DIFFUSION IN COATINGS: INSIGHTS FROM MOLECULAR SIMULATIONS

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Formulating Functional Films and Coatings IV

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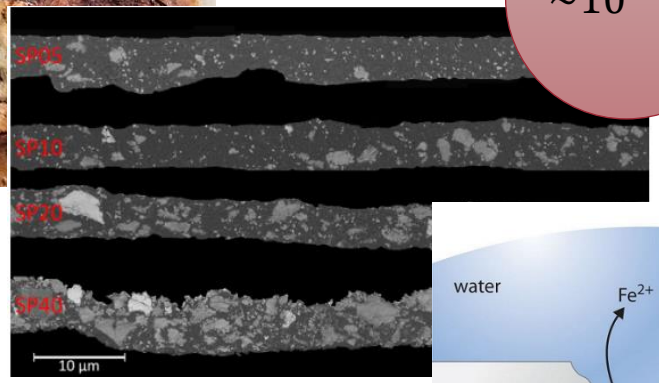
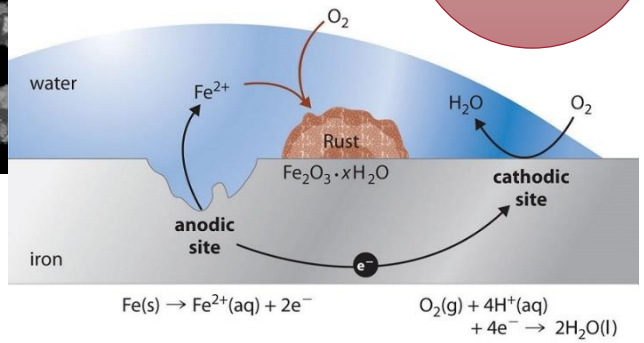
Corrosion protection across time and space

$\sim 10^{0}$m

$\sim 10^{-3}$m



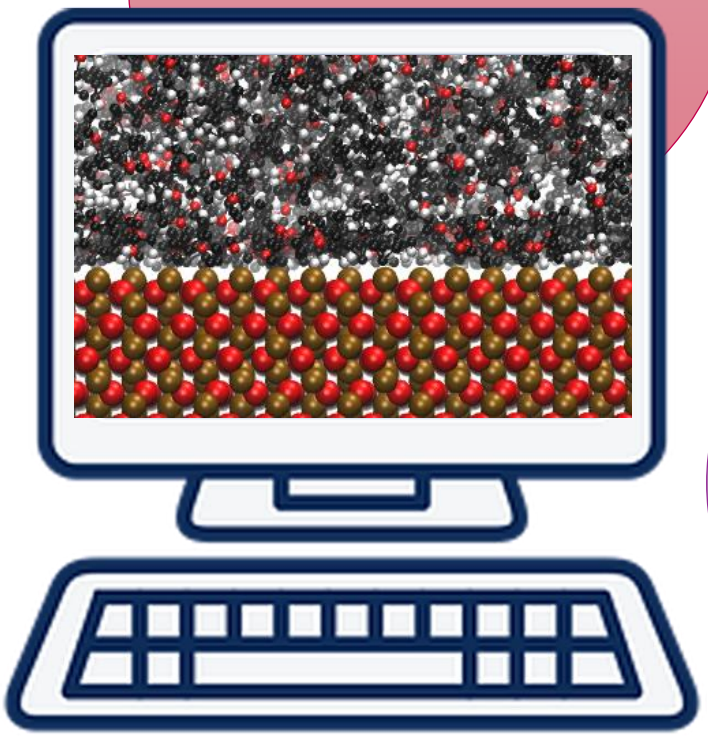
$\sim 10^{-6}$m



$\sim 10^{-9}$m

Modelling approach

Construct realistic models of polymer-solid systems.

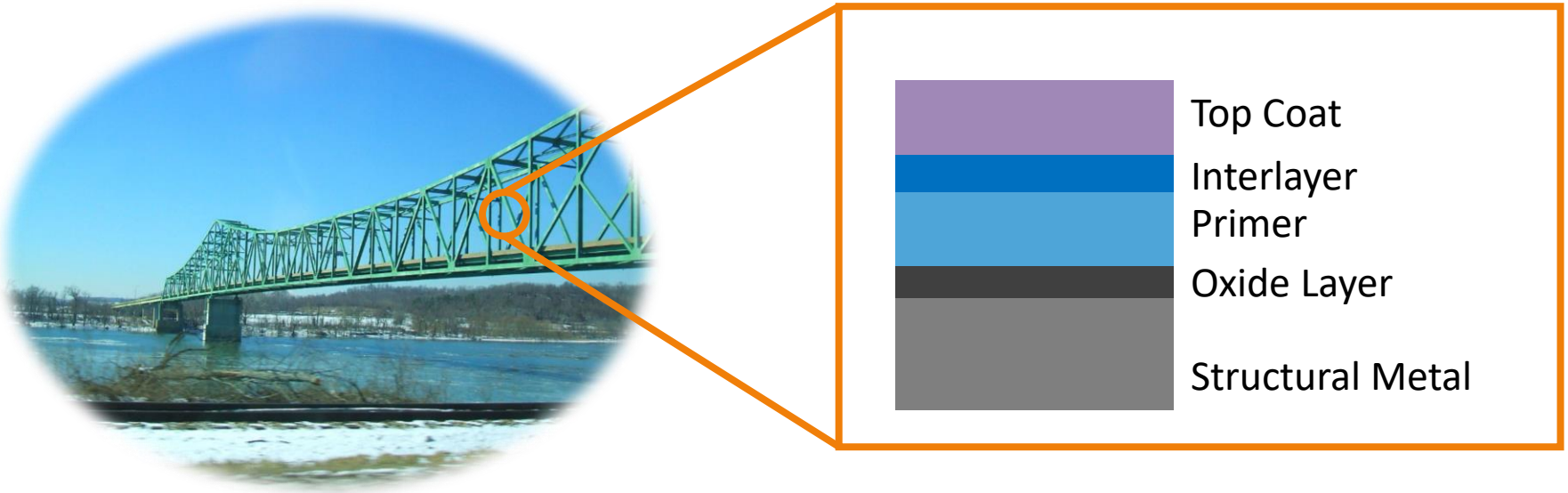


Identify transport mechanisms, bottle necks and energy barriers.

