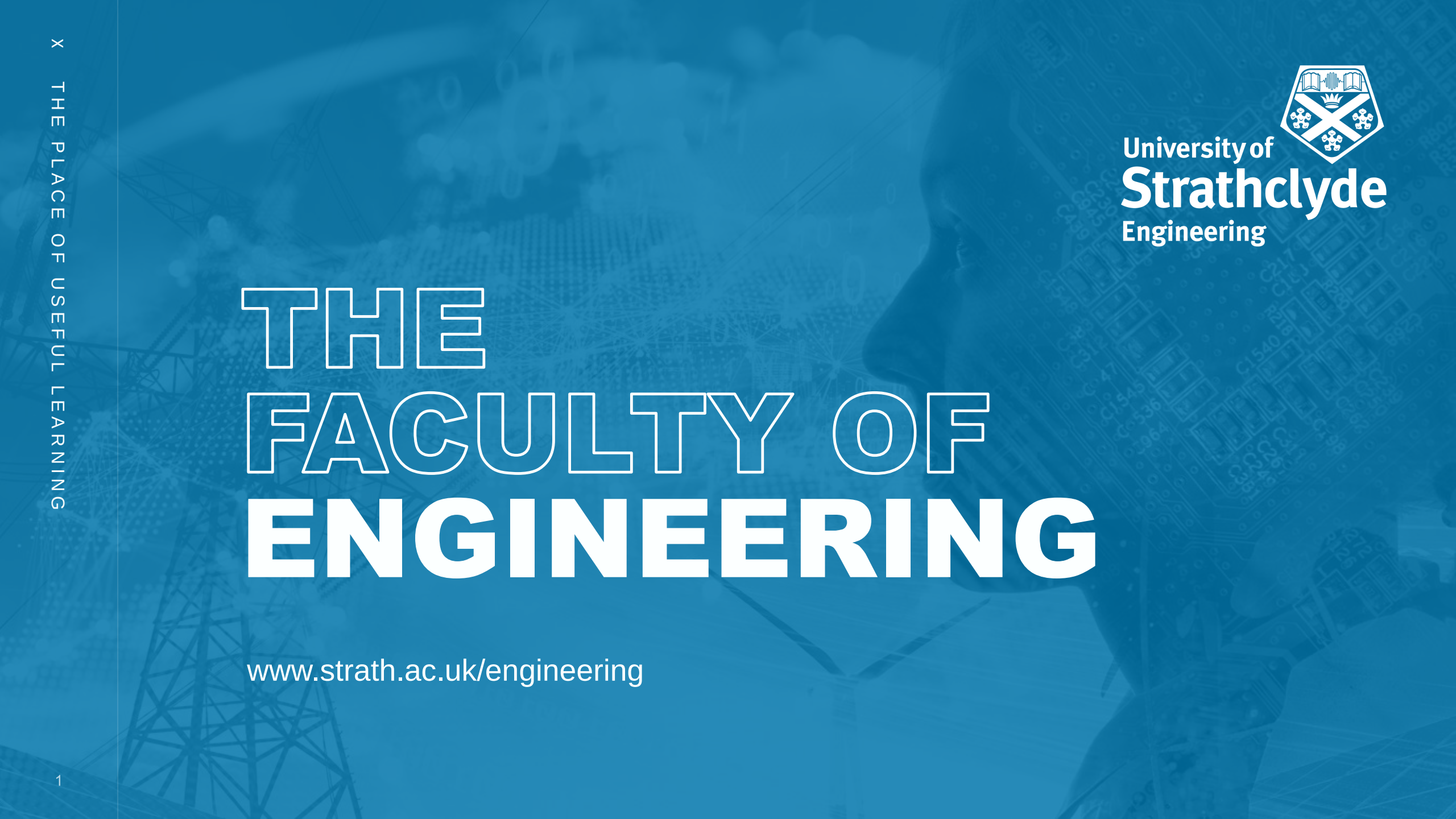
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Atomistic Simulations of Polymers for Sustainable Food Packaging Design

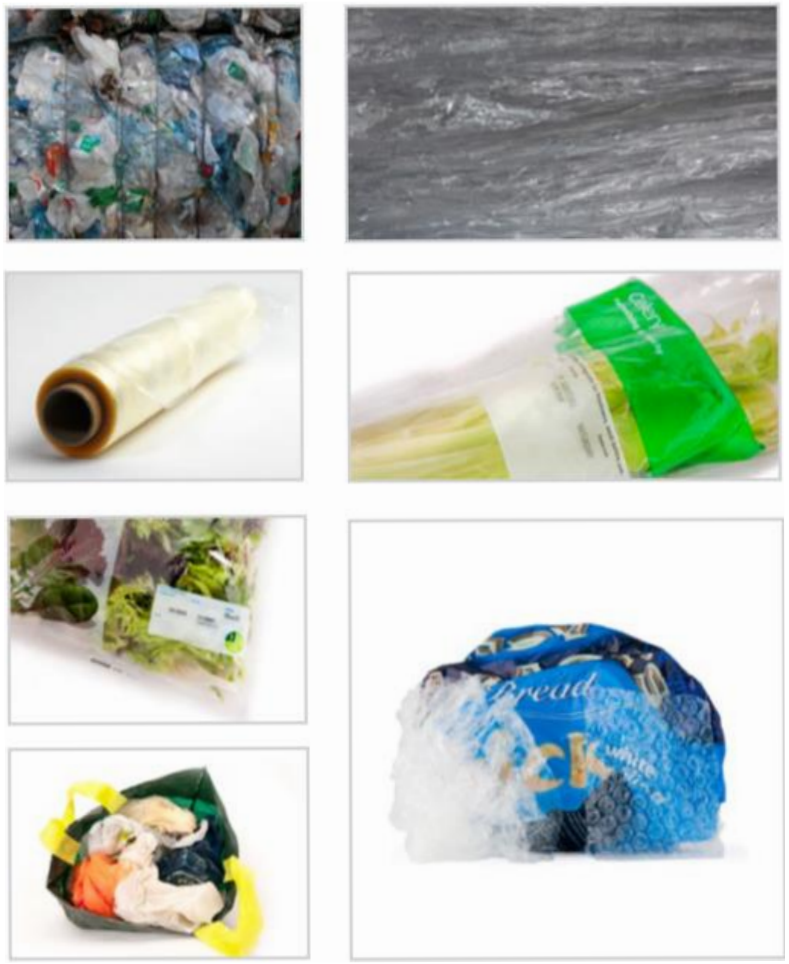
Nisha Middleton
MDAnalysis UGM
Sep 2023

Plastic Film Packaging

Increases shelf life of food

Lightweight, transparent, flexible

Multilayer components



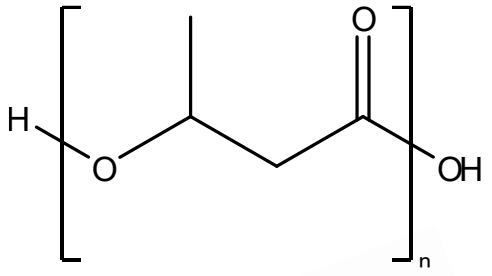
Nearly 1/4 of UK consumer plastic[1]

