

¹Department of Bioengineering, Rice University

Archit A. Chabbi ¹ María Ley Flores ² Juan J. de Pablo ^{2,3}

²Pritzker School of Molecular Engineering, The University of Chicago

³Materials Science Division, Argonne National Laboratory

Background

Polyolefin-like Polymers

Polyolefins, particularly **polyethylene**, are polymers used in **consumer plastics** (Figure 1) [1].

- Used to produce packaging film, grocery bags, food containers, etc.
- Known for having highly favorable physical properties and low-cost production

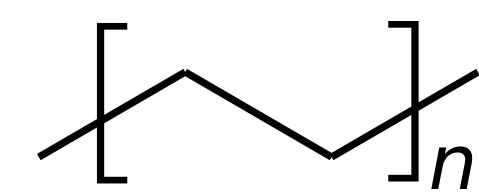


Figure 1. Chemical structure of polyethylene.

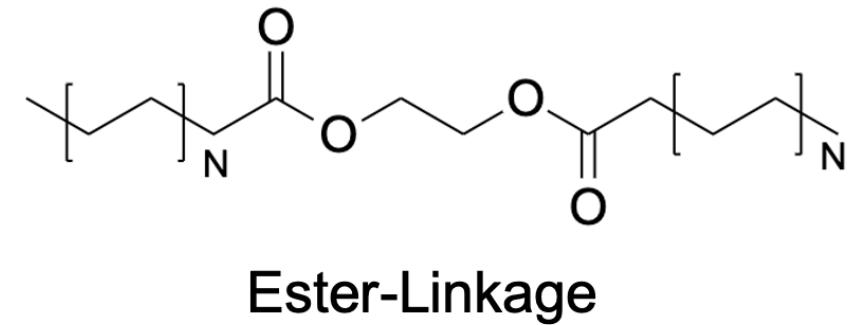
However, polyolefins contribute to the largest fraction of **global plastic waste generation**.

- Current recycling efforts are largely **mechanical** and inefficient
- Chemical recycling** has potential, but is currently **ineffective** due to the **high energetic cost** of breaking down the **carbon-carbon σ bond**

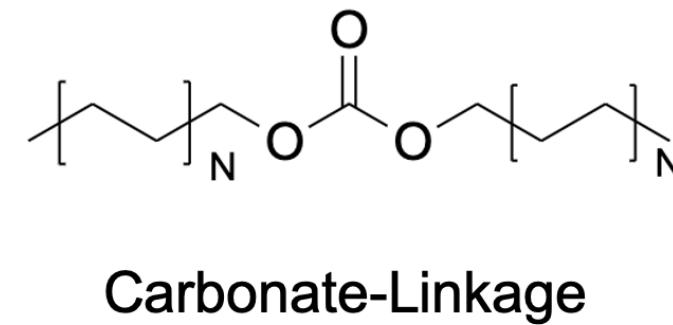
Insertion of Cleavable-Moieties into Polyethylene

Incorporating **chemically active functional groups** into polyethylene chains will lower the energy barrier for degradation via **glycolysis** or **hydrolysis**.

