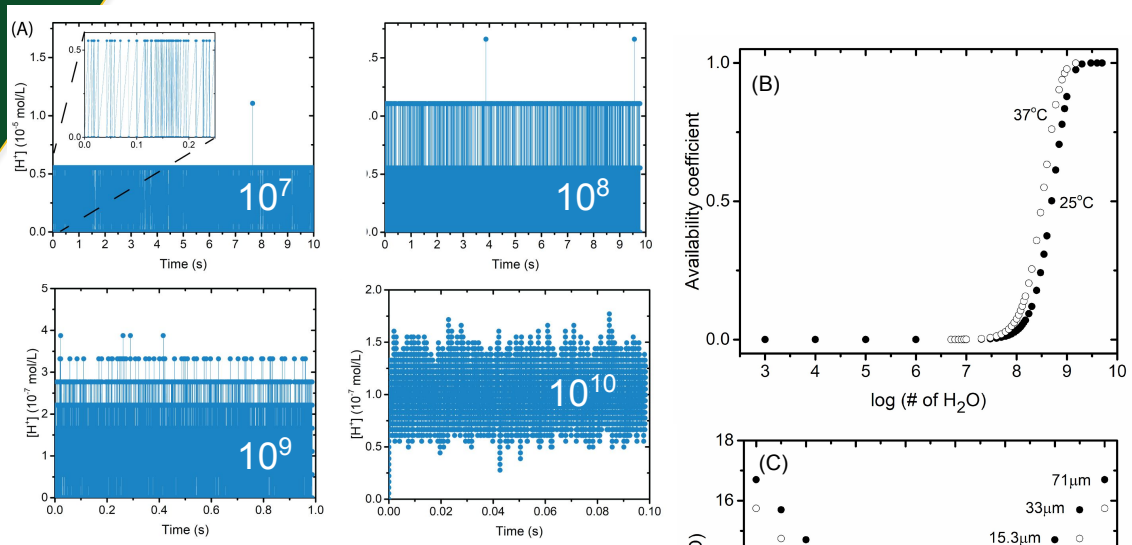
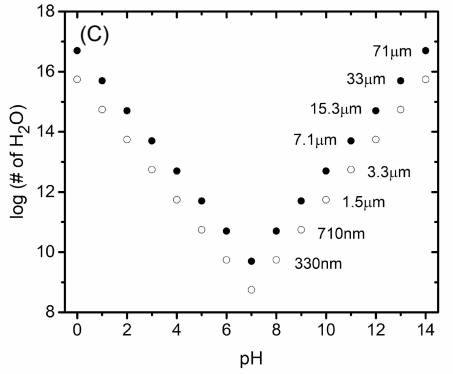
A stochastic description of pH within nanoscopic water pools





A. Fluctuating proton concentrations in pools of 10^7 – 10^{10} waters. Only the largest pool has bulk-like pH.

B. Availability coefficient calculated from the simulations, measuring the sustained presence of protons in water pools. Converges to 1 when the pool becomes bulk-like.

C. Minimum pool radius for which a pH is thermodynamically defined and bulk-like. Open circles are for pools where the availability coefficient is 1, closed circles also satisfy the criterion that water ions are present almost 100% of the time.

Scientific Achievement:

A computational study of the kinetics of water ions in pure water pools too small to have a pH has enabled water ion availability as a function of pool size to be quantified across a broad scale. The results provide a definition of effective pH and estimates of ion pair lifetimes in the pool environment.

Significance and Impact:

The catalytic microenvironment in artificial and natural systems often involves aqueous environments too small to have a bulk-like pH. This work provides a means of assessing instantaneous and average water ion concentrations and lifetimes in these environments, refining our ability to understand how water and water ions participate in the chemistry. The findings apply to many types of confined aqueous environments in inorganic, organic and biological systems.

Research Details:

- Detailed stochastic simulations of water autoionization and ion recombination, capturing ion pair reactions for Poisson distribution analysis
- Stochastic simulations are compared to molecular dynamics for 64-water pools, evaluating the effect of assuming the pools are well-mixed
- Ion pair lifetimes show that lifetimes increase with pool size, going through a maximum, then decreasing as the water ion recombination rate dominates the kinetics
- Definition of a new quantity, an availability coefficient, to measure the transition from fluctuating populations of ion pairs to bulk-like pH

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