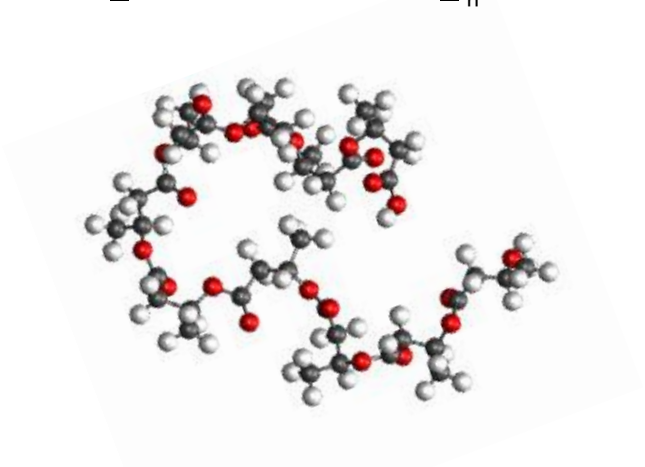
Only 7% currently recycled in UK[1]

Increasing demand for sustainable alternatives

1. The UK Plastics Pact Annual Report 2021-2022

Polyhydroxybutyrate (PHB)



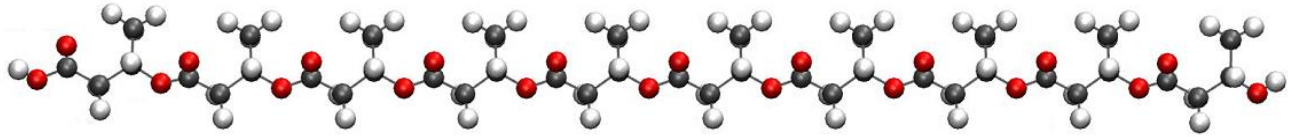


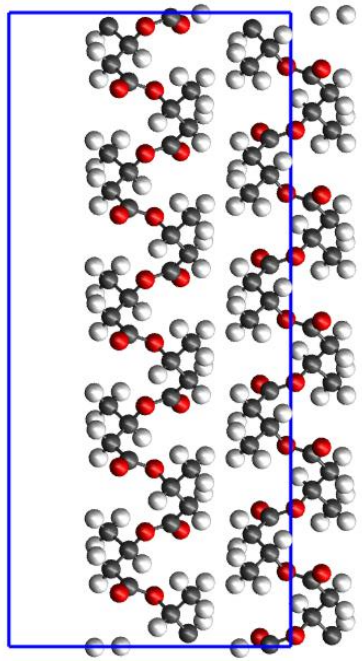
- Bioderived and biodegradable
- Semicrystalline polymer
- Thermal and barrier properties comparable to conventional plastics
- Pure PHB can be brittle due to high crystallinity
- Can be tailored through copolymerisation and addition of fillers and plasticisers

Research Objective

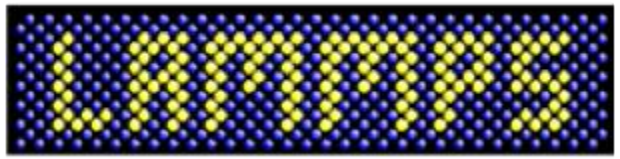
Use molecular dynamics to investigate barrier properties by simulating diffusion of oxygen and water through the amorphous polymer matrix.

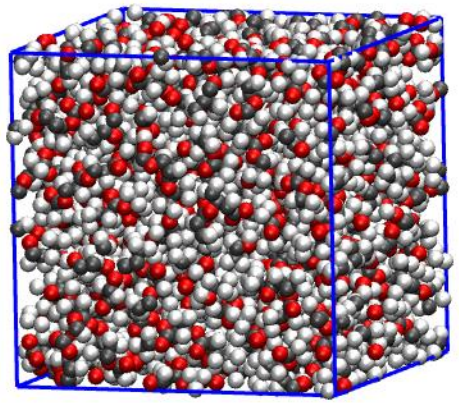
Simulation Method





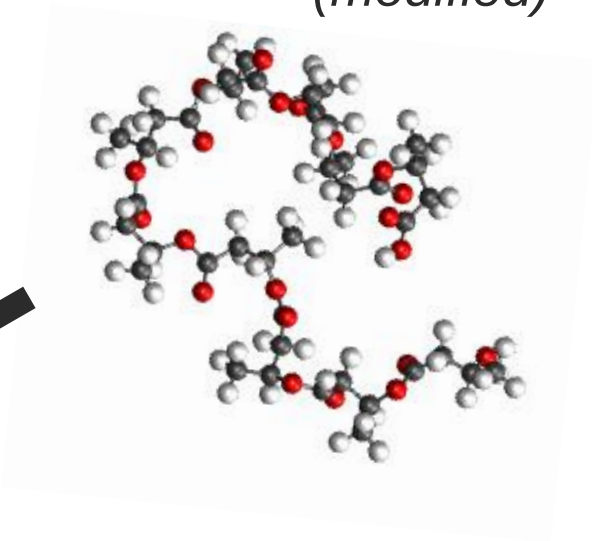
PHB α-crystal





amorphous polymer

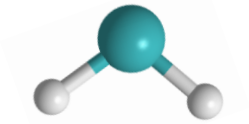
General Amber Force Field[1] (modified)



