NANOSYSTEMS:
PHYSICS, CHEMISTRY, MATHEMATICS

SUPPLEMENTARY MATERIALS

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# Effect of nanoscale water media confinement on the approach curve in SICM

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**Supplementary materials**

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## 1. Model scheme and boundary conditions

The model consists of a domain filled with electrolyte (regions 1, 2) (Fig. S1). The pipette wall (region 3) is not included in the computational domain. The total size of the computational domain is $10 \times 10$ $\mu$m. An axisymmetric problem is solved (AE – axis of symmetry). The approach curve of the nanopipette toward the sample is investigated. The approach is simulated step by step: at each step the distance between the pipette and the sample is decreased. When this distance becomes smaller than a given parameter (40 nm), a subdomain beneath the pipette wall (region 2) is defined within the electrolyte. In region 2, confinement conditions of the water medium are imposed (see main text, Modeling section).

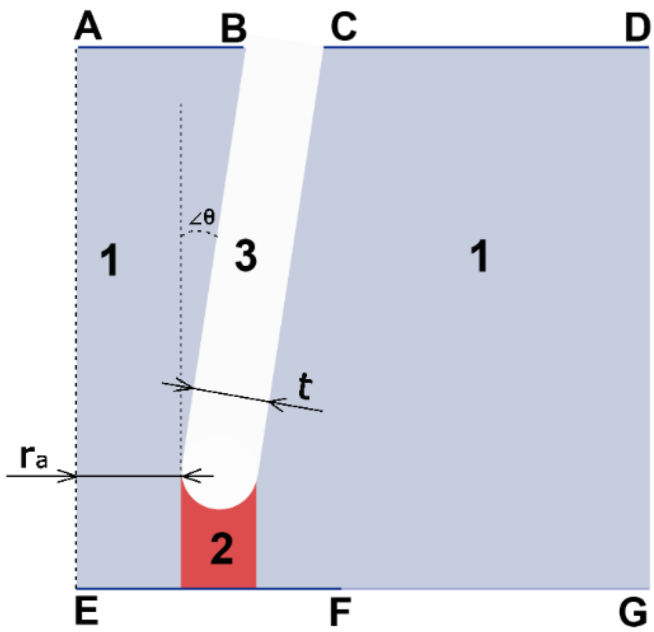



FIG. S1. Axisymmetric model scheme (AE – axis of symmetry). $t$ – NP wall thickness, $r_a$ – aperture radius, $\theta$ – half-cone angl.

In this model, confinement effects are introduced by functional dependencies of ion diffusion coefficients and solvent viscosity on the pipette–sample distance. The model is described by the equations of electrostatics and charged particle transport in an electric field (Tertiary Current, with no electroneutrality condition) and by laminar flow equations (Laminar Flow), where solvent velocity arises due to electroosmotic flow.

Tertiary Current
Initial conditions: concentration $C = C_0$, potential $V = 0$ throughout the domain.

Boundary conditions:
AB, CD: ion concentrations $C = C_0$;
CD: $V = 0$ V;
AB: $V = V_0$, $V_0 < 0$.
Surface charge density $\sigma_{pip}$ is applied at the boundaries where the pipette wall and the sample (EF) are in contact with the electrolyte.

TABLE S1. Main model parameters

| Parameter | Value | Units | Symbol |
|---|---|---|---|
| Pipette aperture radius | 40 nm | nm | $r_a$ |
| Pipette wall thickness | 42 nm | nm | $t$ |
| Tangent of internal half-cone angle | 0.02 | – | $\tan\theta$ |
| Electrolyte concentration | 150 mM | mMol/L | $C_0$ |
| Bath electrode potential | 0 V | V | – |
| Pipette electrode potential | $-1$ V | V | $V_0$ |
| Pippette surface charge density | $-30$ | mC/m$^{-2}$ | $\sigma_{pip}$ |
| Sample surface charge density | ($-120$:$-30$) | mC/m$^{-2}$ | $\sigma$ |

In region 2 (Fig. S1), the ion diffusion coefficients depend on the pipette–sample distance. The initial bulk diffusion coefficient is multiplied by a correction factor $K_{\text{diff}}(z)$ (Fig. S2, Table S2).

## 2. Correction factors for ion diffusion coefficients

TABLE S2. Values of $K_{\text{diff}}(z)$

| Distance to sample (nm) | $K_{\text{diff}}$ |
|---|---|
| 50 | 1 |
| 40 | 1 |
| 30 | 1 |
| 20 | 1 |
| 15 | 0.95 |
| 8 | 0.05 |
| 5 | 0.01 |

## 3. Correction factors for solvent viscosity

Initial conditions: velocity and pressure = 0 throughout the domain. Boundary conditions for solvent flow velocity: Electroosmotic Velocity condition is imposed on all pipette walls and on the sample surface (EF). The electroosmotic flow velocity is defined using the zeta-potential and the Smoluchowski equation.

