Modeling a Two-Stage Thermoset with a Glass Fibre Sizing using Molecular dynamics

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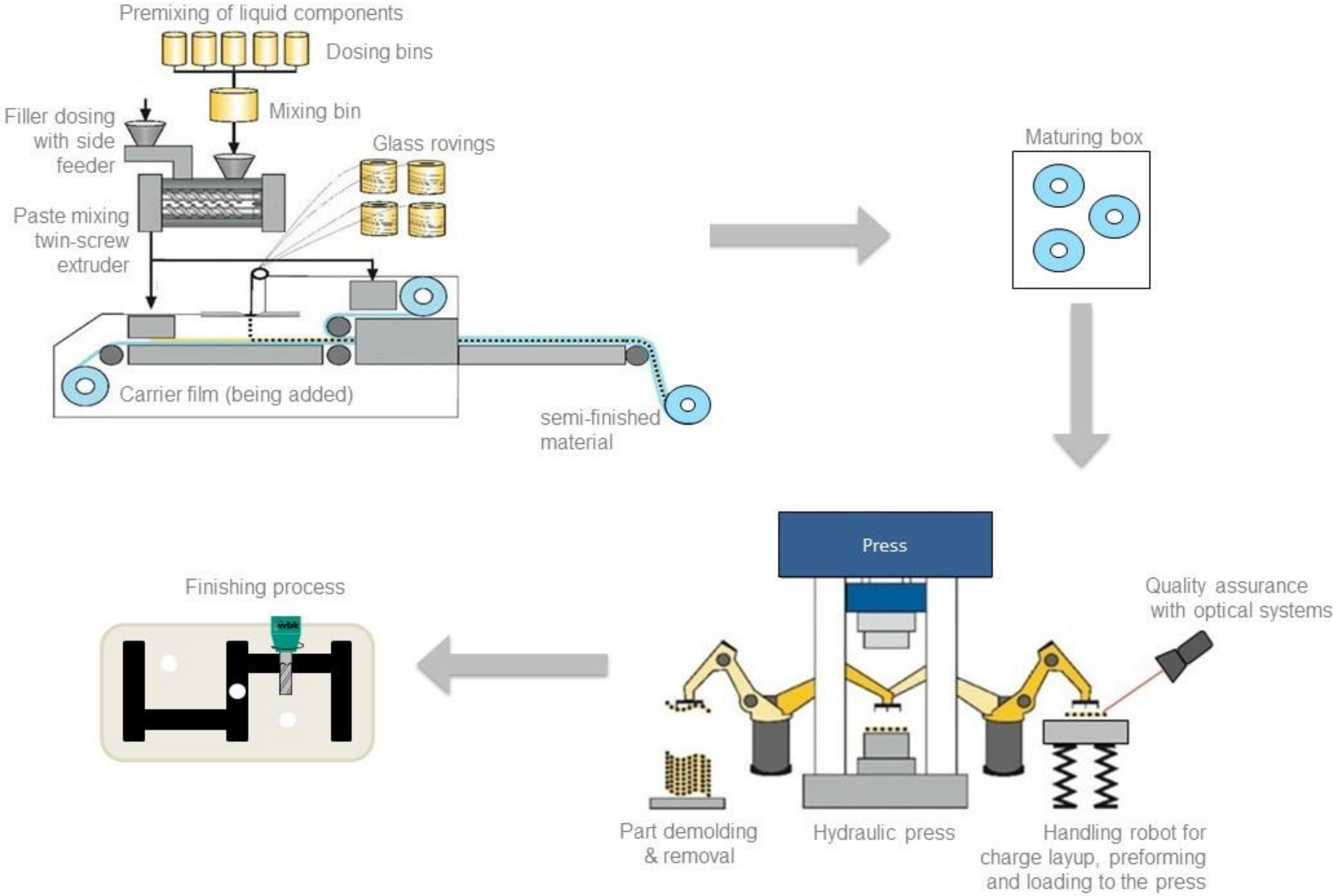
Brief “history” of fiber-reinforced polymers (in cars)

- 1960s-1970s fiberglass! Light weight and rigid, not great in a car crash
- 1990s polymer (plastic) body panels (Saturn), in order to be safe in a car crash, the plastic panels had to be too thick, ended up weighing more than steel panels with worse performance
- 2000s-now Fiber-reinforced polymer (FRP) (better fiberglass and carbon-fiber reinforced polymer) : high performance materials used in aerospace and high performance cars, often use woven fiber sheets embedded in the polymer
- Why does my Toyota still have primarily steel components? Also, why did SpaceX abandon FRPs for stainless steel for its “Starship” rocket program?
  FRPs are not well enough understood to ensure processing will yield material/parts with properties that are consistent enough to ensure reliability without testing

Sheet molding compound process chain



- In first process epoxy resin components are mixed and blended with chopped fibers (~room temperature process)
- Curing is a two-stage process with potentially a large time between
- Fibers in the resin are also bonded to the epoxy during the curing process

Some relevant questions that can be addressed using molecular dynamics:

- **Mechanical properties evolution during curing** while the FRP (thermoset) is being processed (typically in hot press). To model this process (using a continuum model) these evolving properties needs to be known.
  - It is very difficult to measure evolution of these properties experimentally.
  - We can measure these properties in a simulation.
- **Polymer Matrix-Fiber interfacial properties:** Fiber pull-out is a failure of the interface between the polymer matrix and the fiber surface
  - Can we model and characterize the interfacial properties?
  - Why does the system fail here?
- **Resulting polymer network properties** (in progress) **:**
  - The all-atom simulations yield a realistic polymer network at different stages of the curing process. Can we use this knowledge to realistically coarse-grain and get a better understanding of these materials?

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Reaction and Characterisation of UPPH using molecular dynamics

work with Felix Schwab (*1st Gen. IRTG PhD student*)

Motivation:

- Material properties of the thermoset UPPH depend on degree of cure ζ^α and temperature Θ.
- The curing process involves significant changes in ζ^α and Θ.
- Experimentally determining material properties curing the cure would be extremely difficult
- In a simulation we can freeze ζ^α (i.e. stop further reactions) and hold Θ constant at any point
- Gain a better understanding of the behavior and characteristics of the system during curing

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PAPER
Felix K. Schwab and Colin Denniston
Reaction and characterisation of a two-stage thermoset using molecular dynamics

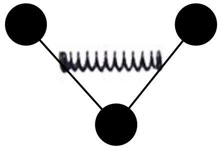
Force Field (Compass)

Non-Bonded interactions include a Coulomb term and a van der Waals term:

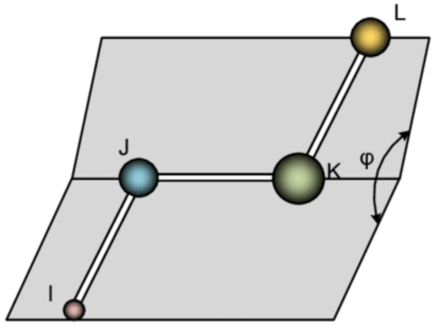
$$E_{elec}(r) = \frac{1}{4\pi\varepsilon_o}\frac{q_iq_j}{r} \qquad E_{vdw}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

Bonded interactions include a 2-body harmonic bond term, a 3-body angle term, and a 4-body dihedral term class2 potentials (mixed terms included):

