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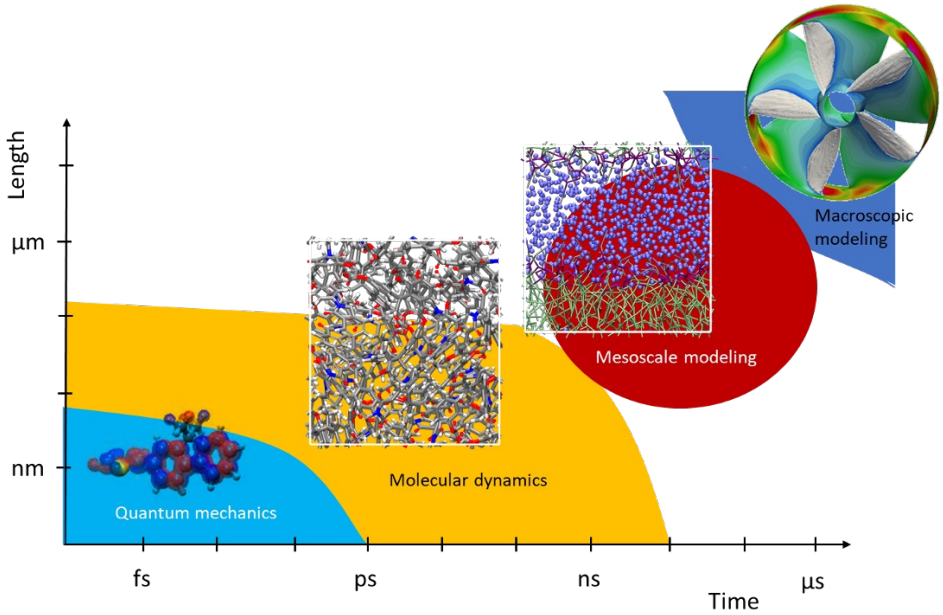
MedeA Training: Multiscale Modeling of Polymers Using the *MedeA Environment*



Marianna Yiannourakou and Jörg Hill

Materials Design, Inc.

27 October 2022

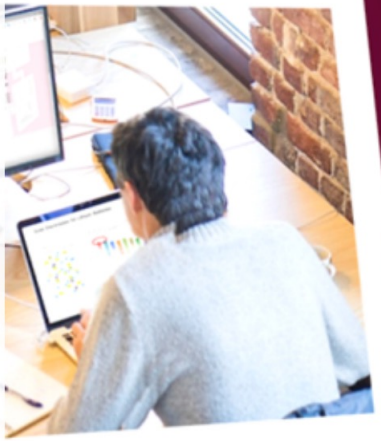
Materials Design UGM

UGM 2022

The Materials Design annual user event will be online for 2022.

Plenary Speakers include:

Prof. Jeffrey Grossman
Prof. Georg Kresse
Dr. Carla Verdi
Prof. Jörg Behler
Dr. Jozef Bicerano



https://ugm.materialsdesign.com/

Materials Design UGM Training Series

- Share the plenary sessions with your colleagues!
  - Registration details

    https://www.ugm.materialsdesign.com
- We will be recording this session
  - Upcoming sessions are posted on the UGM site
  - Watch any of our earlier webinars anytime www.materialsdesign.com/webinars
- Brief survey
  - Take a 2 minutes brief survey at the end of the webinar
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

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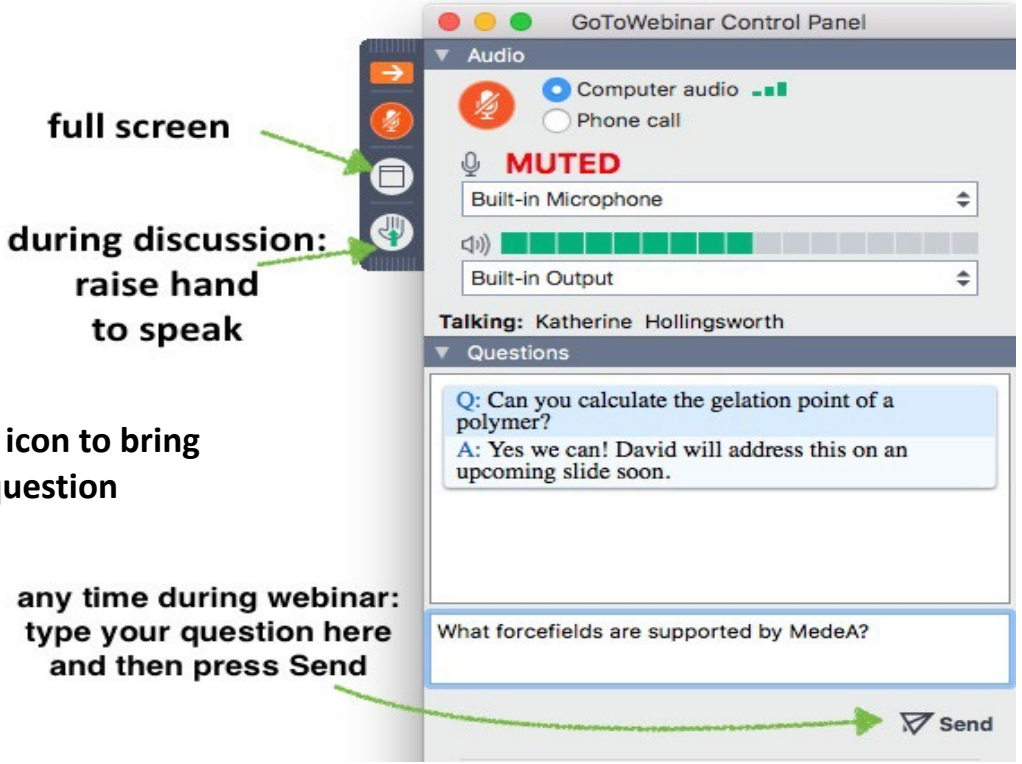
Webinar Speakers

Dr. Rene Windiks ***Dr. Marianna Yiannourakou*** ***Dr. Jörg Hill***

Training & Support Team

Xiaoli Liu	Shubham Pandey	René Windiks	Thomas Nilson	Garrett Tow	David Reith
Presenter	*Presenter*				*Moderator*

Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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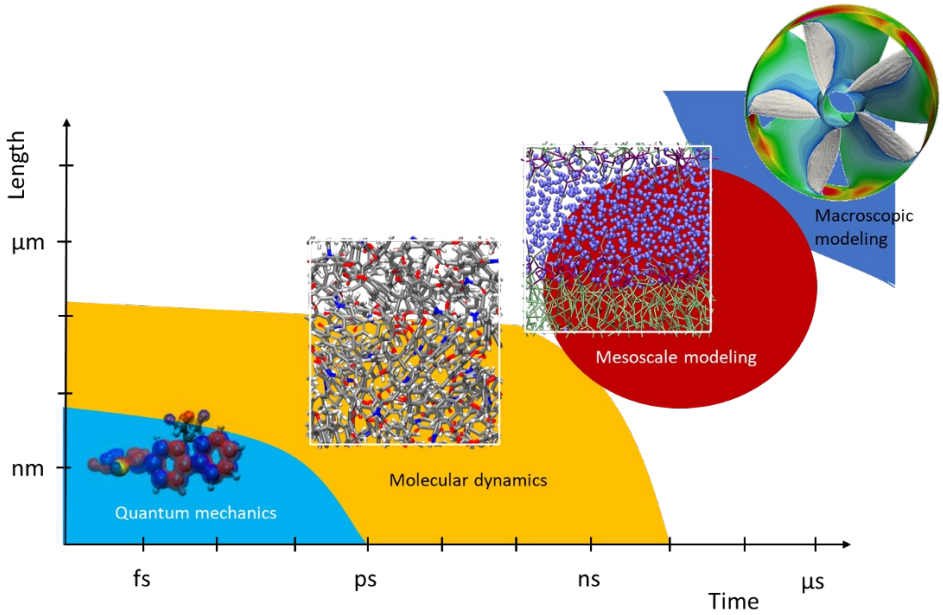

