Numerical Modeling of Nanopipettes for Electrophysiology and Imaging

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Introduction: Pipettes are the gold standard in electrophysiology, and can image electrolyte-based systems. Numerical modeling of fluid flow through nanopipettes under varying conditions[1] and upon approach to surfaces[2] is well established. The present work builds upon these existing models by accounting for additional effects that become significant as pipette diameter shrinks further into the nanoscale regime.

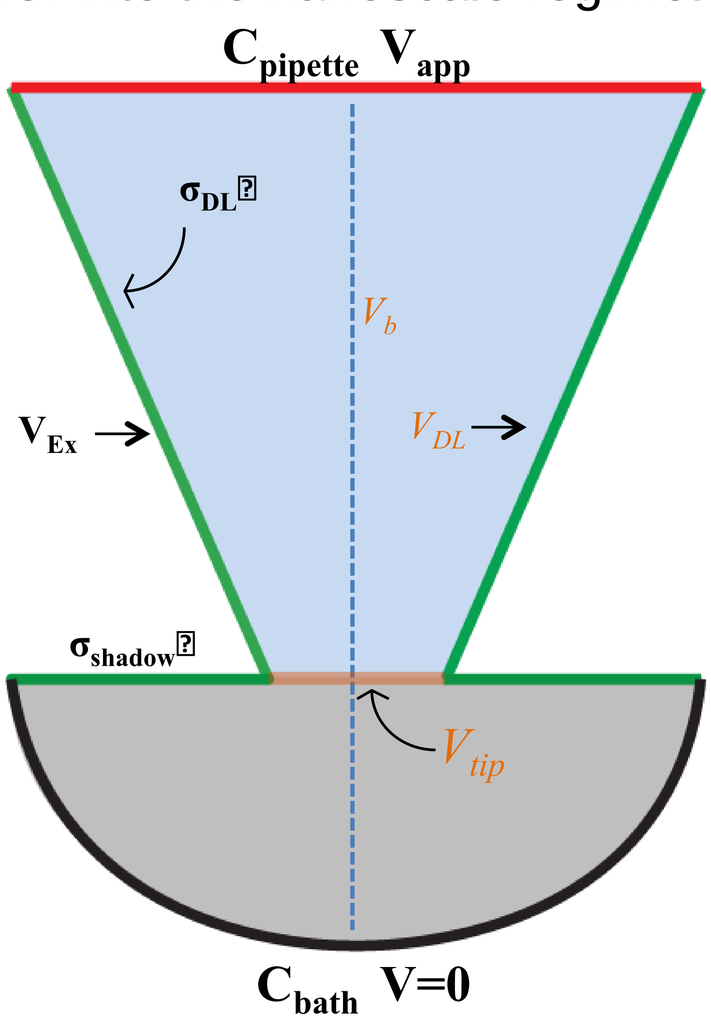

Figure 1. Geometry and boundary conditions. Black parameters applied to system. Orange parameters yielded by solution.

Computational Methods: Poisson-Nernst Planck equations, with additional expressions for glass surface chemistry and electric field effects through the pipette wall.

$$N_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla V$$

$$\nabla^2 V = \frac{-F}{e} \sum z_i c_i \qquad V_0 = V_{DL} + \frac{s_s}{C_{stern}}$$

$$[H]_0 = [H]_b e^{-(V_0 - V_b)/V_T} \qquad D_{pip} = \frac{V_{Ex} - V_0}{e_{pip} d_{pip}}$$

$$s_s = \frac{-q\Gamma}{1 + [H]_0 10^{pK}} \qquad s_{DL} = s_s + D_{pip}$$

N_{ii} = species flux; D_i = diffusion coefficient; c_i = species concentration; z_i = valence; F = Faraday constant; R = gas constant; T = temperature; V = potential; ε = permittivity; σ = charge density; [H] = proton concentration; V_T = thermal voltage; D_{pip} = displacement field; d_{pip} = pipette wall thickness; q = elementary charge; Γ = surface binding site density, pK = binding equilibrium constant

Results: Determined nanopipette tip potential for a variety of conditions.

