A New SAFT-VR Mie Density Functional Theory for Predicting the Surface Tension and Interfacial Properties of Fluids of Chain Molecules

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A Helmholtz free energy density functional is developed to describe the vapor-liquid interface of molecular chains. The functional is based on the statistical associating fluid theory for variable range Mie potentials (SAFT-VR Mie). A standard perturbative density functional theory (DFT) is constructed by partitioning the free energy density into a reference term which incorporates all of the short-range interactions, and is treated locally, and an attractive perturbation which incorporates the long-range dispersion interactions. This new SAFT-VR Mie DFT formalism is used to examine the effect of molecular chain length on the surface tension of freely-jointed tangent Mie spheres, that is, bond distances are kept constant at a value equal to the diameter of the monomeric spheres forming the chains, with no further intramolecular interactions. The theory is validated against computer simulation results for Mie molecular chains made up to six Mie spherical units. We also use accurate coarse-grained (CG) force fields obtained for the successful SAFT-VR Mie formalism for selected substances of industrial interest, including water, carbon dioxide, and some alkanes, to predict the interfacial properties of these molecules. It is very gratifying that a DFT based on SAFT-VR Mie free energy, in combination with the use of coarse-grained intermolecular potentials, can provide an accurate quantitative description of the surface tension, not directly accessible from the equation of state, of both the model and experimental systems.