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Outline

- Properties calculated from correlations: P3C
- Forcefields: accuracy and coverage
- Building systems
- Example 1: Properties calculated from molecular dynamics simulations: LAMMPS
- Example 2: Properties calculated from Monte Carlo simulations: GIBBS
- Example 3: Advanced workflows for property calculation: Building & LAMMPS & GIBBS
- Applications Summary

- Properties calculated from correlations: P3C
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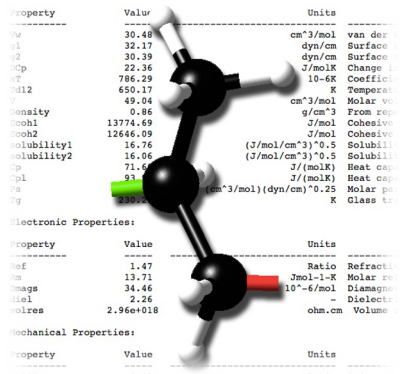


P3C

Polymer **P**roperty **P**rediction Using **C**orrelations

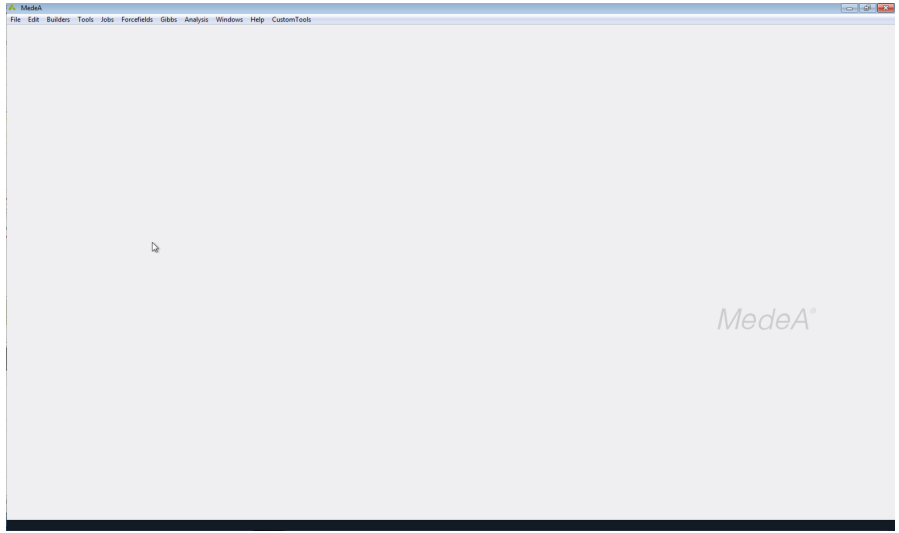
https://www.materialsdesign.com/datasheet/P3C

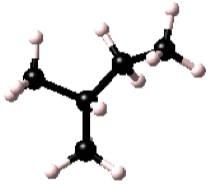
MedeA P3C employs the core methodology described by Jozef Bicerano* sometimes known as the Synthia method originally developed at Dow Chemical.
The MedeA P3C implementation extends the original methodology with a number of additional correlations for specific properties.

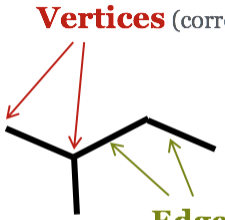
* J. Bicerano, Prediction of Polymer Properties, Marcel Dekker, Inc. (2002)

P3C for homo- and co-polymers

- Calculation of a wide range of polymer properties based on topological descriptors
- A property is calculated from a correlation based on connectivity indices
- It applies to polymers containing C, N, O, H, F, Si, S, CL and Br atoms
- It allows the use of designer correlations







Vertices (correspond to non-H atoms)

Edges
(correspond to bonds between non-H atoms)

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Properties calculated from correlations: P3C
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Building systems
Example 1: Properties calculated from molecular dynamics simulations: LAMMPS
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Summary – Conclusions

Forcefields

Accuracy and Coverage

https://www.materialsdesign.com/forcefields

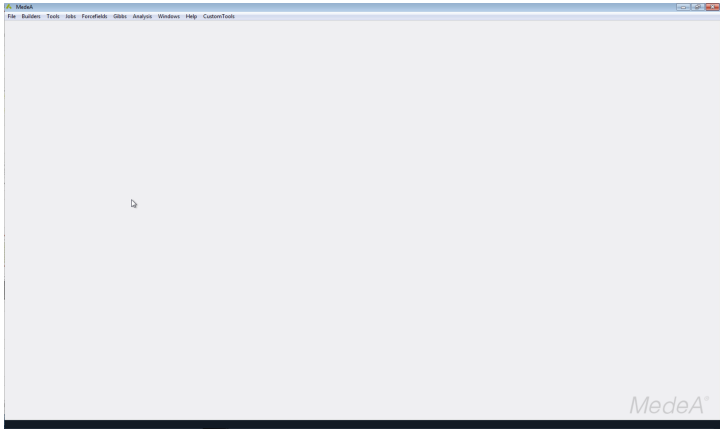
In *MedeA*, forcefields are the basis for many atomistic simulations. Forcefields allow simulators to study systems with thousands of atoms and over many configurations.

In all cases, *MedeA* provides open access to forcefield parameters, and all supporting information, such as atom assignment rules. For any simulation, it is straightforward to access the parameters that were employed in that particular calculation, making it easy to document, assess, and reproduce calculation results.

Available forcefields (FF) in *MedeA*

1. Inorganic
2. Organic
3. Metallic
4. Noble
5. Semiconductor
6. NIST
7. Mesoscale
8. ReaxFF
9. MLPs

- **All-atoms***:
  - **pcff/pcff+**
  - oplsaa, oplsaa+
  - compass/compass+
  - gaff
- **United Atoms*:**
  - AUA/AUA+
  - TraPPE-UA+
- **Coarse-grained*:**
  - Martini-2
  - Martini-3
  - SPICA