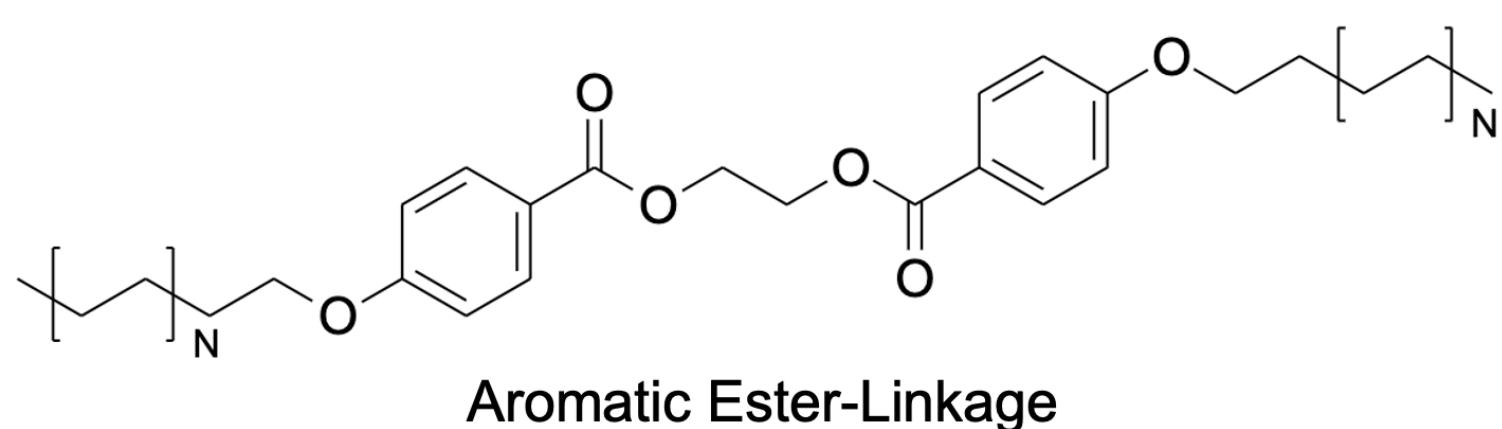
- Groups of interest are **ester**, **aromatic-ester**, **anhydride**, and **carbonate** linkages (Figure 2)
- Thermophysical properties** of these candidate polymers can be evaluated against those of commercial polyethylene as potential **alternatives**



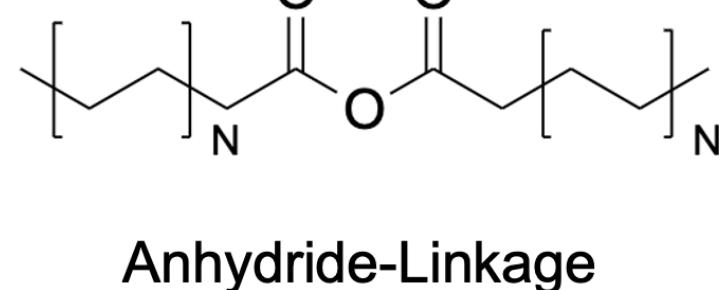
Ester-Linkage



Carbonate-Linkage



Aromatic Ester-Linkage



Anhydride-Linkage

Figure 2. Polyethylene chains featuring cleavable bonds inserted in the middle of the backbone.

Molecular Dynamics Simulations

Molecular dynamics (MD) simulations are a **computational method** of analyzing the movement of particles in a system over time ⇒ **faster** and more **efficient** than physical experimentation.

MD simulations calculate the forces acting on each atom according to a **force field** and solve **Newton's equations of motion** numerically (Figure 3).

$$E_{total} = \sum_{bonds} K_r(r - r_{eq})^2 + \sum_{angles} K_\theta(\theta - \theta_{eq})^2 + \sum_{torsions} \left\{ \frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)] \right\} + \sum_{vdW} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{ele} \frac{q_i q_j e^2}{r_{ij}}$$

