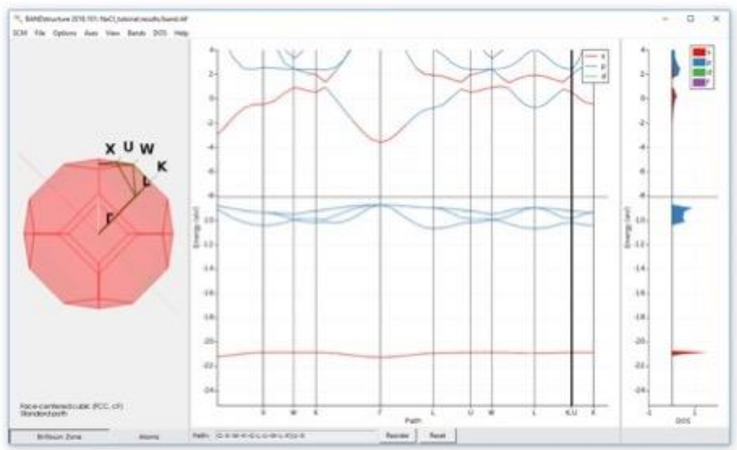
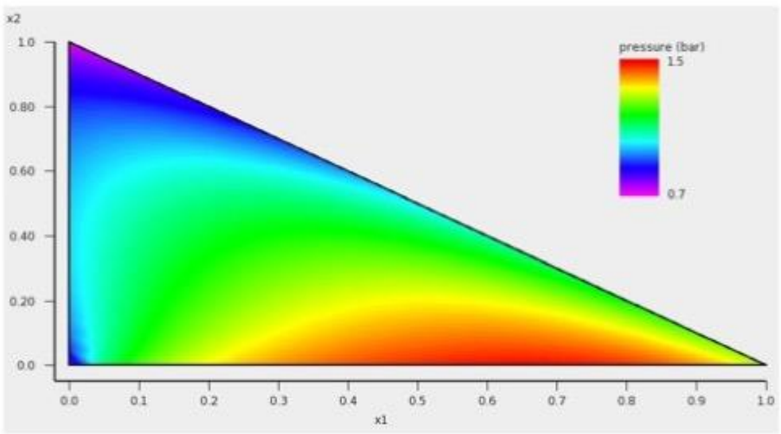
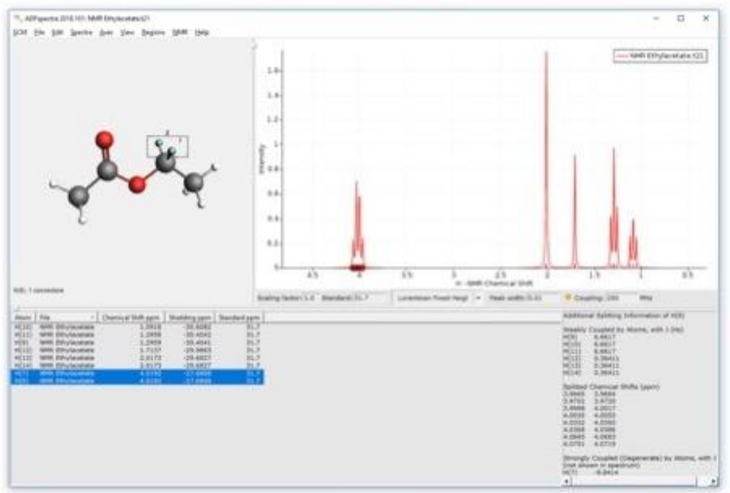
Also working with KAIST on ACE-Reaction (+ machine learning)
Y. Kim, J. W. Kim, Z. Kim and W. Y. Kim, Chem. Sci. 2018, 9, 825; JPCA 2019, 123, 4796.

ACE-Reaction: automated reaction rates



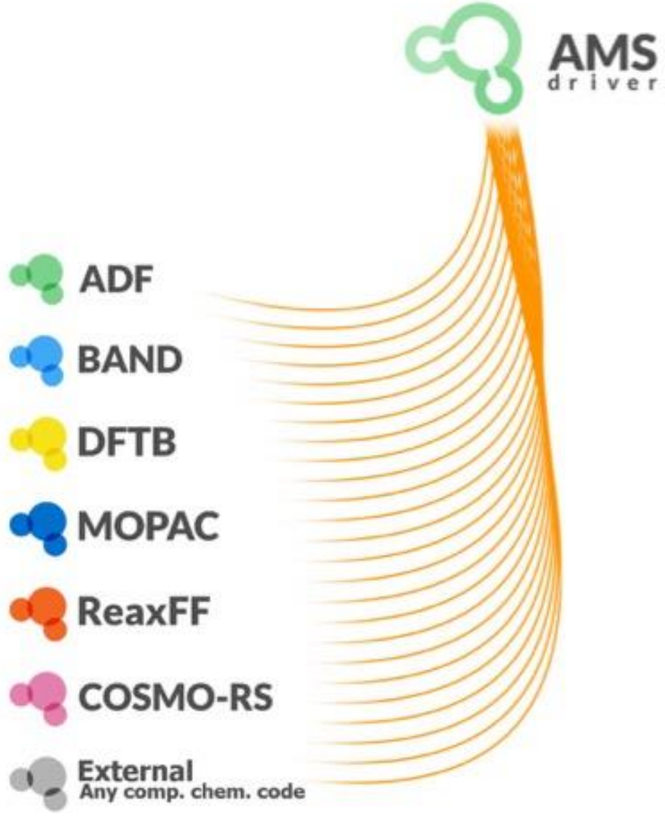
Y. Kim, J. W. Kim, Z. Kim and W. Y. Kim, Chem. Sci. 2018, 9, 825; JPCA 2019, 123, 4796.

