Atomistic and Mesoscopic Modeling of Structure-Property Relations in Polymers

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Molecular-based approaches for understanding and tailoring structure-property-processing relations in materials, based on the fundamental principles of quantum and statistical mechanics, have gained ground in academic research and industrial practice. The broad spectra of length and time scales governing structure and dynamics in real-life materials have demanded the advancement of multiscale modeling strategies, involving several levels of representation, to bridge atomistic constitution and interactions with macroscopic properties.

We will discuss three examples of molecular modeling of structure-property relations in polymeric materials: (a) prediction of linear and nonlinear rheological properties of high-molecular weight polymer melts, such as polyethylene and cis-1,4 polyisoprene, through hybrid particle-field mesoscopic simulations employing slip-springs to represent entanglements and parameterized on the basis of atomistic calculations[1),2)]; (b) tracking structural relaxation in polymer glasses, such as polystyrene, as a sequence of elementary transitions between basins on their energy hypersurface, with transition rate constants computed from atomistic infrequent-event analysis[3)]; (c) quantifying the morphology developing upon crystallization of polyethylene films formed from the melt through the Machine Direction Orientation process[4)]. In each example we will outline how scale-hopping algorithms can be devised, based on rigorous statistical mechanical principles, to meet the challenges of long time and length scales in polymers in a computationally tractable way. The computational results lead to property predictions that are validated by available experimental measurements and elucidate molecular-level processes that are critical to materials design.

References

1) Sgouros, A.P.; Megariotis, G.; Theodorou, D.N. *Macromolecules* **2017**, *50*, 4524.

2) Vogiatzis, G.G.; Megariotis, G.; Theodorou, D.N. *Macromolecules* **2017**, *50*, 3004-3029.

3) Vogiatzis, G.G.; van Breemen, L.C.A.; Hütter, M.; Theodorou, D.N. *Molec. Syst. Des. Eng.* **2023**, *8*, 1013-1029.

4) Anogiannakis, S.; Venetsanos, F.; Theodorou, D.N. *Macromolecules* **2024**, *57*, 7331-7346.