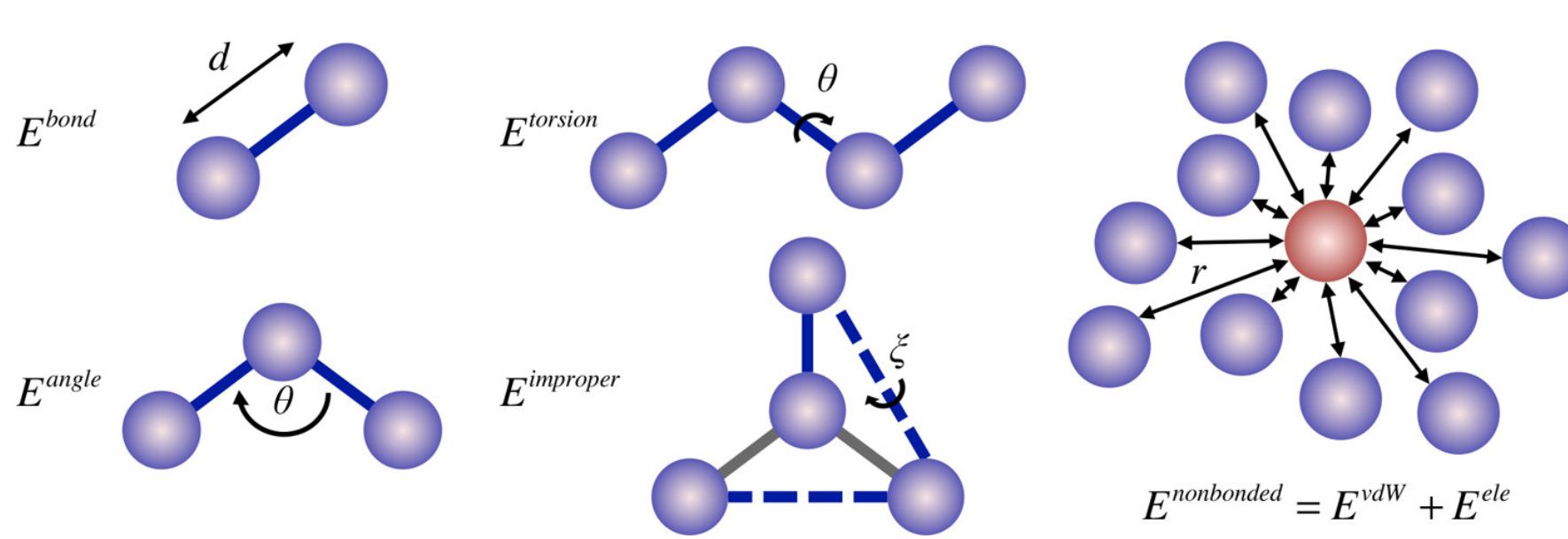


Figure 3. (Top) The **OPLS** force field potential energy equation used in this work [2]. Forces are calculated from the derivative of the potential: $\vec{F} = -\frac{\partial E}{\partial \vec{r}}$. (Bottom) Schematic illustrating the force field parameters.

This study utilizes a **united-atom representation**, where hydrogen atoms are incorporated implicitly within the carbon atoms.

Objective

The objective of this study is to **develop structure-property relationships** of polyethylene chains containing **cleavable bonds** via MD simulations.

The MD simulation data will then be used to **train machine learning models** that can **predict the thermophysical properties** of different configurations of these polymers.

Methods

1. Generate molecule topologies

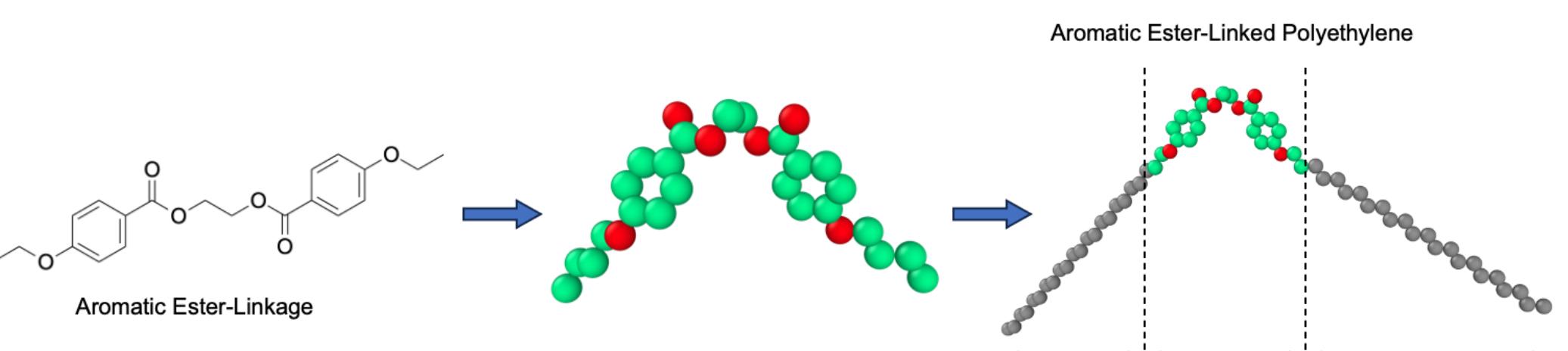


Figure 4. Topology generation of a chain with an aromatic-ester linkage inserted into a polyethylene backbone.

