Chi Parameters from Simulations

Scott Milner [C, S]
Department of Chemical Engineering, The Pennsylvania State University, University Park, PA
stm9@psu.edu

The Flory–Huggins χ parameter describes the excess free energy of mixing and governs phase behavior for polymer blends and block copolymers. For chemically distinct nonpolar polymers, χ is dominated by mismatch in cohesive energy density. For chemically similar polymers, the entropic part of χ arising from non-ideal packing can be significant. To investigate this, we perform molecular dynamic (MD) simulations for bead-spring chains differing only in stiffness. Using thermodynamic integration, we extract χ as low as 10^{-4} per monomer, in good agreement with field-theory based predictions of Fredrickson et al. We also obtain χ for the archetypical coarse-grained model of enthalpic polymer blends: flexible bead-spring chains with different LJ interactions between A and B monomers. Using this χ and self-consistent field theory (SCFT), we predict the interfacial profile for phase-separated binary blends, in good agreement with MD simulations for immiscible blends. Applied to atomistic simulations, our method should be able to predict χ for new polymers from chemical structures.