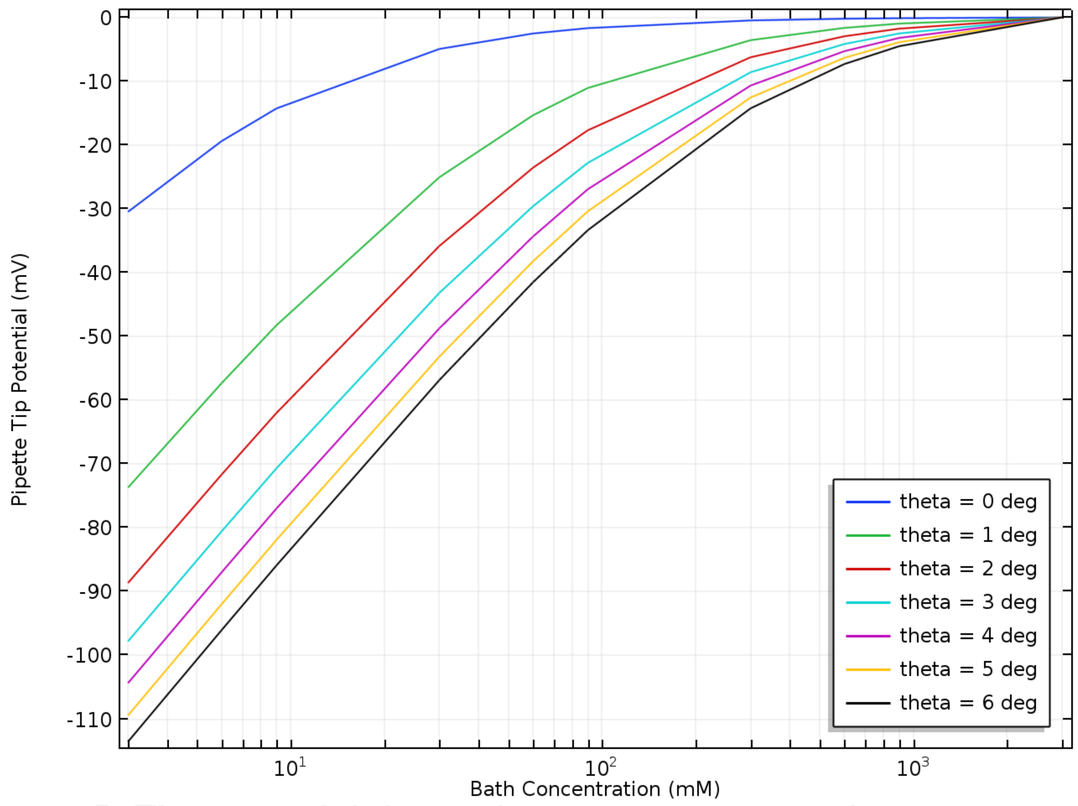

Figure 2. Tip potential dependence on concentration, cone angle

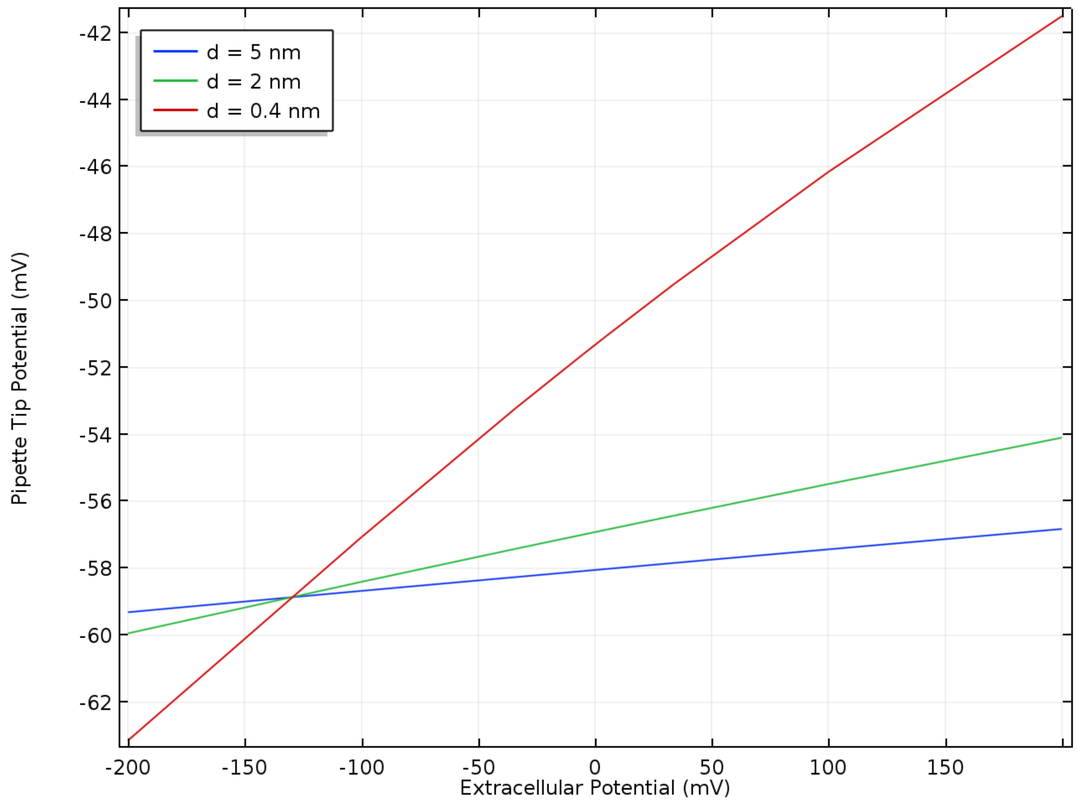

Figure 3. Tip potential dependence on electric field through the wall

Conclusions:

- Pipette tip potential primarily a function of cone angle and concentration gradient; mostly independent of radius
- Electric field through pipette wall can drastically swing tip potential
- pH, surface site density, and equilibrium constant also can modulate tip potential and sensitivity to field through wall
- Tip potential changes caused by changes in surface charge density at end of pipette

References:

1.White HS, Bund A, "Ion Current Rectification at Nanopores in Glass Membranes", *Langmuir*, 24, 2212-2218 (2008)
2.Edwards MA, Unwin PR, "SICM: A model for experimentally realistic conditions and image interpretation", *Analytical Chemsitry* 81, 4482-4492 (2009).

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