2. Insert molecules into simulation box and minimize energy

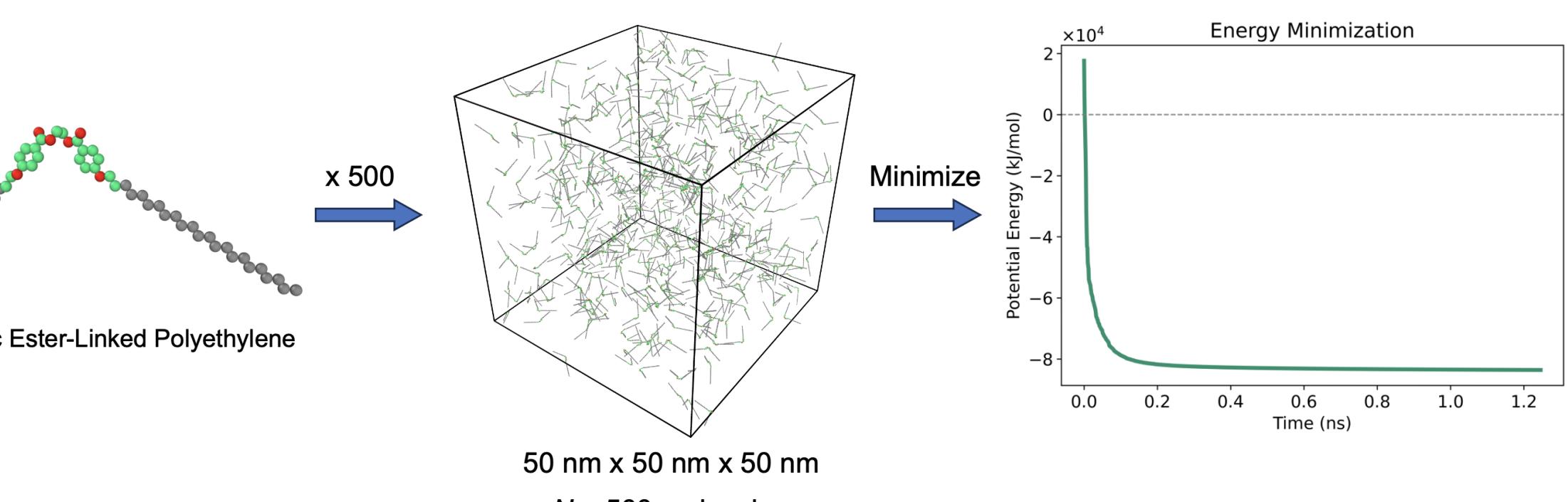


Figure 5. Molecules are first inserted into simulation box. System energy is then minimized to reach lowest energy state.

