Structure and Dynamics of Water at the Interface with Phospholipid Membranes and Rigid Graphene Sheets

Giancarlo Franzese [C, S] and Carles Calero
Seccio 039; de Fisica Estadistica i Interdisciplinaria--Departament de Fisica de la Materia Condensada, Universitat de Barcelona, Barcelona, Spain
gfranzese@ub.edu

An accurate description of the structure and dynamics of interfacial water is essential for phospholipid membranes, since it determines their function and their interaction with other molecules, and for nanostructured carbon materials, as in man-made superhydrophobic materials, carbon-based filtration membranes, or cryomicroscopy at hydrated graphene interfaces. We study, by all-atom molecular dynamics simulations, water confined in stacked phospholipid membranes with hydration from poor to complete [1]. We find that the water dynamics is dramatically slowed down by reducing the hydration level, as in the experiments [2, 3, 4]. We identify three different regions in the interface where water molecules exhibit distinctive dynamical behavior. We show that the slow-down is a consequence of (i) the robustness of water-lipid hydrogen bonds, which are more frequent the lower the hydration of the membrane, and (2) the longer lifetime of water-water hydrogen bonds the lower the hydration. By adopting a sensitive local order metric recently proposed by Martelli et al., measuring the degree of overlap of the local environment with the structures of perfect ice, we find that water acquires a high intermediate range order (IRO) within 1 nm from the membrane interface, i.e. with the same distance where its dynamics slows down [5]. Surprisingly, we show that at distances as far as $\simeq$ 2.5 nm from the interface, although the bulk-like dynamics is recovered, the IRO of water is still slightly higher than that in the bulk under the same thermodynamic conditions. Therefore, the water-membrane interface has a structural effect at ambient conditions that propagates further than the often-invoked 1 nm length scale. Next, we study the crystallization and dynamics of water in a rigid graphene sieve [6]. We find that the diffusion of water confined between parallel walls depends on the plate distance in a non-monotonic way and is related to the water structuring, crystallization, re-melting, and evaporation for decreasing inter-plate distance. Our results could be relevant in those applications where water is in contact with nanostructured carbon materials and could help us to understand the role of water at biomembrane interfaces.

References:

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