https://www.materialsdesign.com/forcefields

* FF available for use in *MedeA LAMMPS, MedeA GIBBS*

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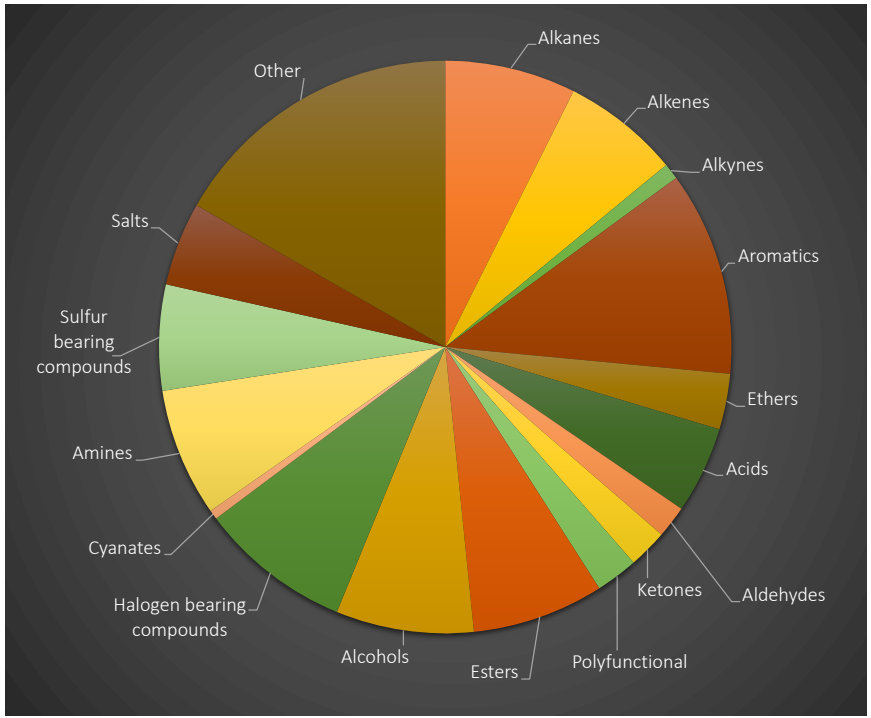
PCFF+ coverage for molecular species

- 2,150 compounds (mostly organic species)



Forcefield coverage in *MedeA* 3.6

Forcefield	Full coverage	Missing nonbond terms	Missing covalent terms
pcff+	95 %	3 %	2 %
pcff (original)	53 %	4 %	44 %

pcff+ extensions / improvements done to achieve agreement of densities under ambient conditions within 1% of experiment and flag anything outside of 2% as requiring further investigation (normal boiling point and other temperatures are also often used, particularly for lighter compounds)

Accurate description of relatively small molecules including specific functional groups results in accurate description of larger molecules including the same functional groups.

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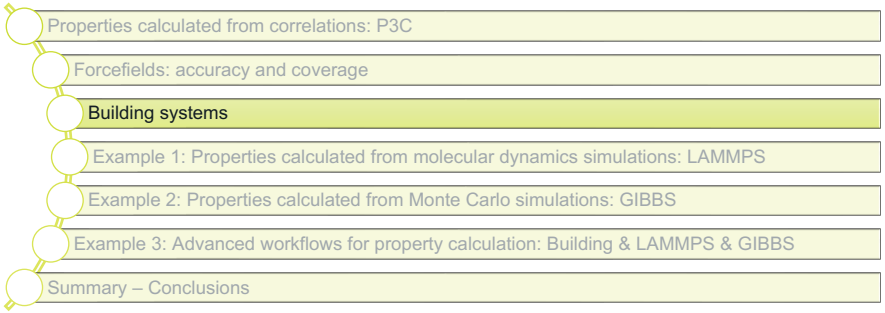

Building Systems

Polymer builder, Amorphous Materials Builder, builder for coarse-grained systems, Thermoset builder

Polymer Builder

- Build polymers from pre-defined or custom monomers
  - Library of commonly encountered monomers
  - Sketch monomers in MedeA
- Apply rules for composition, orientation and stereochemistry
  - Homopolymers
  - Co-polymers (alternating, block or random)
  - Backbone dihedral angle
  - Capping of head and tail
  - Meso diad probability

Polymer Builder

- Example: Building bisphenol-A-polycarbonate (10 monomers)

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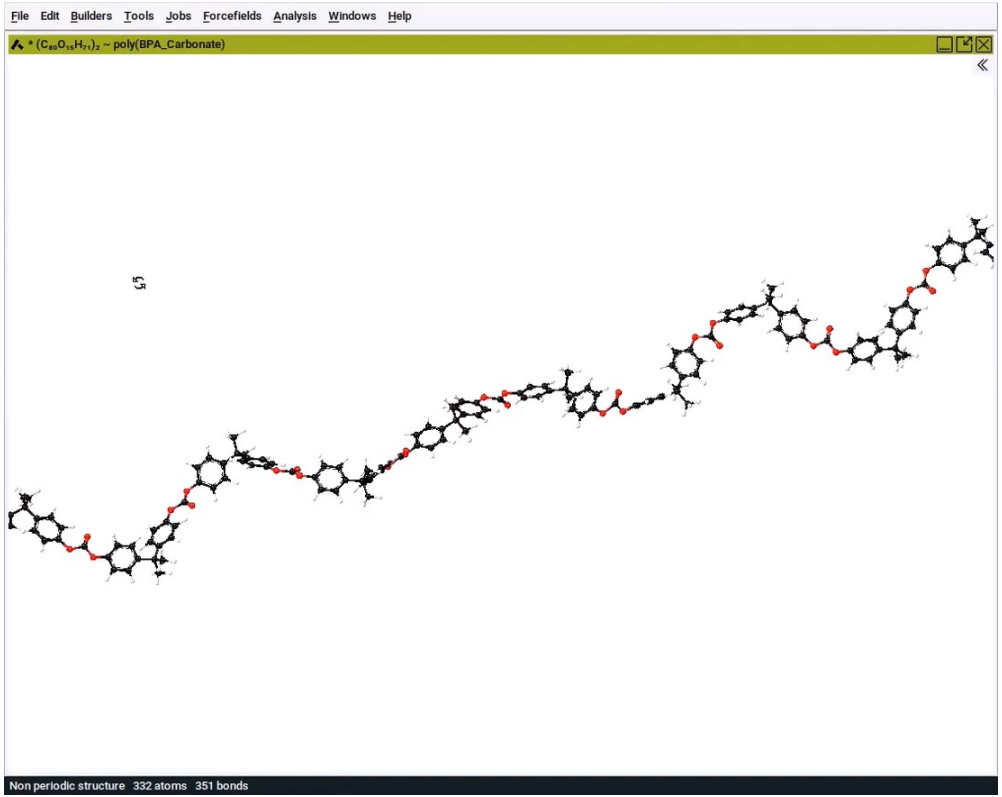
Amorphous Materials Builder

- Build amorphous materials such as
  - Molecular liquids or mixtures of liquids
  - Rubbery or glassy materials (polymers, oxides)
  - Layered systems
  - Gas penetrant organic or inorganic systems in membranes or coatings
- Mix arbitrary number of components
  - Atoms or ions
  - Molecules (flexible, with rotatable backbone or rigid)
  - Periodic systems (P1)

Amorphous Materials Builder

- Example: Build amorphous bisphenol-A-polycarbonate (10 monomers, 5 chains at 0.8 g/cm^3)