3. Run simulations and compute thermophysical properties of system

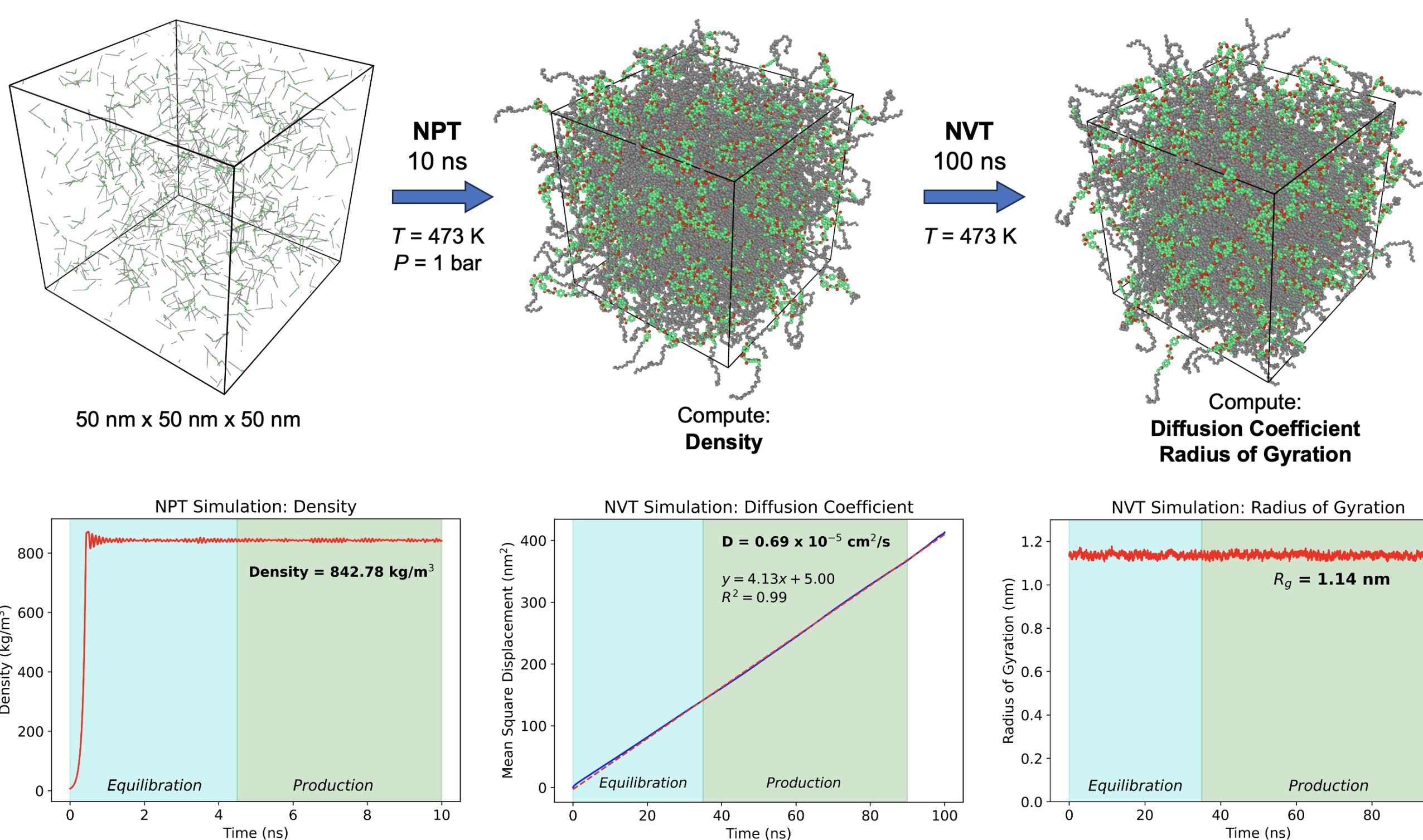


Figure 6. (Top) System is first simulated with an NPT (constant pressure and temperature) ensemble, followed by an NVT (constant volume and temperature) ensemble. (Bottom) **Density** is computed during the NPT run after system is equilibrated. **Diffusion coefficient D** is computed during the NVT run using linear regression of **MSD** with the Einstein relation: $MSD \equiv \langle |x(t) - x(0)|^2 \rangle = 6Dt$. The **radius of gyration R_g** is also computed during the NVT run.

4. Train Gaussian process regression models with simulation data

Gaussian process regression (GPR) is a non-parametric, supervised machine learning model.

