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Interfacial water thickness at inorganic nanoconstructs and biomolecules: Size matters

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ABSTRACT

Water molecules in the proximity of solid nanostructures influence both the overall properties of liquid and the structure and functionality of solid particles. The study of water dynamics at solid–liquid interfaces has strong implications in energy, environmental and biomedical fields. This article focuses on the hydration layer properties in the proximity of Carbon Nanotubes (CNTs) and biomolecules (proteins, polypeptides and amino acids). Here we show a quantitative relation between the solid surface extension and the characteristic length of water nanolayer (δ), which is confined at solid–liquid interfaces. Specifically, the size dependence is attributed to the limited superposition of nonbonded interactions in case of small molecules. These results may facilitate the design of novel energy or biomedical colloidal nanosuspensions, and a more fundamental understanding of biomolecular processes influenced by nanoscale water dynamics.

1. Introduction

Water at solid–liquid nanoscale interfaces shows properties significantly different from those in the bulk region. This altered behavior is manly due to nonbonded interactions with the solid phase, which are able to confine some layers of water molecules and to modify the structural and dynamic characteristics of the solvent at the interface [1]. The solid–liquid interactions at the nanoscale induce water molecules to form a structured solid-like layer (also known as nanolayer or hydration layer/shell [2]) with increased density [3,4]. Moreover, in such nanoconfined condition the self-diffusivity of water is generally reduced and the viscosity is dramatically increased [5,6].

Several experimental and modeling techniques have been employed to investigate the peculiar properties of interfacial water. For example, by using nano-ultrasonic technique, Mante and colleagues observed the high mass density and the elastic modulus of water at alumina-water interfaces [7]. The mechanical anomalies of the hydration water layer, including the largely enhanced viscosity and non-squeeze-out fluidity, have been also studied by surface force apparatus [8], scanning force microscopy [9] and atomic force microscopy [10]. Atomistic simulations, e.g. Molecular Dynamics (MD), are also powerful methods for studying the distribution and mobility of nanoconfined water [11,12]. Recently, MD simulations and theoretical analogies with the properties of supercooled water have unveiled a scaling behavior for the self-diffusion coefficient of water in more than sixty confined configurations [1]. From the computational perspective, scaling laws are highly desirable as they allow to upscale results from time-consuming simulations, thus coping with the multi-scale nature of atomistic or other microscopic simulators [13–15]. Moreover, the scaling behavior in [1] has been further validated by recent, independent neutron experiments measuring the mobility of nanoconfined water [16,17].

A broad variety of energy, environmental and biomedical applications take advantages of the peculiar properties of nanoconfined water [18,19]. For example, the reduction of water self-diffusion coefficient in the proximity of contrast agents for magnetic resonance imaging leads to significant enhancements in diagnostic performances [20]. Water hydration shell rearrangement has been also identified as a key ingredient for the insertion of anti-cancer drugs into the DNA minor groove [21,22]. Moreover, the peculiar heat and mass transport properties of nanolayer are responsible for the outstanding thermo-physical properties of nanofluids [23,24], which are mainly investigated for energy [25] or biomedical [26] applications.

On the other hand, water at solid–liquid interface plays a fundamental role in controlling the activity and functionality of solid nanostructures [27,28]. In particular, protein folding, molecular recognition, self-assembly and aggregation are strongly influenced by the thickness of water layer confined at the surface [29–31]. For example, stability and conformation of Amyloid plaques, which are associated with several neurodegenerative diseases such as

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Alzheimer and Parkinson, are regulated by the quantity of water adsorbed at the surface [32–34]. The structural changes of dioleoylphosphatidylcholine (DOPC) bilayer are promoted by its progressive hydration [35], and the binding process at protein interfaces is also facilitated by a network between adhesive water molecules at the surface [36]. Moreover, changes in the hydration layer depth around DNA are also observed during the transition from helix to coil configuration [37]. The clustering and aggregation dynamics of suspended nanoparticles (e.g. graphene) are also influenced by the thickness of nanoconfined water [38,39].

These examples show a crucial role for the water layer at nanoscale interfaces: on one hand, it modifies the overall properties of surrounding liquid; on the other hand, water at nanoscale interfaces strongly alters the dynamics of solid phase itself. Hence, a more quantitative understanding of the extension and properties of the hydration level is fundamental in many emerging nano- and biotechnology applications.