bonds



angles

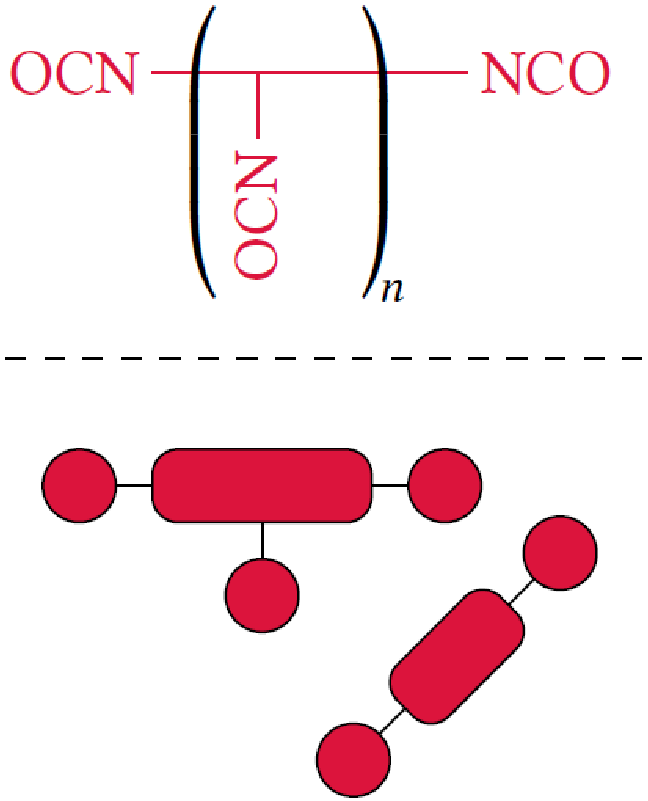


dihedrals

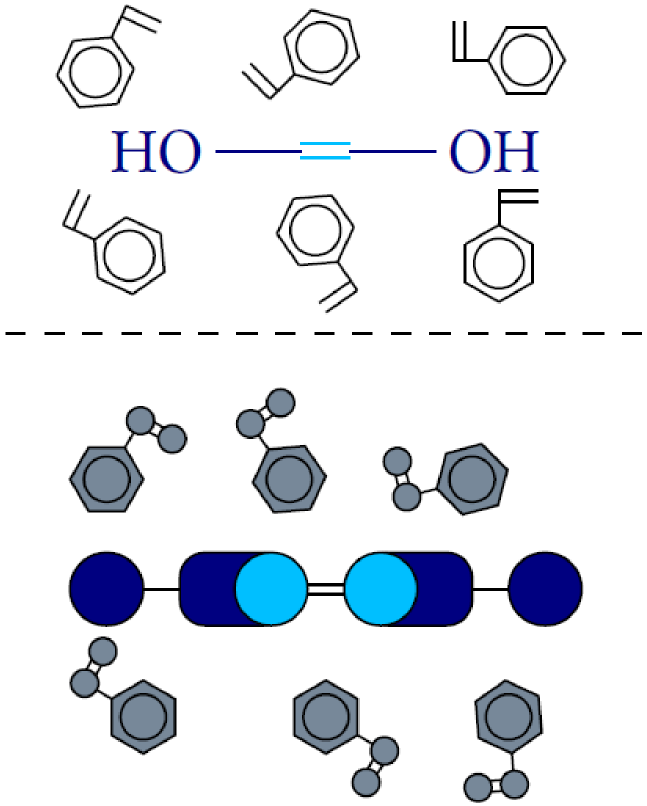
Simulations are done using LAMMPS, with some modifications based on bond forming routines of Timothy Sirk

Composition and reactions

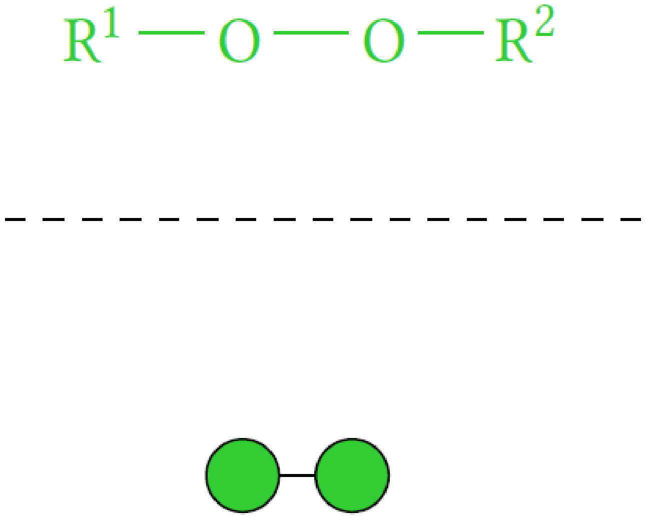
- resin of interest: unsaturated polyester-polyurethane hybrid (UPPH)
- used UPPH resin is based on Aliancys’ Daron AQR 1009 resin
- Components:



Polymeric Isocyanate

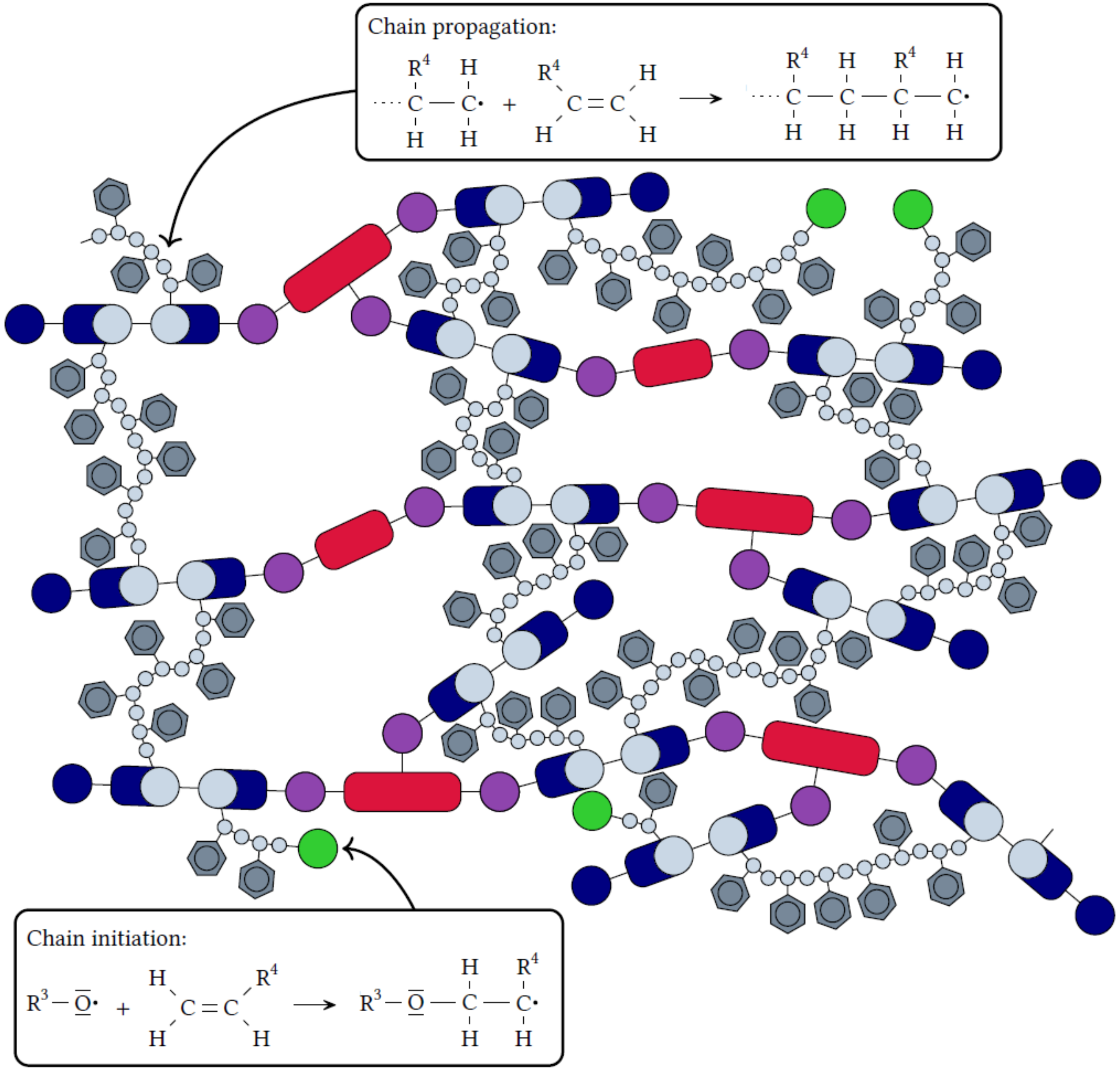


Unsaturated Polyester Polyol dissolved in Styrene



Organic Peroxide

Two-stage curing: → Radical polymerisation: cross-linking



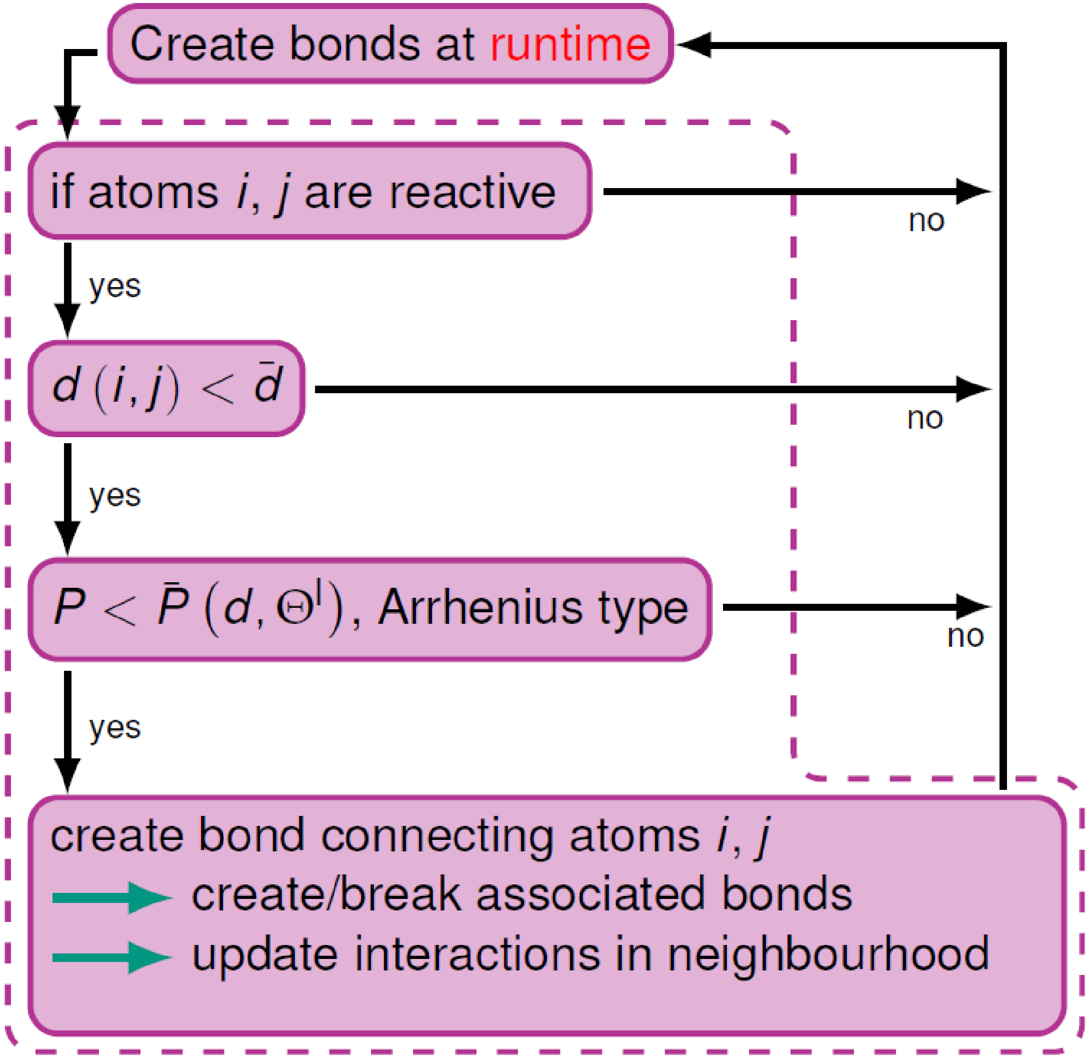
Chain propagation:

