Interfacial Properties and Structure of Polymeric Blends and Solutions from Interfacial-SAFT (iSAFT) Density Functional Theory

A. Dominik^{S} and W.G. Chapman^{C}
Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX, U.S.A.
wgchap@rice.edu

Interfacial properties play an essential role in applications of great industrial importance, such as adhesion, polymer coating and thin films, paints, separations, catalysis, wettability and emulsions. This has motivated studies of complex macromolecular systems (hydrocarbons, proteins, polymers) in confined geometries, and at solid-fluid and fluid-fluid interfaces. As properties of complex chemical systems are being tailored at the nanoscale, a molecular level understanding of the interplay between interfacial properties, fluid structure, and macroscopic properties of the material is necessary. Experimental investigation of interfacial phenomena is hampered by the small scale of the systems. Molecular simulation provides an alternative to experimental techniques, but is computationally expensive, and thus often limited to short-chain molecules. Consequently, substantial efforts have been directed towards developing a theory for structure and thermodynamics of inhomogeneous polymeric solutions and blends

We have recently developed a new density functional theory (DFT) to describe phase behavior and microstructure of mixtures of polymeric fluids in inhomogeneous environments. The theory is based on Wertheim's thermodynamic perturbation theory for association; it treats the polyatomic system as a mixture of strongly associating monomers. The theory is formulated in terms of segment density; therefore it offers the simplicity and computational efficiency of an atomic DFT. This feature of iSAFT makes it best suited for modeling interfacial properties and structure of chains of several hundreds or even thousands of segments. We demonstrate the success of the theory in capturing the effects of size and shape of the fluid molecules and system parameters such as fluid-fluid and surface-fluid interaction strengths on fluid structure and interfacial properties. Our DFT shares a common basis with the Statistical Associating Fluid Theory (SAFT), one of the most accurate and widely used theories for bulk polymer solutions. This self-consistency of the bulk and interfacial models enables us to predict the interfacial properties of the considered systems with a set of molecular parameters obtained from the readily available bulk properties. We compare results from iSAFT to molecular simulations, as well as experimental data for interfacial tension and molecular structure of realistic systems comprising polymer melts, blends and solutions.