WEBINAR

Mesoscale Simulations

Jörg-Rüdiger Hill
Materials Design

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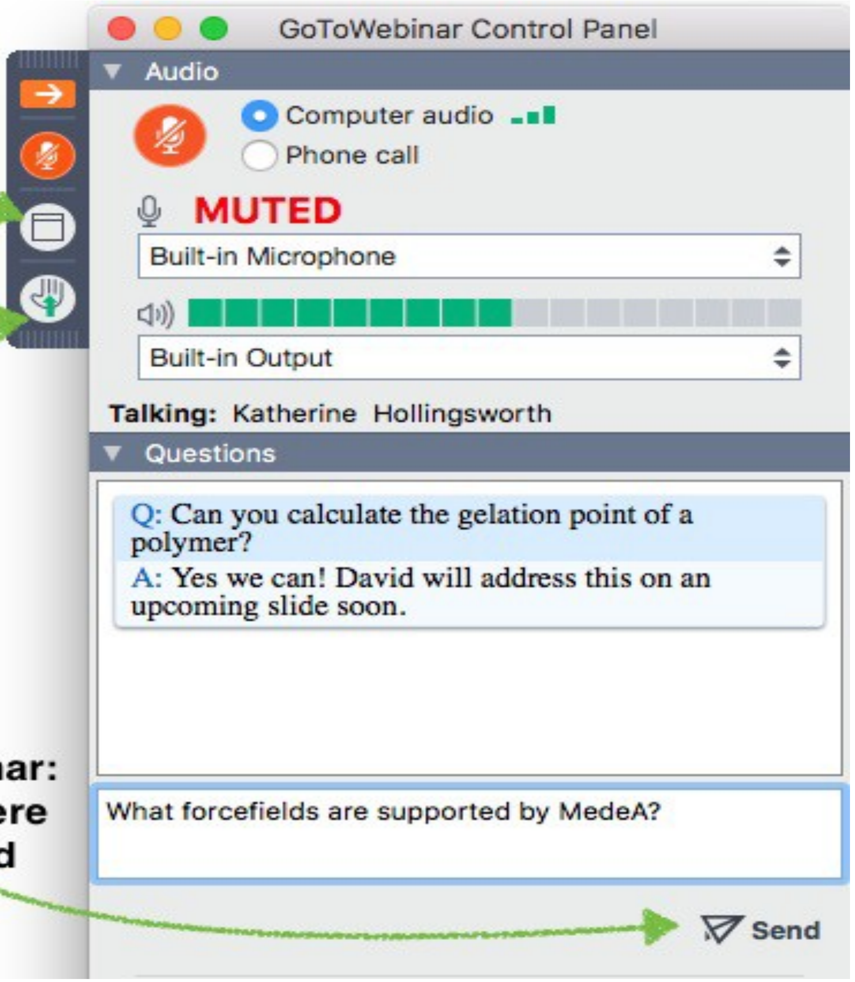

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Webinar Speakers

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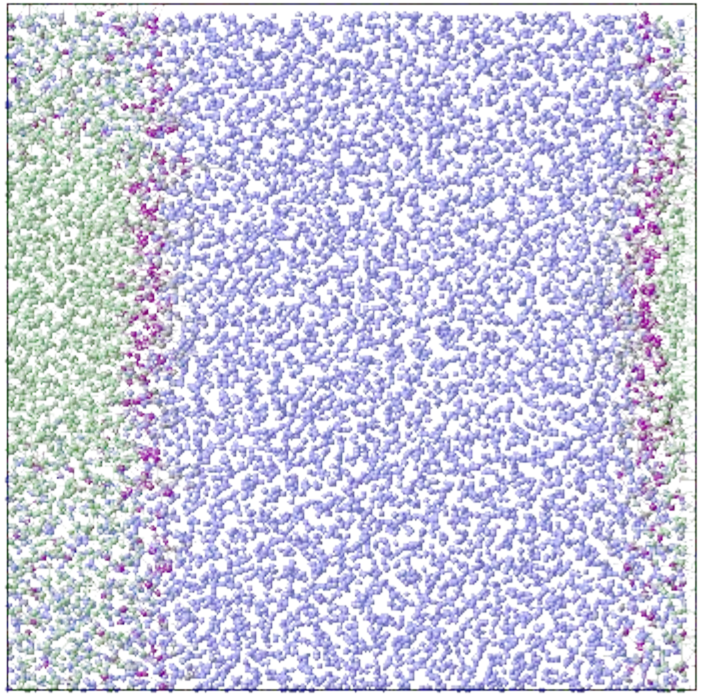
Outline

- What is mesoscale modeling?
- Theoretical background
- Mesoscale forcefields
- Application examples
- Mesoscale modeling with MedeA 3.1



What Is Mesoscale Modeling?

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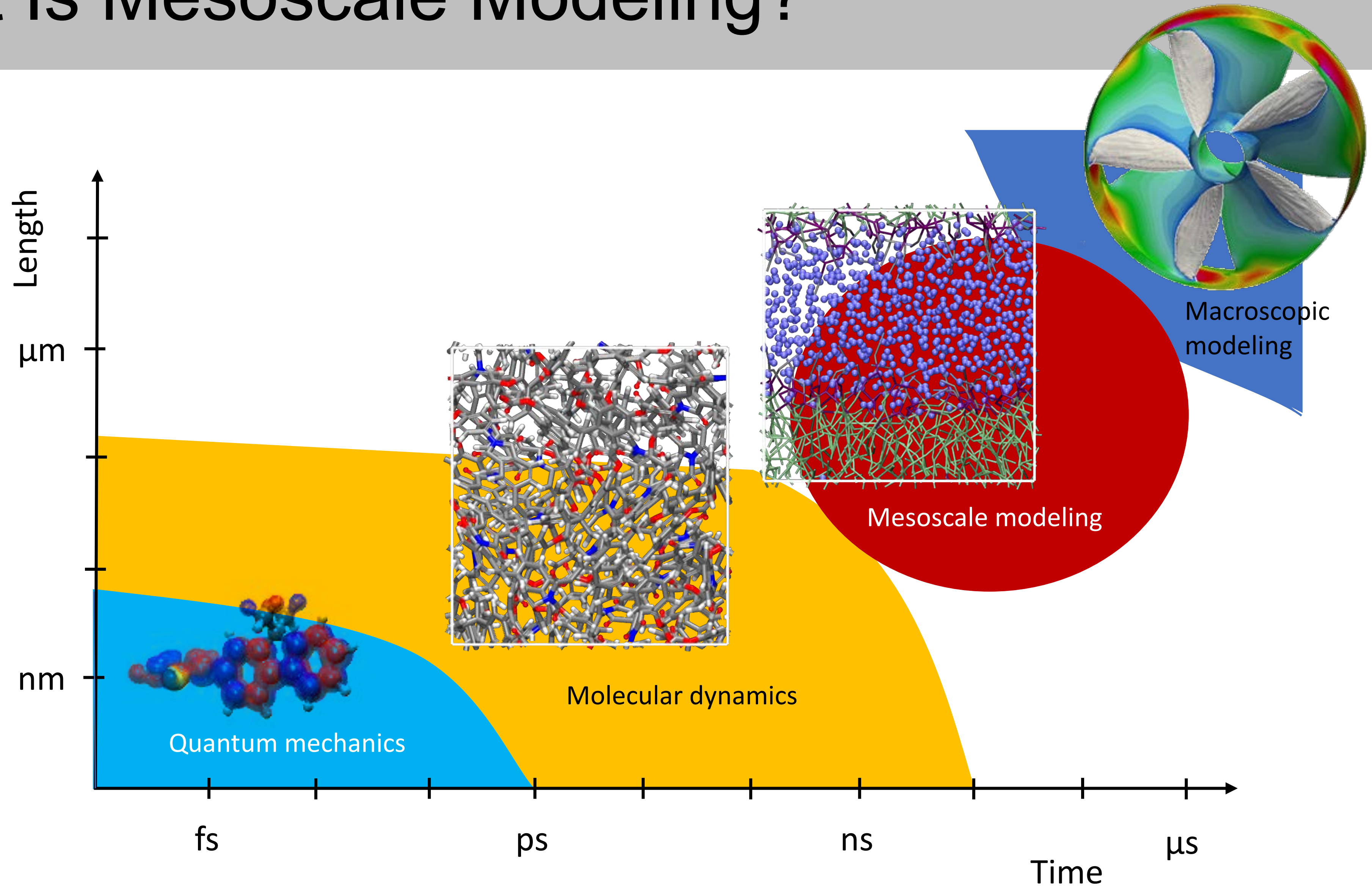
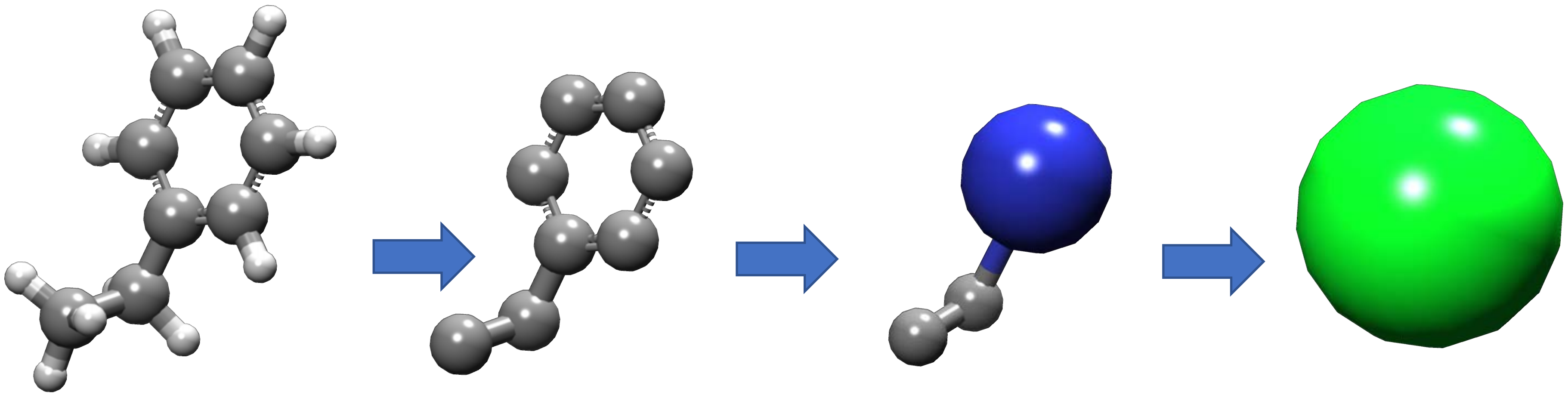


What Is Mesoscale Modeling?