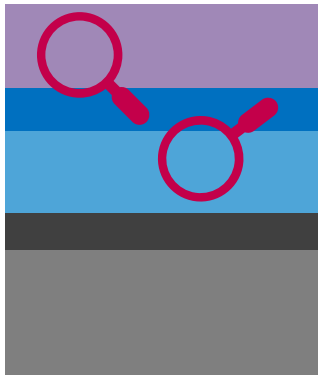
Provide fundamental understanding on molecular level transport and energy barriers

Paint

- Paint is an organic coating applied to a substrate
- Formulated product - COMPLICATED
  - Binder, Thinner, Filler, Additives…
- Primary function is to protect the substrate
- Wide range of applications
  - Aerospace, automotive, food packaging…



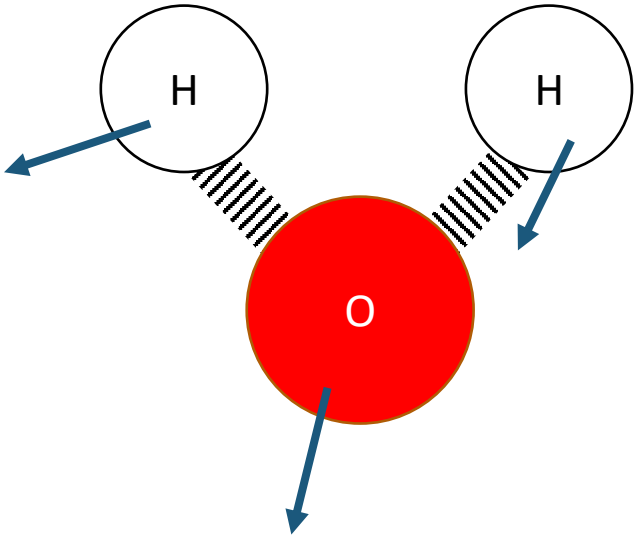
Aim and approach



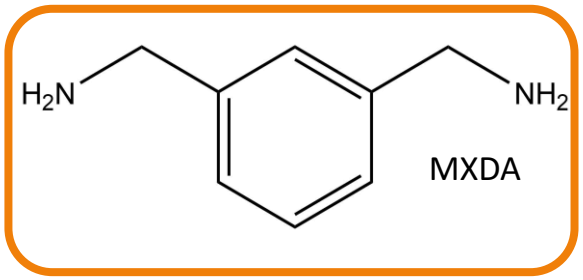
- **Aim**: How do water and ions reach the surface?
- **Approach**: Create realistic cross-linked structure with different water/ion concentrations in

Molecular Modelling

- Each atom is represented as a single bead with specific parameters
  - e.g. radius, interaction, charge
- These beads are joined by springs to build up molecules
  - Plus angle/dihedral
- Molecular dynamics integrates through time using Newton's equations of motion



Epoxy resin



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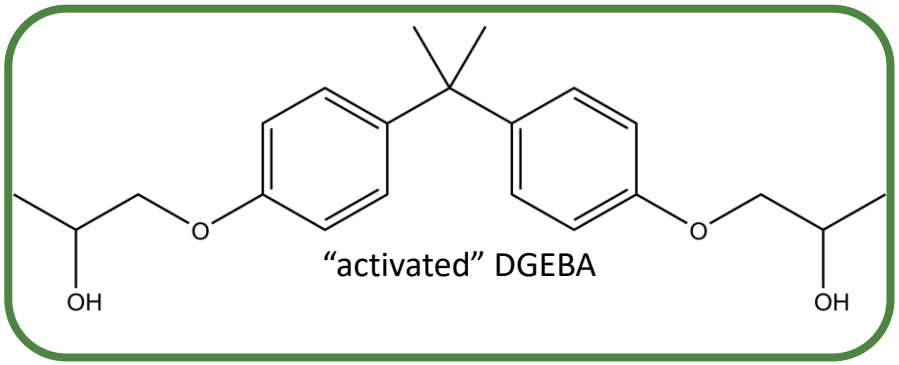
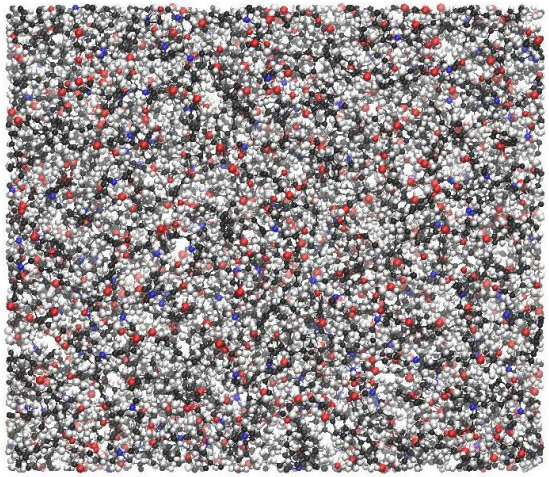


Temperature
(Pressure)