$$\cdots\overset{\mathrm{R^4}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot + \overset{\mathrm{R^4}}{\underset{\mathrm{H}}{}}\mathrm{C{=}C}\overset{\mathrm{H}}{\underset{\mathrm{H}}{}} \longrightarrow \cdots\overset{\mathrm{R^4}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{R^4}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot$$

Chain initiation:

$$\mathrm{R^3}-\overline{\mathrm{O}}\cdot + \overset{\mathrm{H}}{\underset{\mathrm{H}}{}}\mathrm{C{=}C}\overset{\mathrm{R^4}}{\underset{\mathrm{H}}{}} \longrightarrow \mathrm{R^3}-\overline{\mathrm{O}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{R^4}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot$$

Reaction algorithms


Create bonds at runtime

if atoms *i*, *j* are reactive

no

yes

$d\left(i,j\right) < \bar{d}$

no

yes

$P < \bar{P}\left(d, \Theta^{\mathrm{l}}\right)$, Arrhenius type

no

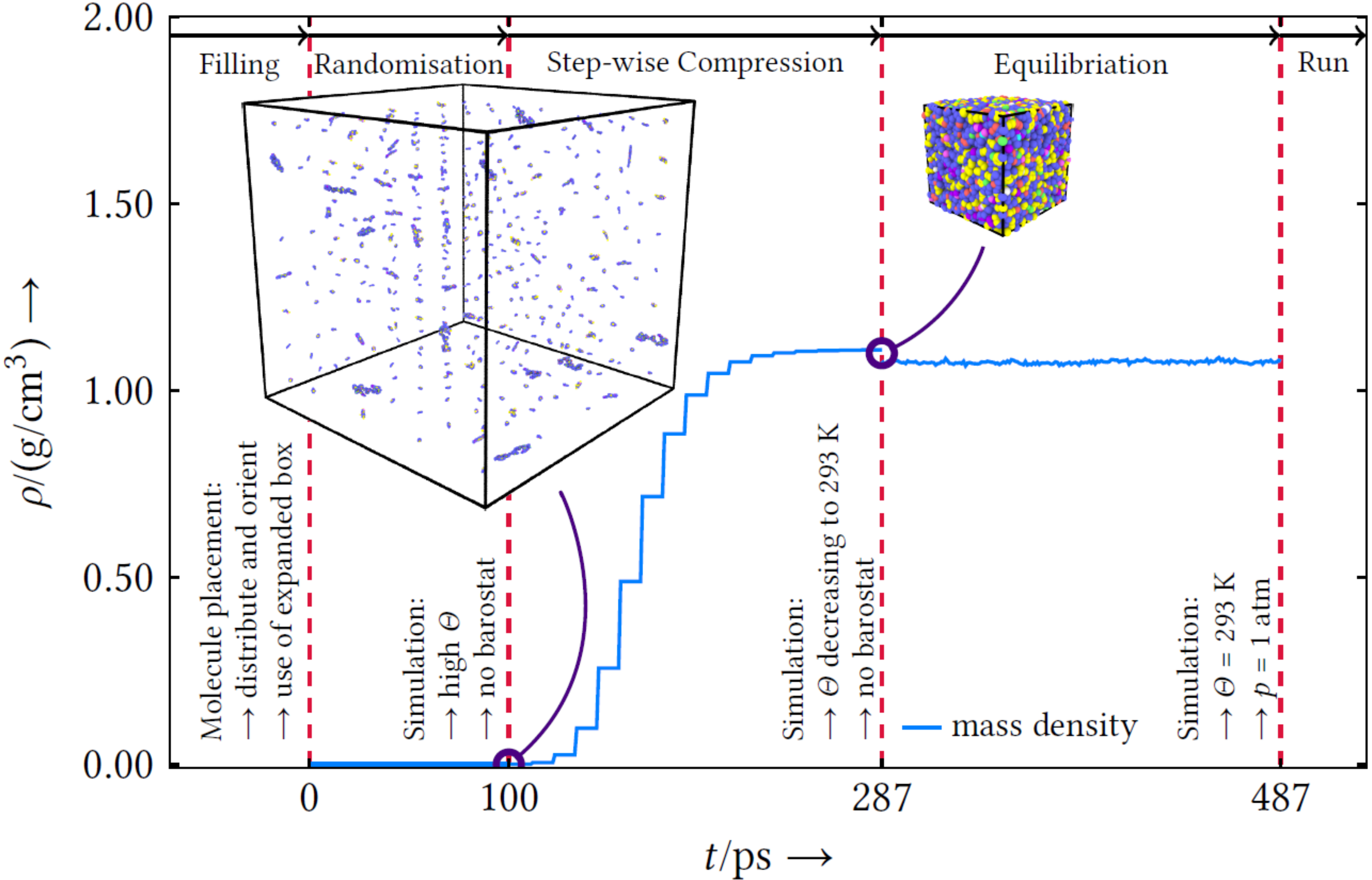
yes

create bond connecting atoms *i*, *j*

→ create/break associated bonds

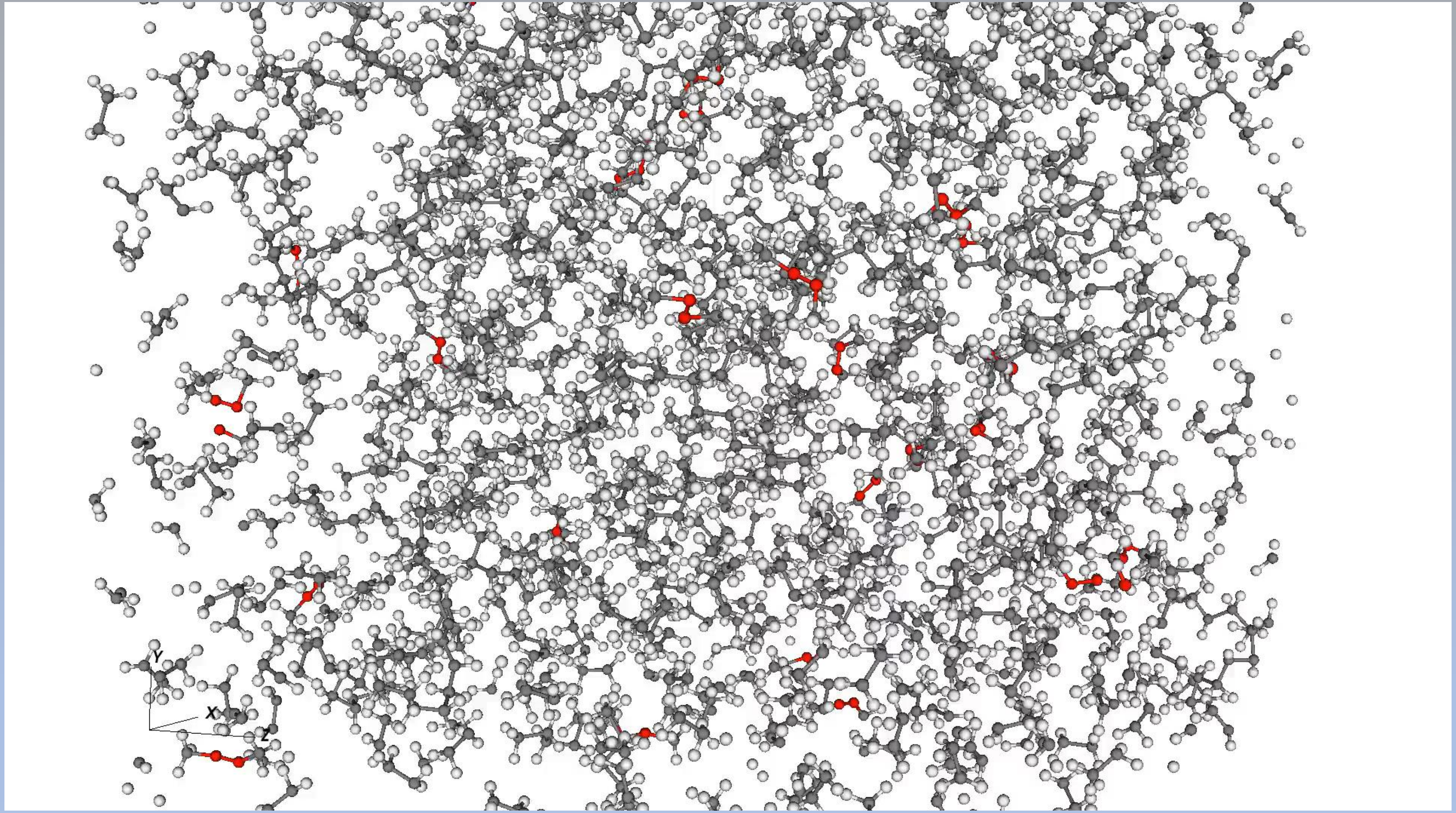
→ update interactions in neighbourhood

- Basis:
  - LAMMPS' *fixes bond/create* and *bond/break*
  - algorithms used by Elder, Andzelm and Sirk (2015)
  - probalistic criterion based on Okabe *et al.* (2013, 2016)
- Bond dissociation:
  - Peroxide groups cleave above 60 ℃
- Bond formation:
  - Urethane reaction: side reaction after main reaction
  - Radical reaction: auxiliary charges to mimic free electrons