- Modeling on time and length scales larger than atomistic modeling
- Groups of atoms are usually placed together in „beads“ (united atom approaches are a first step)
- One bead can also represent multiple molecules, e. g., three water molecules
- Beads can have bonds
- Forcefields are usually non-transferable
- Coarse-grained and dissipative particle dynamics (DPD) simulations

What Is Mesoscale Modeling?

Coarse graining of a styrene monomer



atomistic

united atom

coarse grained 1

coarse grained 2

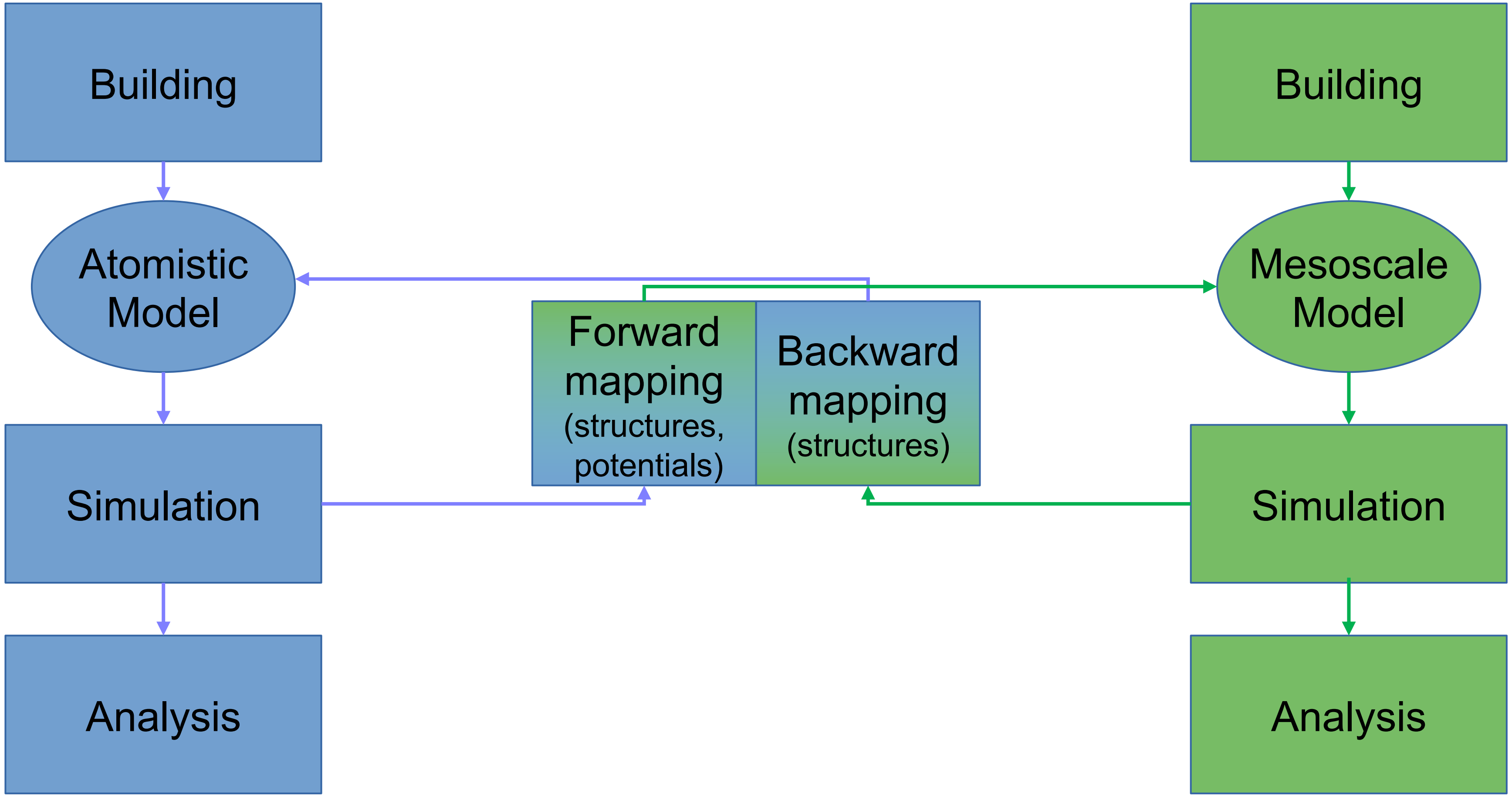
Theoretical Background

Theoretical Background

- Mesoscale models
  - Reduce number of particles
  - Smoothen potential energy surface
  - Allow longer simulation of larger systems (microseconds and tens of nanometers)
  - Lose details of system
- Building of mesoscale models
  - Direct
  - Conversion of atomistic models
- Mesoscale models can be converted to atomistic models (needs additional information)
- Forcefields
  - Designed for larger groups of molecules (Martini, SPICA)
  - System specific (fitted to atomistic data)

Theoretical Background

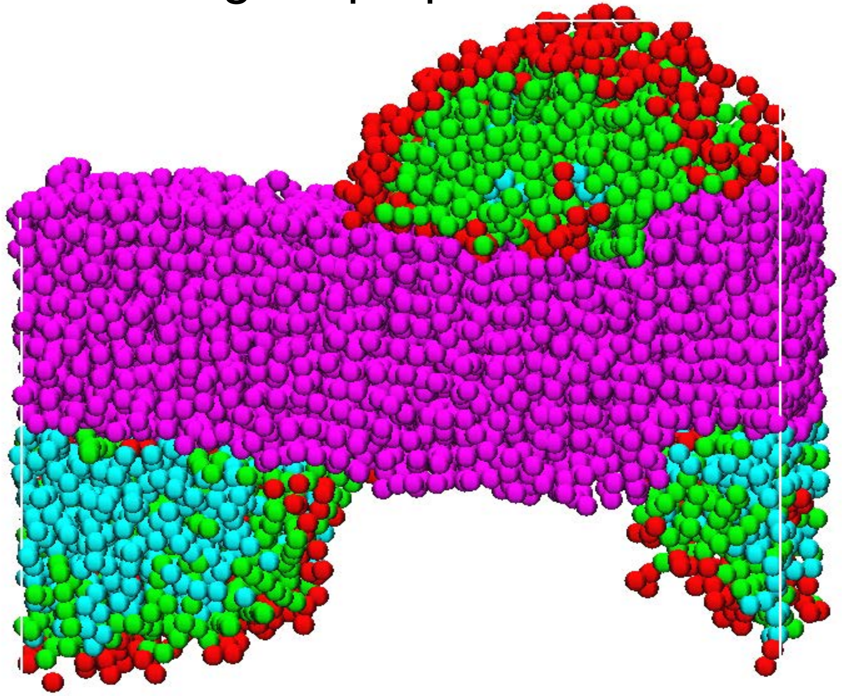
- Users expect smooth switching between atomistic and mesoscale simulations



Theoretical Background

Types of mesoscale simulations

- Coarse-grained simulations
  - Interaction of hard particles representing more than one atom
- DPD simulations
  - Stochastic technique for simulating the dynamic and rheological properties of fluids (hydrodynamics)
  - Soft interaction potential
  - Fluid elements instead of particles
  - Momentum is conserved locally
  - Beads can be tied together with soft springs



Mesoscale Forcefields

Mesoscale Forcefields

Functional form is usually the same as for atomistic forcefields

$$E = E_{bond} + E_{angle} + E_{non-bond}$$

with

$$E_{bond} = \sum_{i=0}^{n} K_b (r - r_0)^2$$

$$E_{angle} = \sum_{i=0}^{n} K_a (\cos\theta - \cos\theta_0)^2$$

$$E_{non-bond} = \sum_{i<j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6} \right] + \sum_{i<j} \frac{q_i q_j}{4\pi\epsilon_0 \epsilon_r r}$$