Cross-link
Density

Composition



Structure

Pore size distribution

Dynamics

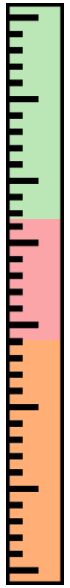
Water and polymer mobility

Diffusion coefficient

Interactions

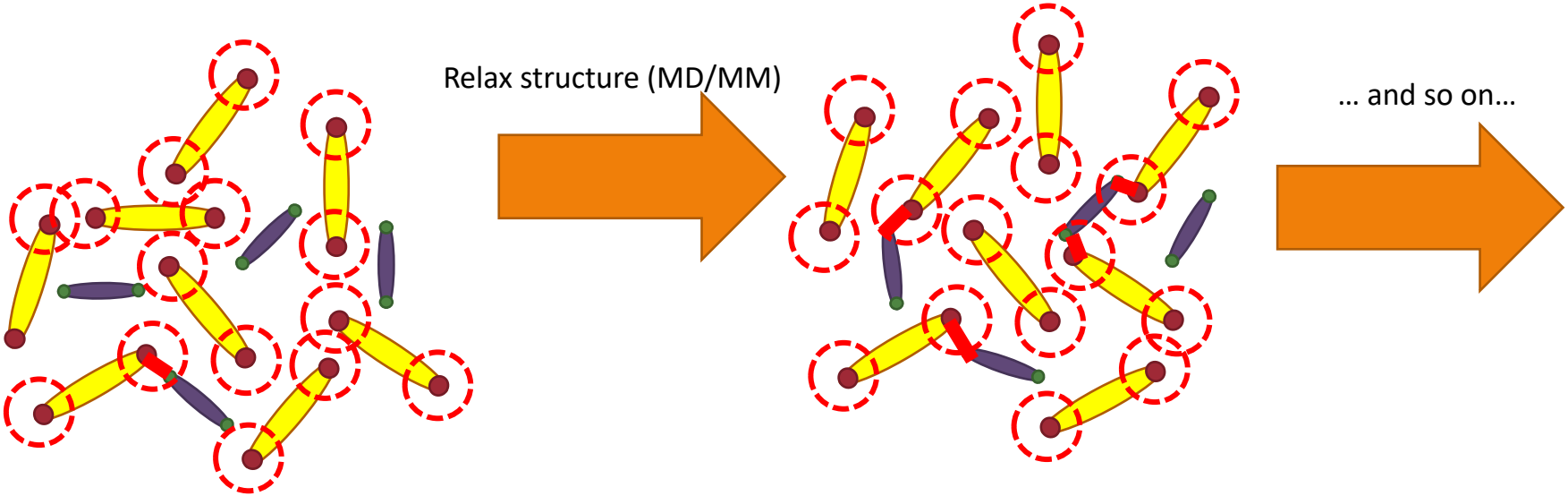
Location of water

Hydrogen bonds



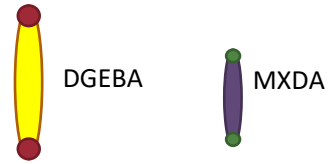
Cross-linking procedure

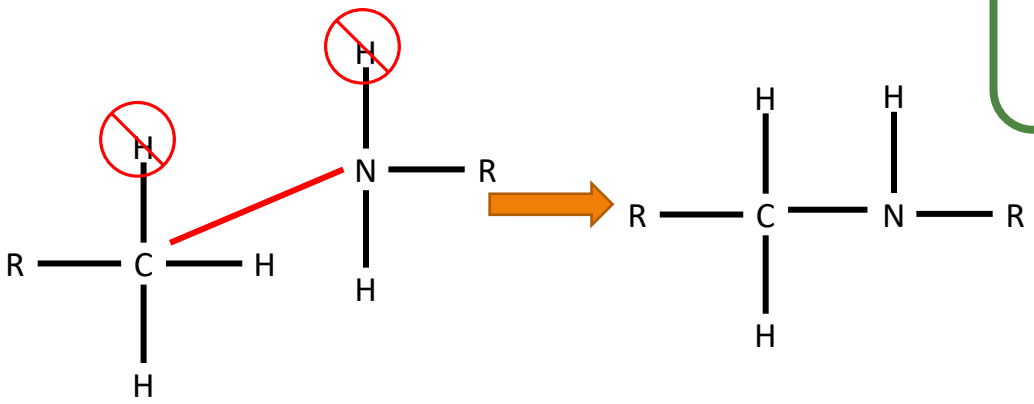
1. Equilibrate system
2. Create new bonds between reactive species within cut off distance
3. Relax new network
4. Repeat until desired amount of cross-linking

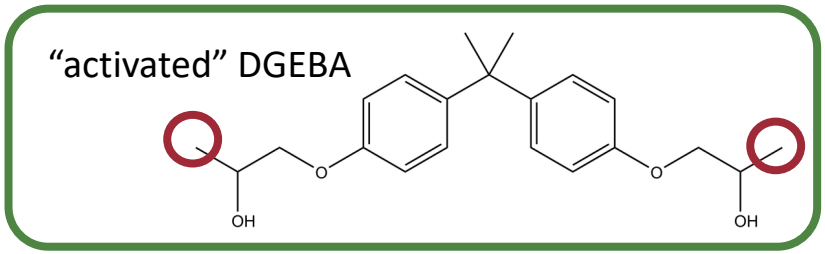


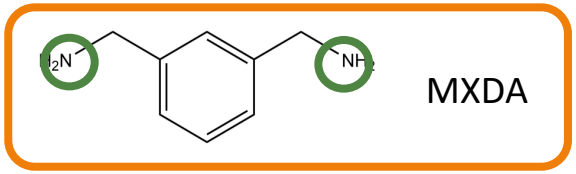
Cross-linking procedure

1. Equilibrate system
2. Create new bonds between reactive species within cut off distance
3. Relax new network
4. Repeat until desired amount of cross-linking
5. Remove excess H's and update charges
6. Final equilibration run