Two systems sizes:

- small: approx. 14,000 atoms, three different variants
- large: approx. 112,000 atoms

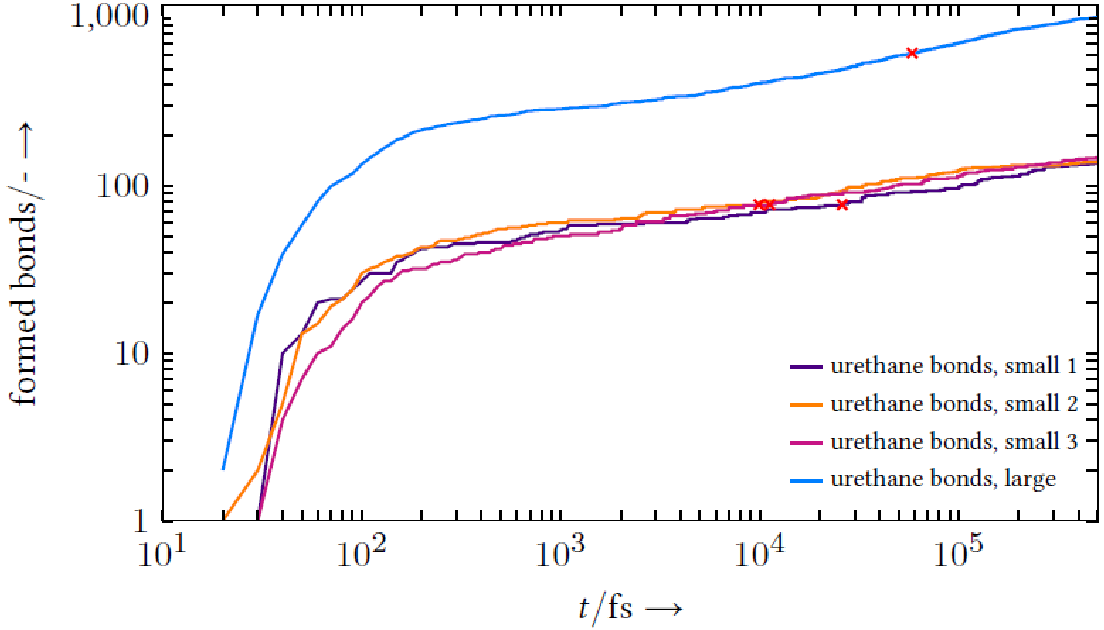

Y
X
Z

Assumption:

- urethane reaction reaches max. 50% conversion (to avoid dense network)

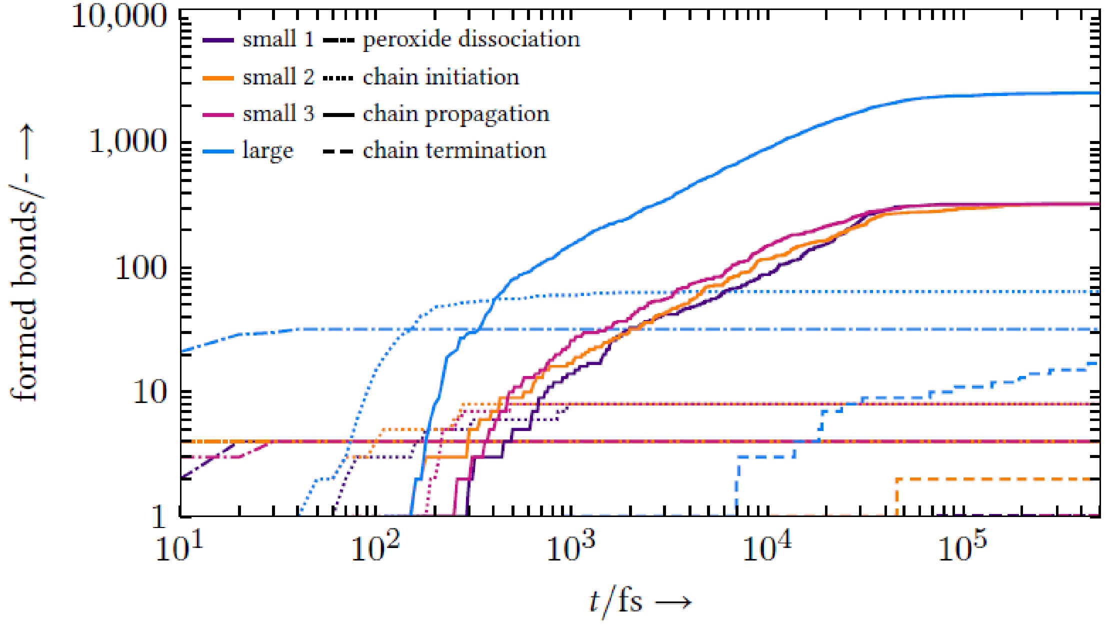
Urethane reaction: x marks 50% conversion

$\Theta = 313\,\mathrm{K}$, $p = 1\,\mathrm{atm}$



Radical reaction:

$\Theta = 418\,\mathrm{K}$, $p = 98.69\,\mathrm{atm}$



Cross-linkers: volatile organic compound

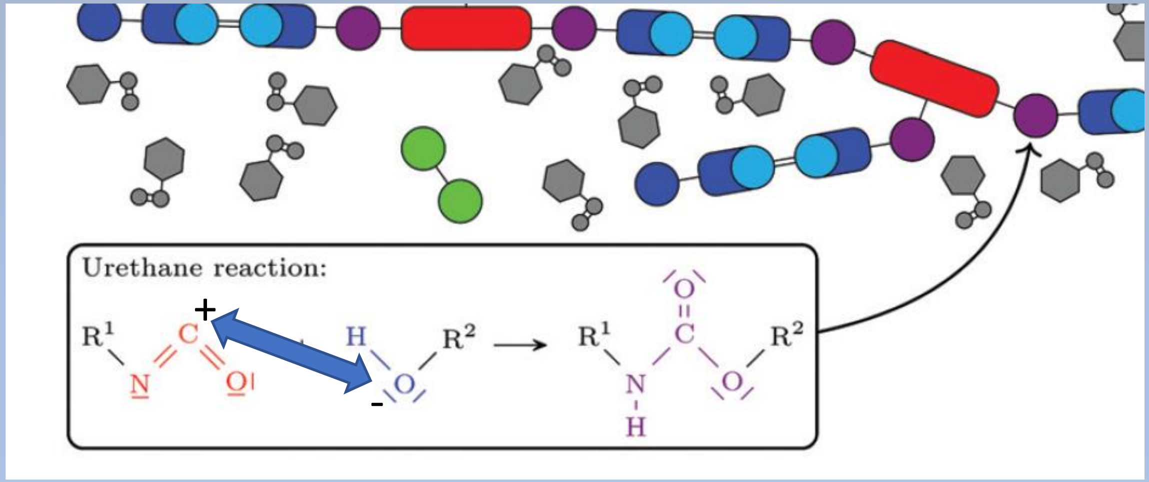
	small system	large system
remaining styrene	$4.01\% \pm 0.57\%$	4.39%

Volume shrinkage:

	small system	large system	Verleg/Hummer (2006)
total reaction	$-5.33^{+0.24}_{-0.20}\%$	-5.11%	$-5.6\%..-7.5\%$
radical reaction	$-4.70^{+0.34}_{-0.30}\%$	-4.59%	—