Mesoscale Forcefields

DPD uses a different approach

$$f_i = \sum_{j \neq i} (f_{ij}^C + f_{ij}^D + f_{ij}^R)$$

with

$$f_{ij}^C = Aw(r)$$
$$f_{ij}^D = -\gamma w(r)^2 \left(\vec{r}_{ij} \cdot \vec{v}_{ij}\right)$$
$$f_{ij}^R = \sigma w(r) \alpha (\Delta t)^{-1/2}$$
$$w(r) = 1 - \frac{r}{r_C}$$

A and γ: Forcefield parameters, $\sigma = \sqrt{2k_B T \gamma}$

α: Random number from Gaussian distribution with zero mean and unit variance

r_C: Cutoff

Mesoscale Forcefields

Common mesoscale forcefields

- Martini (https://cgmartini.nl)
  - Developed for biomolecules (lipids etc.)
  - Extended to cover some polymers (PE, PP, PS, PEG, PSS, P3HT, PDADMA, PAMAM), ionic liquids
  - Targets structural, elastic, dynamic and thermodynamic properties
  - Usually 4 heavy atoms → 1 bead

- SPICA (surface property fitting coarse graining, https://www.spica-ff.org)
  - Developed for surfactants/water systems (alkanes, ethers, alcohols)
  - Targets thermodynamic properties: surface/interfacial tension and density

- Many custom made forcefields

Mesoscale Forcefields

Development of custom forcefields

- Forcefields are created by matching atomistic molecular dynamics trajectories
  - Boltzmann inversion for bonded potentials
  - Iterative Boltzmann inversion
  - Inverse Monte Carlo
  - Force matching
  - Relative entropy method
- Academic codes exist
  - Versatile Object-oriented Toolkit for Coarse-graining Applications – VOTCA
  - MagiC

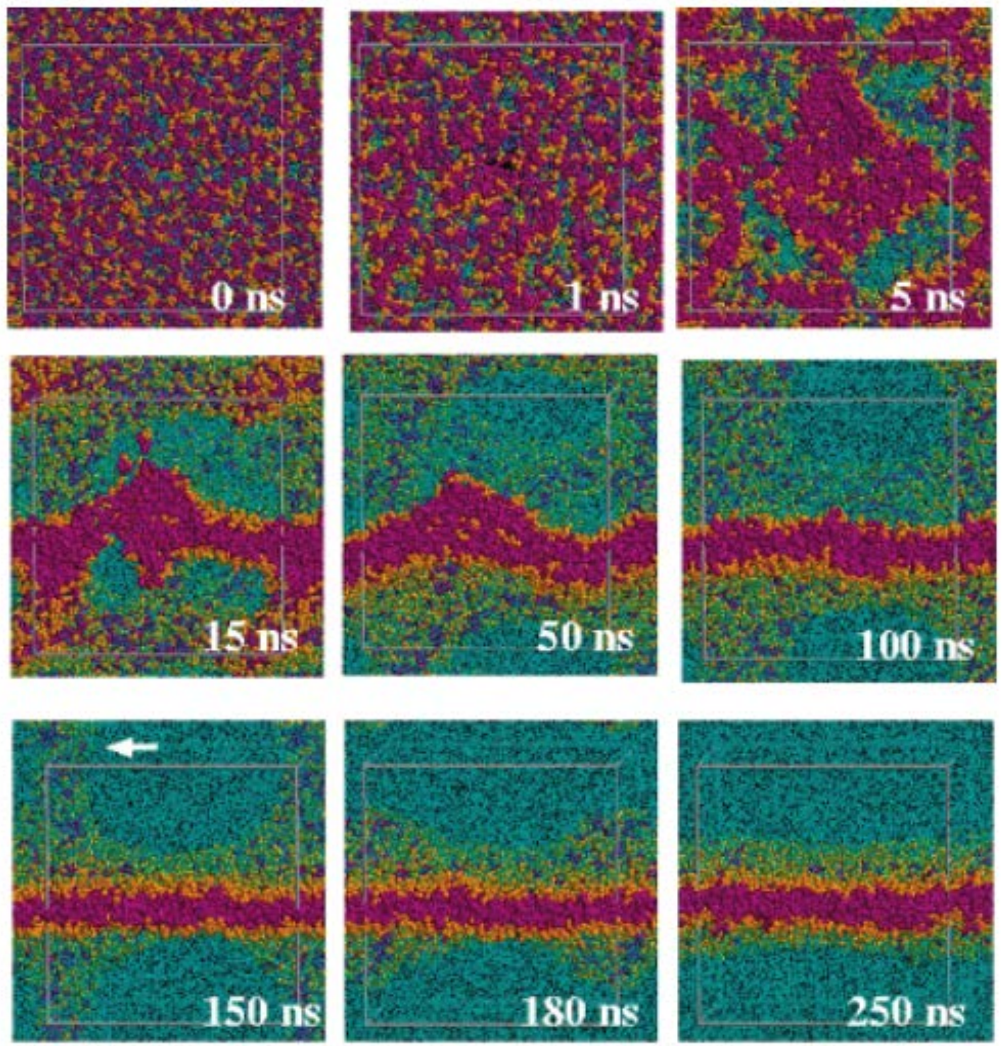
Application Examples

Application Examples

- Self-assembly of a lipid bilayer in water, Martini forcefield
  - S. J. Marrink, A. H. de Vries, A. E. Mark, J. Phys. Chem. B (2004), **108**, 750-760
  - S. J. Marrink, H. J. Risselada, S. Yefimov, D. P. Tieleman, A. H. de Vries, J. Phys. Chem. B (2007), **111**, 7812-7824
- Thermoset polyester coating, Martini forcefield
  - Rossi et al., Macromolecules (2011), **44,** 6198 - 6208
- Extraction with ionic liquids, Martini forcefield
  - L. I. Vazquez-Salazar, M. Selle, A. H. de Vries, S. J. Marrink, P. C. T. Souza, Preprint at ChemRxiv
- Mechanical properties of epoxy resin, custom forcefield
  - A. V. S. S. Prasad, T. Grover, S. Basu, Int. J. Eng. Sci. Technol. (2010), **2,** 17-30

Self-assembly of Lipid Bilayer

- Self-assembly of a lipid bilayer in water
- 1600 DPPC lipid and 60000 coarse-grained water molecules randomly distributed, 1 µs simulation time
- Martini forcefield
- Bilayer is forming after around 100 ns



Thermoset Polyester Coating

- Construction of mesoscale model of thermoset used in steel coating consisting of
  - Building monomers and polymers
  - Building amorphous system
  - Cross-linking to form thermoset
- Equilibration runs of 1 µs, cross-linking for 0.1 µs

Macromolecules

ARTICLE

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A MARTINI Coarse-Grained Model of a Thermoset Polyester Coating

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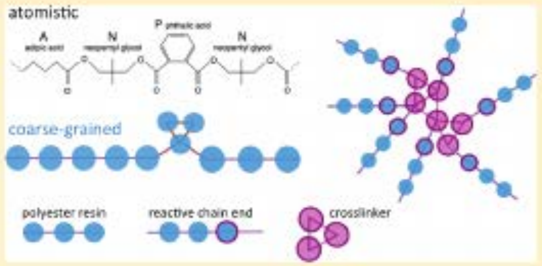
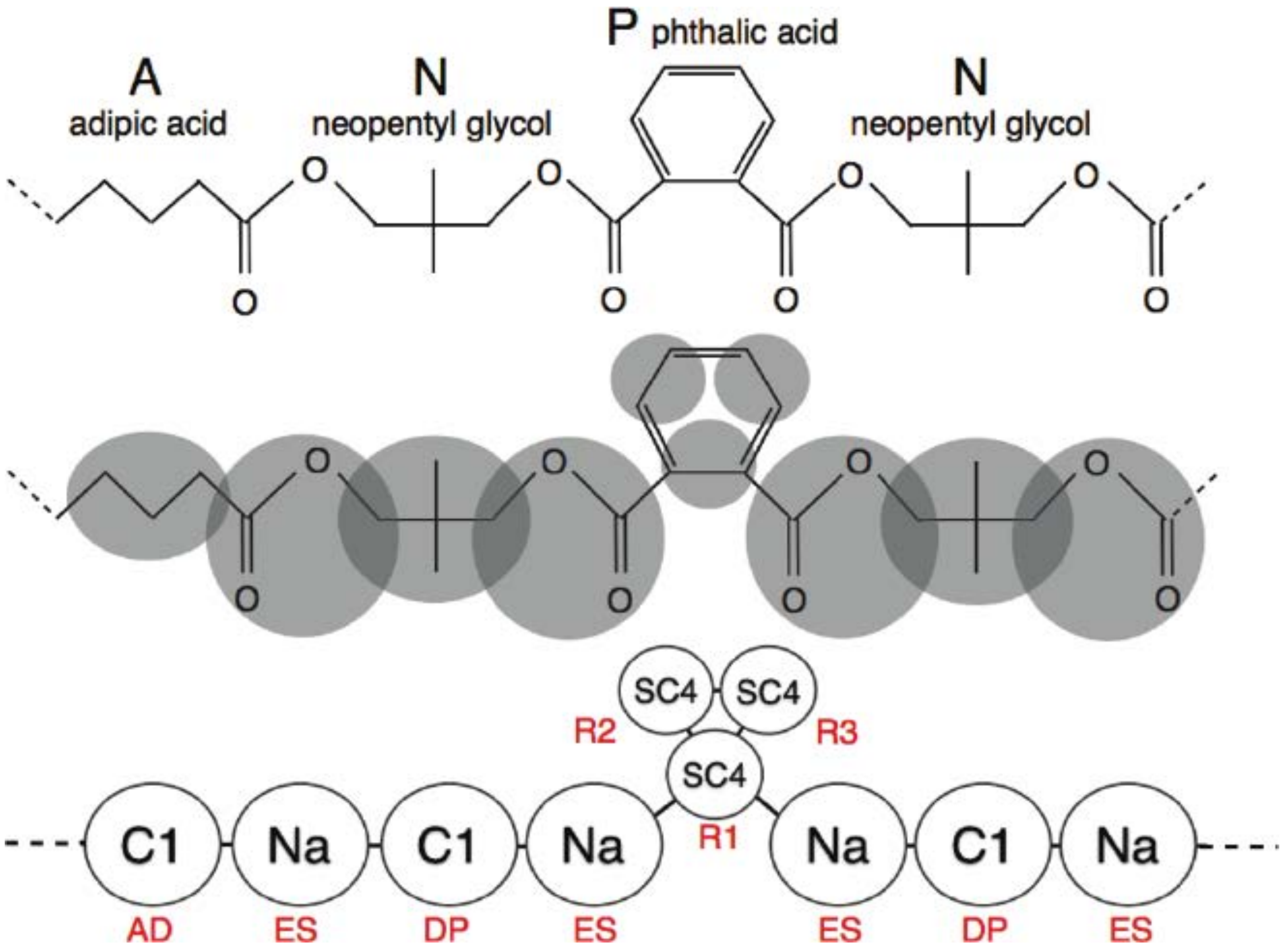
Supporting Information