**Laminar Flow**

Initial conditions: in the model domain, the flow velocity and excess pressure relative to the atmosphere are set to zero. Boundary conditions for solvent flow velocity: the Electroosmotic Velocity condition (see main text, Modeling section) is

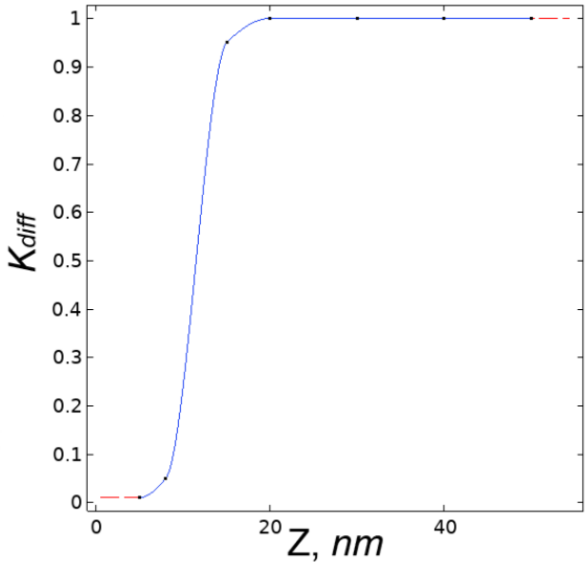



FIG. S2. Correction factor $K_{\text{diff}}(z)$ for ion diffusion coefficients depending on pipette–sample distance

TABLE S3. Values of $K_v(z)$

| Distance to sample (nm) | $K_v$ |
|---|---|
| 50 | 1 |
| 40 | 1 |
| 30 | 1 |
| 20 | 1 |
| 15 | 1.05 |
| 10 | 2 |
| 7 | 7.14 |
| 5 | 10 |

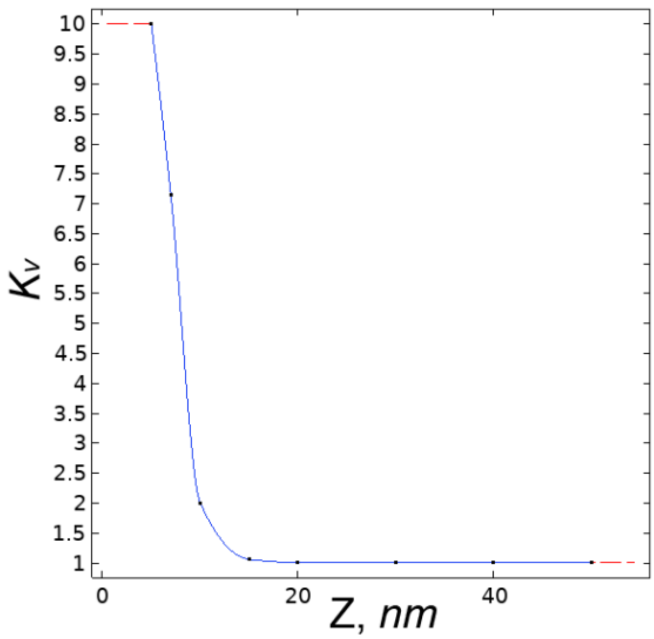
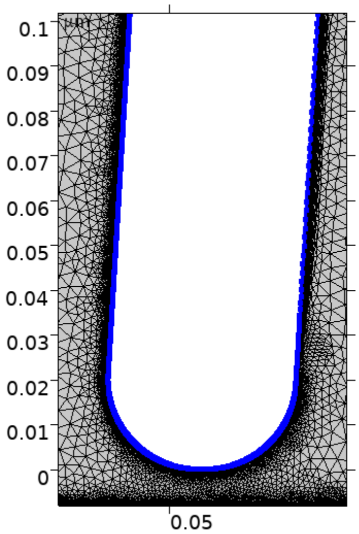


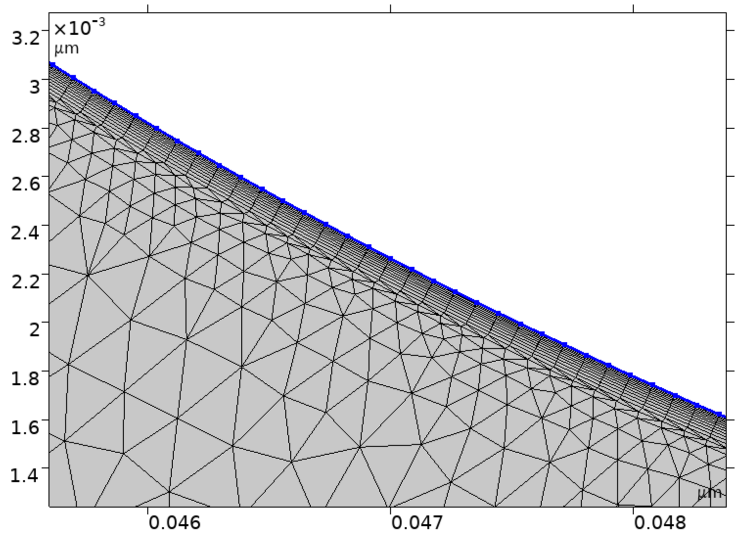

FIG. S3. Correction factor $K_v(z)$ for solvent viscosity depending on pipette–sample distance applied along all pipette boundaries and on the sample surface EF. The electroosmotic flow velocity is determined using the zeta potential according to the Smoluchowski equation. In region 2 (Fig. S1), the solvent viscosity is set as a function of the pipette–sample distance. The bulk viscosity value in region 2 is multiplied by a correction factor $K_v(z)$ (Fig. S3, Table S3).

## 4. Mesh parameters

A triangular mesh was used for the simulations. The cell size depends on boundary conditions. The smallest element size was set to 0.1 nm on the inner pipette surface and on the sample surface (EF). Boundary layer meshing was applied along the pipette walls, resulting in layers with element thickness of ∼0.01 nm perpendicular to the pipette surface (Fig. S4B).




(A)




(B)

FIG. S4. Overview of the mesh fineness and quality across the computational domain (A); zoomed-in view near the nanopipette surface (B)