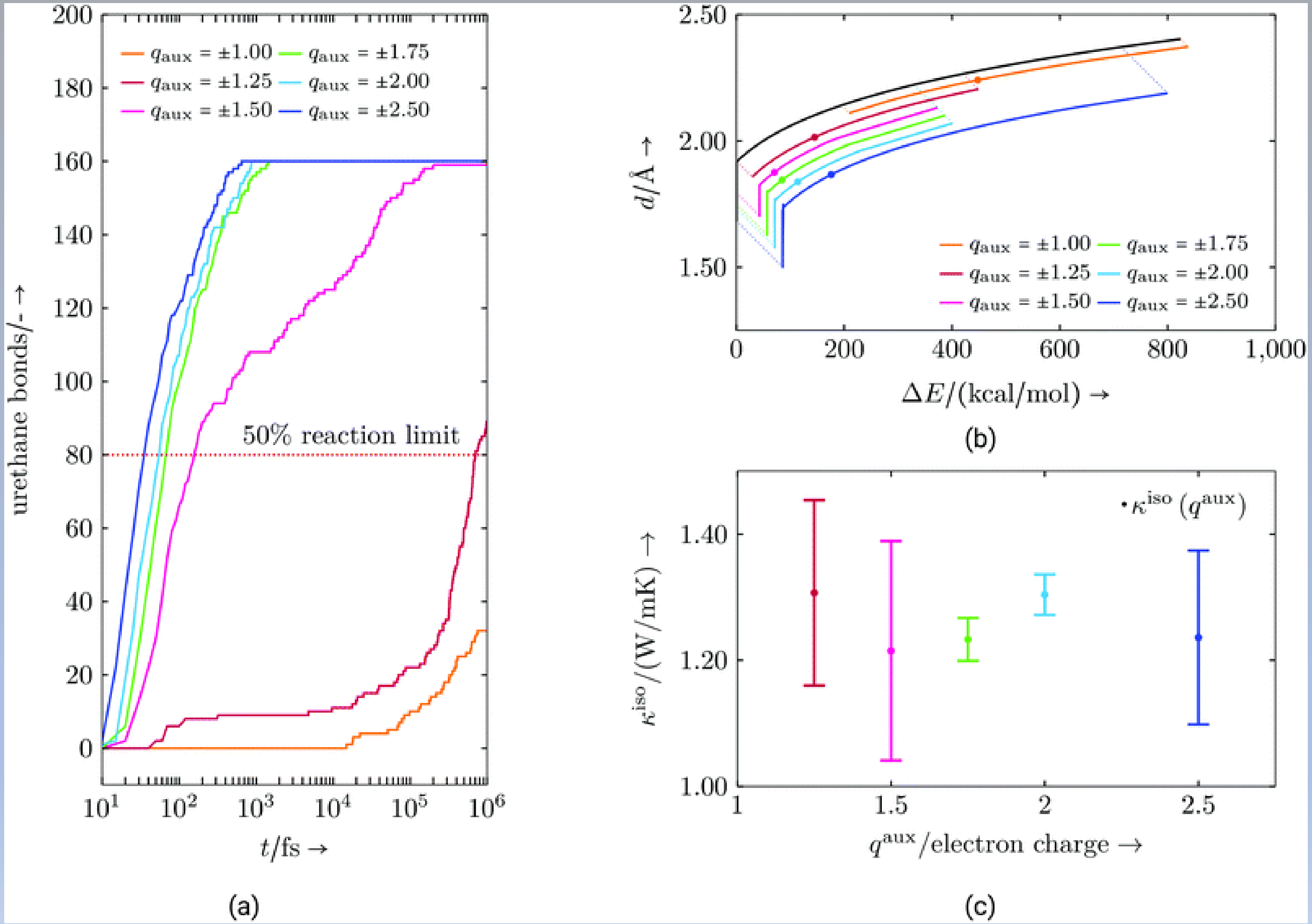
Cheats:

- The time for some reactions to complete is too slow (for MD time scales) primarily because it takes a long time for reaction partners to find each other (via weakly driven diffusive motion).
- Perfect mixed initial state helps, but to further enhance reaction partners finding each other we add “auxiliary charges” to electrophile and nucleophile centers until they have found a partner (only acting between these centers, does not interact with other charges in the system)



- The goal is not to track the time evolution but to create a reasonable polymer network as a function of the degree of cure and temperature.
- We hope the slightly altered dynamics still yield similar network properties as a function of the degree of cure.

Effect of auxiliary charge on polyurethane reaction



(a)

(b)

(c)

Molecular Dynamics: Material Properties

Preliminaries:

- Θ and ζ are varied, relevant ranges:
  - urethane reaction: $\zeta^{\mathrm{u}} = \{0, 50\}\,\%$, $\Theta = \{273, 313\}$ K
  - radical reaction: $\zeta^{\mathrm{r}} = \{0, 20, 40, 60, 80, 100\}\,\%$, $\Theta = \{273, 313, 398, 438\}$ K
- material properties evaluated: c_{V}, κ, α, Θ^{g} and K
- not evaluated: G and η, but possible via simulating a dynamic mechanical analysis
- notation for degree of cure:
  UxRy, e.g. U50R20 means 50% urethane conversion, 20% radical conversion
- rating of results is qualitatively in range and tendency of values
  - comparison with common thermoset values found in Mark (2007)
    and Granta Design CES EduPack (version 2018) ($\approx$ fully cured, ≈ 298 K, ≈ 1 atm)

Molecular Dynamics: Material Properties

Bulk Modulus (MPa):

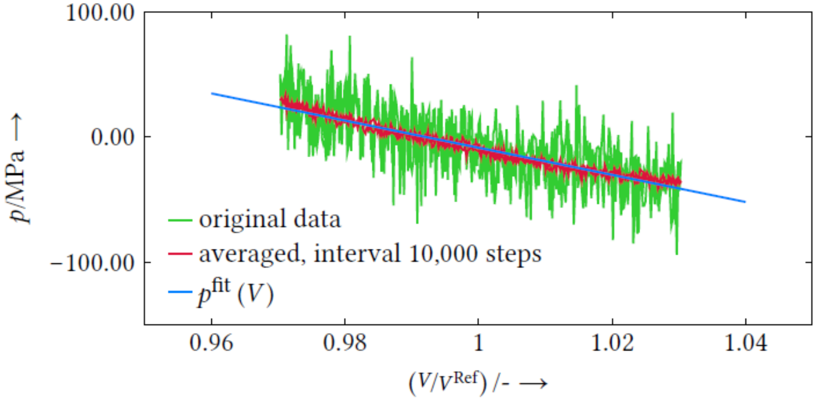
- thermodynamic relation:

$$\boxed{\frac{1}{K} = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{\Theta}}$$

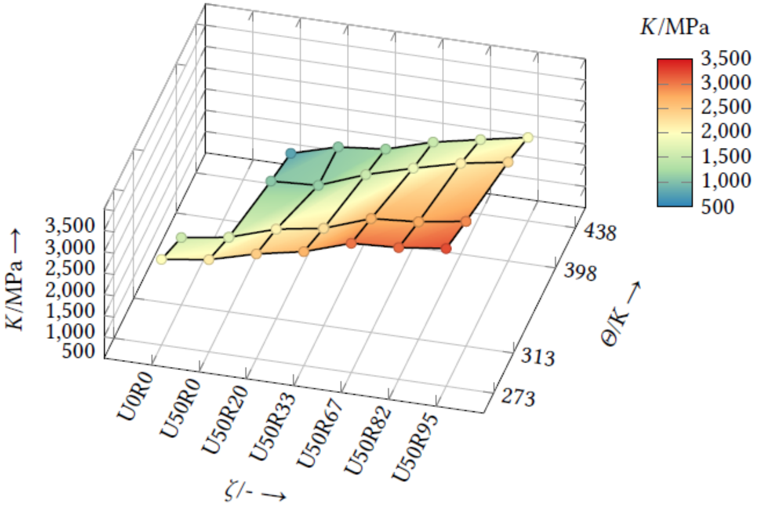
cf. Landau (1959)

- simulation:
  - large system, deformation of simulation box, $\Delta L = 1\%$ (uniformly)
  - equilibrated for $t = 1$ ns (NPT), then evaluation run for up to 6 ns (NVT)
  - single simulations ran with *fix nve/limit*
- evaluation:
  - linear fit
- comparison:
  - range: e.g. 3,200 to 6,120 MPa
  - tendency: de-/increases with Θ/ζ

Example: U50R0 at $\Theta = 398\,\mathrm{K}$



K over parameter range:



Molecular Dynamics: Material Properties

Specific Heat Capacity at Constant Volume (J/kgK):

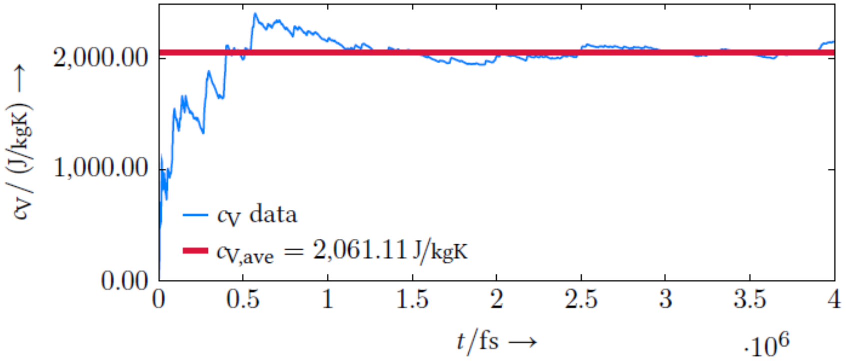
- from statistical mechanics:

$$\boxed{c_V = \frac{1}{m}\,\frac{\langle {e^{\text{tot}}}^2\rangle - \langle e^{\text{tot}}\rangle^2}{k_B\Theta^2}}$$