1. Wang, Junmei, et al. Journal of computational chemistry 25.9 (2004): 1157-1174.

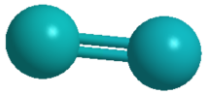
Simulation Method

H_2O

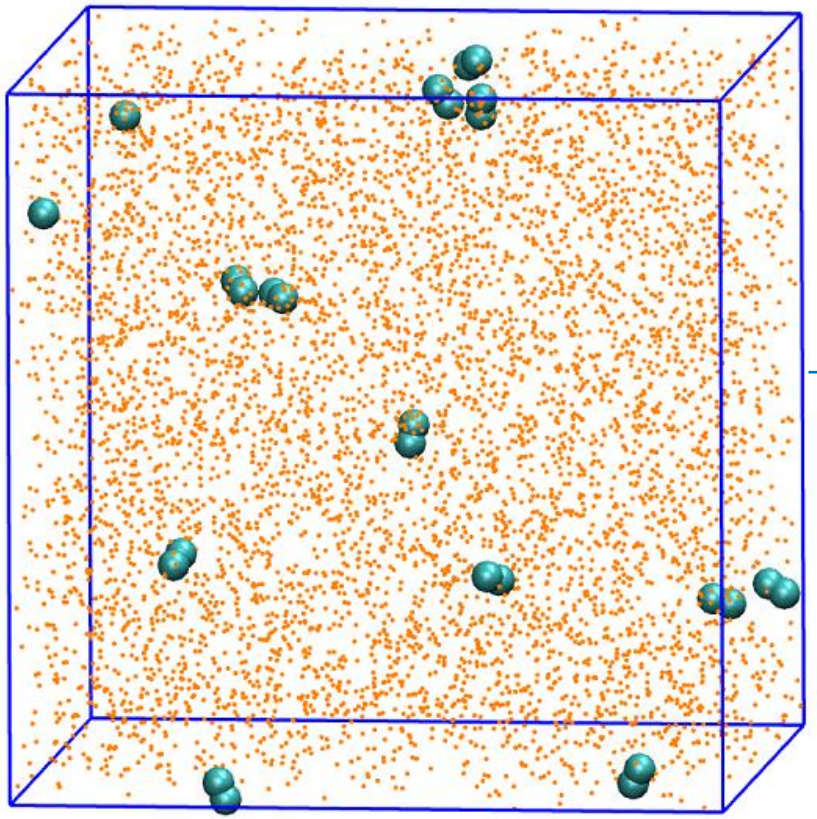


SPCE model[1]

O_2



Monticelli model[2]



1ns NPT equilibration → 200ns NVT production run

1. Berendsen, Herman JC, J. Raul Grigera, and Tjerk P. Straatsma. Journal of Physical Chemistry 91.24 (1987): 6269-6271
2. Javanainen, Matti, Ilpo Vattulainen, and Luca Monticelli. The Journal of Physical Chemistry B 121.3 (2017): 518-528.

Post-Simulation Analysis

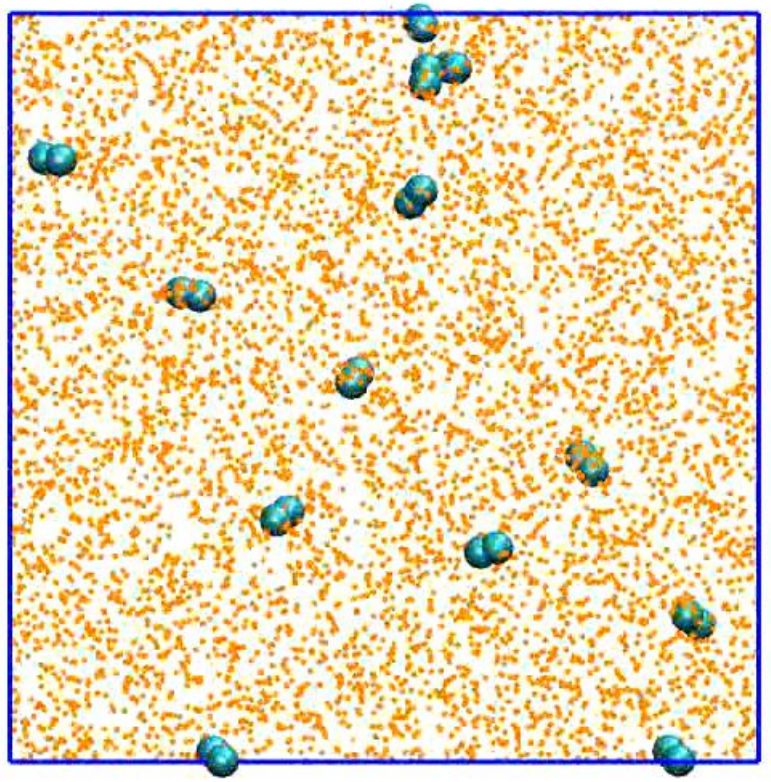
`MDAnalysis.analysis.msd`

class `MDAnalysis.analysis.msd.EinsteinMSD`

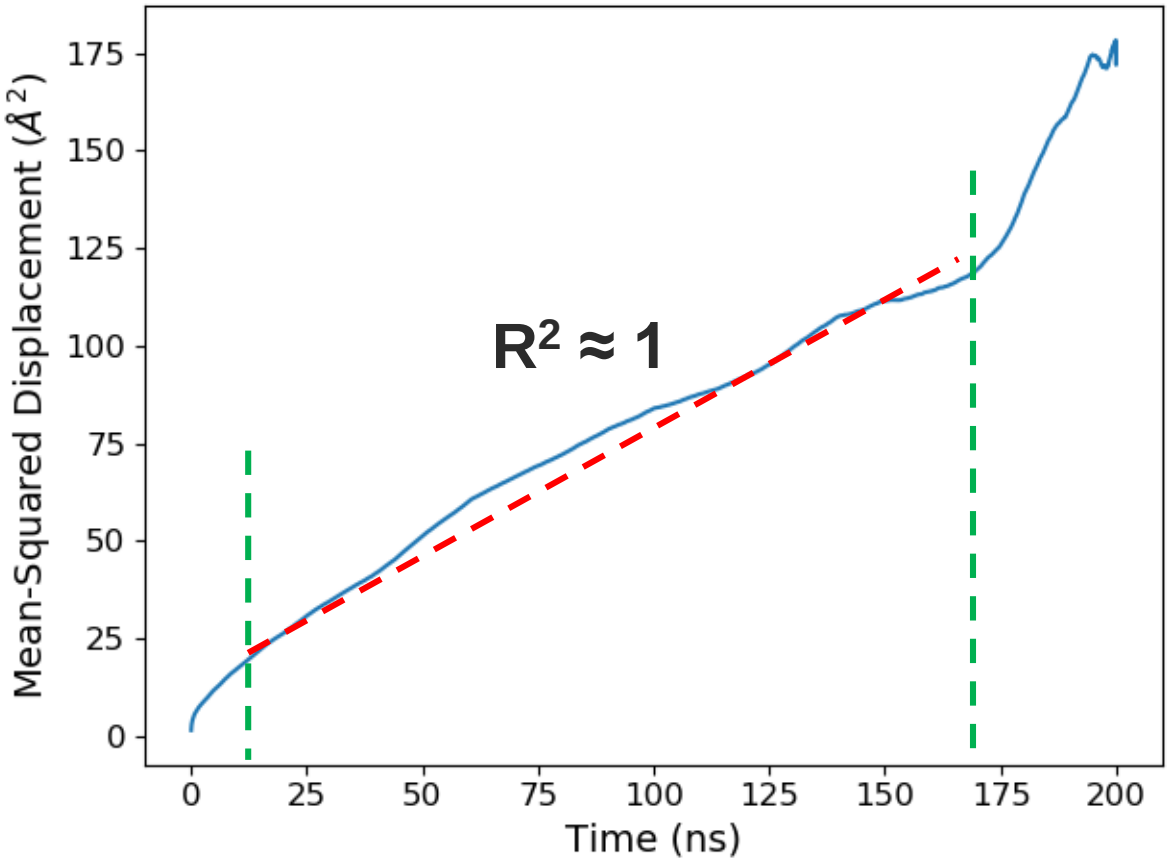
Mean squared displacement:

$$MSD(r_d) = \left\langle \frac{1}{N} \sum_{i=1}^{N} |r_d - r_d(t_0)|^2 \right\rangle_{t_0}$$

r = coordinates
d = dimensionality
N = number of atoms
$\langle \rangle_{t0}$ = average over time origins



Post-Simulation Analysis



$$MSD(r_d) = \left\langle \frac{1}{N} \sum_{i=1}^{N} |r_d - r_d(t_0)|^2 \right\rangle_{t_0}$$

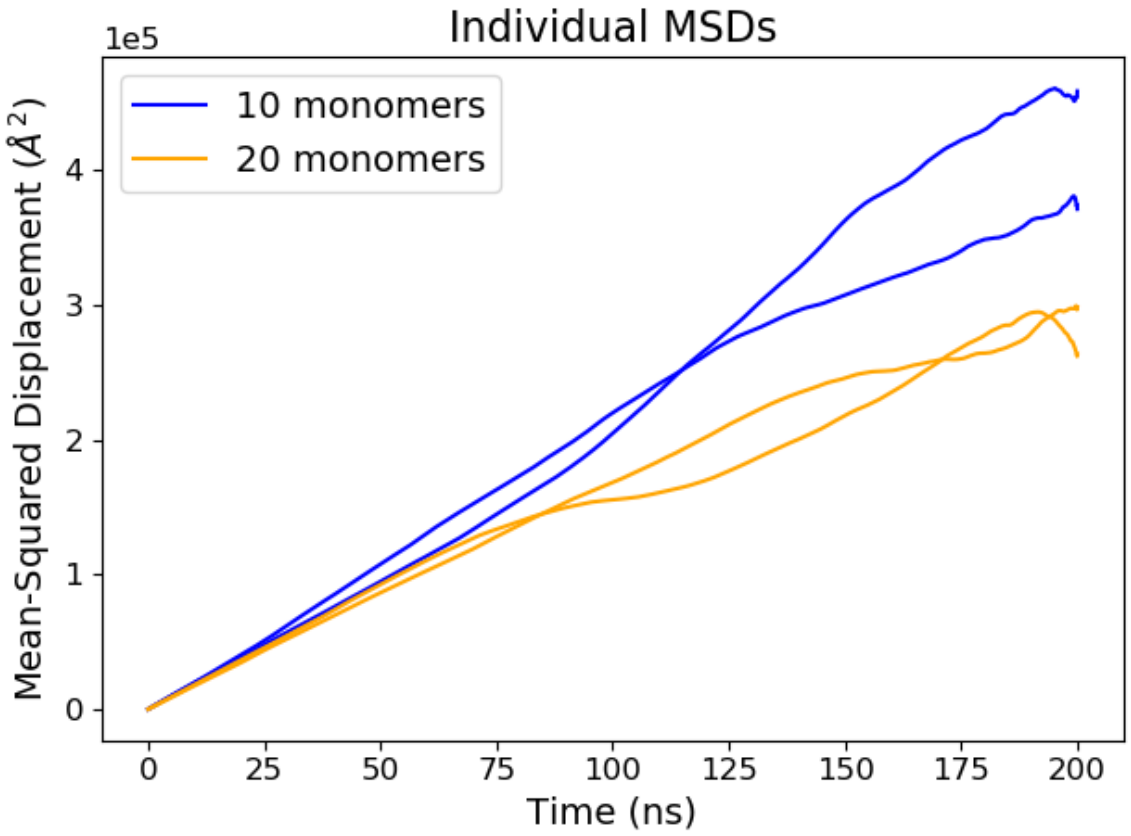
from scipy.stats import **linregress**

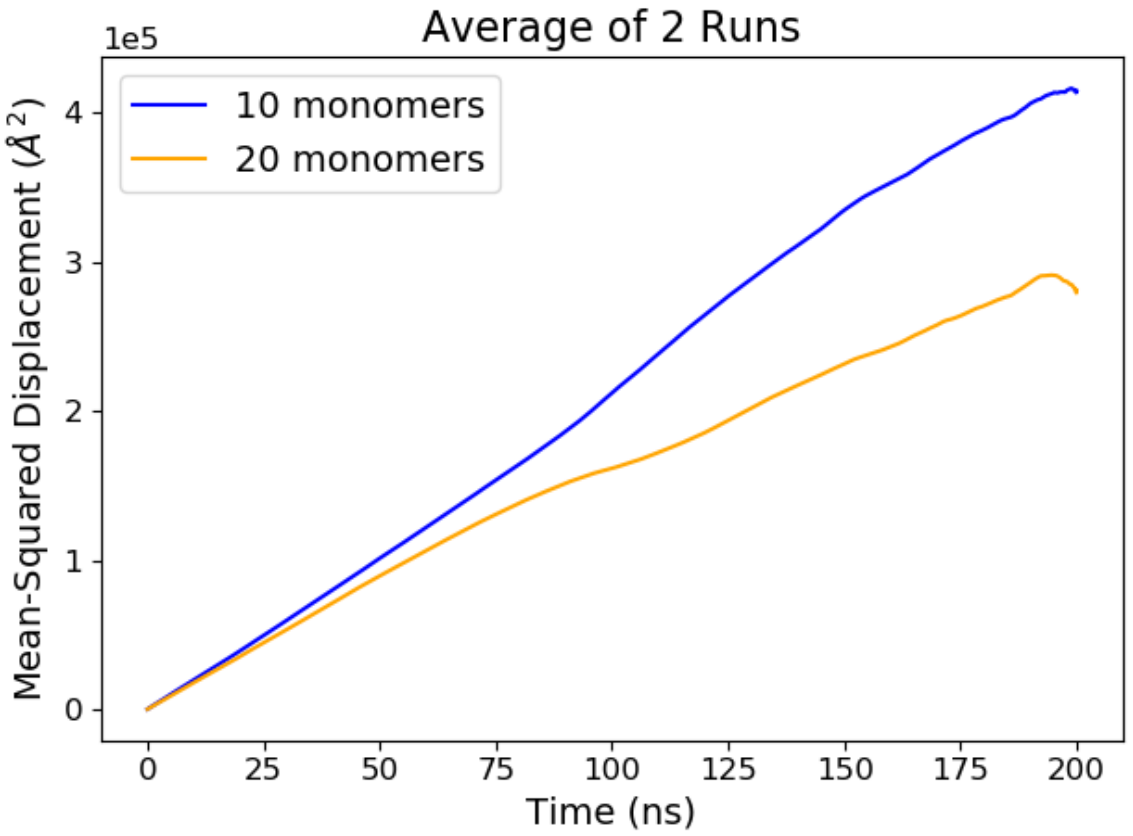
Linear regression model used to calculate diffusion coefficient (D)