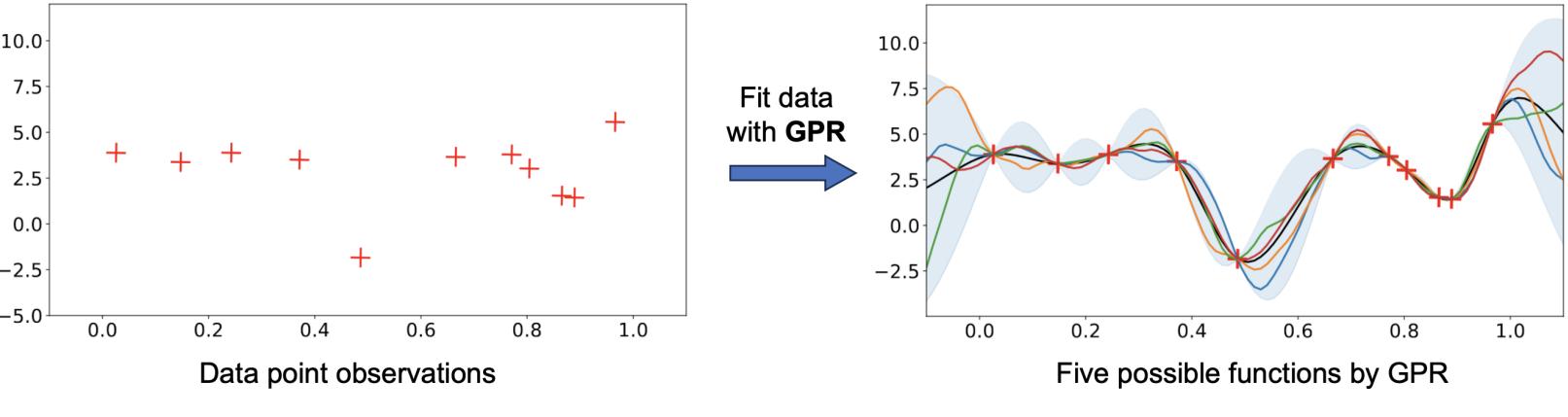


Figure 7. A regression example. (Left) Observed data points. (Right) Five sample functions that fit the data.

Results

MD Simulation Data

Simulations were run for all linkages from 20-200 backbone atoms at temperatures of 373-573 K.

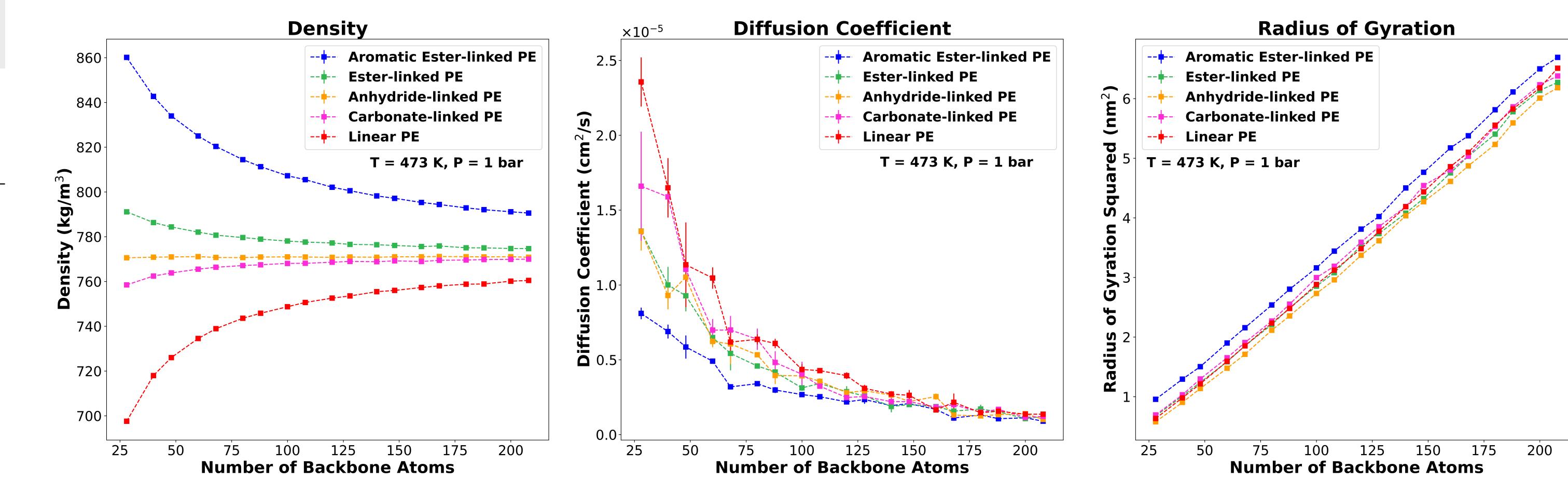


Figure 8. Data for all functional groups at $T = 473$ K and $P = 1$ bar. Properties were compared to those of polyethylene.