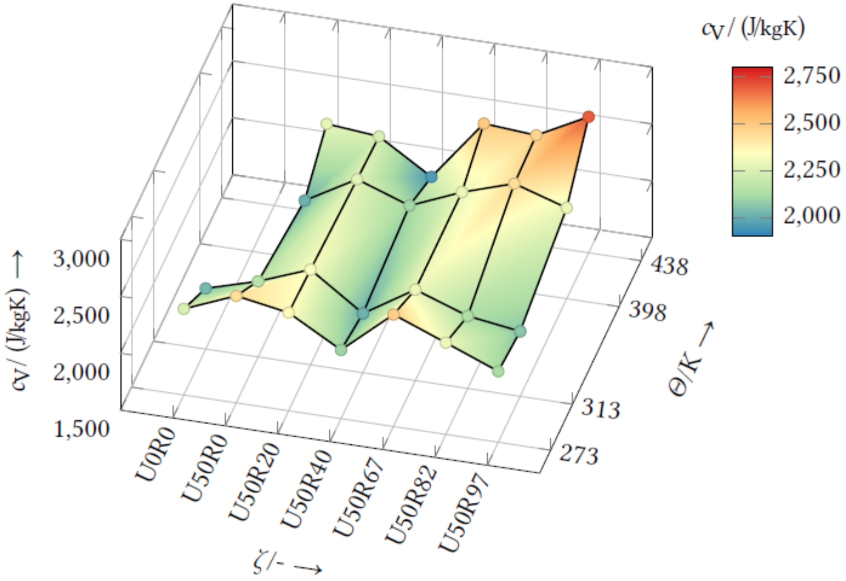
cf. Frenkel and Smit (2002), k_B: Boltzmann constant

- simulation:
  - small systems
  - equilibrated for $t = 1$ ns (NPT), then evaluation run for up to 5 ns (NVT)
- evaluation:
  - cumulative average for each small system
  - weighted average of all three small systems
- comparison:
  - range: e.g. 1,180 to 1,770 J/kgK
  - tendency: rising values with Θ, rough development with Θ, cf. Warfield *et al.* (1959, 1960)

Example: U50R72 at $\Theta = 313\,\text{K}$



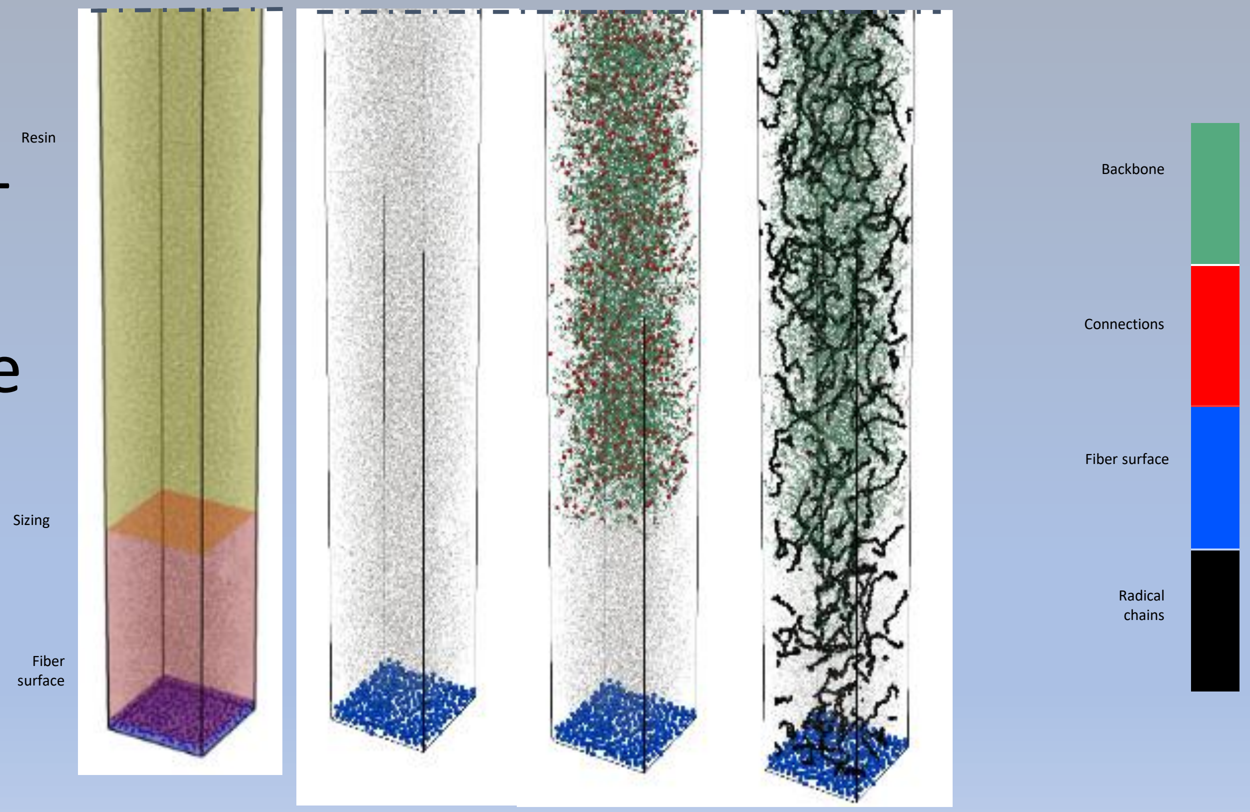
c_V over parameter range:



Polymer Matrix-Fiber interfacial properties

work with Lukas Schöller (*2nd Gen. IRTG PhD student*)

- Fiber pull-out is a failure of the interface between the polymer matrix and the fiber surface
  - Why does the system fail here?
- Does the fiber affect the polymer-matrix in its proximity?
- How does the matrix attach to the sizing during curing?



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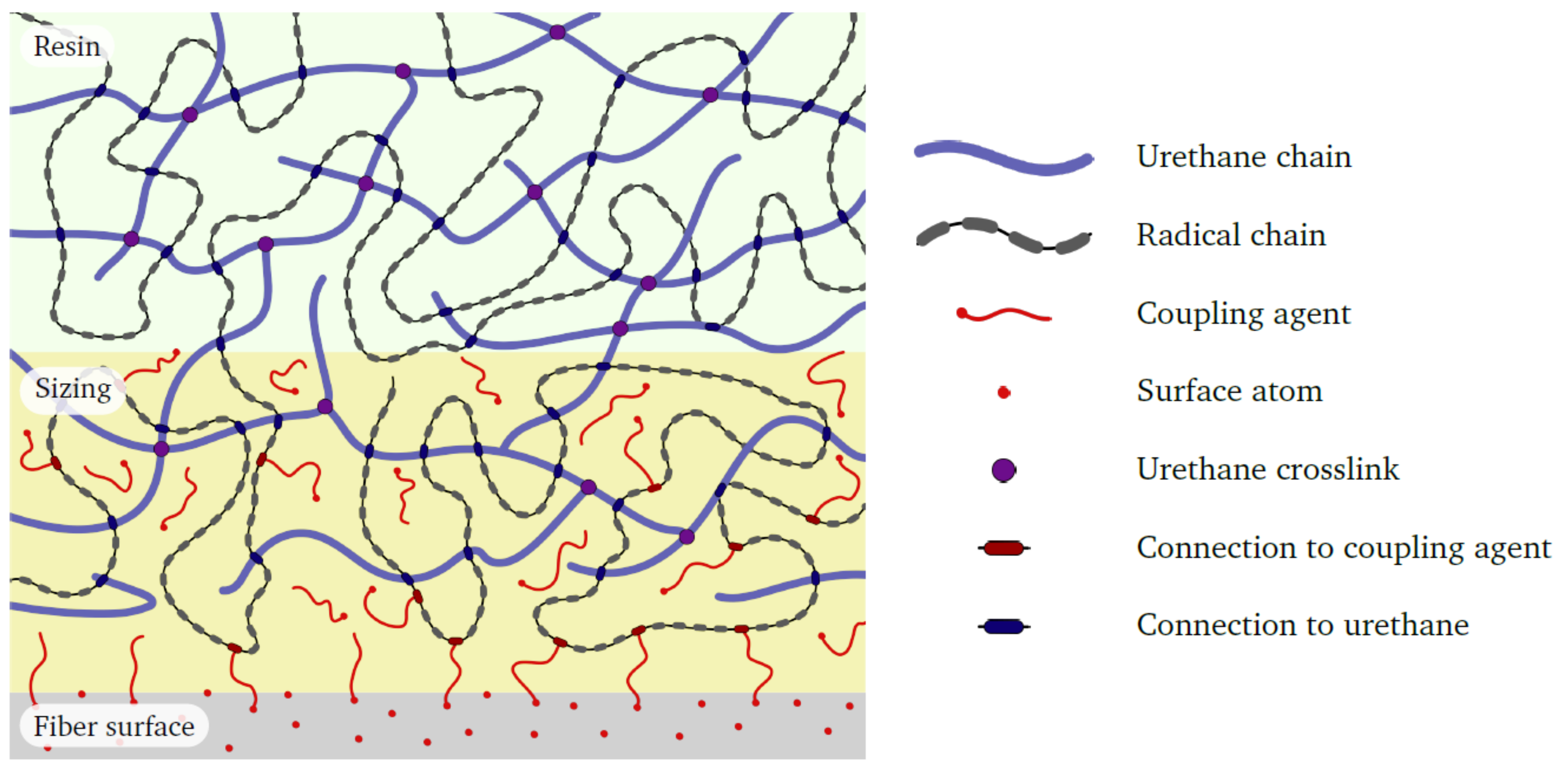
System:



