# Molecular Dynamics Simulation of Oxygen Diffusion through Self-assembled Monolayers

P. Srivastava[S] and W.G. Chapman
*Department of Chemical and Biomolecular Engineering, Rice University, Houston, U.S.A.*

P.E. Laibinis[C]
*Department of Chemical Engineering, Vanderbilt University, Nashville, TN, U.S.A.*
*paul.e.laibinis@vanderbilt.edu*

We have used molecular dynamics (MD) simulations to investigate the influence of molecular structure on the ability of various self-assembled monolayers (SAMs) to act as barrier films against through-film oxygen transport, as relevant to the use of these films in corrosion inhibition. Our motivation for this work comes from prior experiments performed using cyclic voltammetry and electrochemical impedance spectroscopy, that showed that the coating resistances of n-alkanethiolate (CnS) SAMs on copper increase dramatically with the chain length (n) of $n \geq 16$, and are negligible, in comparison, for $n \leq 12$. To gain insight into the structural features responsible for these observations, we performed MD simulations of oxygen transport across SAMs of different chain lengths, on gold and copper, using the "z-constraint algorithm". Our MD simulations reveal that, for increases in the thickness of these coatings by only a few angstroms in the transition region of $n \approx 16$, the free energy barrier towards oxygen transport increases by ~20 kJ/mol. The MD simulations also showed that the free volume alignment within these films has a huge impact on the diffusivities of oxygen through them. The barrier resistances offered by these films towards oxygen transport, as calculated by the MD simulations, were a function of the crystallinity of the center region of the SAMs. The lack of a crystalline region within SAMs for $n \leq 12$ and the growth of a crystalline region within the interior of SAMs for $n \geq 16$ appear most responsible for the experimentally observed trends.