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} MSD(r_d)$$

Einstein diffusion regime when R^2 and log-log slope ≈ 1

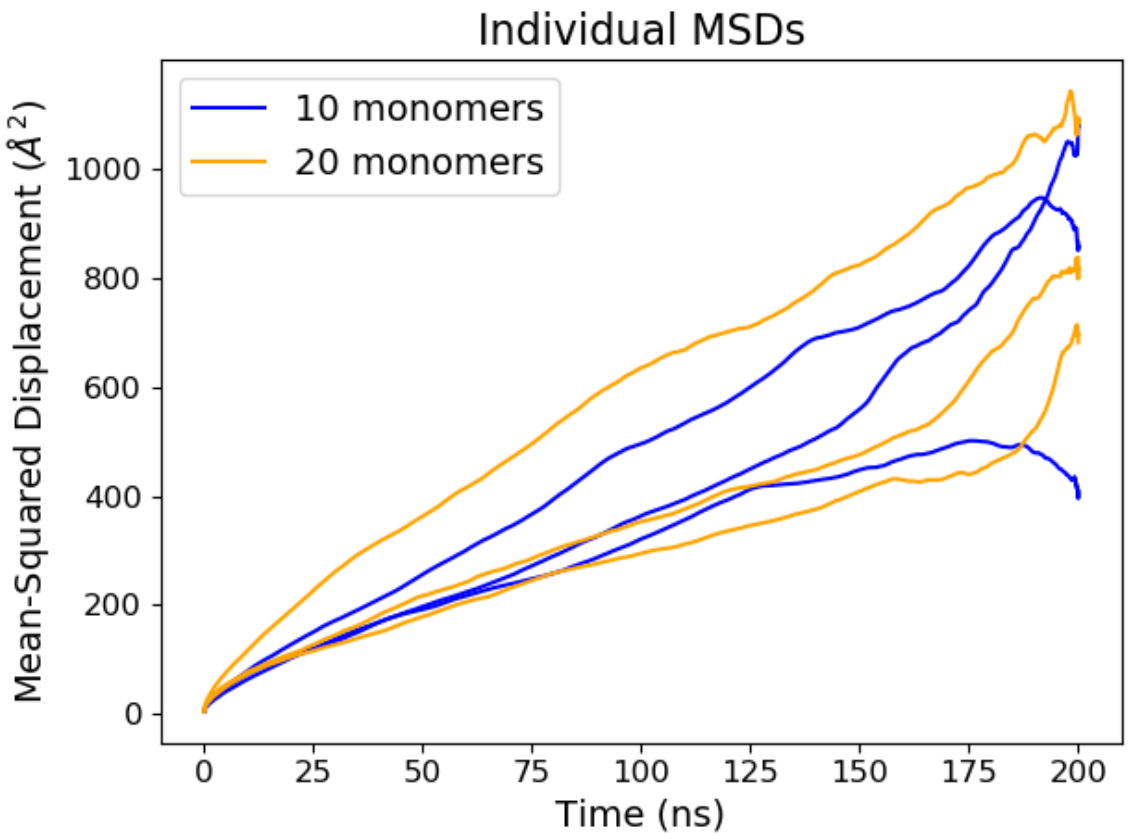
Oxygen Diffusion at 500K

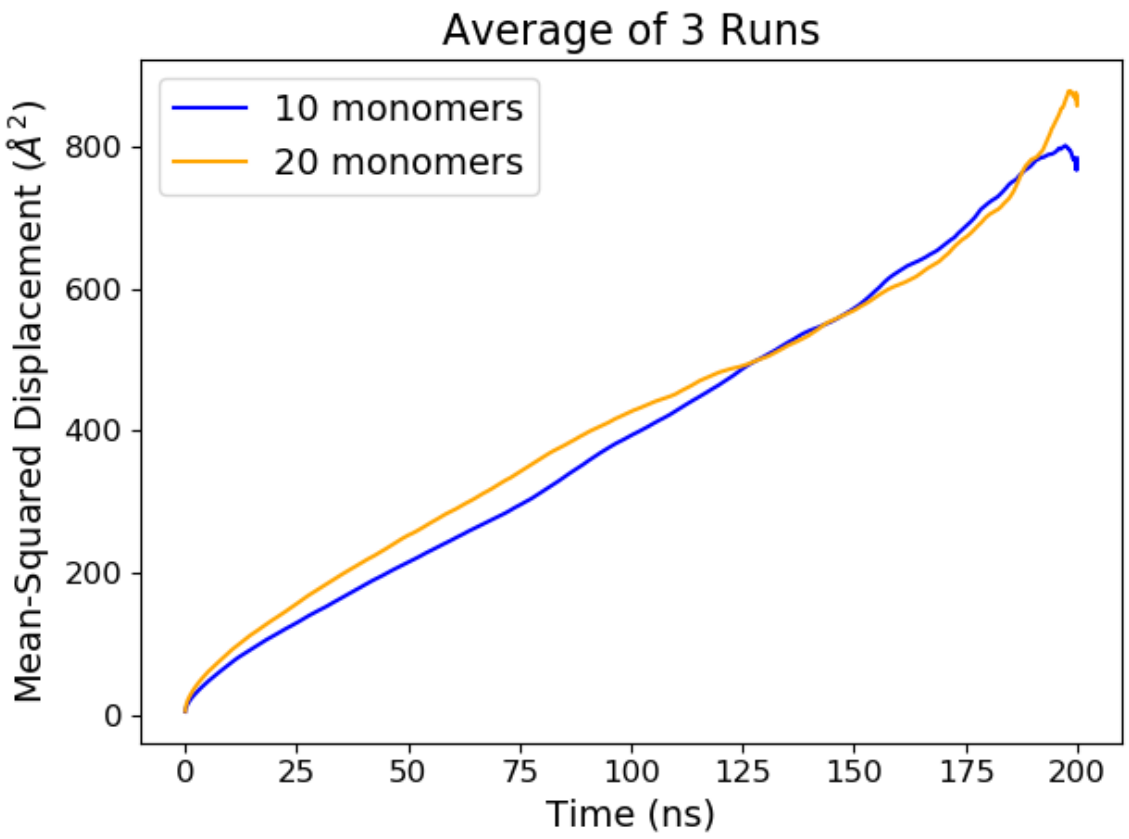