- Resin: Same UPPH as before, will follow same curing protocol
- Fiber: E-glass. As the coupling agent interacts primarily with the Si atoms on the fiber surface so we can skip most of the details of the fiber itself and represent it with appropriately spaced configuration of fixed Si atoms.
- Sizing: …it's a secret…

Sizing

- Sizing is a bit of a black-box technology as size formulations are kept secret. As a result, understanding in the literature is quite limited and fragmented.
- Main components are:
  - The **film former** is mainly intended to protect the fiber during processing. Must be compatible with the matrix material (UPPH) so we take it as identical.
  - The **coupling agent** reacts (bonds) with the fiber surface as well the resin.
- Looking at different sources it seems that the primary coupling agent for polyesters appears to be γ-methacryloxypropyltrimethoxysiline (γ-MPS) so we will use that.
- However, the hydrolyzed γ-MPS undergoes a **condensation process** where the hydroxyl groups form hydrogen bonds with other hydroxyl groups, followed by the formation of covalent bonds while losing a water molecule

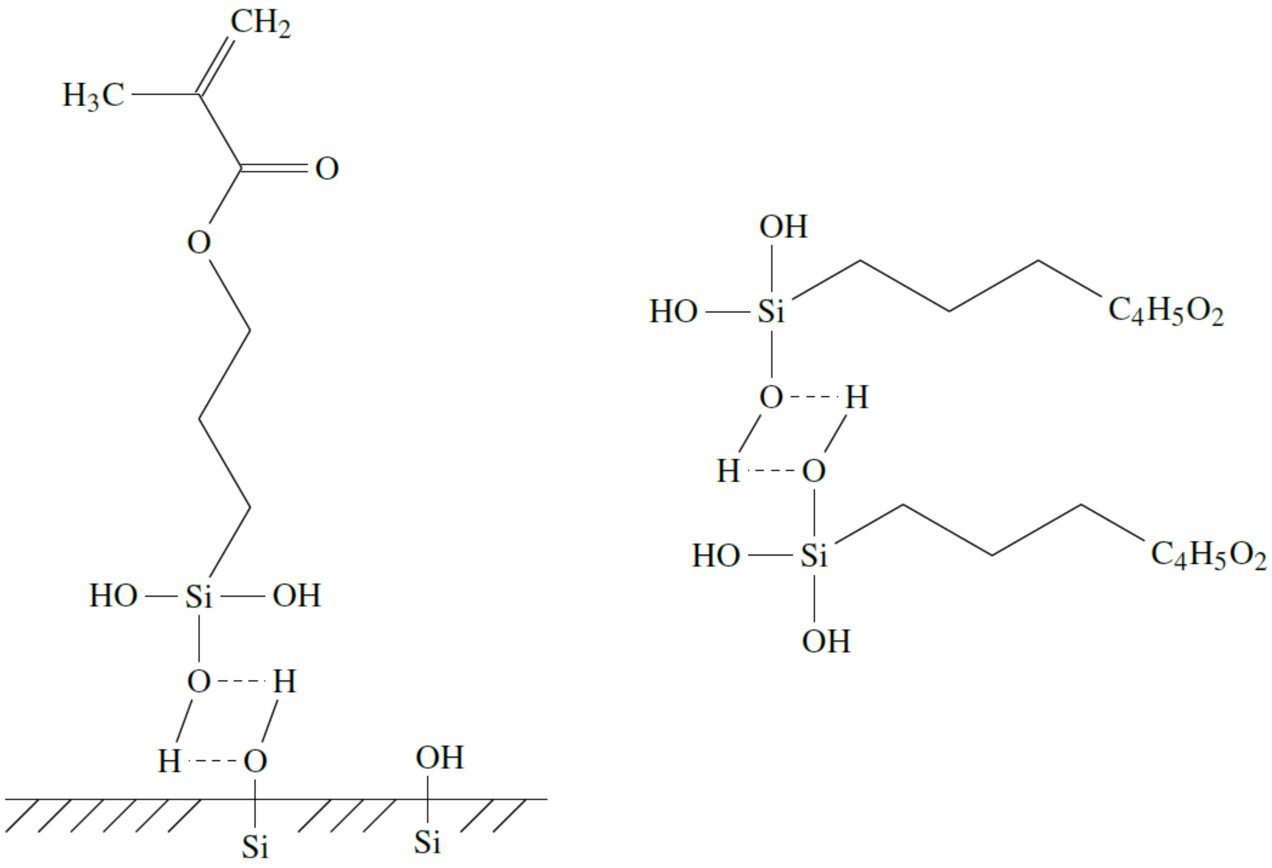
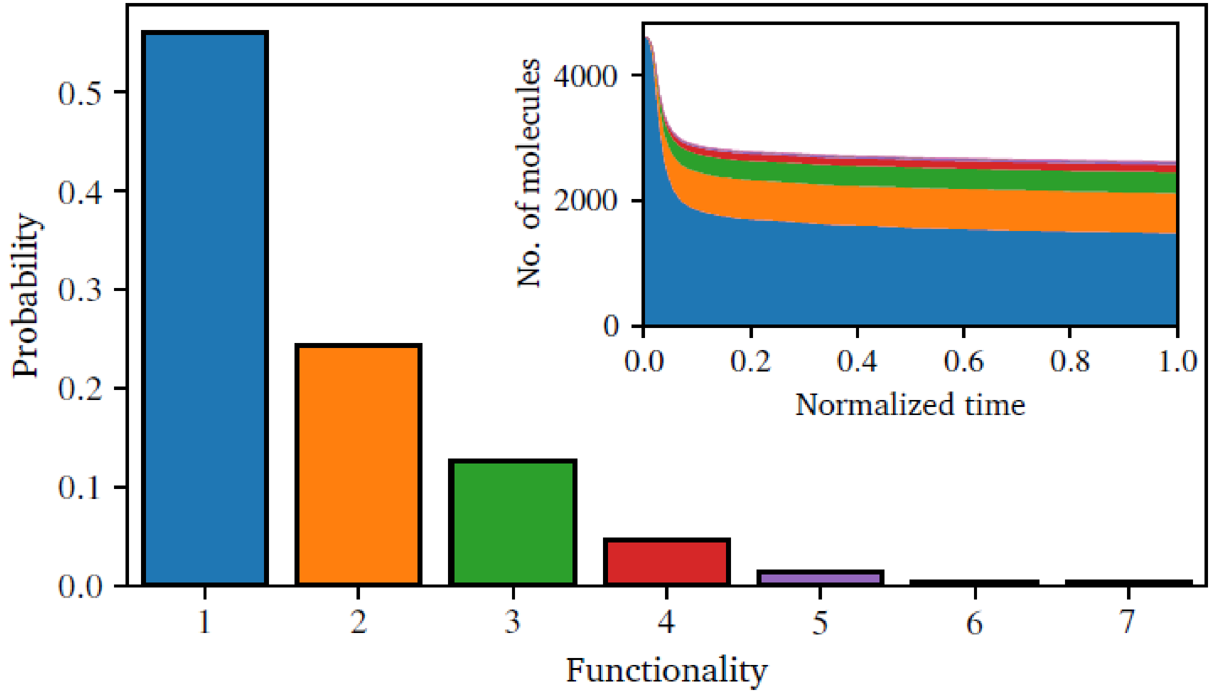
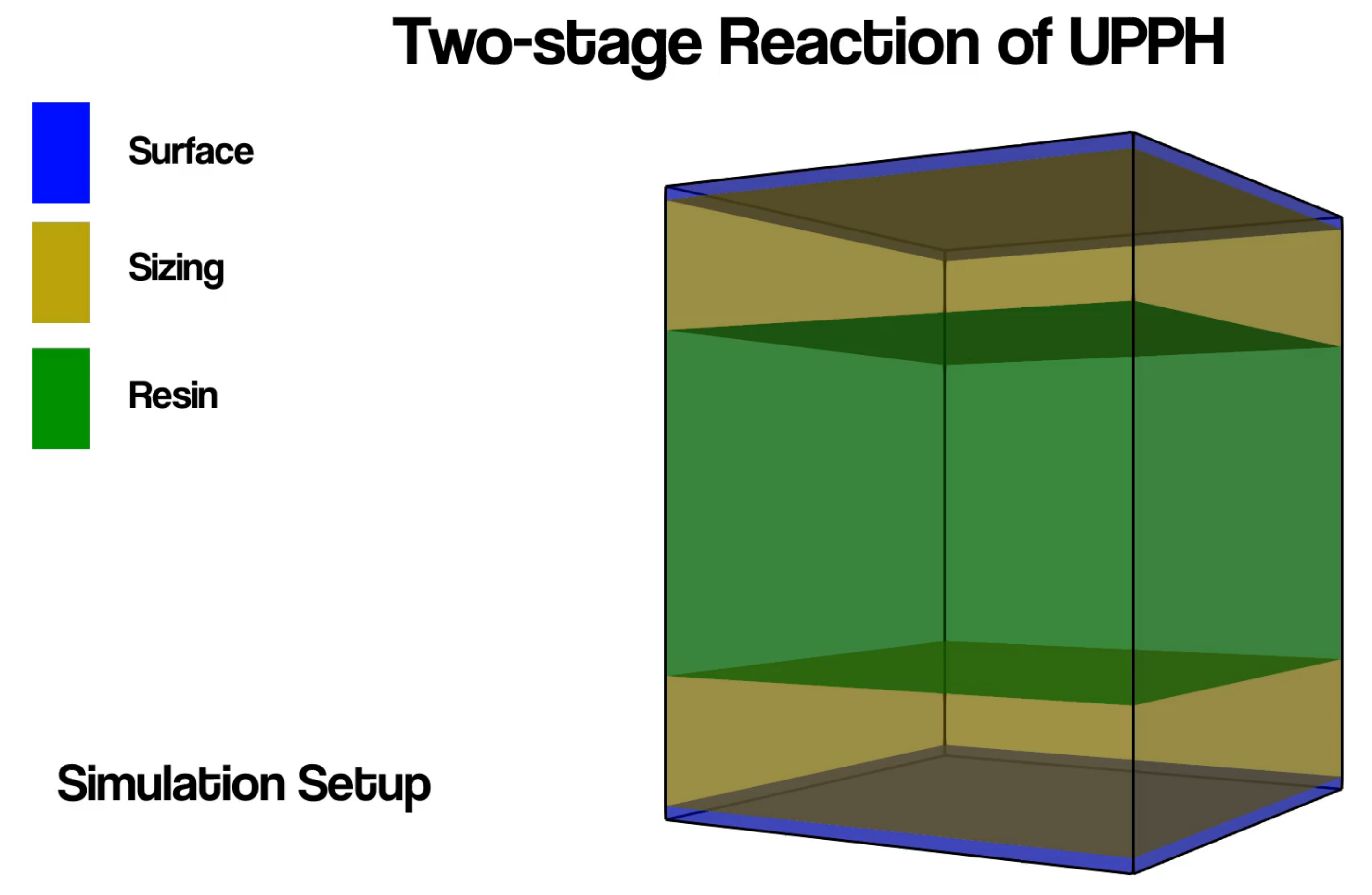


