Chemistry & Materials with the Amsterdam Modeling Suite: Polymers

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Amsterdam Modeling Suite

- **ADF:** powerful molecular DFT
  - Spectroscopy: NMR, EPR, VCD, UV, XAS
  - Advanced solvation / environments
  - Reactivity, Bonding analysis

- **BAND:** periodic DFT
  - (2D) Materials, spectroscopy, analysis
- **Interface with and binaries for QE**

- **DFTB & MOPAC**
  - fast electronic structure

- **ReaxFF:** Reactive MD
  - Dynamics of large complicated systems

- **COSMO-RS:** fluid thermodynamics
  - VLE, LLE, logP, solubility

- **Integrated GUI:** use out of the box

- **AMSDriver:** complex PES tasks

- **PLAMS:** python scripting workflows & automation
Background: SCM, ADF & AMS

- ADF = first DFT code for chemistry (1970s) Baerends@VU (>’73), Ziegler@Calgary (>’75)
- SCM: Spin-off company 1995
- 20 people (10 senior PhD’s) + 3 EU fellows
- Many academic collaborators / EU networks
  - ~150 authors
  - New functionality
- SCM: development, debug, port, optimize, docs & support

articles & patents in materials science with “density functional theory”, Nat. Mat. 4619
ADF: Molecular DFT

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


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

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

- Integrated Graphical Interface:
  - Easy set up & analysis
  - Switch: ADF, BAND & Quantum Espresso

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

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

periodic energy decomposition analysis (tutorial)
L. Pecher and R. Tonner
WIREs CMS, (2018)
DFTB: ‘fast DFT’ for molecules & periodic material

**Approximated DFT**
- Nearest neighbor & minimal basis
- Tabulated elec & rep. parameters:
  - Grimme GFN-xTB ($Z = 1-86$)
  - 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


**Standard forcefields vs ReaxFF**

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

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

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

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

Dynamic bond orders: depending on distance
ReaxFF: applications

Li battery discharge: J. Electrochem. Soc. 161, E3009 (2014); PCCP, 17, 3383 (2015), tutorial

Hydrogen embrittlement of steels

Crystallization TiO$_2$ nano-particles in water

Pd-catalysed CO oxidation GCMC+ReaxFF
ReaxFF tools in Amsterdam Modeling Suite

ChemTraYzer: Automated rates & pathways
New: Analyze surface reactions

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

epoxy + amine

Modulus, yield point

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

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

Properties of cross-linked epoxy polymers

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

Polymer 158, 354 (2018)
Properties of cross-linked epoxy polymers

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

From Stress-Strain:
- Yield point(s)
- Strain ratios

Odegard group

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.

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

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

Polymer mixture design with COSMO-RS

- COSMO-RS: mixture thermodynamics
  - 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

\[ N_{p/s} - \text{Number of moles of polymer/ solvent} \]
\[ \phi_{p/s} - \text{Volume fraction of polymer/ solvent} \]
\[ \chi_{ps} - \text{Flory-Huggins Parameter} \]

\[ \frac{\Delta G_{\text{mix}}}{RT} = N_p \ln(\phi_p) + N_s \ln(\phi_s) + N_s \phi_p \chi_{ps} \]
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
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
PLAMS: python scripting

Links all modules + various tools
→ workflows & screening
→ (custom) post-processing
→ rapid prototyping
ReaxPro: Reactive Process Design as a Multi-scale / Multi-equation Problem

Chemistry & Mass Transport

- kMC: Zacros, CFD: Catalytic FOAM

EU project 2019-2023

Industrial partners: BASF, JM, DowDuPont, Shell