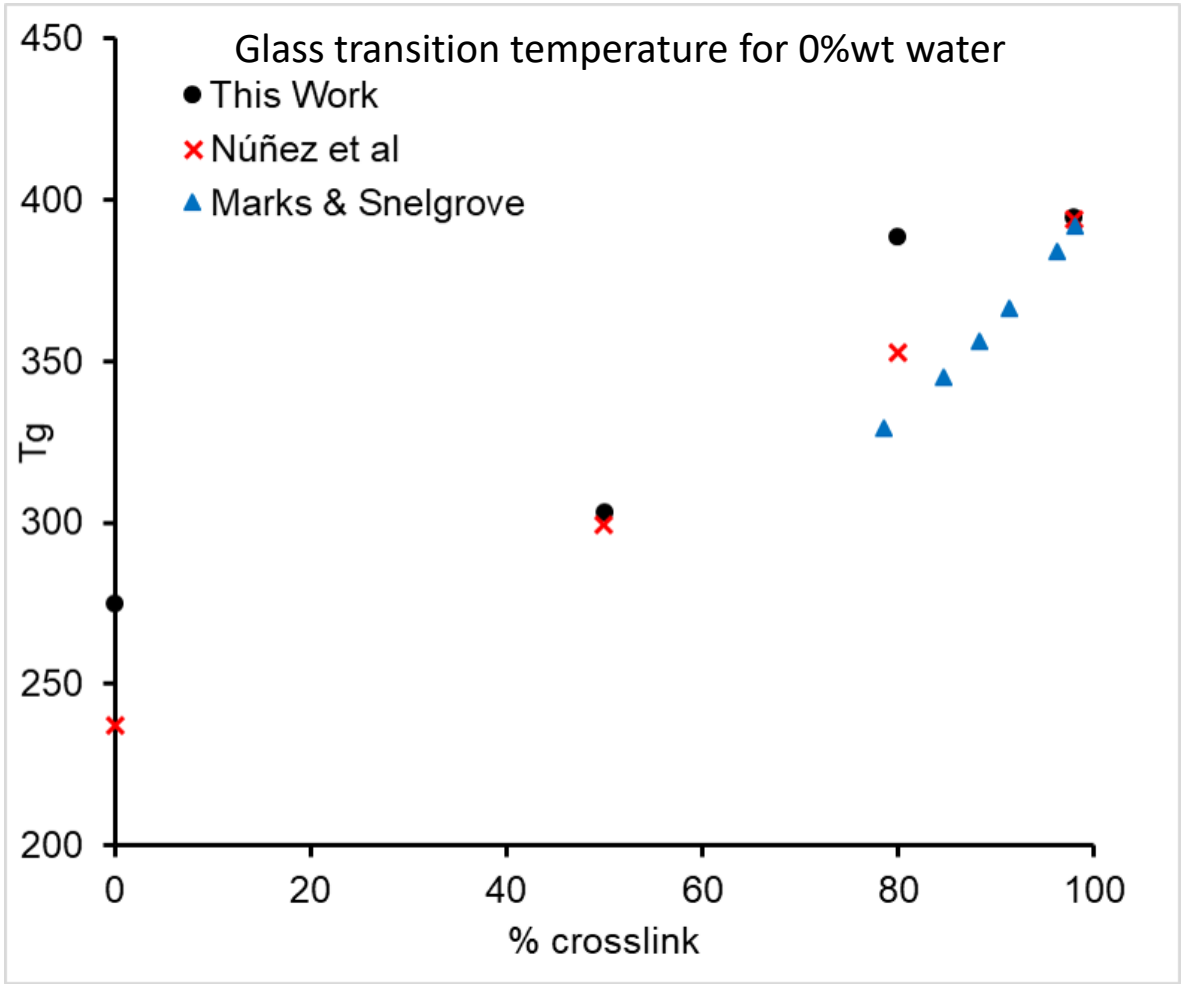








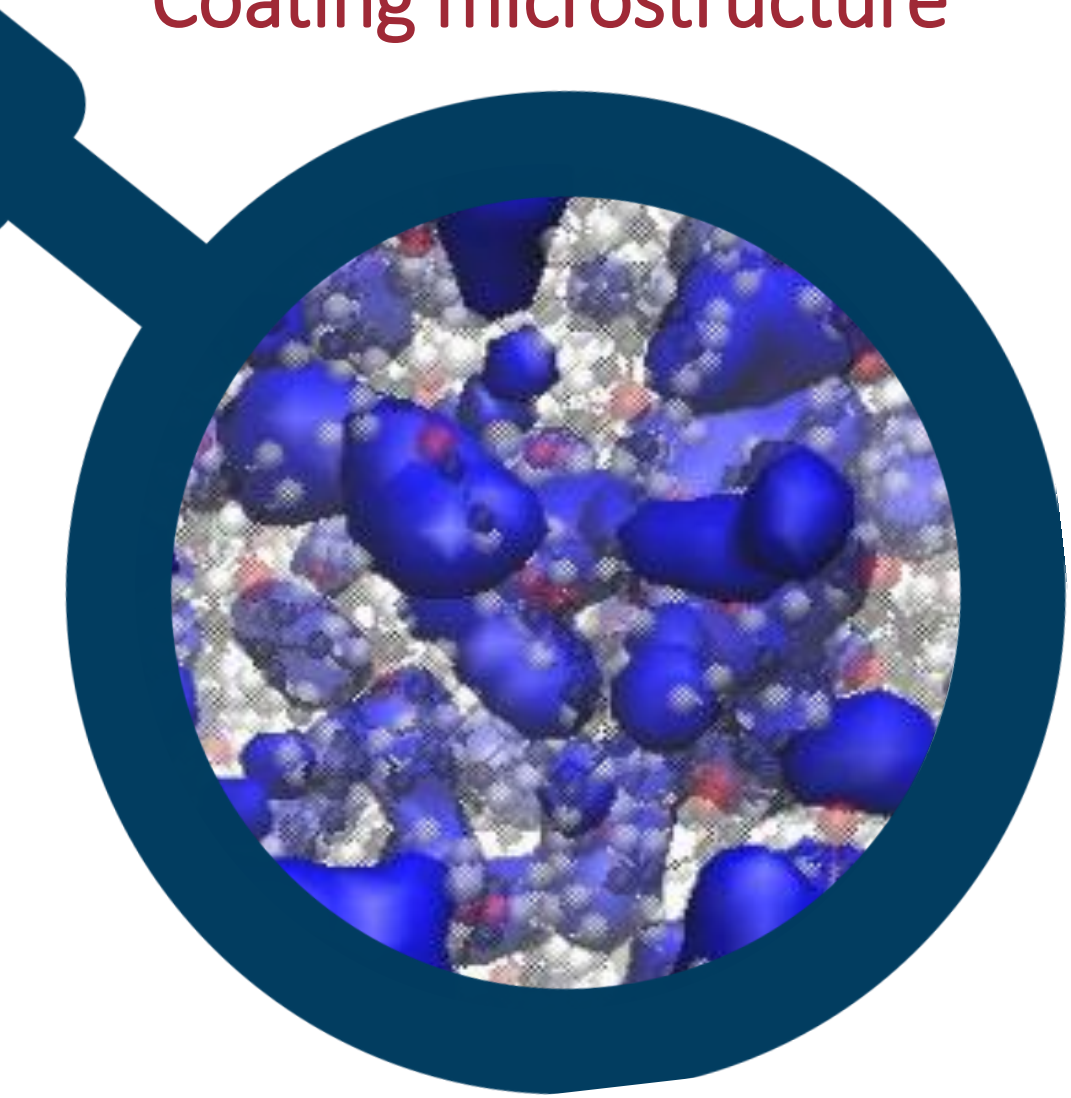
Model Validation



Confirmed model validity through glass transition temperature and density.