Oxygen diffuses more in 10 monomer system due to chain relaxation timescales

Oxygen Diffusion at 300K

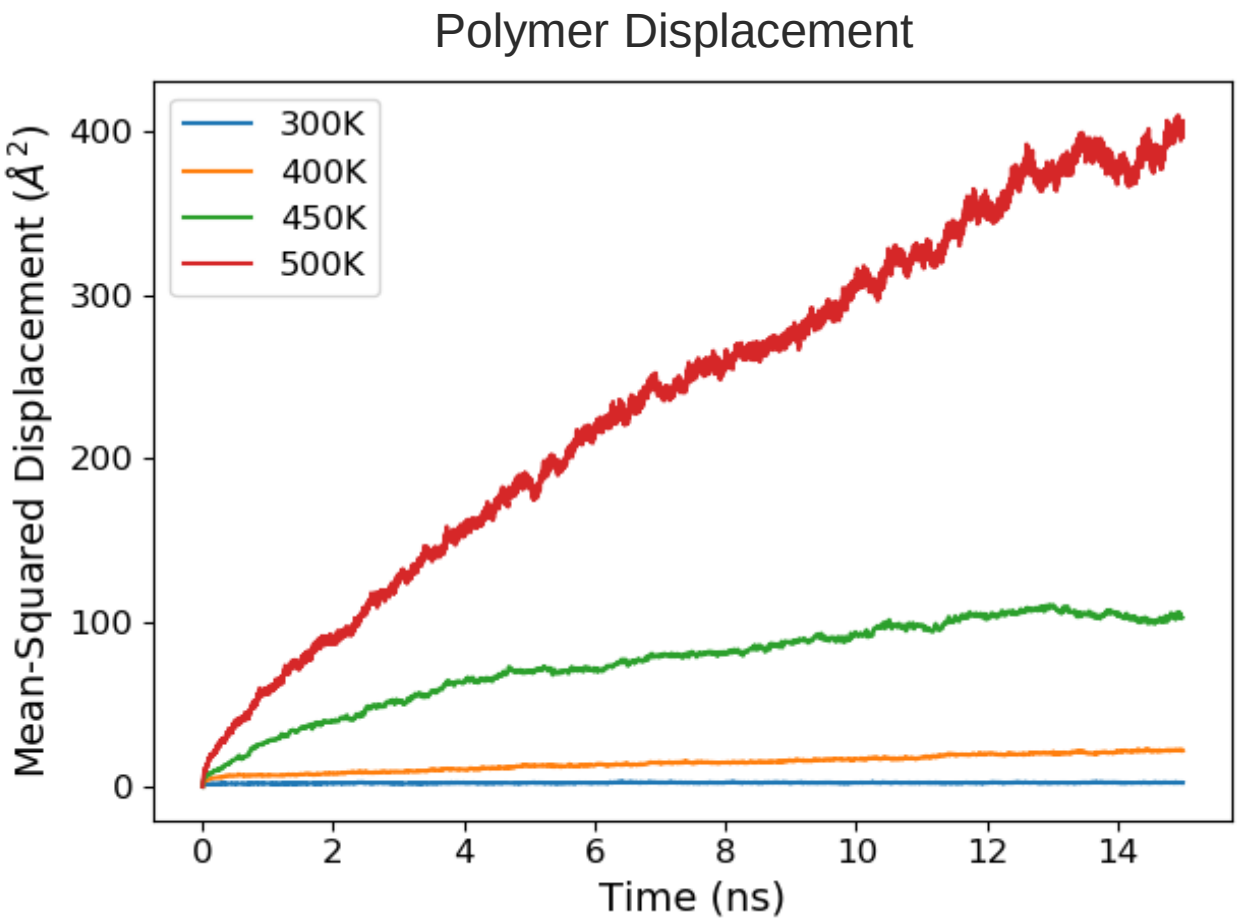




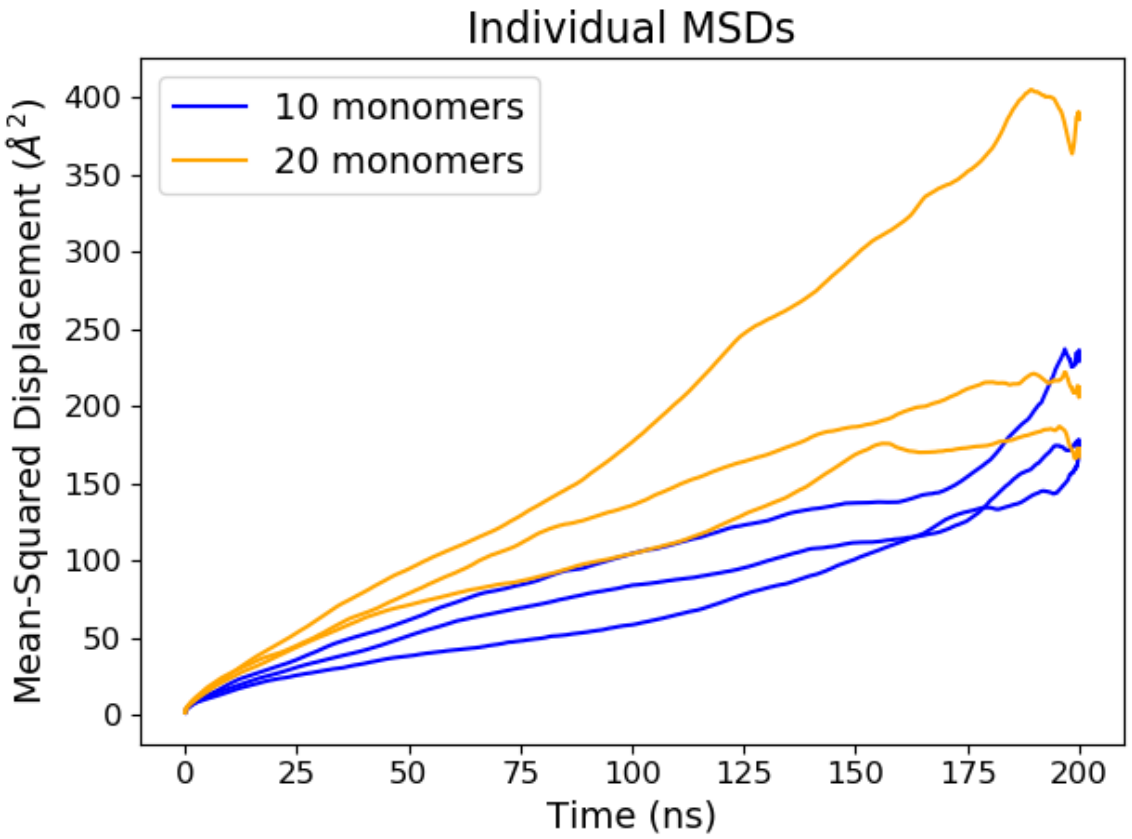
At 300K diffusion is limited by polymer chain mobility

