Molecular dynamics simulation study of the role of nanometer scale structure on interfacial energy

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Recent experiments have demonstrated that the interfacial energy of a surface consisting of domains commensurate in size with solvent molecules depends non-monotonically on its composition, which is in contrast to the prediction of the conventional continuum thermodynamic model. In order to obtain further insight into the role of nanometer scale structure on interfacial energy, we carried out molecular dynamics simulations of an aqueous solution of nano-particles with stripe-like, alternating hydrophilic and hydrophobic SAM domains, where the compositions and stripe widths resemble those in experiments. We find via simulation that as the width of the hydrophobic stripes decreases, water molecules more closely approach the hydrophobic domains, indicating a stronger cavitation effect, which reduces the work of adhesion. At the same time, as the width of the hydrophilic stripes increases, on average each ligand in the hydrophilic domains is able to make more hydrogen bonds with the surrounding water molecules, indicating an enhanced affinity of the hydrophilic domains for the solvent, which substantially increases the work of adhesion. Both effects depend on stripe width but oppose each other as the stripe width of the hydrophobic and hydrophilic domains changes. We conclude that the observed non-monotonic behavior of the work of adhesion and interfacial energy is due to the competition of these two effects combined with the complex way in which domain size in these types of mixed SAMs evolves with composition.