

 WATER DYNAMICS AT SURFACES

Patterning polarity

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The way that water molecules interact and move on different surfaces has fascinated scientists for many years. Nature has mastered the use of hydrophilic and hydrophobic interactions to guide highly complex processes. Protein folding dynamics, for example, are affected by the way that water molecules arrange and move in the proximity of the amino acids at the protein surface. Understanding the deep secrets that regulate water dynamics on solid surfaces can help to define material design principles useful in applications like water filtration, adsorption, chromatography and catalysis. Of course, water–surface interactions are strongly influenced by the number of polar or non-polar chemical groups on the surface. However, Jacob Monroe and Scott Shell report in *PNAS* that the specific patterns of hydrophilic and hydrophobic functionalities also have a large effect on water dynamics on the surface.

In their previous study, Shell’s group collaborated with the group of

Songi Han, who used NMR techniques to look at water diffusivities around silica nanoparticles exhibiting different levels of hydrophobicity, which were attained by changing the concentration of hydroxyl groups on the silica surface. A surprising and marked decrease of water diffusivity was observed above a certain hydroxyl concentration; however, this behaviour could not be reproduced by molecular dynamics simulations of silica surfaces decorated with different concentrations of randomly distributed hydroxyl groups. “At the time, we hypothesized that water dynamics might depend not only on the surface density, but also on the arrangement of hydroxyl groups on the surface — for example, whether or not –OH groups were evenly dispersed or clustered into small islands,” explains Shell. “Indeed our further simulations then confirmed that different patterns of hydroxyls could give rise to distinct water mobilities.”

In the present study, Shell and Monroe wanted to investigate what range of water dynamics is achievable only through surface patterning of hydrophobic and hydrophilic functionalities. In order to study the patterning in isolation from other effects, such as average coverage, the team used a genetic algorithm to generate a large variety of surface patterns. They chose one hard and one soft surface — crystalline silica and mixed methyl and hydroxyl terminated self-assembled monolayers, respectively — and a “toy” Lennard-Jones surface that does not form hydrogen bonds with water. Molecular dynamics simulations were then performed to identify any signatures of the surface patterning in the water mobility. “In other words, we were looking for universal fingerprints in the water that would tell us about its dynamics,

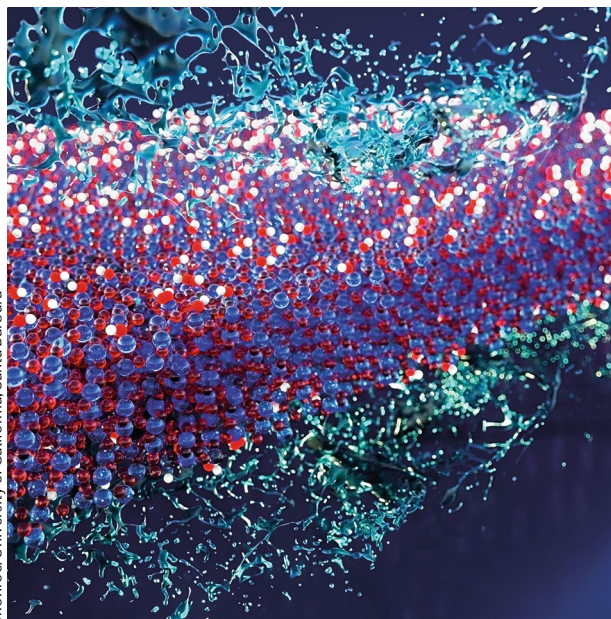
without needing to know the surface details,” clarifies Shell.

Shell and Monroe found that clustering of hydrophobic groups leads to faster water mobilities. Specific hydrophobic patterns can be used to attain water mobilities comparable to those on randomly patterned surfaces while using only half the number of hydrophobic groups. However, the patterning effect is only observed for surfaces bearing functional groups able to form hydrogen bonds with water or that prefer oriented interactions with the water molecules. The effect was not observed for the toy Lennard-Jones surfaces, suggesting that water dynamics are predominantly influenced by short-range, anisotropic interactions. This is in contrast to what was previously observed for thermodynamic properties that seem to also be sensitive to longer-range, isotropic attractions. Finally, surfaces with a high affinity for small methane-like hydrophobic molecules and/or characterized by high orientational entropy of the surface water lead to faster water diffusivities. “These results are exciting because they suggest a deep connection between water structure, thermodynamics and dynamics at the interface, and may lead to new theories for understanding water dynamics near complex molecules and surfaces,” says Shell. Monroe concludes: “If the dynamics of water at the interface is of interest, then the density of functional groups alone does not provide enough information — their arrangement should also be considered when analysing and designing interfacial materials.”

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ORIGINAL ARTICLE Monroe, J. I. & Shell, M. S. Computational discovery of chemically patterned surfaces that effect unique hydration water dynamics. *Proc. Natl Acad. Sci. USA* **115**, 8093–8098 (2018)

FURTHER READING Schrader, A. M. et al. Surface chemical heterogeneity modulates silica surface hydration. *Proc. Natl Acad. Sci. USA* **115**, 2890–2895 (2018)



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