Fig. 3 Hydrogen bonds of the coupling agent γ-MPS at the gla surface (left) and with other coupling agent molecules (right).

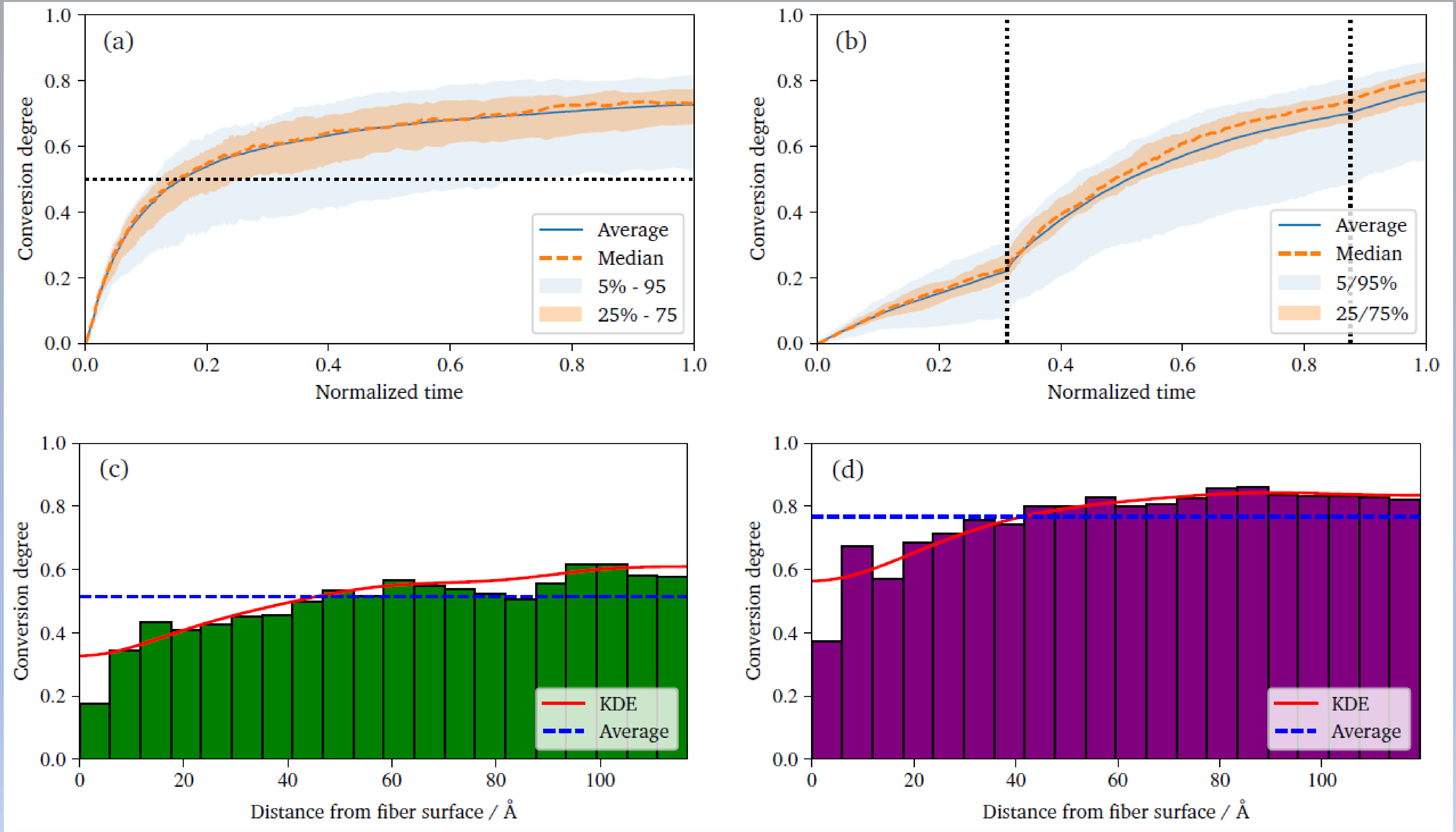


The condensation reaction is followed by the previous two-stage reaction of UPPH



Polyurethane reaction

Radical polymerization



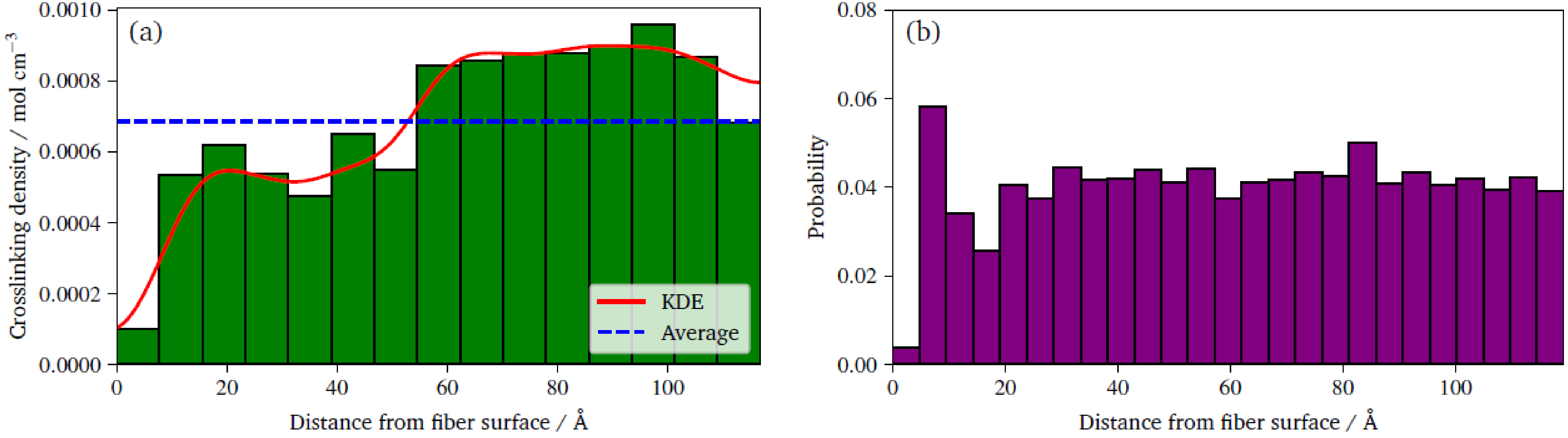


Fig. 8 (a) Spatial distribution of the crosslinking density of the polyurethane reaction at 50 % conversion degree. (b) Spatial distribution of the relative frequency of radical chains at the end of the radical polymerization. In addition to the histograms, the averages and a KDEs are displayed.

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Conclusions

- Ideal mixing significantly speeds up the curing process
- Material properties measured were consistent with experimentally known values (where available) with the exception of the glass transition temperature.
- We can use MD to study the full fiber+sizing+resin system but trade secrets mean it is difficult to exactly match a specific commercially available fiber/size
- Probably there are low concentration components of the size that limit the condensation but we don’t know what they are. Nevertheless, the resulting system should be reasonably represented.
- The presence of the fiber slows the radical reaction somewhat, probably by blocking diffusion of styrene molecules
- The properties of the polymer matrix change as we approach the interfacial region
  - lower conversion ratio for the reactions
  - lower crosslink density
- To do:
  - How does the change in properties of the polymer matrix affect material properties in the interfacial region
  - coarse-grain the move to larger scales