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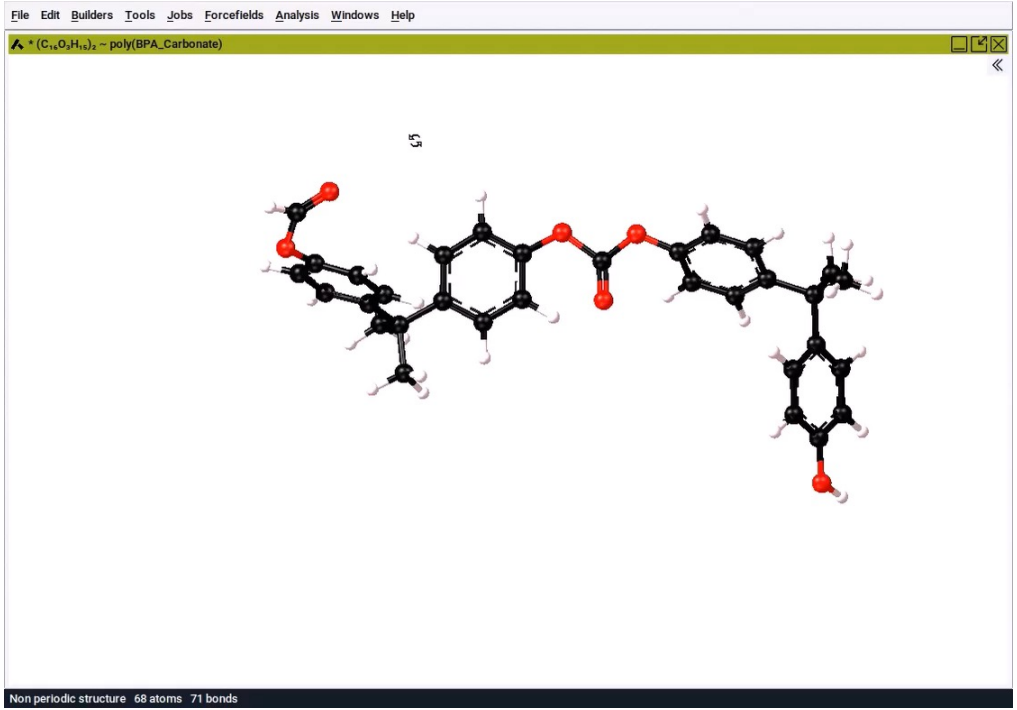
Builder for Coarse-Grained Systems

- Create coarse-grained systems from scratch
  - By sketching
  - With the polymer builder
  - With the amorphous materials builder
  - With the thermoset builder
- Map atomistic to coarse-grained systems
  - Select atoms to map to one bead on screen
  - Set bead types
  - Save mapping in file for reuse

Builder for Coarse-Grained Systems

- Example: Map atomistic model of bisphenol-A-polycarbonate to Martini beads



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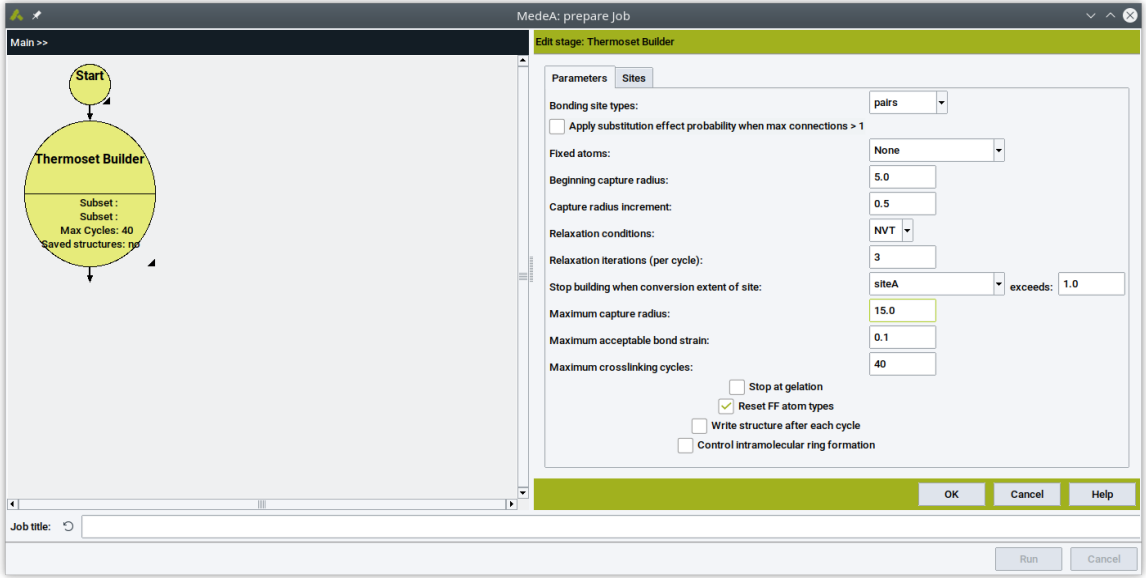
Thermoset Builder

- Build thermosets
  - Cross-link amorphous systems
  - Bonds are created in cycles with a growing capture sphere around each cross-linking site
  - Cross-linking sites can be user defined
  - Each cycle ends with a short molecular dynamics run followed by a minimization



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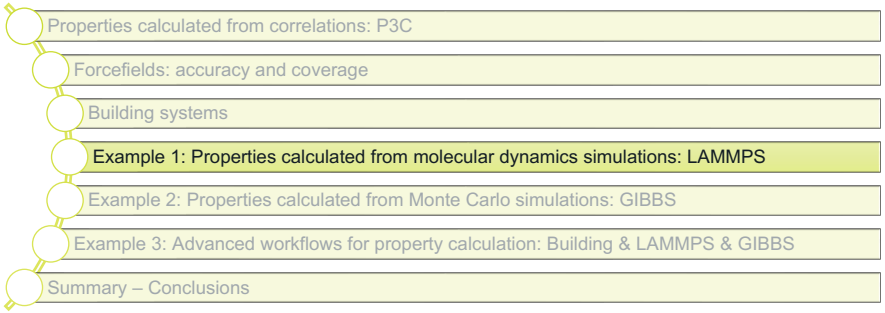


Example 1: Properties calculated from molecular dynamics simulations: LAMMPS

Calculating elastic constants for bisphenol-A-polycarbonate

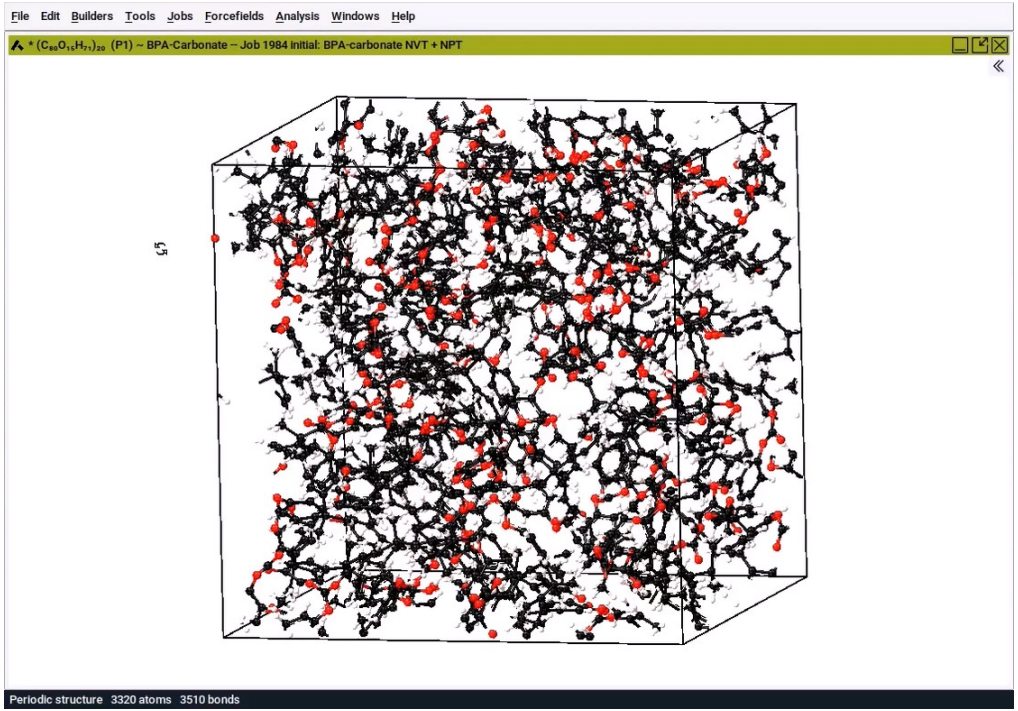
Tutorial: Calculating elastic constants for bisphenol-A-polycarbonate