ABSTRACT: We hereby present a coarse-grained model of a typical polyester resin for coil coating applications. We validate the model via comparison with experimental data. The interactions between coarse-grained particles are described by the MARTINI force-field [Marrink et al. et al. J. Phys. Chem. B 2007, 11, 7812]. Our model and molecular dynamics simulation protocols include the description of a hardener and the formation of cross-links between the hardener and the polyester resin. We perform experimental tests on the thermodynamic and mechanical properties of the system, and compare them with molecular dynamics simulations. The model estimates the glass transition temperature of the coating within 30 K of the experimental measurement. The model captures correctly the broadening effect of cross-linking on the glass transition, and on the temperature dependence of the elastic response of the polyester resin.

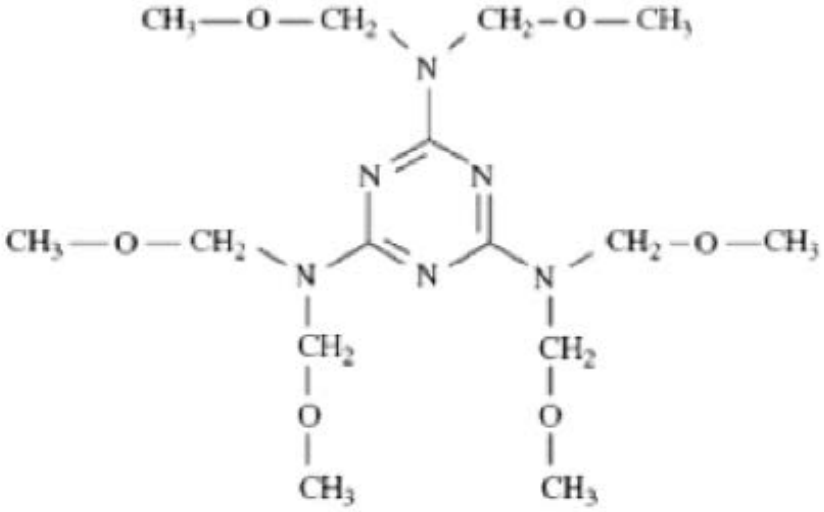


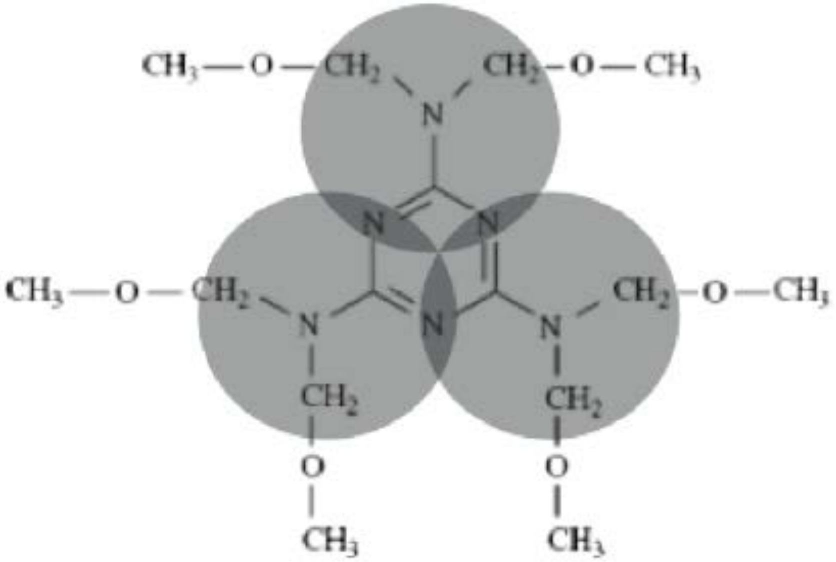
Thermoset Polyester Coating

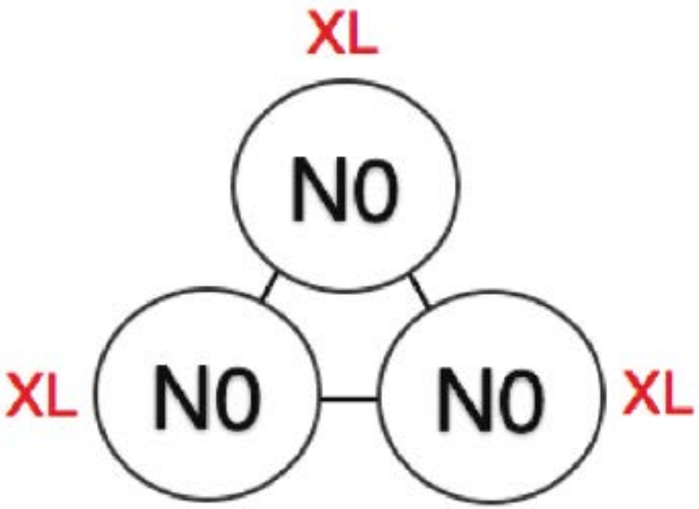
- Polymer



- Cross-linking agent

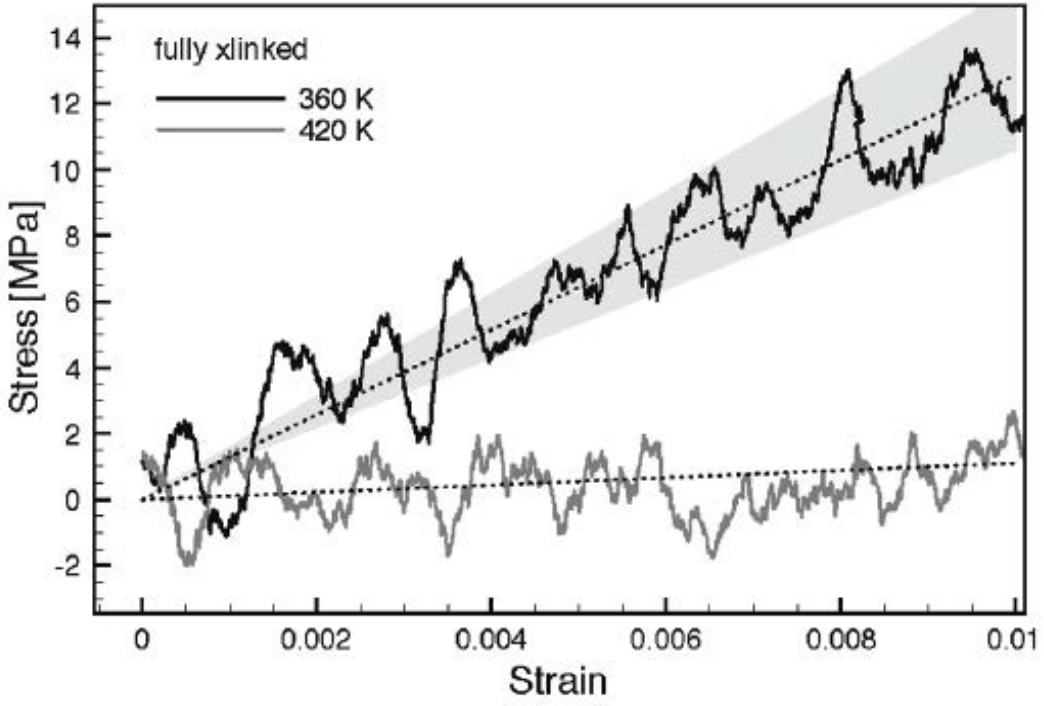






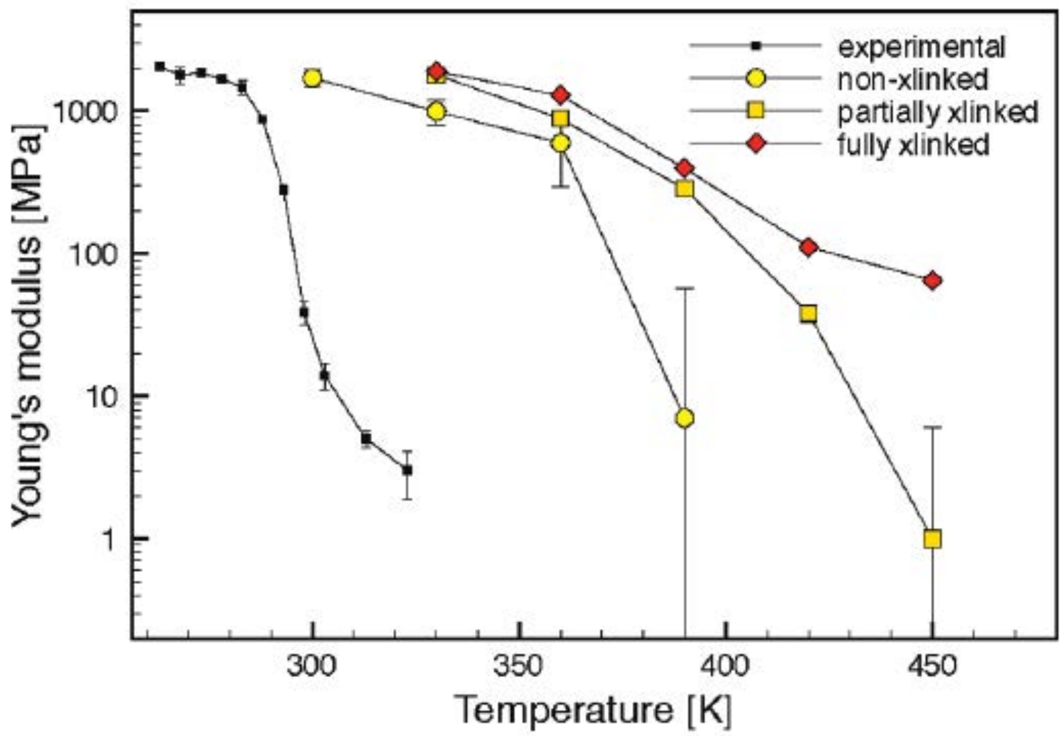
Thermoset Polyester Coating