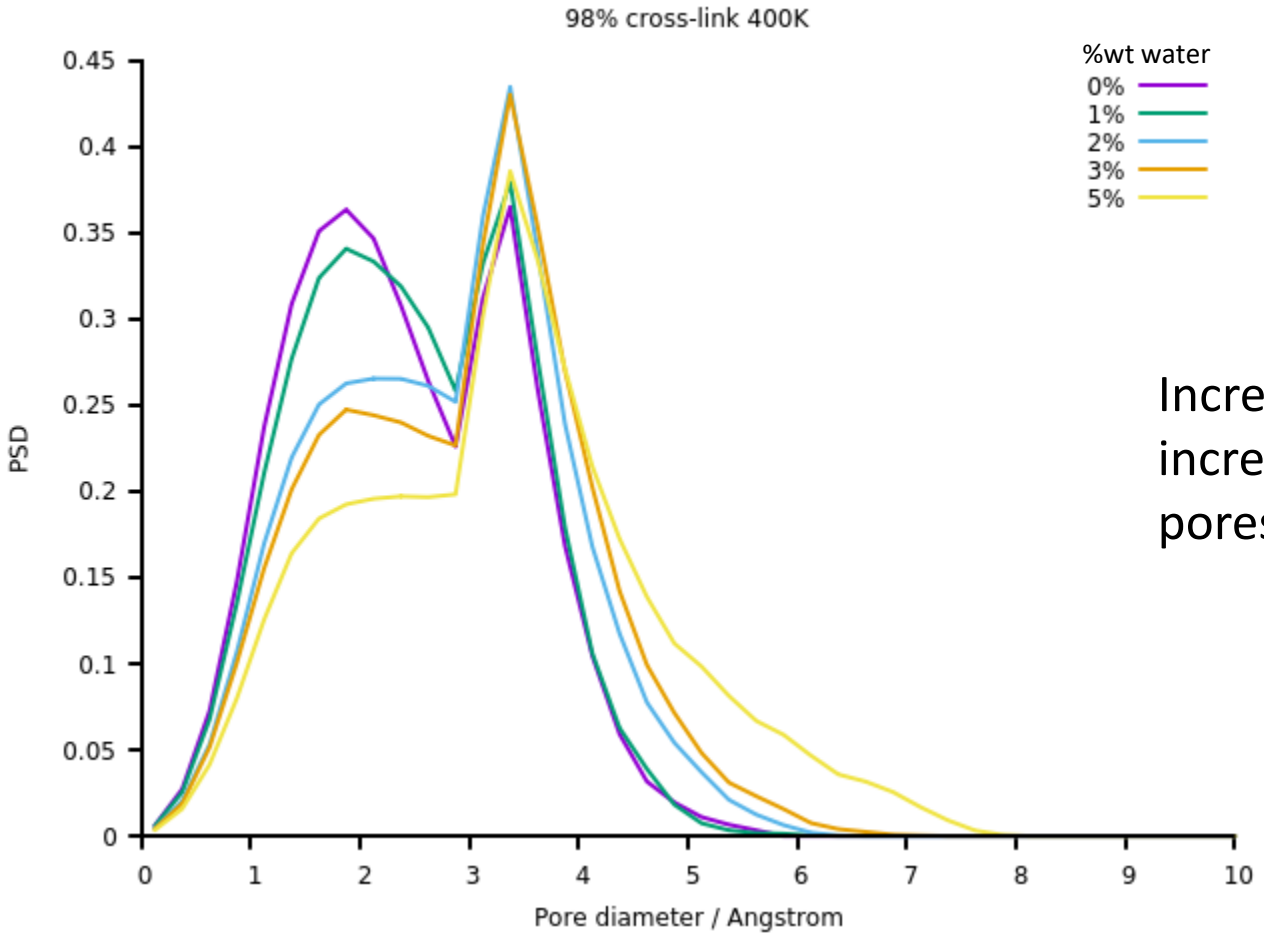
L. Nunez *et al J thermal anal calor* (2007) 70 9-17
M. J. Marks and R. V. Snelgrove *ACS Appl. Mater. Interfaces* (2009) 1 921-926

Coating microstructure



- Free volume found as isolated voids or pores for all systems considered
- Quantify pore size distribution in different coating conditions

Water content



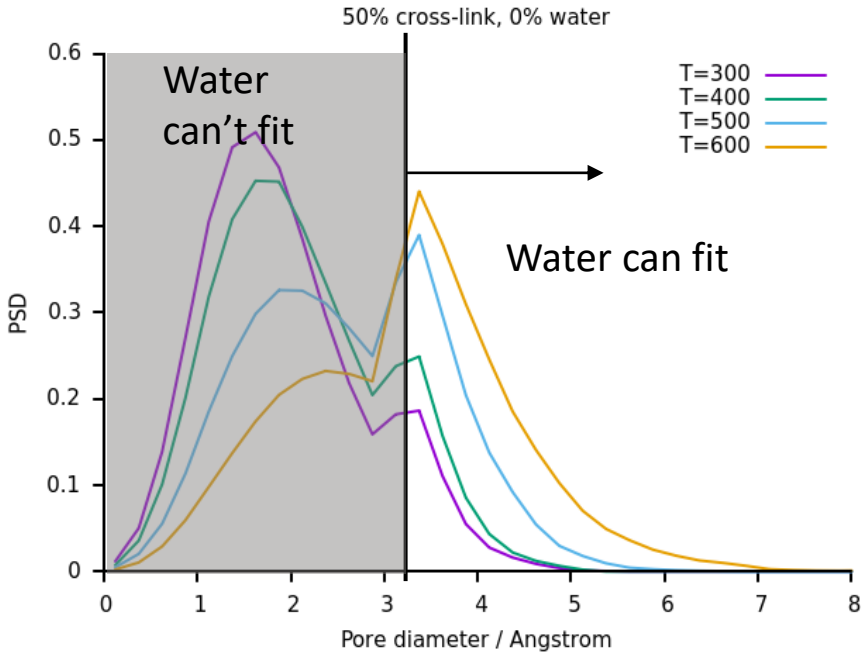
Increasing water content increases proportion of large pores