LAMMPS

- Geometry optimization and molecular dynamics using atomistic and coarse-grained forcefields
- NVE, NVT and NPT ensembles
- Properties such as
  - Cohesive energy density
  - Thermal conductivity
  - Viscocity
  - Diffusion
  - Surface tension
- LAMMPS interface is based on flowcharts

LAMMPS

- Example: Calculating elastic constants for bisphenol-A-polycarbonate



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LAMMPS

- Results can be found in Job.out (exp. Young modulus: 2.0 – 2.4 GPa, Poisson ratio 0.37)

Elastic constant matrix (GPa):

	1	2	3	4	5	6
1	5.0137	2.6157	3.1534	-0.0563	0.6456	0.1208
2	2.6157	4.2360	2.3400	0.1226	-0.1324	-0.2147
3	3.1534	2.3400	4.5410	0.0282	-0.2157	0.1591
4	-0.0563	0.1226	0.0282	1.3340	-0.1330	0.0173
5	0.6456	-0.1324	-0.2157	-0.1330	0.8542	-0.0251
6	0.1208	-0.2147	0.1591	0.0173	-0.0251	1.1822

Modulus	Voigt	Reuss	Hill	
Bulk	3.33	3.26	3.30	GPa
Shear	1.05	0.81	0.93	GPa
Young's	2.86	2.25	2.56	GPa
Longitudinal	4.74	4.35	4.54	GPa
Poisson's ratio	0.3572	0.3848	0.3707	
Pugh's ratio	3.1669	4.0068	3.5331	

Pugh's ratio k is a descriptor for ductility, see S F Pugh, Phil. Mag. 45 (1954) 823-843
k = B/G > 1.75 ductile, otherwise brittle

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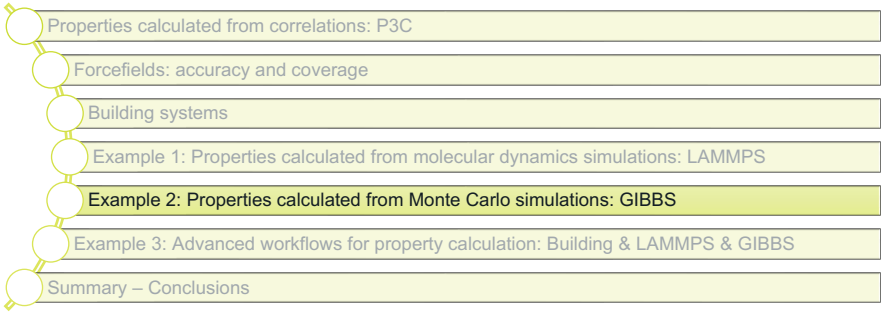


Example 2: Properties calculated from Monte Carlo simulations: GIBBS

Solubility of O_2 in PS

Tutorial: Permeability of O_2 in Polystyrene http://my.materialsdesign.com/tutorials

Example: Solubility of O_2 in Polystyrene

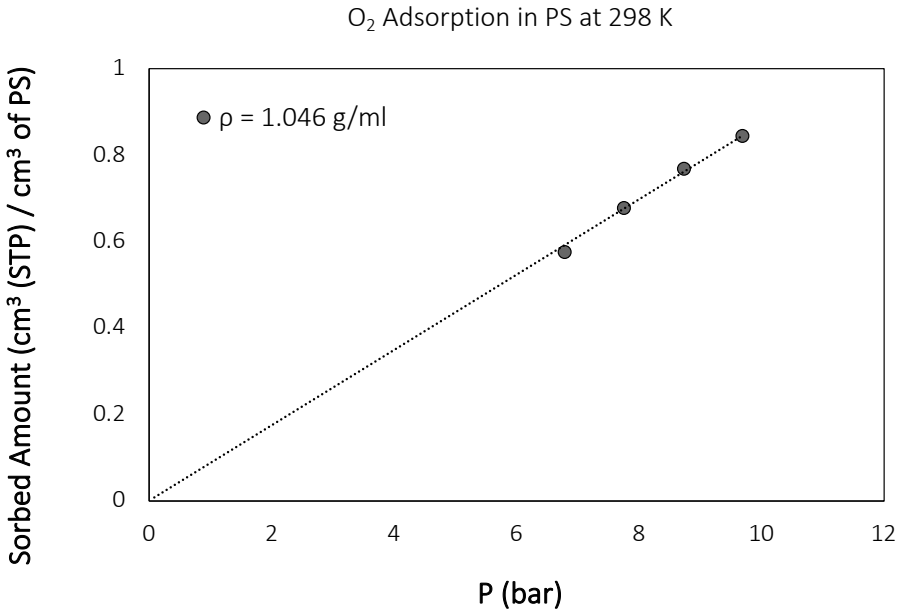
Pressure dependence of solubility of O_2 in atactic PS at 298K

- $S = \frac{C_{O_2}}{P_{O_2}}$

where O_2 is the concentration of the gas in the polymer and, P_{O_2} is the pressure of the gas

- *S = 0.872 10^{-6} cm^3 (STP) / cm^3 of PS / Pa*

Note: 0.85 cm^3(STP)/cm^3 of PS corresponds to ~2.4 molecules per simulation box



Experimental density: Zoller & Walsh (1995), p133

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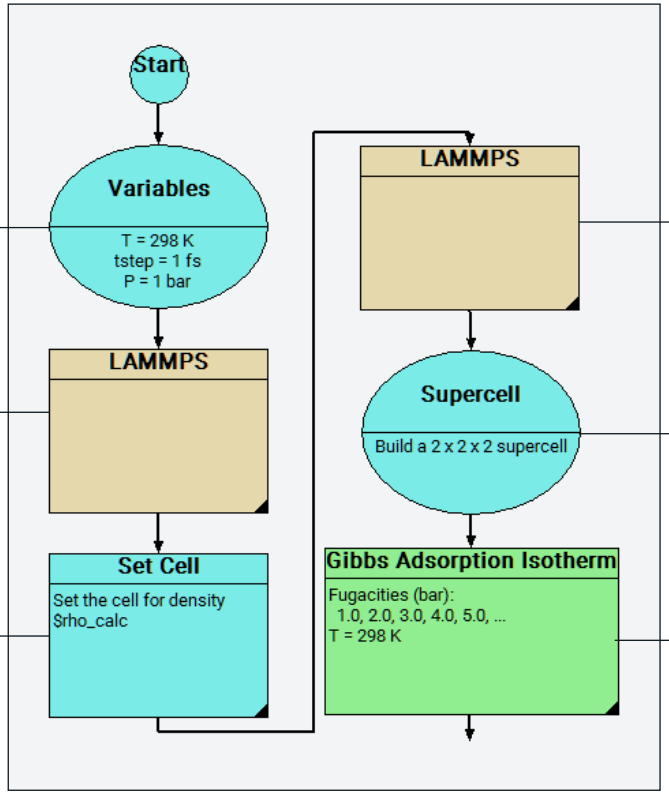
Example: Solubility of O_2 in Polystyrene



