Supporting Information: Improved Sampling in Ab Initio Free Energy Calculations of Biomolecules at Solid-Liquid Interfaces: Tight-Binding Assessment of Charged Amino Acids on TiO_2 Anatase (101)

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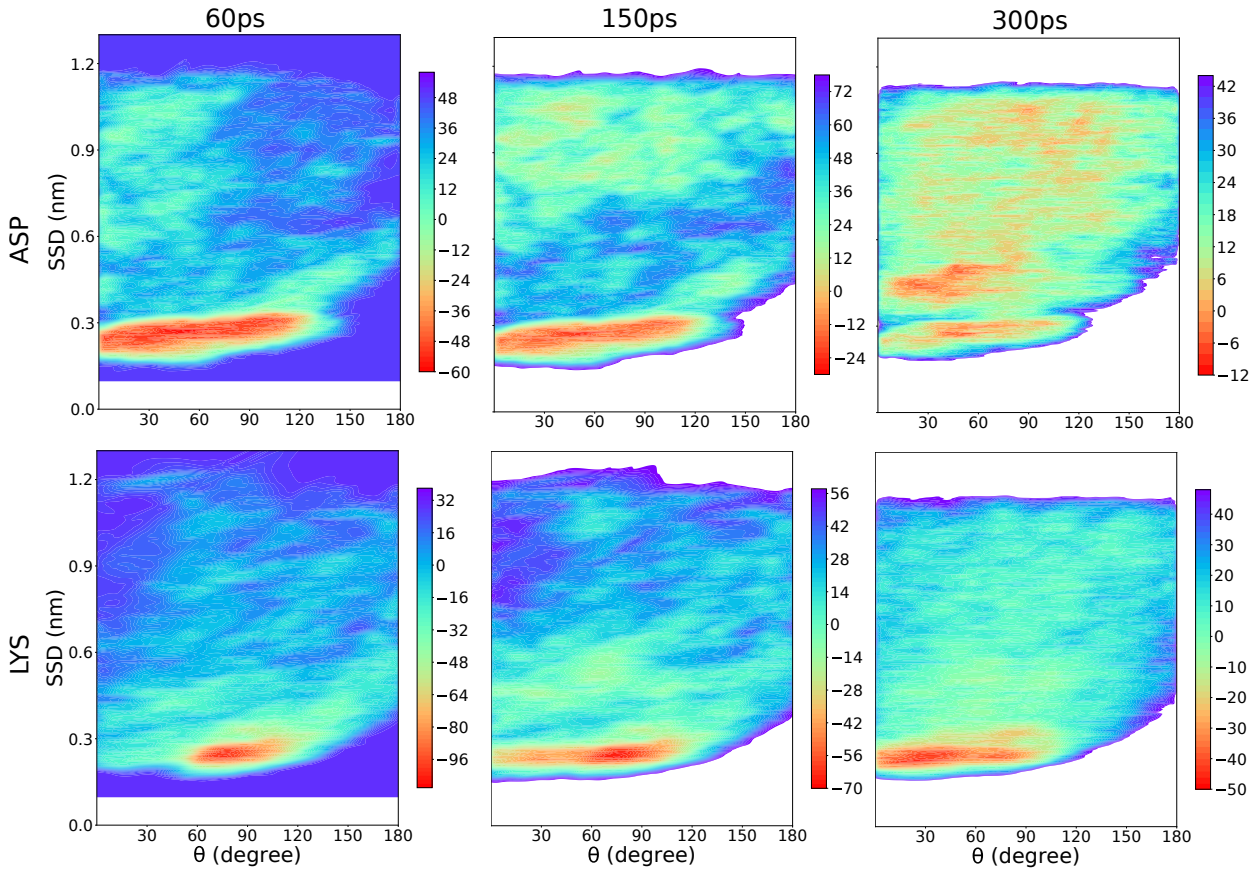

Figure S1. 2D histograms of the accumulated bias potential for the two CVs, SSD and θ, implemented in the Metadynamics simulation at different intervals of time. A single global minima is present for Lys and Asp as function of θ, thus the free energy profile is mostly driven by the SSD variable. Asp is more free to to span the rotational space once is it adsorbed while Lys presents a preferential orientation around $\theta = 30^o$ in the converged profile.

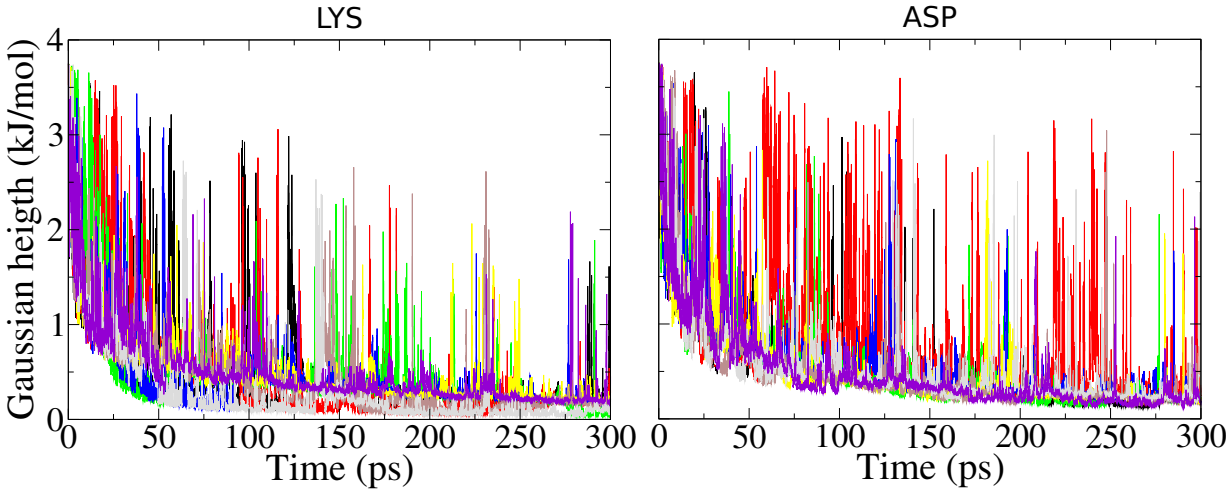

Figure S2. Variation of the Gaussians height driven by the bias factor during the Metadynamics simulation. The values for the 8 walkers are plotted for both Lys and Asp systems. Within 50 ps the starting value of 3.5 kJ/mol decays by 80% and it oscillates around a final values of 0.05 kJ/mol. The spikes represent the sampling of unexplored regions of the phase space.