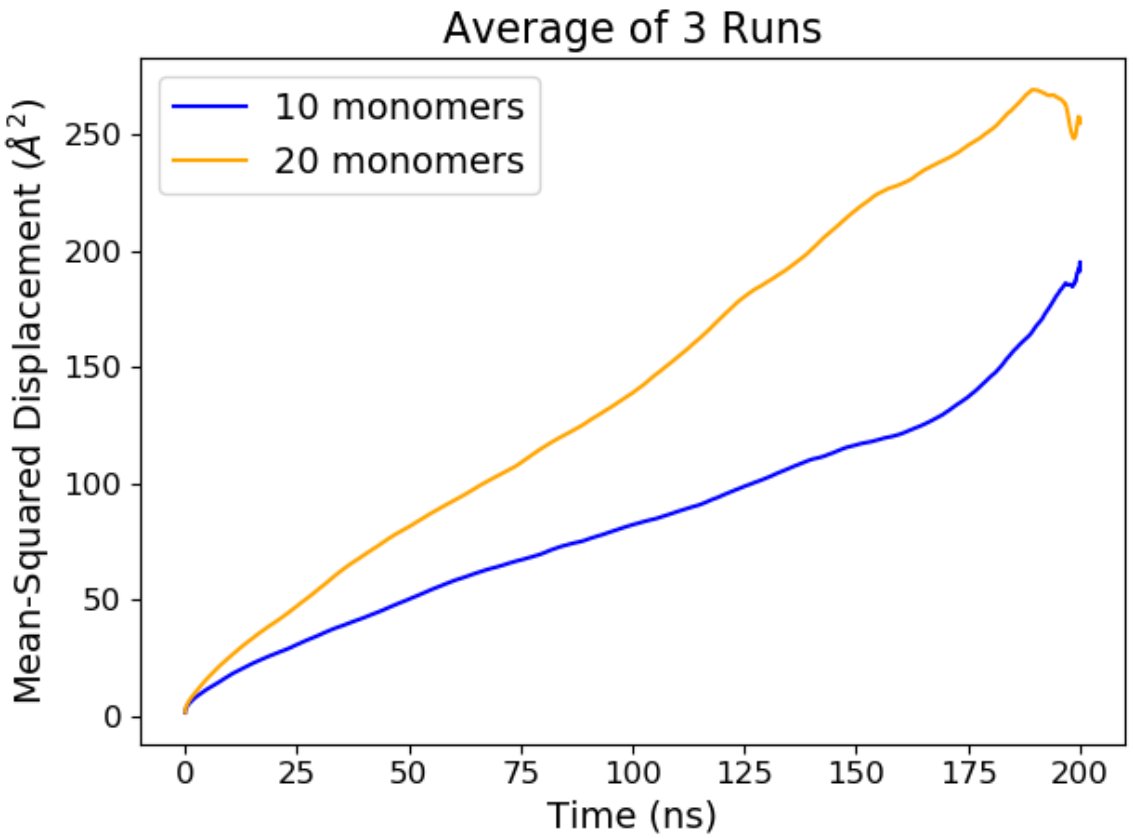
Polymer Chain Mobility

- Higher D values at higher temperatures due to increased polymer chain mobility
- At 300K PHB model is **below** glass transition temperature