Set the values of certain variables to be used in the simulations (T, MD timestep, P)

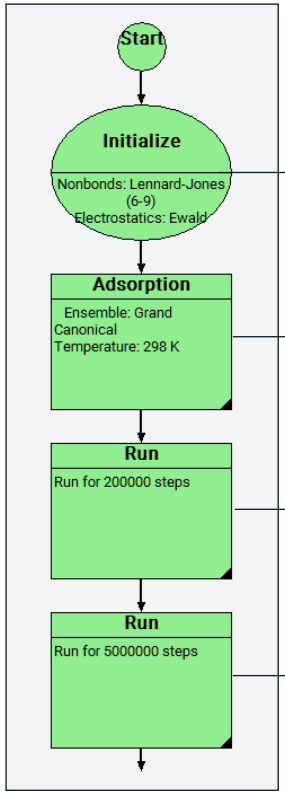
Run 1 short equlitration MD (NVT) run and 1 production MD (NPT) run

Adjust system's density to the calculated average density (or e.g. the experimental density) for a given pressure

Run a short MD equilibration (NVT) run to relax the system after density adjustment

Create a supercell

Run a MC (GCMC) run to calculate an entire isotherm for a range of fugacities



Initialize MC

Set up input for the sorption simulation (T, sorbent, adsorbates)

Run 1 short equilibration MC (GC) run

Run 1 production MC (GC) run

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Example: Solubility of O_2 in Polystyrene

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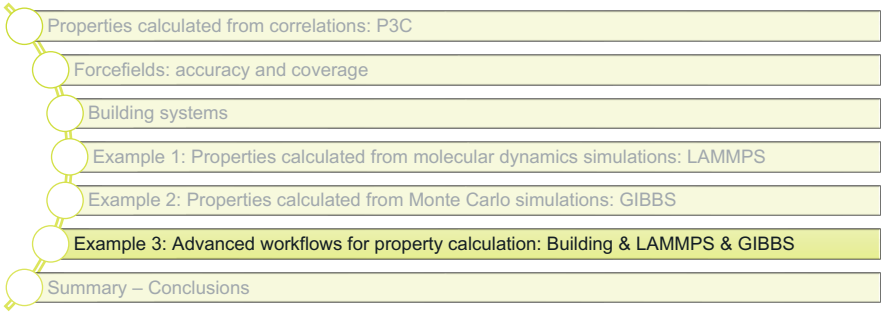


Example 3: Advanced workflows for property calculation: Building & LAMMPS & GIBBS

Permeability of O_2 in PS: LAMMPS & GIBBS

Tutorial: Permeability of O_2 in Polystyrene http://my.materialsdesign.com/tutorials

Permeation and Permeability

Permeation is usually described experimentally by a **permeability coefficient**, P, defined by[1]:

$$P = \frac{(quantity\ of\ permeant) \times (membrane\ thickness)}{(area) \times (time) \times (pressure\ drop\ across\ membrane)}$$

which is equivalent to the following:

$$P = D \times S$$

where D denotes the diffusivity, and S the solubility.

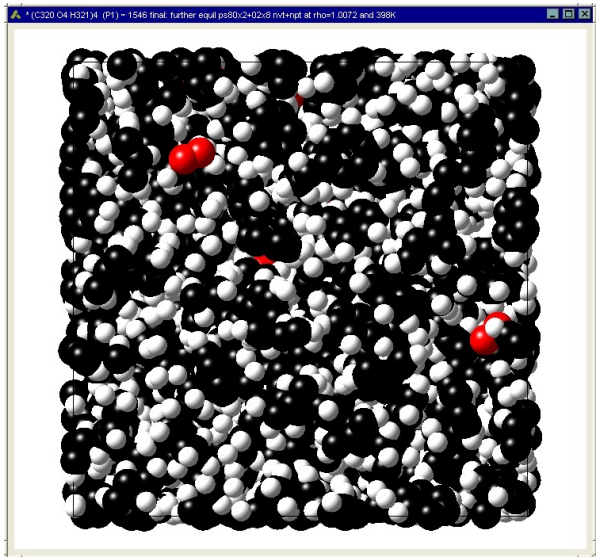
In atomistic simulations of gas penetrant systems, D can often be obtained directly using molecular dynamics simulation, while S can be obtained by Monte Carlo methods.

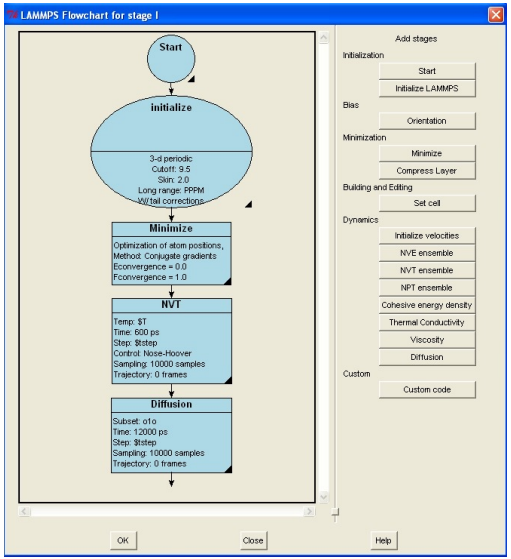
1. see, for example, Polymer Handbook, J. Brandrup & E.H. Immergut (eds)

Example: Diffusivity of O_2 in Polystyrene

System Studied

Model system containing 2 atactic PS molecules with DP=80, with 8 added oxygen molecules (2580 atoms total), with Diffusion Flowchart





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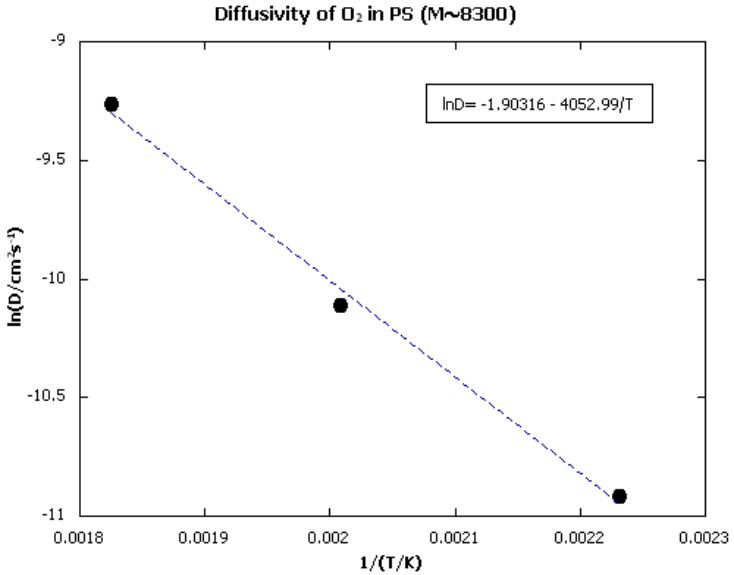
Diffusivity of O_2 in Polystyrene