Size of water = 3.16 Angstrom

Pore size distribution

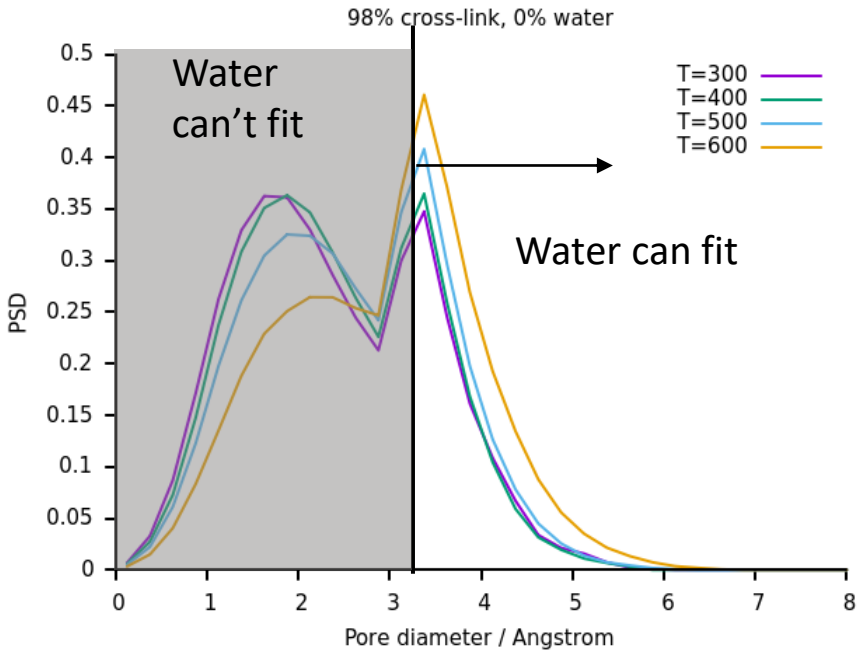
Low Crosslink

Proportion of large pores dramatically increases with temperature



High Crosslink

Much less change in proportion of large pores



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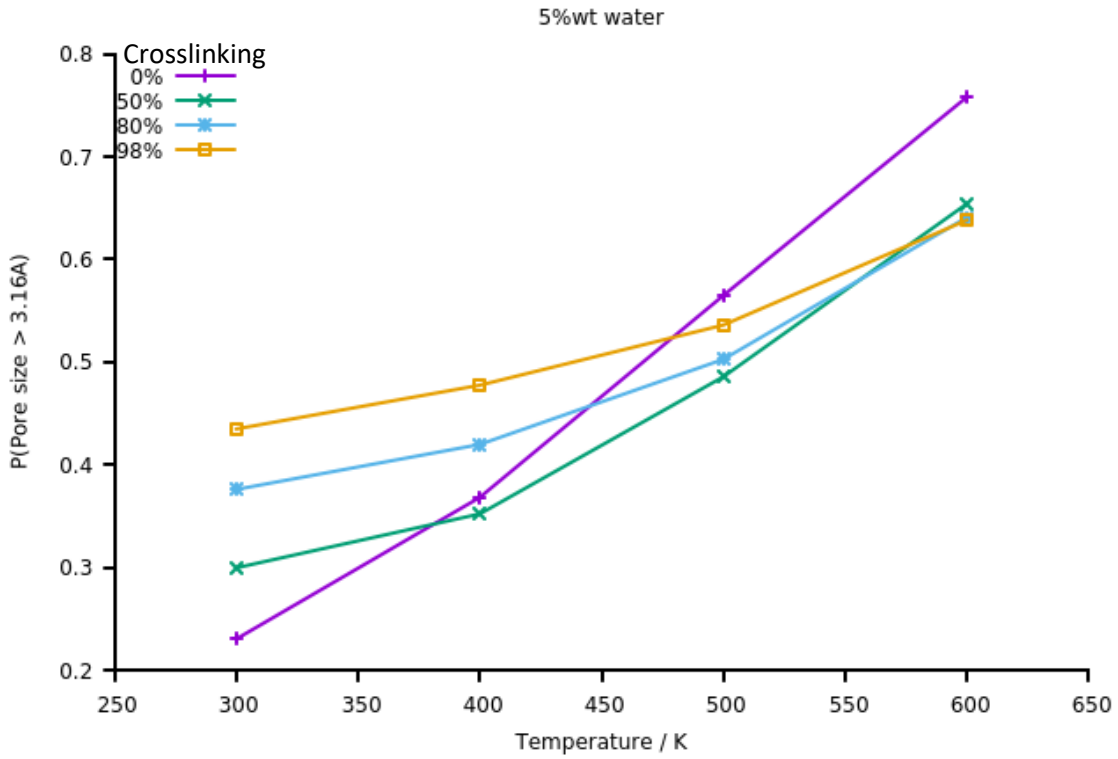
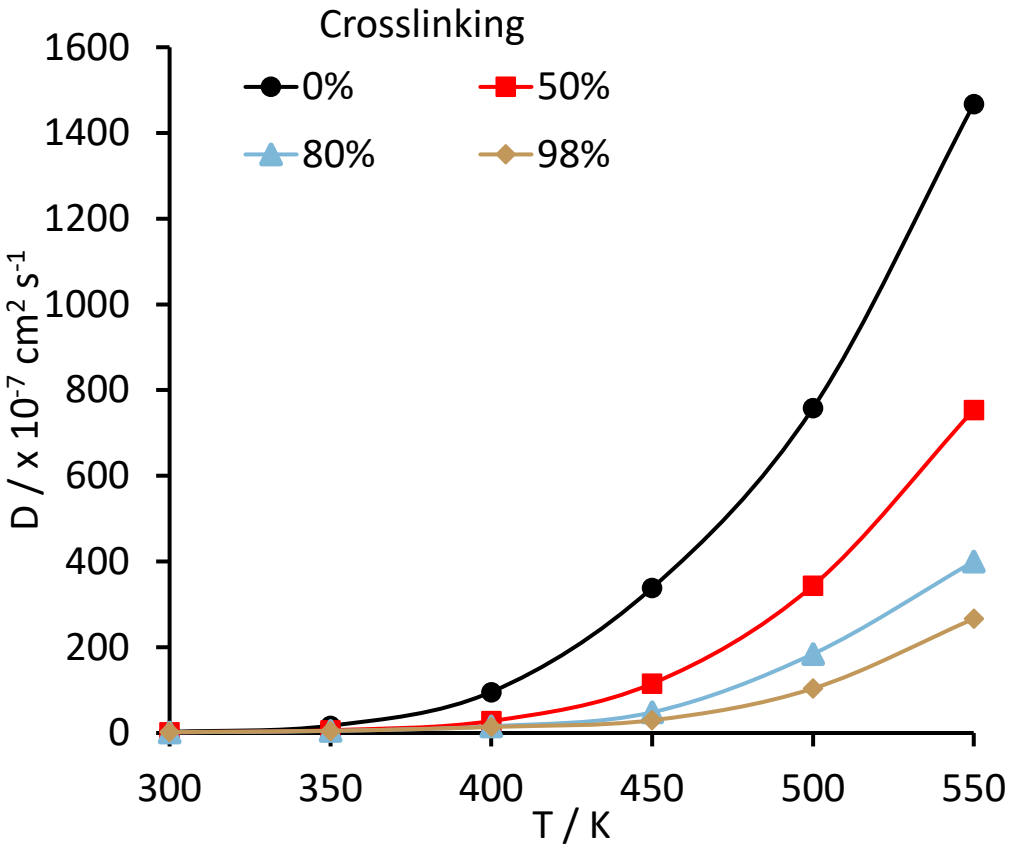