- Stress-strain curves for fully cross-linked system at different temperatures



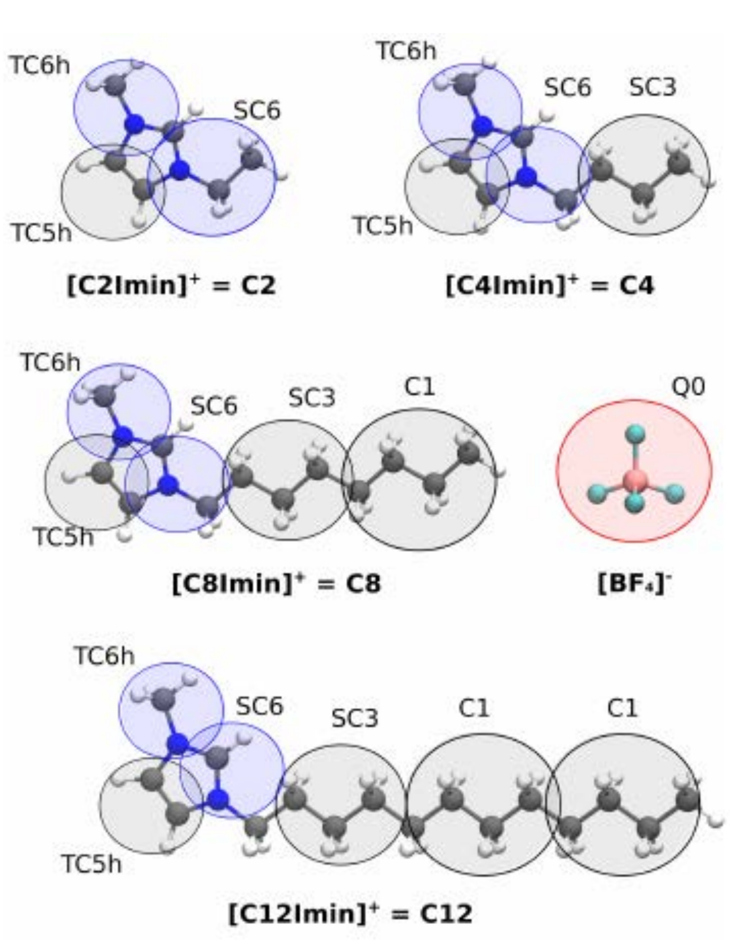
Thermoset Polyester Coating

- Young‘s modulus as function of temperature



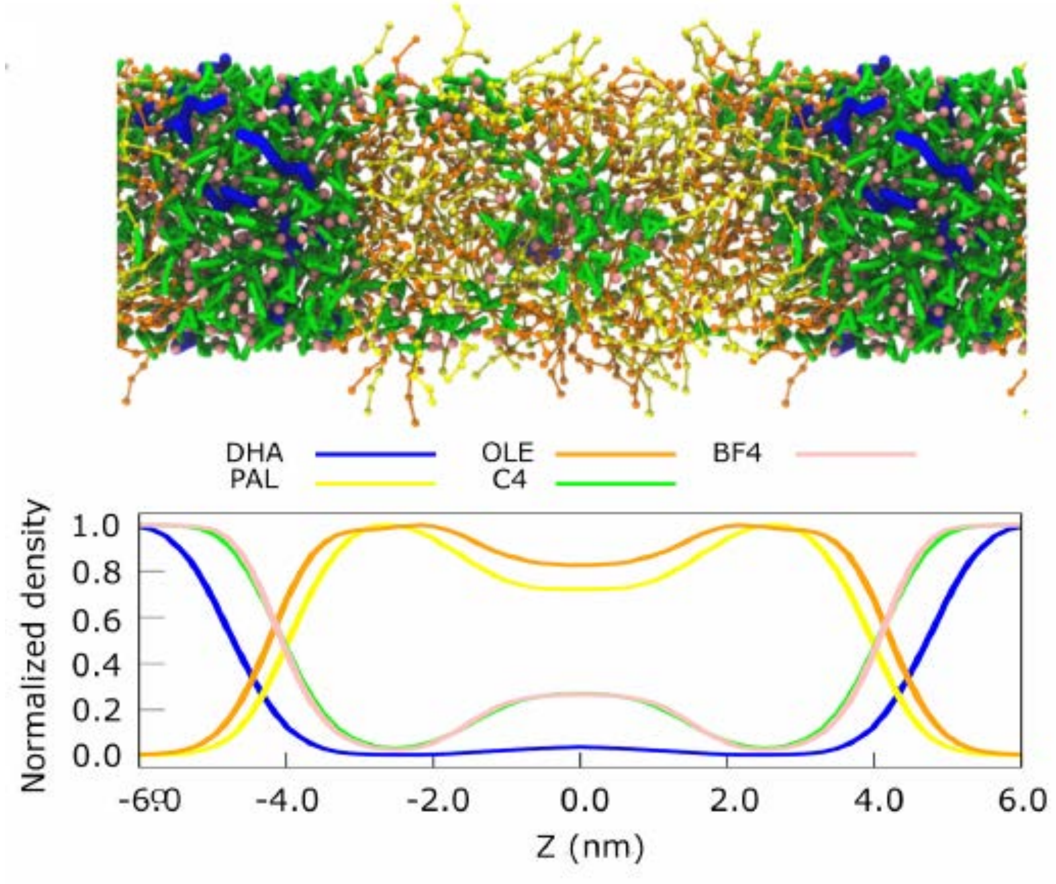
Extraction With Ionic Liquids

- Ionic liquids can be used to extract compounds from mixtures
- Martini forcefield was used to simulate extraction of omega-3 polyunsaturated fatty acid from mixture with saturated fatty acids (fish oil: oleic and palmitic acid and docosahexaenoic acid)
- Partial charge model for ions
- 5 x 5 x 13 nm, 4.4 μs runs



Extraction With Ionic Liquids

- Clear separation of unsaturated fatty acid (DHA) and saturated fatty acids (OLE, PAL) at end of simulation



Pictures from preprint of L. I. Vazquez-Salazar, M. Selle, A. H. de Vries, S. J. Marrink, P. C. T. Souza

Extraction With Ionic Liquids

- Selectivity can be calculated from Gibbs energies

IL	ΔG^{DHA} (kJ/mol) *-octane / +octane*	ΔG^{OLE} (kJ/mol) *-octane / +octane*	ΔG^{PAL} (kJ/mol) *-octane / +octane*	Selectivity *-octane/+octane*
C2	-10.5 ± 0.3 / -11.8 ± 0.2	24.2 ± 2.1 / 27.4 ± 0.3	27.8 ± 0.3 / 35.2 ± 0.2	$765*10^3$ / $6011*10^3$
C4	-8.8 ± 1.0* / -16.8 ± 2.8	12.9 ± 0.3* /16.0 ± 3.4	17.2 ± 0.1* / 20.4 ± 1.7	$5*10^3$ / $418*10^3$