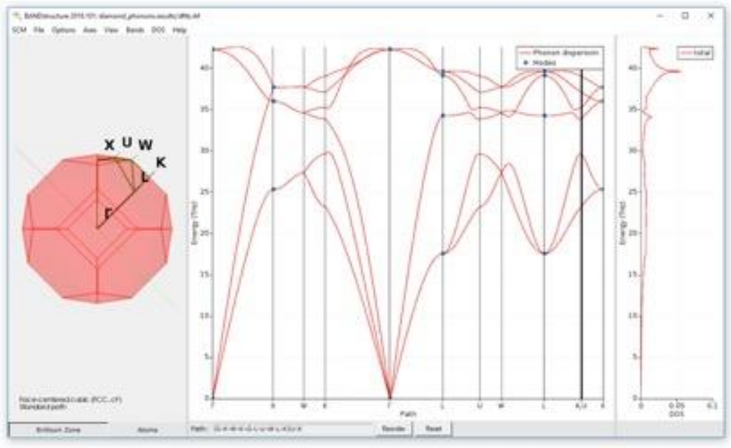
1 GUI: build, run & analyze

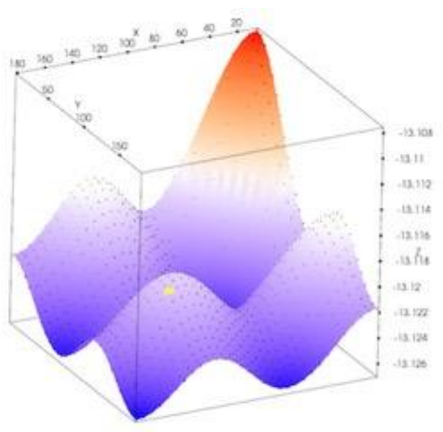










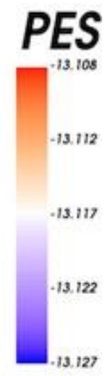
The AMS driver: decouple from Engine

- Frequencies (+ analysis) & phonons
- Stress & elastic tensors
- Scan (multiple) coords, any periodicity
- Geometries, TS, IRC
- Advanced Molecular Dynamics
- (Grand Canonical) Monte Carlo