- At low temperature, pore size increases with crosslinking.
- At high temperature, all crosslinked samples have similar pore sizes

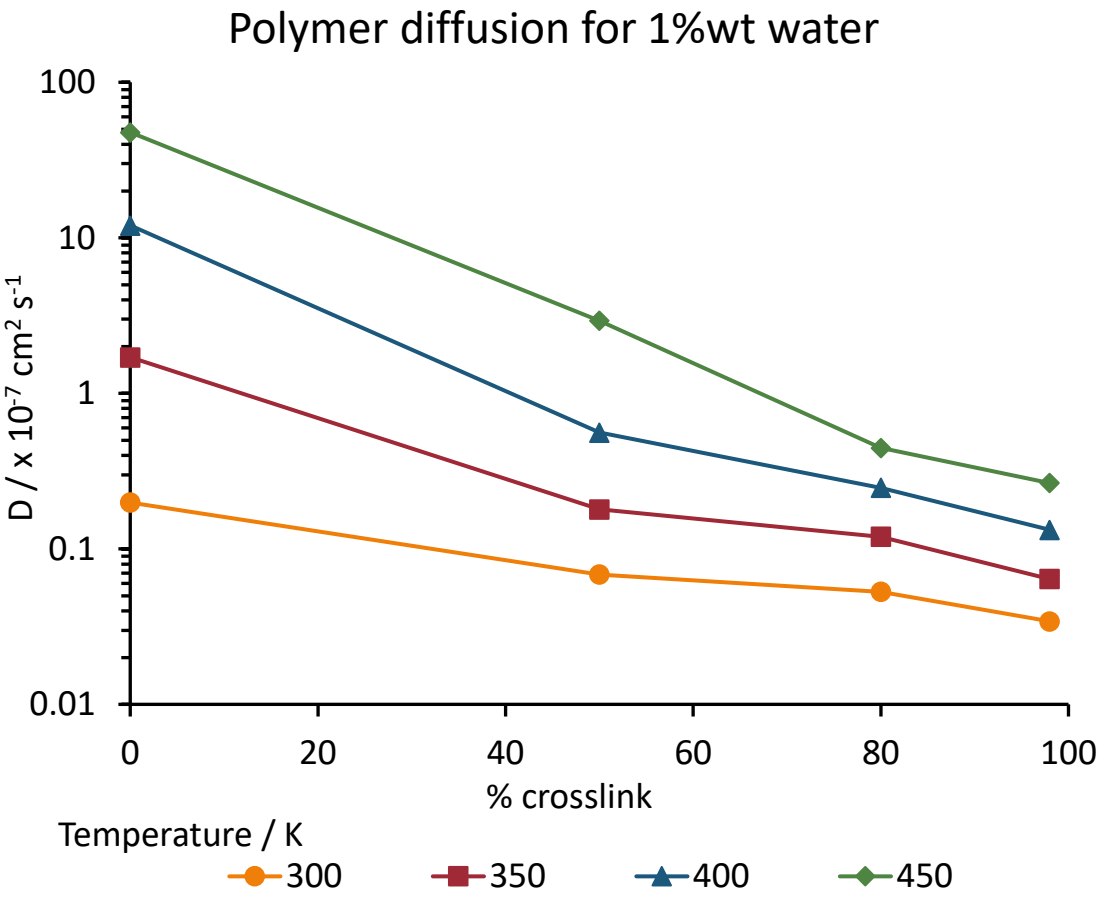
Water diffusion



Dramatic decrease in water diffusion with crosslinking (despite larger pores in PSD)

Polymer chain mobility

Water diffusion



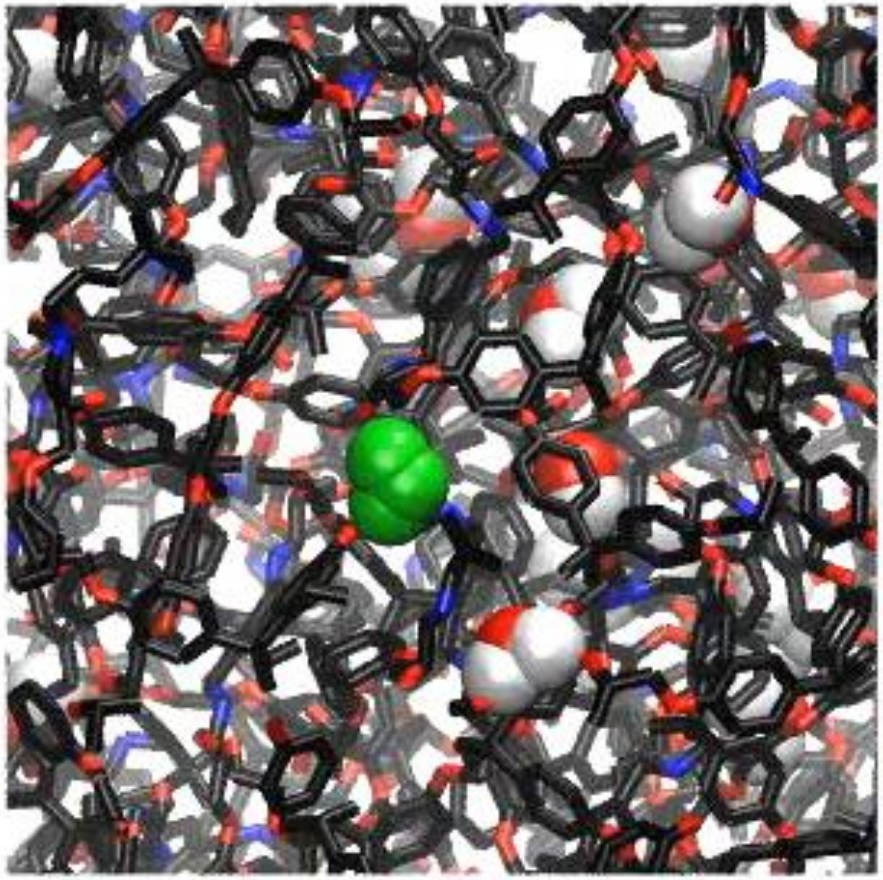
Dramatic decrease in water diffusion with crosslinking (despite larger pores in PSD)

