

7th of November 2024
12:00 h

Zoom Virtual Meeting:

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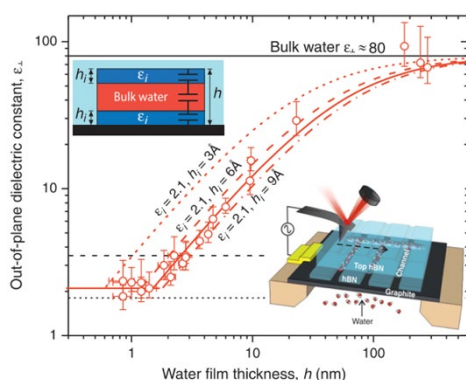
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Dr. Laura Fumagalli
University of Manchester

Unraveling the dielectric properties of interfacial and nanoconfined water



The dielectric polarization properties of near-surface and nanoconfined water have long been a subject of investigation¹⁻³ due to their critical role in various phenomena, including intermolecular forces, ion and molecular solvation, transport, and chemical reactions⁴⁻⁶. While there have been extensive theoretical and computational studies in recent years⁷⁻¹⁰, experimental evidence remains scarce due to technical challenges in measuring these properties in just few molecular layers of water near surfaces. After briefly presenting our experimental approach — based on highly sensitive scanning probe microscopy methods capable of probing local impedance¹¹⁻¹³ — I will present our recent findings on the dielectric constant of water near and confined between van der Waals crystals^{14,15}. Our experiments revealed the presence of an interfacial water layer with dielectric properties significantly different from

those of bulk water. In the direction perpendicular to the surfaces¹⁴, we found that interfacial water exhibits an anomalously low dielectric constant under moderate confinement, down to strong confinement (~ 1 nm). Conversely, in the in-plane direction¹⁵, the dielectric constant of interfacial water remains bulk-like under moderate confinement and increases to ferroelectric-like values under strong confinement. Furthermore, we observed that its in-plane conductivity also increases, reaching superionic values for quasi-2D water (1-2 nm). These findings offer new insights into various physical, chemical, and biological processes, and provides feedback for theoretical models that describe near-surface water and water-mediated interactions.

- (1) Stern, O. Zur theorie der elektrolytischen Doppelschicht *Elektrochem. Angew. Phys. Chem.* **30**, 508-516 (1924).
- (2) Bockris, J. O. M., Devanathan, M. A. V. & Muller, K. On the structure of charged interfaces. *Proc Roy. Soc. Lond. A Math. Phys. Sci.* **274**, 55–79 (1963).
- (3) Conway, B. E., Bockris, J. O. M. & Ammar, I. A. The dielectric constant of the solution in the diffuse and Helmholtz double layers at a charged interface in aqueous solution. *Trans. Faraday Soc.* **47**, 756-766 (1951).
- (4) Born, M. Volumen und hydrationswärme der ionen. *Z. Physik* **1**, 45-48, doi:doi.org/10.1007/BF01881023 (1920).
- (5) Nandi, N., Bhattacharyya, K. & Bagchi, B. Dielectric relaxation and solvation dynamics of water in complex chemical and biological systems. *Chem. Rev.* **100**, 2013-2046, doi:10.1021/cr980127v (2000).
- (6) Israelachvili, J. N. & Pashley, R. M. Molecular layering of water at surfaces and origin of repulsive hydration forces. *Nature* **306**, 249250 (1983).
- (7) Bonthuis, D. J., Gekle, S. & Netz, R. R. Profile of the static permittivity tensor of water at interfaces: consequences for capacitance, hydration interaction and ion adsorption. *Langmuir* **28**, 7679-7694 (2012).
- (8) Schlaich, A., Knapp, E. W. & Netz, R. R. Water dielectric effects in planar confinement. *Phys. Rev. Lett.* **117**, 048001 (2016).
- (9) Muñoz-Santiburcio, D. & Marx, D. Confinement-controlled aqueous chemistry within nanometric slit pores. *Chem. Rev.* **121**, 62936320, doi:10.1021/acs.chemrev.0c01292 (2021).
- (10) Matyushov, D. V. Dielectric susceptibility of water in the interface. *J. Phys. Chem. B* **125**, 8282-8293 (2021).
- (11) Fumagalli, L., Ferrari, G., Sampietro, M. & Gomila, G. Dielectric-constant measurement of thin insulating films at low frequency by nanoscale capacitance microscopy. *Appl. Phys. Lett.* **91**, 243110 (2007).
- (12) Fumagalli, L., Esteban-Ferrer, D., Cuervo, A., Carrascosa, J. L. & Gomila, G. Label-free identification of single dielectric nanoparticles and viruses with ultraweak polarization forces. *Nat. Mater.* **11**, 808-816 (2012).
- (13) Gramse, G., Edwards, M. A., Fumagalli, L. & Gomila, G. Dynamic electrostatic force microscopy in liquid media. *Appl. Phys. Lett.* **101**, 213108 (2012).
- (14) Fumagalli, L. *et al.* Anomalously low dielectric constant of confined water. *Science* **360**, 1339-1342 (2018).
- (15) Wang, R. *et al.* In-plane dielectric constant and conductivity of confined water. *arXiv:2407.21538* (2024).