

# Molecular origins of the zeta potential

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Non-equilibrium molecular dynamics simulations of electroosmotic flow between parallel slabs of the hydroxylated (110) rutile (TiO<sub>2</sub>) surface were utilized<sup>1</sup> to estimate aqueous solution streaming mobilities, which were converted to zeta-potentials via the commonly used Helmholtz-Smoluchowski equation. A range of rutile surface charge densities (0.1 to -0.4 C/m<sup>2</sup>), corresponding to pH values between about 2.8 and 9.4 in RbCl, NaCl, and SrCl<sub>2</sub> aqueous solutions, were modeled and compared to experimental zeta-potential data for TiO<sub>2</sub> particle suspensions. Simulated zeta-potentials are in accord with experimental values including changing from positive to negative values with increasing pH at all RbCl and low NaCl and SrCl<sub>2</sub> concentrations, and remaining positive at higher NaCl and SrCl<sub>2</sub> concentrations. We show that at the molecular-level the ZP arises from the delicate interplay of spatially-varying dynamics, structure and electrostatics in a narrow interfacial region within about 15 Å of the surface, even in dilute salt solutions. This contrasts fundamentally with continuum descriptions of such interfaces, which predict the ZP response region to be inversely related to ionic strength.

This study advances our previous works<sup>2-5</sup> on determination of properties at solid-liquid interfaces.

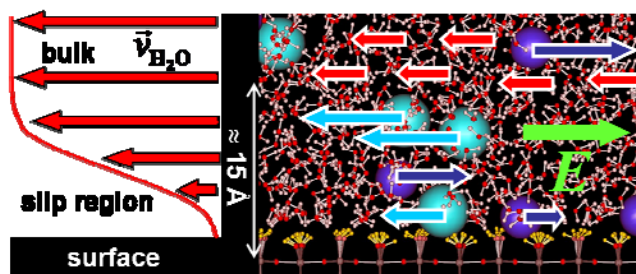


Figure 1: Schematic picture of the molecular origin of electro-osmotic velocity

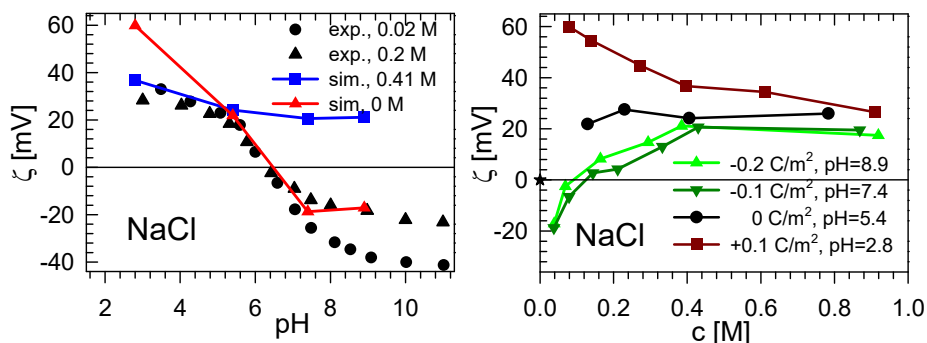


Figure 2: Zeta-potentials from NEMD simulations<sup>1</sup>. Reference experimental data for rutile in NaCl are given as black symbols.

## References

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