Arrhenius plot for O_2 in atactic PS (548K-448K)

- Predicts D ~ **1.87×10^{-7} cm^2s^{-1} at 298K**



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Solubility of O_2 in Polystyrene

Pressure dependence of solubility of O_2 in atactic PS at 298K

- $S = \frac{C_{O_2}}{P_{O_2}}$

where O_2 is the concentration of the gas in the polymer and, P_{O_2} is the pressure of the gas

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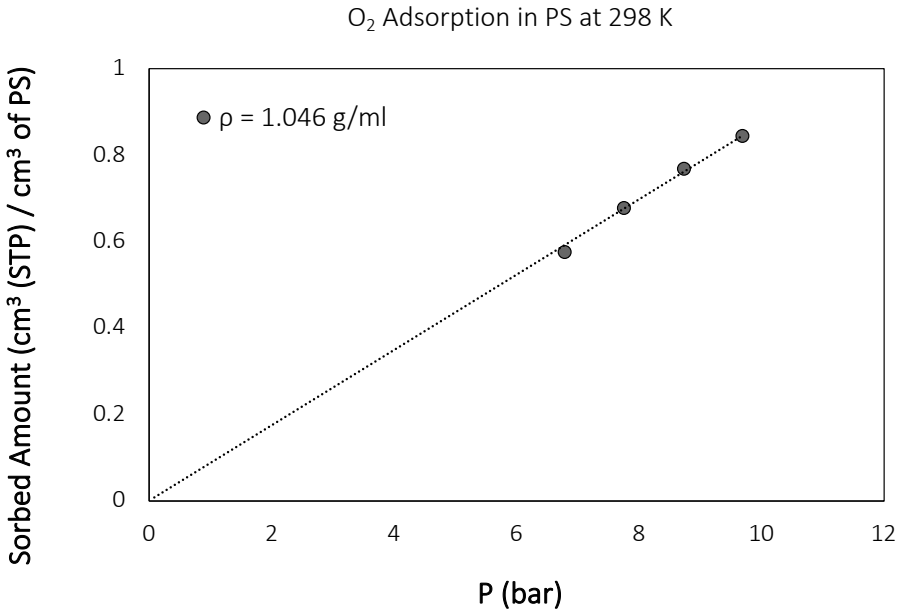
Note: 0.85 cm^3(STP)/cm^3 of PS corresponds to ~2.4 molecules per simulation box



Experimental density: Zoller & Walsh (1995), p133

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Permeation and Permeability

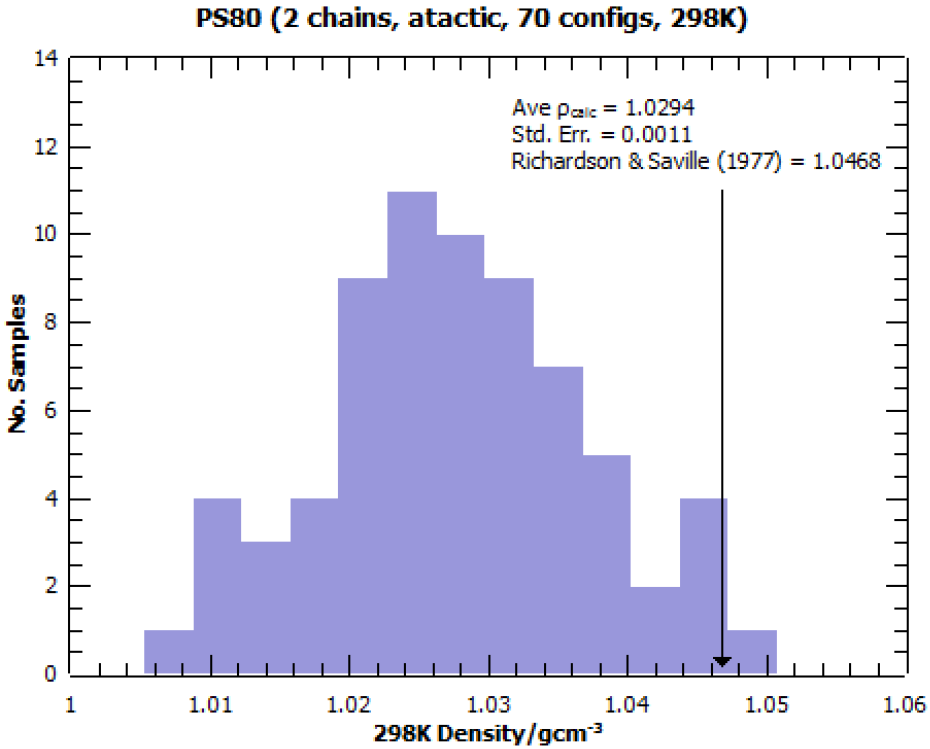
Comparison of calculated and experimental permeability data for O_2 in atactic PS at 298K

	D ($x10^7$)[a] [cm^2/s]	S ($x10^6$)[b] [cm^3(STP)/(cm^3.Pa]	P ($x10^{13}$)[c] [cm^3(STP).cm/(cm^2.s.Pa)]
Calculated	1.87	0.87	1.63
Burmeister et al	-	-	1.35-1.85
Wang & Ogilby	2.0+0.2	-	-
Rharbi et al	1.9+0.05	-	1.71-1.89

References:
Burmeister et al, Polym. Prepr. ACS Div Polym. Chem. **27**, 414 (1986)
Wang & Ogilby, Can. J. Chem. **73**, 1831 (1995)
Rharbi et al., Anal. Chem. **71**, 5045 (1999)

Sampling

- Sampling is crucial for determining the sensitivity of the method and the expected accuracy
- Multiple simulation jobs starting from independent initial configurations are required to allow for the accurate calculation of the desired properties
- The low solubility of O_2 in PS implies that a small variation in the system's density and the local configuration may result in substantial fluctuations of the solubility