Water Diffusion at 300K

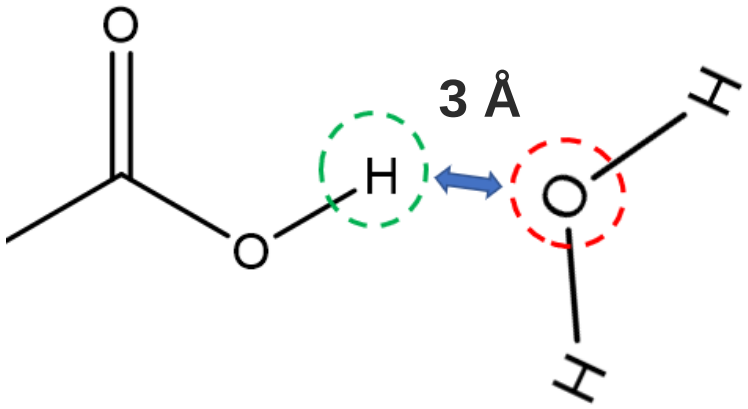


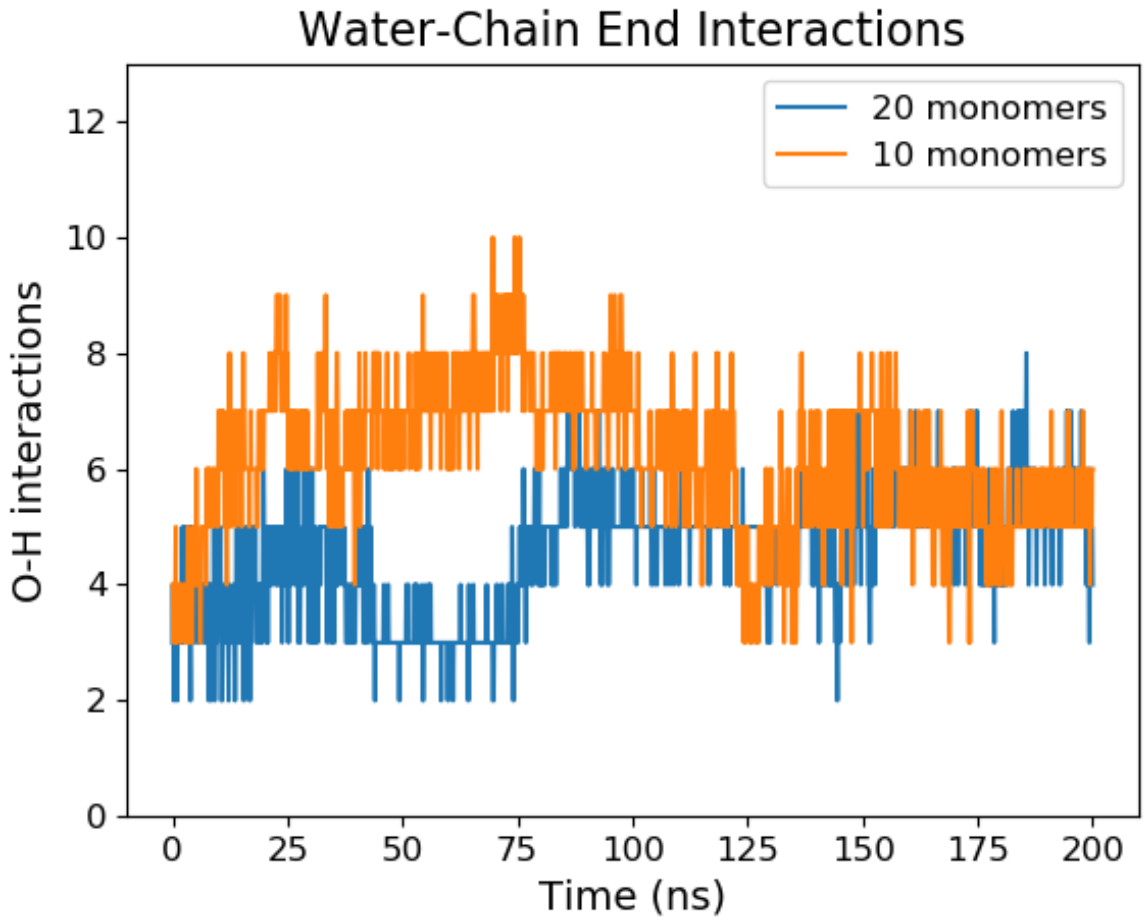


Water diffusion is slower in 10 monomer system

Effect of Chain Ends

- D_{water} lower for 10 monomer chain due to interactions with polar chain ends
- $D_{oxygen} > D_{water}$ since oxygen is non-polar





Diffusion Coefficient

Permeant	System	Temp (K)	D (cm^2/s)
Oxygen	10 monomers	500	3.76×10^{-5}
	20 monomers	500	2.46×10^{-5}
	10 monomers	300	6.05×10^{-8}
	20 monomers	300	5.45×10^{-8}
	Experimental[1]	296	5.26×10^{-8}
Water	10 monomers	300	1.11×10^{-8}
	20 monomers	300	2.23×10^{-8}
	Experimental[1]	298	2.17×10^{-8}

accuracy ± 0.4%

- D values in agreement with experiment
- Higher D at 500K due to polymer chain mobility
- $D_{oxygen} > D_{water}$; PHB stronger barrier against water

1. Follain, Nadege, et al. The Journal of Physical Chemistry C 118.12 (2014): 6165-6177.

Comparison to Other Polymers

	D_{water} ($x10^{-8}$ cm^2/s)	D_{oxygen} ($x10^{-8}$ cm^2/s)
PHB	2.23	5.45
PLA[1, 2]	6.61	7.6
PET[3, 4]	0.85	1.16

PLA = bioderived & biodegradable
PET = petrochemically derived & non-biodegradable

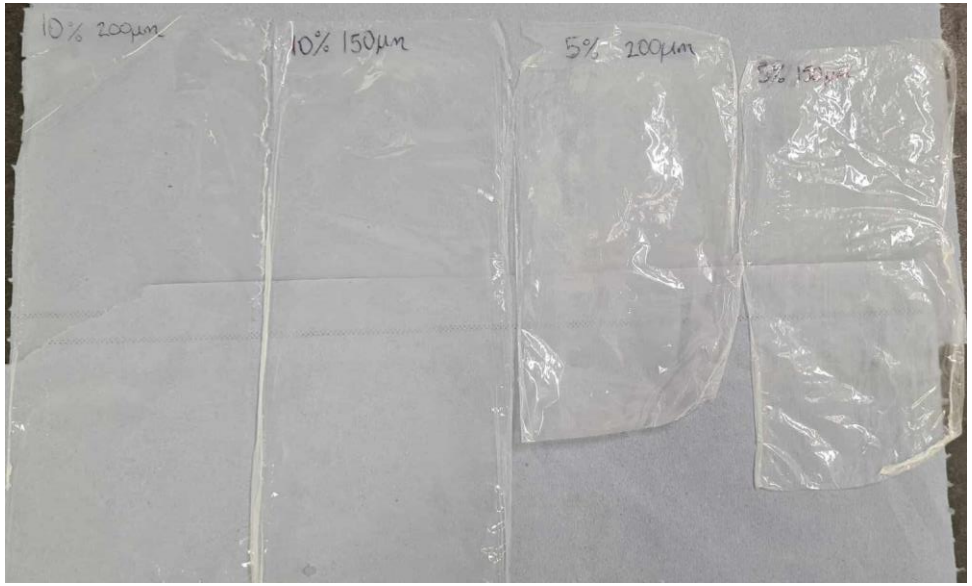
1. Yoon, Jin-San, et al. Journal of applied polymer science 77.8 (2000): 1716-1722.
2. Bao, Lihong, et al. Journal of membrane science 285.1-2 (2006): 166-172.
3. Sammon, C., J. Yarwood, and N. Everall. Polymer 41.7 (2000): 2521-2534
4. Lightfoot, Jasmine C., et al *Macromolecules* 55.2 (2021): 498-510

Conclusions

- Permeant polarity and polymer chain mobility determine diffusion properties
- Diffusion coefficients from simulations are in agreement with experimental values
- PHB is a stronger barrier against water than oxygen
- Barrier properties of PHB make it a promising candidate for food packaging applications

Future Work

- Further analysis of H_2O and O_2 interaction with PHB
- Investigate mechanical properties and crystallinity of PHB films
- Measure barrier properties using a permeation cell with H_2O and O_2
- Study effect of filler particles and plasticisers



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