Goal Gaussian multi-pole (GMP) featurization schemes combined with neural network (NN) regression has recently been demonstrated to yield descriptor sets capable of producing efficient, accurate, and transferable reactive force fields for Density Functional Theory (DFT) calculations that can be scaled to many element systems and long times [1, 2]. These results indicate that GMP—NN based simulations could be used to model reactive polymeric systems which are inherently large from an atomistic perspective and vary wildly in terms of elemental composition (excluding the carbon backbone) and structure.

Aim 1 Establish that previously described methodology for GMP—NN based simulations can be used to accurately predict the behavior of polymeric systems for physically relevant reaction schemes and time scales. The existing mathematical framework for generating GMP based featurization schemes will be employed to describe the local electronic environment of each atom in polymer chains of various molecular weights. Simulations will be built around GMP based descriptors to model the dynamic behavior of polymer chains over varying time scales. The performance and accuracy of these simulations will be assessed by comparing the results to existing molecular dynamics or solution state theory based simulations. This strategy will be extended to model reactive systems, namely well characterized light sensitive polymers. The simulations will capture the behavior of the polymeric system as it undergoes light induced depolymerization. This effort will *simultaneously* capture the energetics of various transition states and the dynamic conformational behavior of the polymer system as it depolymerizes. These results can be evaluated in the context of the published experimental results [3].

Aim 2 Incorporate GMP—NN featurization code into the existing SPARC environment to optimize solution procedure and enable deployment. The recently published SPARC simulation package for ab-initio real-space calculations can run DFT calculations for large systems (100-500 atoms) in just a few seconds which represents an order of magnitude improvement versus state-of-the-art DFT codes [4]. Interfacing the GMP—NN based featurization code with the SPARC code would augment the strengths of each approach by further enhancing the efficiency and scalability of DFT calculations run in this environment without sacrificing accuracy. This would also confer the added benefit of making the GMP—NN code distributable since the SPARC simulation package is an open-source tool.

Aim 3 Demonstrate that the GMP—NN based polymeric simulation results can predict experimental behavior. Polyethylene (PE) chain fragments (MW < 30 kg/mol) interspersed with stimuli responsive monomer will be modeled using the methods and tools outlined in Aim 1 and Aim 2. A variety of stimuli responsive monomers will be screened for their ability to initiate depolymerization of PE at various positions along the chain. The time scale of the simulation will extend beyond the time scale of depolymerization to assess the probable end state of the various PE chain fragments. A collaborator will deliver experimental results which can be used to validate the GMP—NN based approach's ability to accurately assess end states for reactive polymeric systems.

Impact DFT is an established and powerful research tool that has been employed in the fields of chemistry, material science, and biology among others to provide mechanistic insight to chemical processes at an atomic level of detail. Unfortunately, it can be prohibitively complex or computationally expensive to use DFT to model large, heterogenous atomistic systems. These limitations can be overcome by the incorporation of universally applicable featurization schemes such as the GMP—NN based approach laid out in recent publications [1, 2]. This allows researchers to peek behind what was previously a steel curtain to gain insights into the behavior of larger systems or longer time scales. The proposed work could shift the paradigm for atomistic simulations as it has the potential to i) demonstrate the ability of GMP—NN based DFT simulations to model large systems with previously unattainable levels of chemical fidelity and ii) translate these in silico results to tangible improvements in sustainable polymer chemistry. **References** 1) Lei, X. and A.J. Medford, Physical Review Materials, 2019 2) Lei, X. and A.J. Medford, 2021. 3) Phillips, O., et al., Journal of applied polymer science, 2019 4) Xu, Q., et al., 2021.