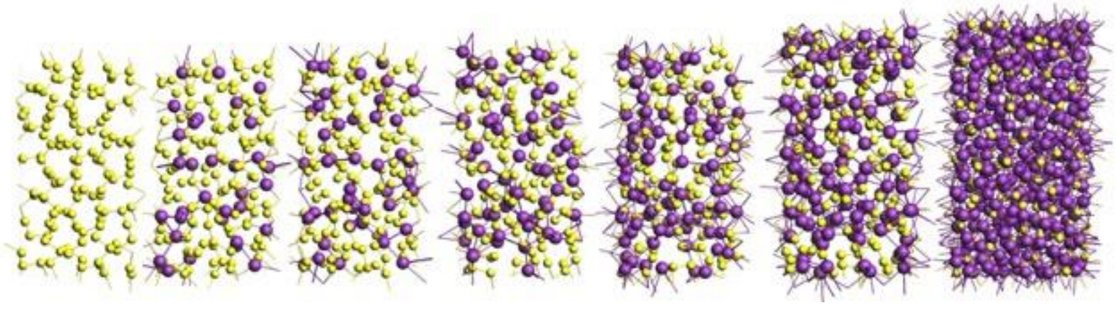




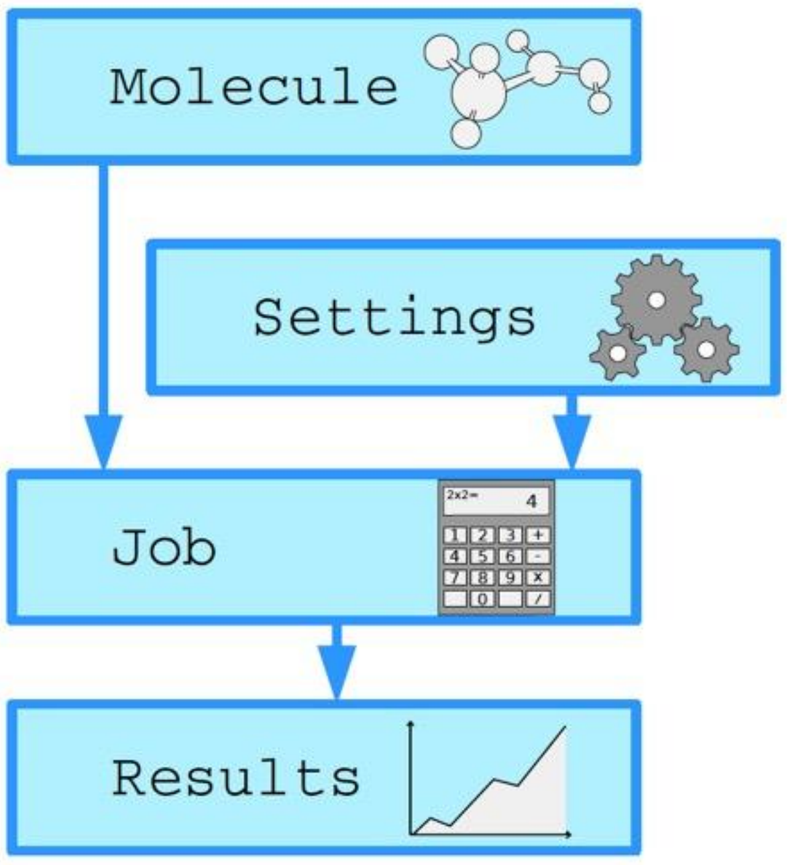


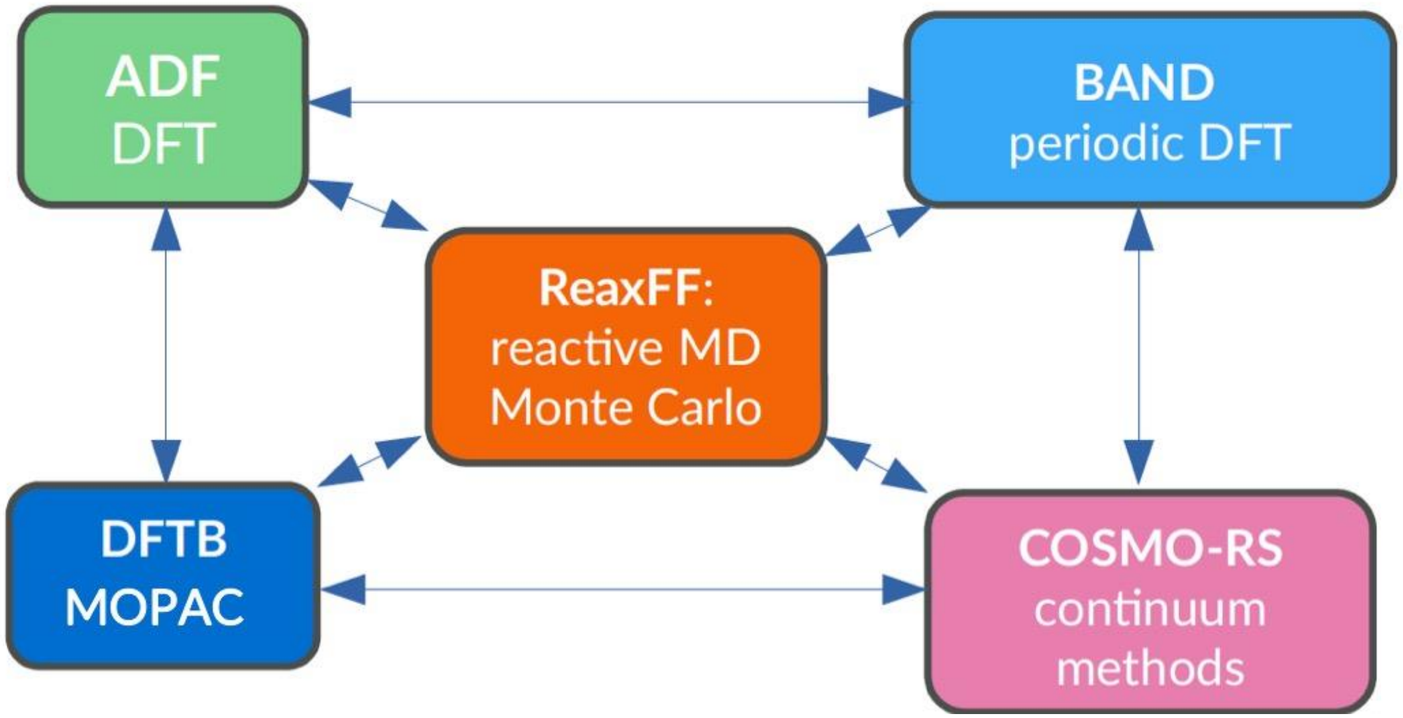


$S_8 \longrightarrow Li_2S_8 \longrightarrow Li_2S_6 \longrightarrow Li_2S_4 \longrightarrow Li_2S_3 \longrightarrow Li_2S_2 \longrightarrow Li_2S$



PLAMS: python scripting





PLAMS python

Links all modules + various tools
→ workflows & screening
→ (custom) post-processing
→ rapid prototyping