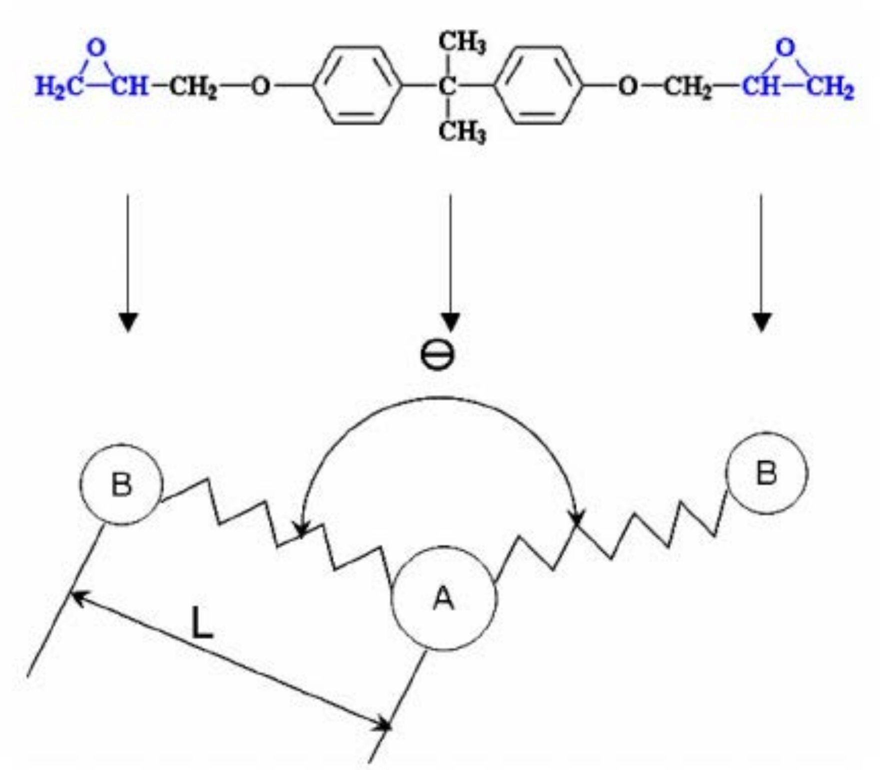
* Free sampling obtained by convention MD simulation was used to estimate the ΔG^{trans} in the case of C4 without octane. For all the other systems, ΔG^{trans} was obtained by US simulations.

- π interactions between unsaturated bonds and imidazolium rings can explain this behaviour
- Effect of co-solvent can be shown

Virtual design of ionic liquids

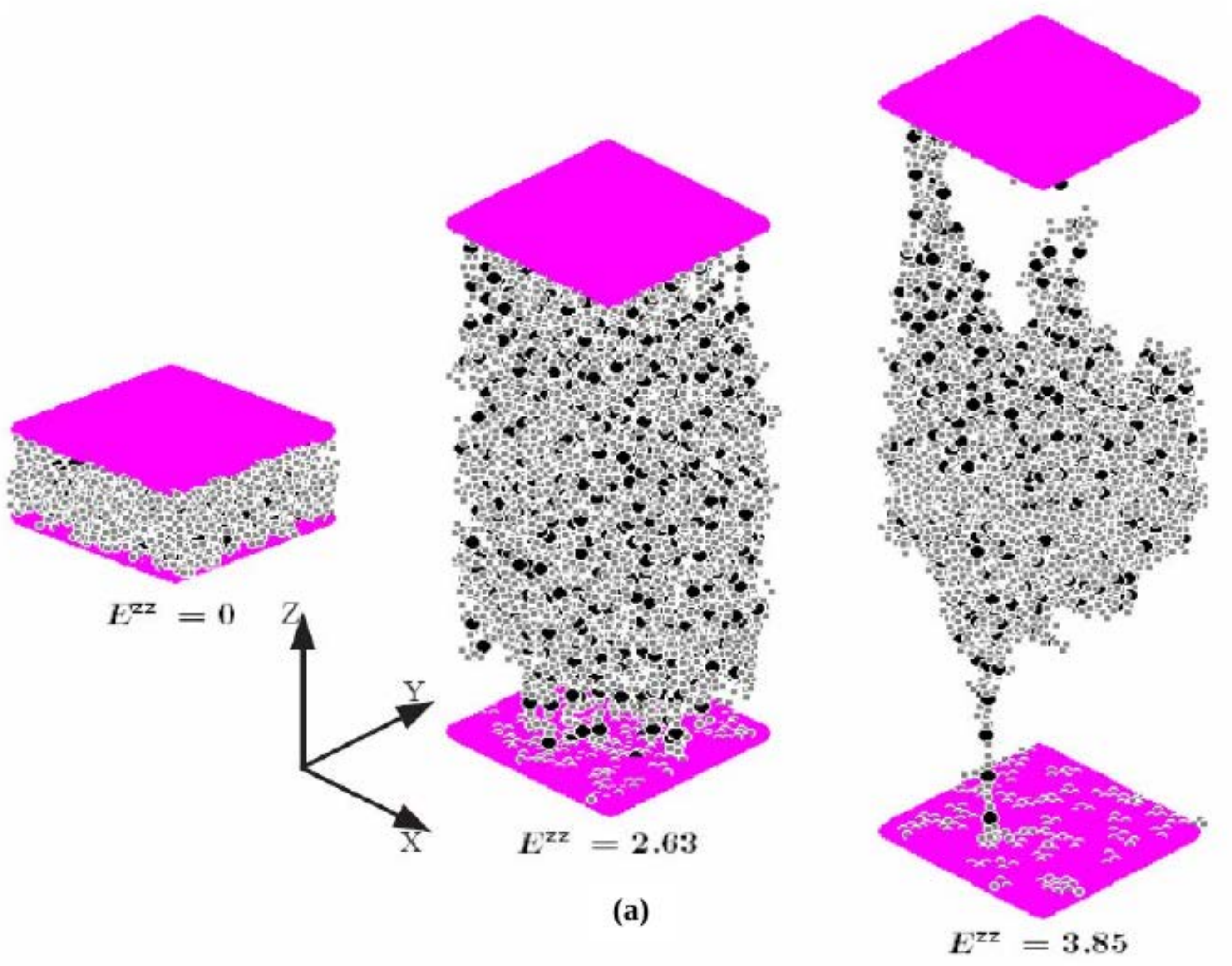
Mechanical Properties of Epoxy Resin

► Mechanical properties of cross-linked diglycidyl ether of bisphenol (A) (DGEBA) as adhesive between two rigid walls



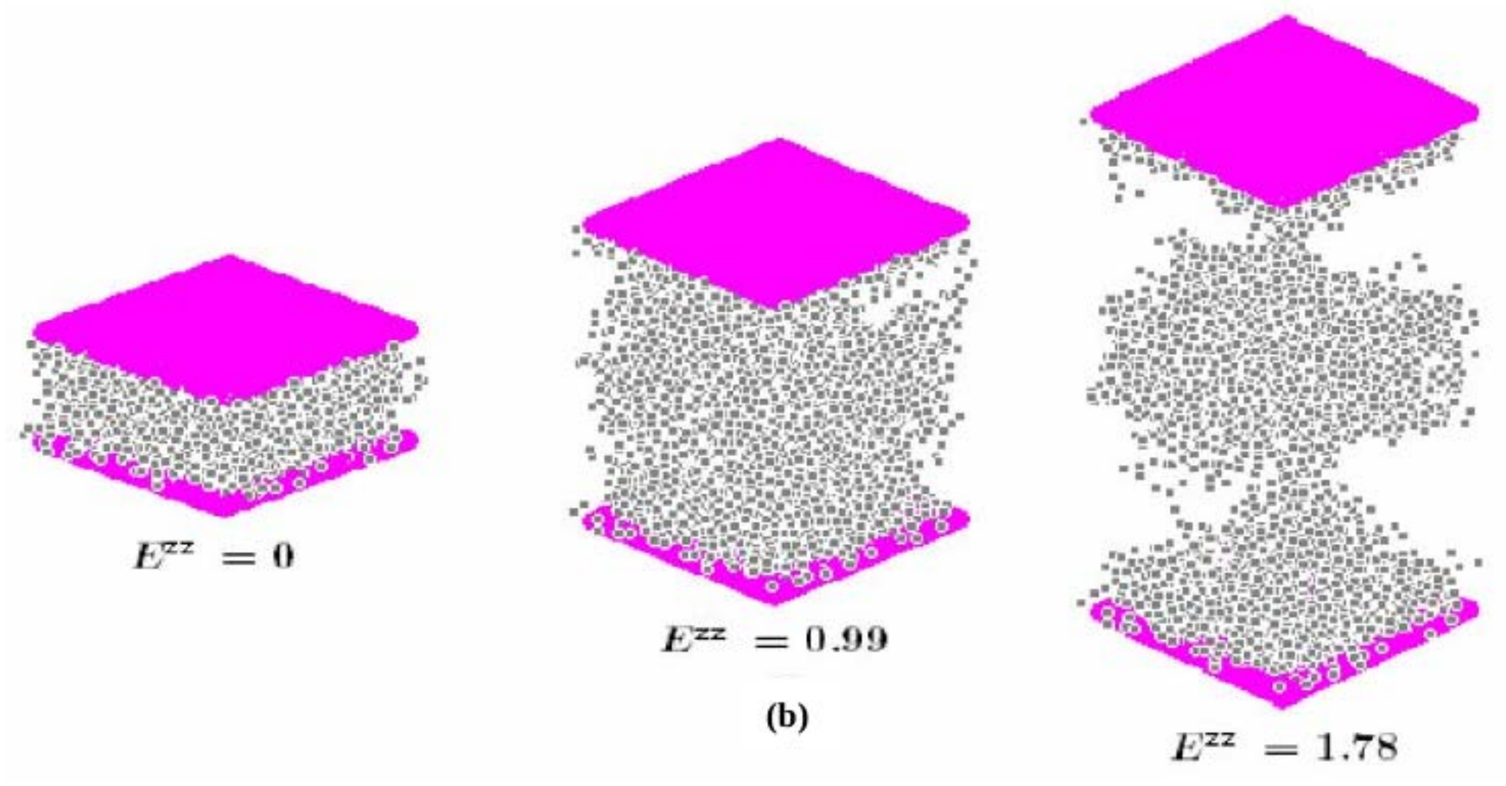
- DGEBA was modeled with three beads
- Cross-linker is represented by one bead which can form four bonds
- System is placed between two walls which are pulled apart