Polymer chain mobility

Lower % crosslink = more flexible

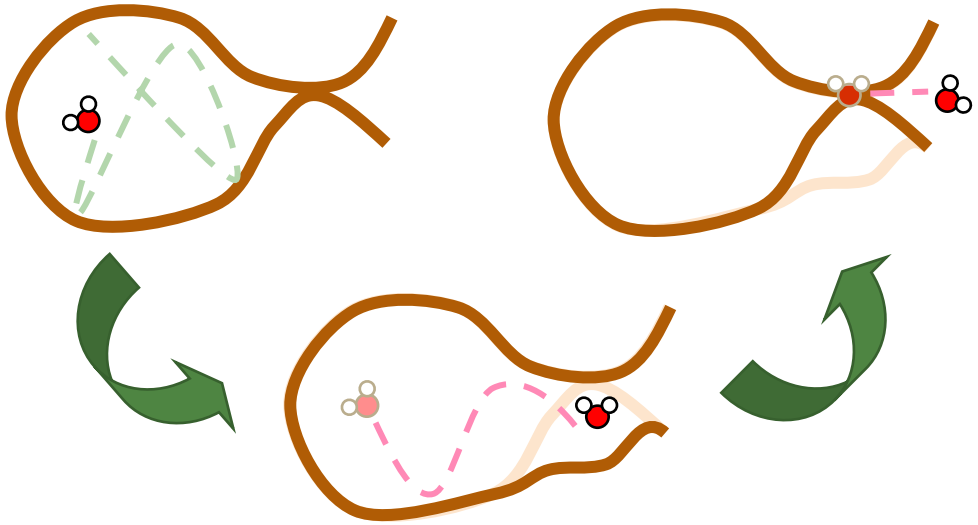
Water moves through polymer through a facilitated “hopping” mechanism

Water diffusion



Summary

- **New Understanding:** Identified the mechanism for water transport through a crosslinked polymer coating



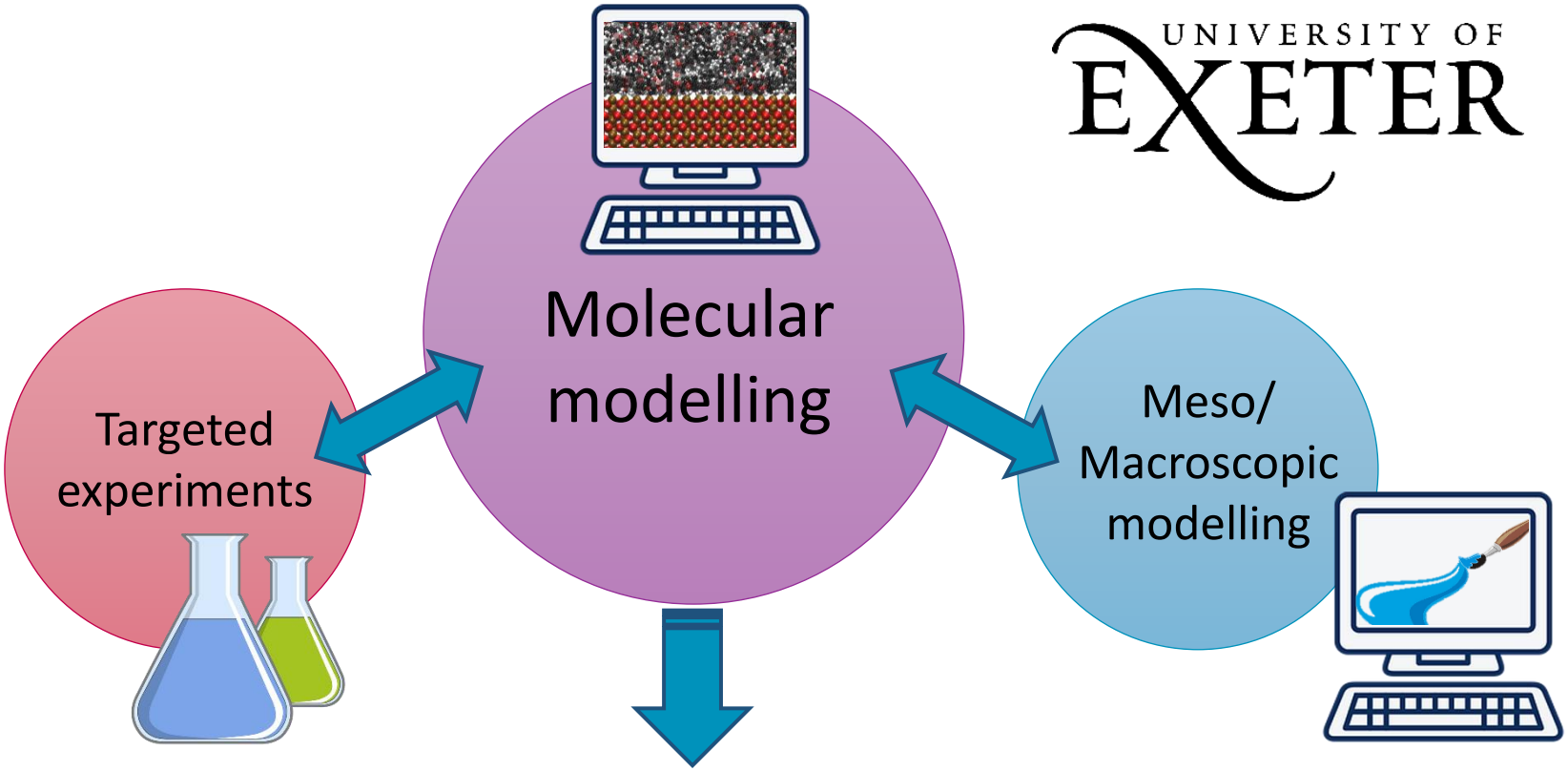
Property	H_2O Diffusion
↑ Temperature	↑↑
↑ Crosslink %	↓
↑ Water %	=

Water diffuses through isolated pores, mediated by polymer motion

Impact

How coating curing and environmental conditions effect the barrier properties of passive coatings

Build up the complexity
Off stoichiometry… Other additives… Ion transport..
Pigments… surfaces…



Increased understanding of coatings and films

Improved products

Acknowledgements

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Dr Melody Obeng

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