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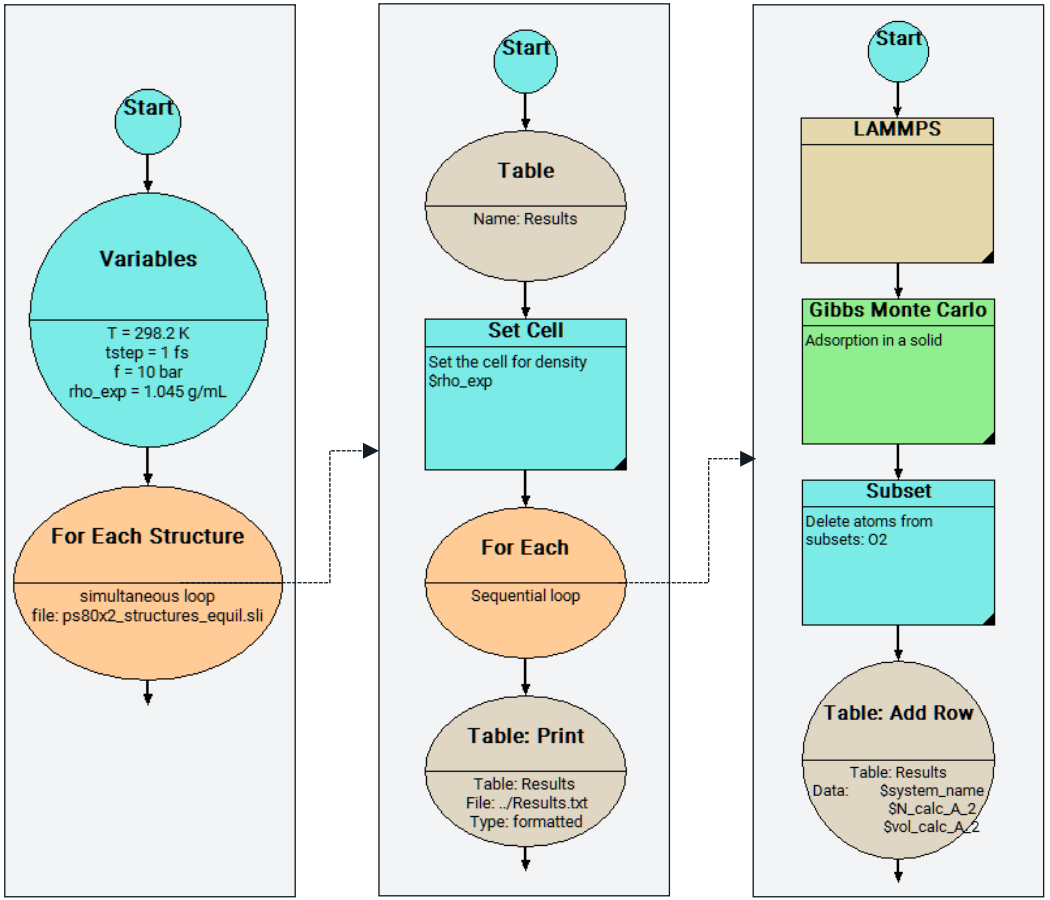
Sampling – Workflows

- Flowcharts can be used efficiently to create workflows that:
  - loop over initial configurations
  - loop over simulation conditions
  - include successive:
    - LAMMPS,
    - GIBBS, and
    - Building/Editing stages
  - schedule tasks to make most efficient use of available compute resources
  - report results and calculated properties in a form that can be further post-processed as appropriate
- Flowcharts can be stored, re-used, and shared



A single flowchart containing a total of 710 GIBBS and 710 LAMMPS simulations

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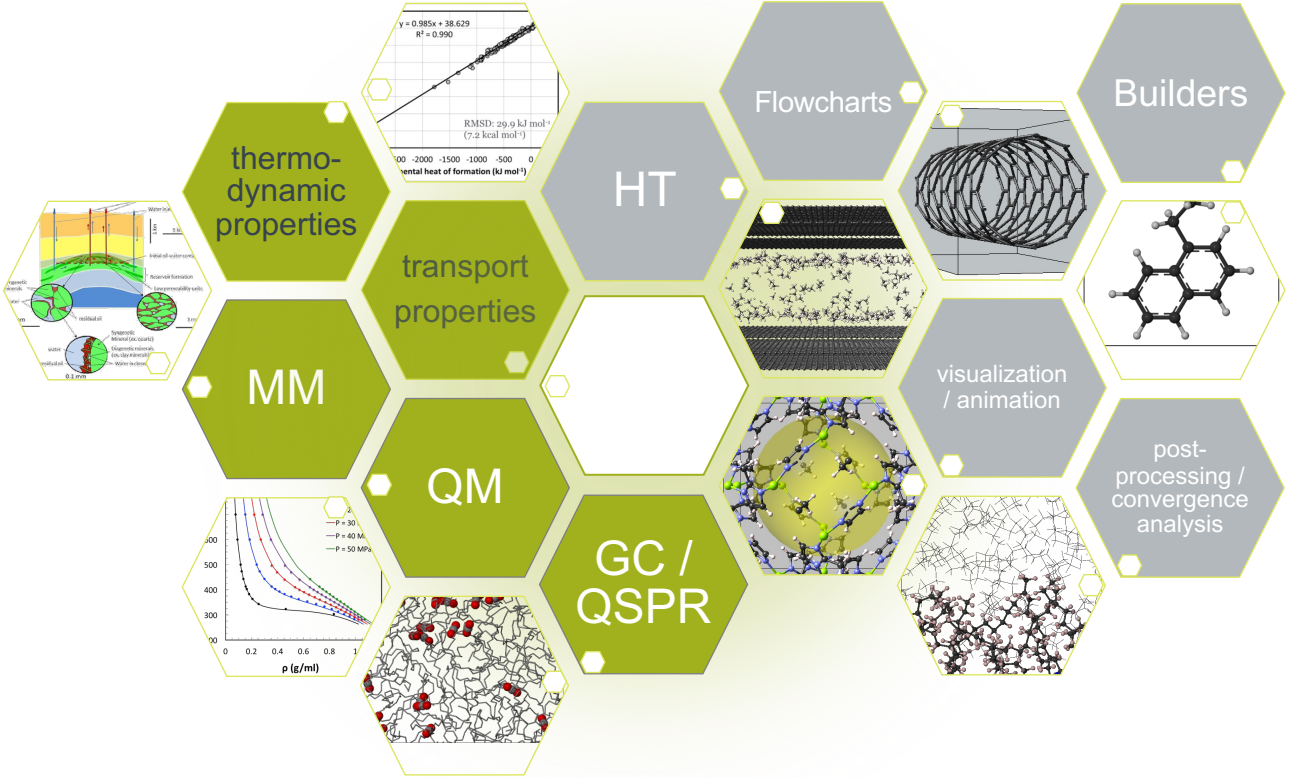
Summary – Conclusions



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Question and Answer Session

Dr. Rene Windiks
Materials Design

Dr. Marianna Yiannourakou
Materials Design

Dr. Jörg Hill
Materials Design

Questions about Materials Design UGM

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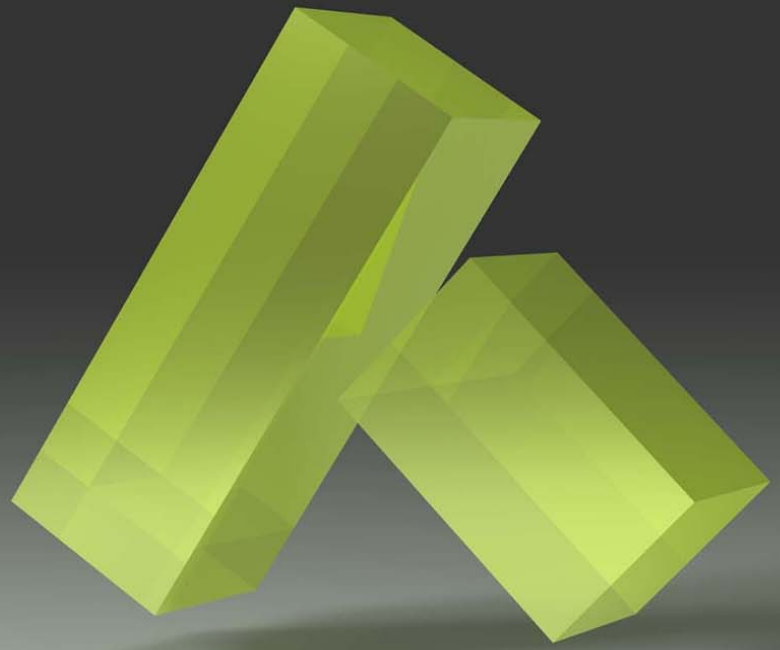

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Innovation by Simulation