Mechanical Properties of Epoxy Resin



Fully cross-linked system

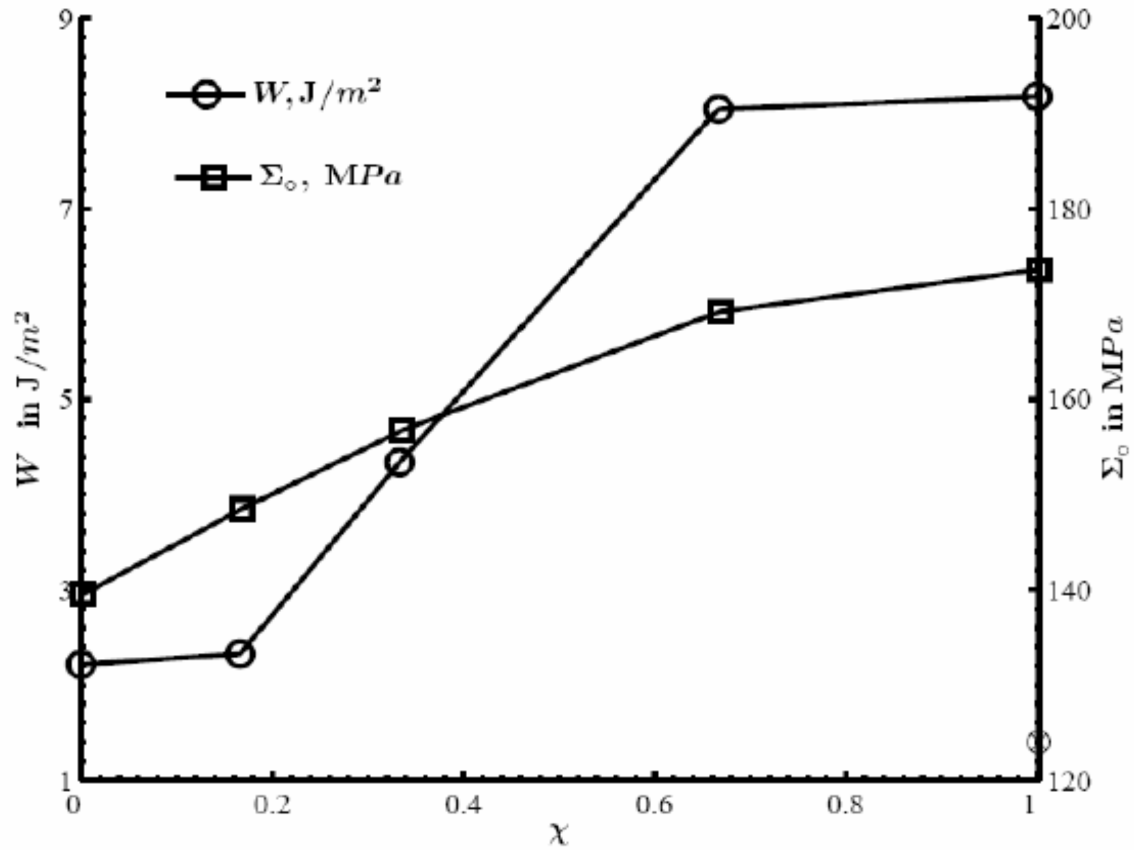
Mechanical Properties of Epoxy Resin



System without cross-links

Mechanical Properties of Epoxy Resin

Adhesion energy W and yield $\sum_0$ as function of degree of cross-linking



Adhesion energy: $W_{calc} = 8\ J/m^2$

$W_{exp} = 2 \ldots 25\ J/m^2$

Mesoscale Modeling With *MedeA* 3.1

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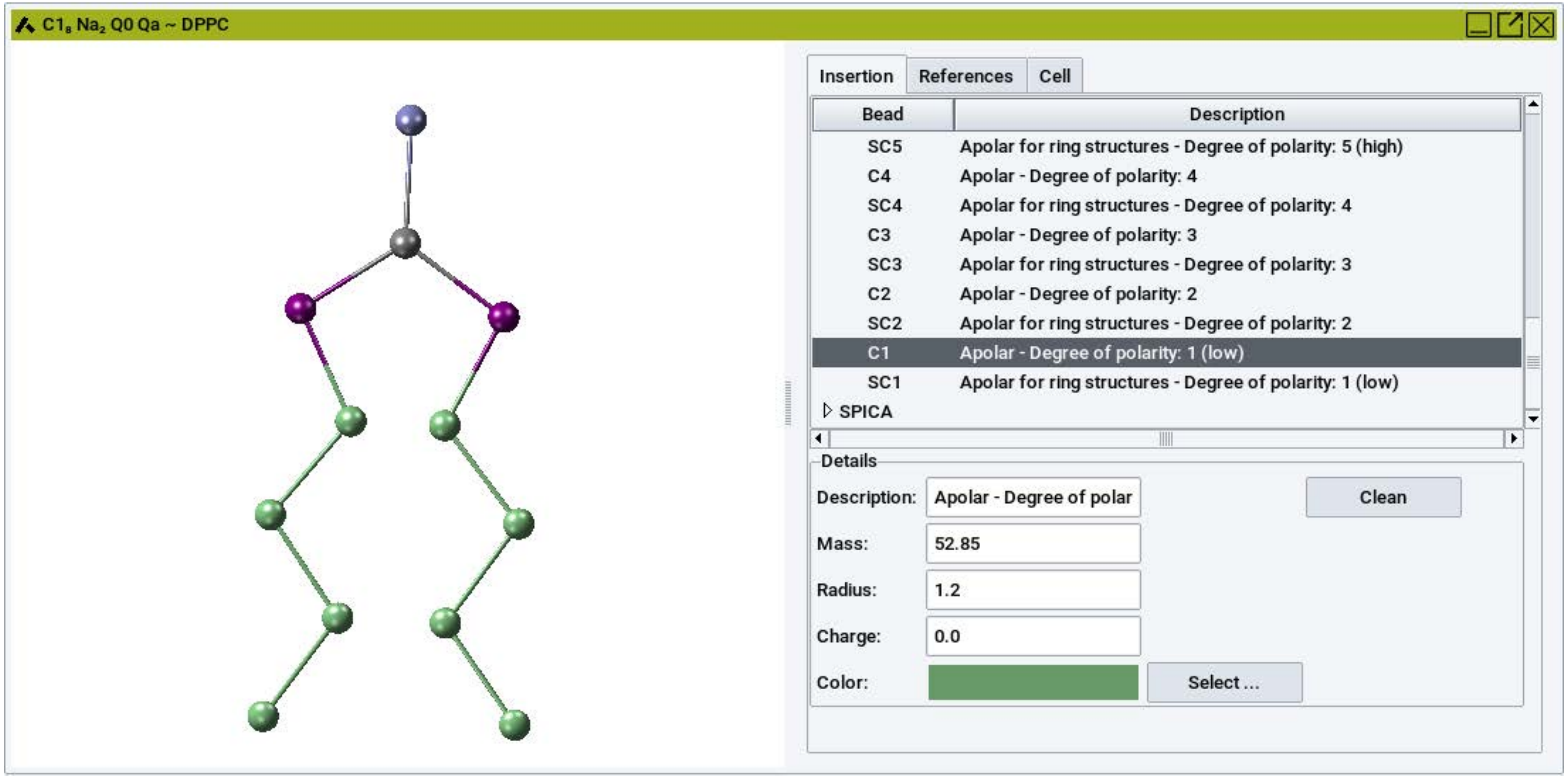
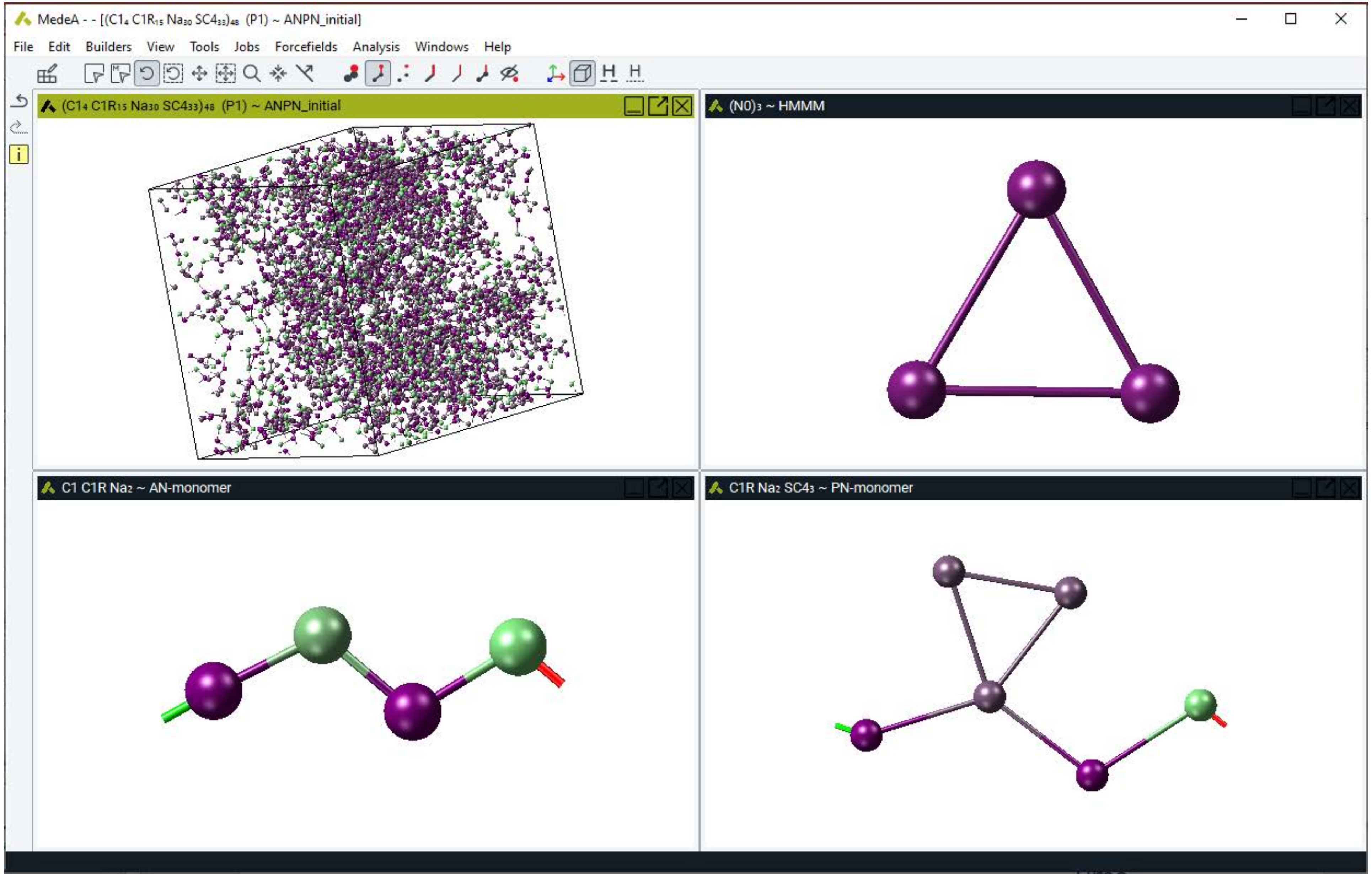
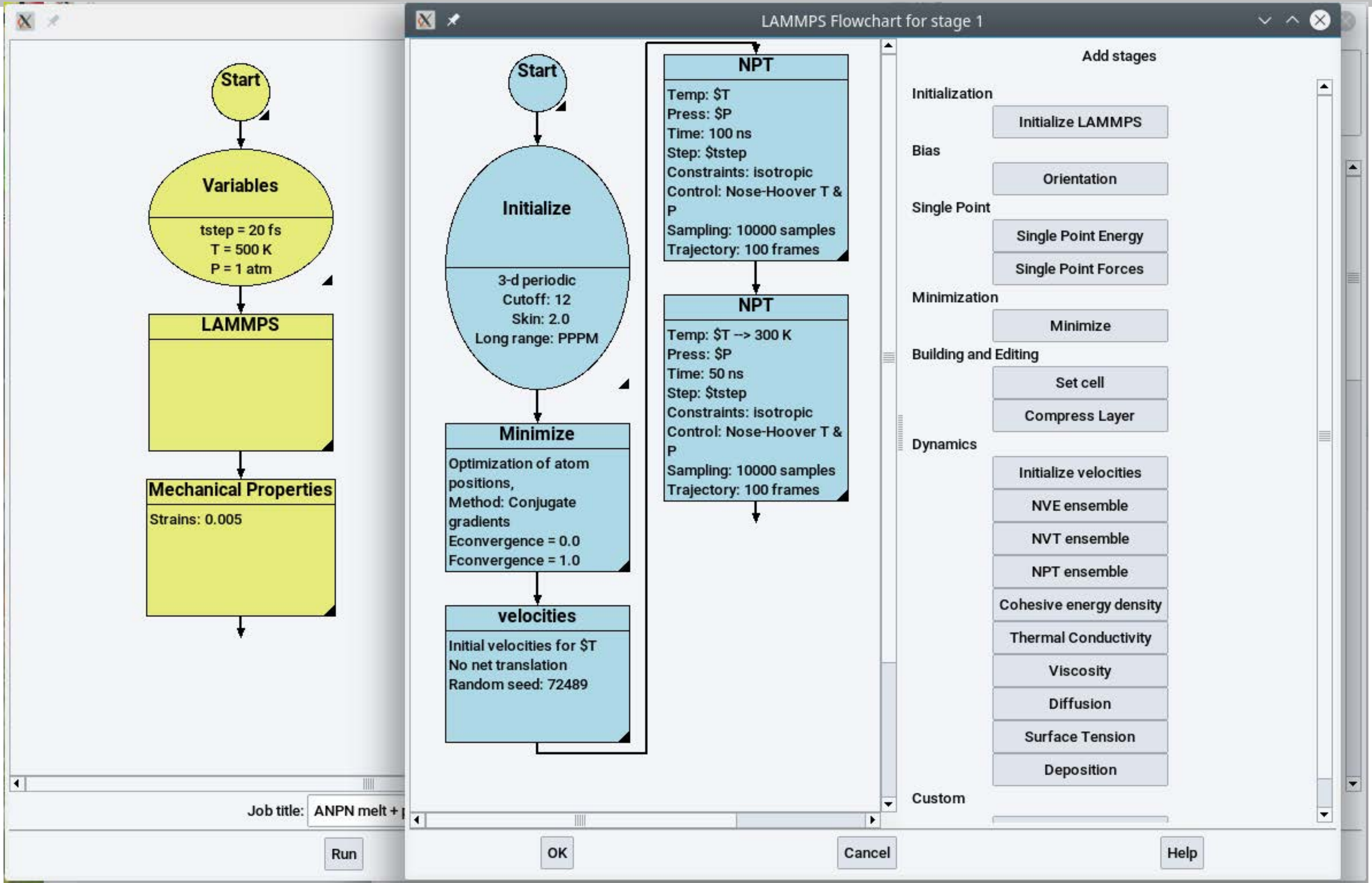


Coarse-grained DPPC molecule

Mesoscale Modeling With *MedeA* 3.1

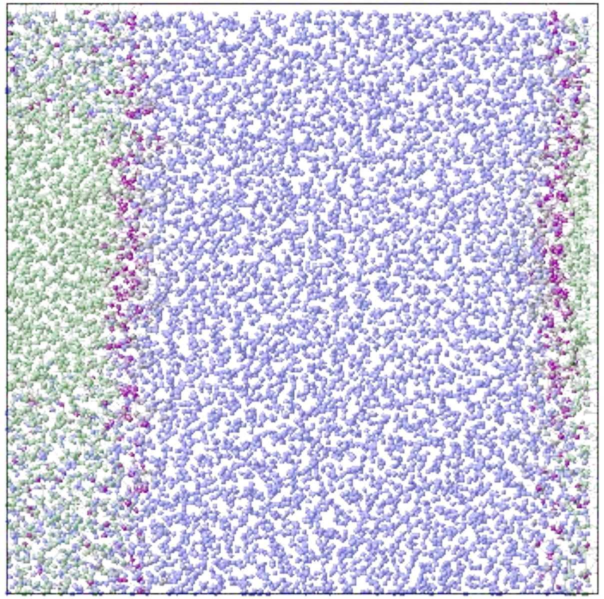


Mesoscale Modeling With *MedeA* 3.1



Mesoscale Modeling With *MedeA* 3.1

- *MedeA* 3.1 supports
  - Sketching of mesoscale systems
  - MARTINI and SPICA forcefields
  - Creation of user defined bead libraries and forcefields
  - Building of polymers, amorphous systems and thermosets for mesoscale systems
  - LAMMPS simulations including Diffusion, Viscosity, Thermal conductivity, Surface tension
  - Hill-Walpole bounds
  - Mechanical properties
  - Deformation



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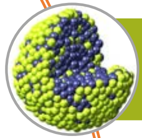
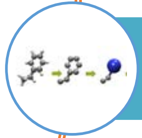
MedeA 3.1 Webinars

June 2020: Elasticity and Beyond – Predicting Mechanical Properties with *MedeA*, by Ray Shan



June 2020: Diffusion by Erich Wimmer and Benoît Minisini

July 2020: VASP 6 by Martjin Marsman



July 2020: Mesoscale Modeling by Jörg-Rüdiger Hill

August 2020: *MedeA* 3.1 by Marianna Yiannourakou, Walter Wolf and Jörg-Rüdiger Hill

Upcoming in the fall of 2020: Additional webinars addressing accuracy and larger scales

MedeA

Innovation by Simulation