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## Long-range interactions induced by oriented water molecules within plasma polymeric subsurfaces

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The common definition of "surface" includes surface atoms and molecules, practically extending at the most three layers –typically up to one nanometer. This definition is justified by the fact that many surface properties such as chemistry, wettability or charge density are determined by the top most surface layer. Far less explored are effects due to interactions with deeper subsurface layers, i.e. the region extending over several nanometers underneath the "surface". This subsurface region, however, might significantly contribute to molecular adsorption at the surface via long-range (i.e. >10 nm) interaction forces.

To make use of such subsurface effects, plasma polymer films (PPFs) with defined architecture in the nanoscale were deposited comprising a hydrophobic-to-hydrophilic vertical chemical gradient structure. The organic/inorganic thin films were generated by depositing 1-15 nm-thick layers of plasma-polymerized HMDSO on a hydrophilic, nanoporous base layer of SiOx (with O2/HMDSO in the plasma). Diffusion of water through the hydrophobic terminal layer is still enabled despite the hydrophobic surface properties yielding hydration of the hydrophobic/hydrophilic subsurface structure as demonstrated by neutron reflectometry measurements. The hydrated films were found to strongly affect protein adsorption at the surface thanks to long-range interaction forces induced by oriented water molecules. Thereby, additional control over adsorption processes and modulation of protein adsorption is enabled which is relevant, e.g., for tissue engineering, wound dressing etc.

Adjusting the thin film architecture of plasma polymer films thus provides an additional parameter to modulate surface properties of materials.

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