Gaussian Process Regression

1-D GPR was performed at a given **fixed temperature** to predict properties given chain length. 2-D GPR was performed for **all linkage types** to predict properties given **chain length and temperature** (Table 1). Figure 9 displays GPR results for predicting **diffusion coefficients** of the **ester-linked PE**.

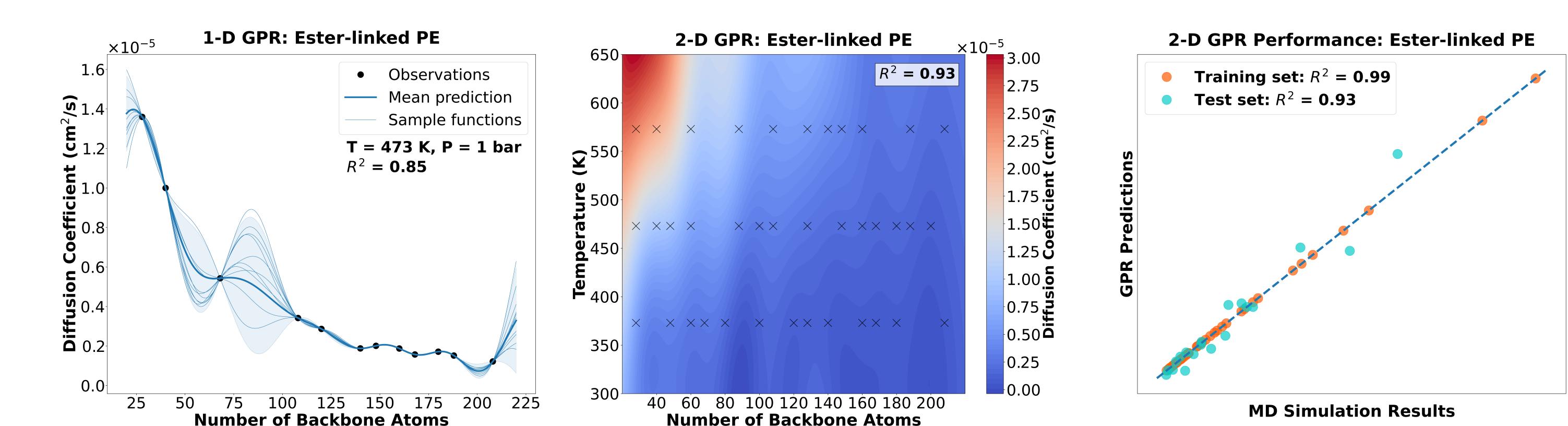


Figure 9. Subset of GPR results. (Left) 1-D GPR at fixed temperature. Highlighted regions indicate uncertainty levels in prediction. (Middle) 2-D GPR results (uncertainty not shown). (Right) Performance results of 2-D GPR model.

Property	Ester	Aromatic-Ester	Anhydride	Carbonate
Density	0.99	0.96	0.97	0.95
Diffusion Coefficient	0.93	0.91	0.92	0.89
Radius of Gyration	0.99	0.98	0.98	0.99

Table 1. R^2 values of all trained 2-D GPR models in this study. All linkage types and properties were evaluated.

Discussion

- Thermophysical properties of polyethylene chains linked with cleavable bonds **closely mimic** those of **linear polyethylene**
- Gaussian process regression has **high predictive capacity** for **modeling the relationship** between molecule configurations and properties

References

- R. Geyer, J. R. Jambeck, and K. L. Law, "Production, use, and fate of all plastics ever made," *Science Advances*, vol. 3, no. 7, 2017.
- W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, "Development and testing of the opls all-atom force field on conformational energetics and properties of organic liquids," *Journal of the American Chemical Society*, vol. 118, no. 45, pp. 11225–11236, 1996.

Acknowledgments

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