In this article, the characteristic length of water nanolayer (δ) adsorbed at the interface is systematically investigated for Carbon Nanotubes (CNTs) and biomolecules (proteins and amino acids). While the relation between surface chemistry and δ has been clarified in previous studies [1,18,40], here the analysis focuses on the link between the size of solid particles and their capability to confine water molecules. MD simulations are first performed to equilibrate the solvated systems; trajectories are then processed and the resulting δ are finally interpreted in the light of the local solid–liquid nonbonded interactions. Results highlight a dependence of the hydration layer thickness on the solid particle size. Specifically, a general law to predict the thickness of hydration layer, and thus the amount of interfacial water, is reported. This approach may help to better understand both colloidal nanosuspensions properties and biological processes involving nanoconfined water. Moreover, the study of hydration layer around amino acids or small peptides could lead to a more fundamental understanding of aggregation, dynamics and functionality of biomolecules.

2. Methods

2.1. Characteristic length of nanolayer

In bulk conditions, water molecules fluctuate with a kinetic energy proportional to k_BT, where k_B is the Boltzmann constant and T the fluid temperature. Approaching to solid surfaces, instead, the state of agitation of the solvent is restrained by interacting potentials with the atoms of solid phase. Hence, a layer of water molecules characterized by a reduced mobility and a more ordered structure is typically formed at the solid–liquid interface. Such layer is usually called nanolayer or hydration layer [2], whose thickness can be quantified by a characteristic length δ [1], which depends on the confining potential.

In the nanolayer, water dynamics is altered by the solid–liquid effective potential $U_{eff} = U_{vdw} + U_c$, where U_{vdw} and U_c are the van der Waals and Coulomb potentials, respectively. Let us consider the i-th solid atom on the Solvent Accessible Surface (SAS [41]) and the direction n orthogonal to the solid surface in the proximity of the i-th atom, then, the solid–liquid effective potential along n can be computed as:

$$U_{eff}(n) = U_{vdw}(n) + \langle U_c \rangle (n). \tag{1}$$

Here, van der Waals interactions are modeled with a 12-6 Lennard–Jones (LJ) model:

$$U_{vdw}(n) = \sum_{k=1}^{N_n} 4\varepsilon_k \left[\left(\frac{\sigma_k}{r_k} \right)^{12} - \left(\frac{\sigma_k}{r_k} \right)^{6} \right], \tag{2}$$

where ε_k and σ_k are the LJ parameters obtained through the Lorentz–Berthelot combination rules between the generic water oxygen with coordinate n and the center of the k-th nearest neighbor. r_k is the Euclidean distance between water oxygen along n direction and the k-th atom. Note that N_n is the amount of nearest neighbors of the i-th atom within the selected computational cut-off radius r_c, which is chosen such that $U_{eff}(r_c) \approx 0$ and vanishing derivative.

Coulomb potential, instead, takes into account the fluctuations of water dipoles due to thermal agitation. Assuming a Maxwell–Boltzmann distribution of the dipoles orientation, the mean Coulomb potential along n is:

$$\langle U_c \rangle (n) = -E\mu_w \Gamma \left(\frac{E\mu_w}{k_BT} \right), \tag{3}$$

where E, μ_w and Γ are the electric strength, the water dipole momentum (7.50×10^{-32} Cm for SPC/E model [1]) and Langevin function, respectively. It is worth to notice that the adopted SPC/E model represents water as a triatomic molecule, which has a single Lennard–Jones site (oxygen atom) and three point charges (both hydrogen and oxygen atoms). Therefore, the thermal fluctuations of the oxygen atom position are neglected for the calculation of U_{eff}; whereas the thermal fluctuations of water dipole around the equilibrium position are taken into account. For this reason, the ensemble average due to the thermal agitation of water molecules has been adopted only for the electrostatic component.

Once U_{eff} is computed along the n direction in the proximity of the i-th atom, a local characteristic length of water nanolayer δ_i can be evaluated. Following the approach in Ref. [1], $\delta_i = n_{i,2} - n_{i,1}$, where $n_{i,1}$ and $n_{i,2}$ are the zeros of equation:

$$U_{eff}(n) + \alpha k_BT = 0, \tag{4}$$

being α related to the degree of freedoms of the water molecules motion. Equation (4) describes a balance between the solid–liquid effective potential (U_{eff}), which causes a reduction of water mobility at the solid–liquid interface, and the kinetic energy of the solvent (αk_BT), which weakens the adsorption of water to the solid surface. In particular, αk_BT is constant along n and it may intersect U_{eff} in two points: $n_{i,1}$ and $n_{i,2}$. The zeros of Equation (4) define the distance δ_i, below which the effective potential is stronger than the thermal energy of water molecules, namely solid–liquid interactions significantly alter water dynamics. In other words, δ_i measures the depth of water layer absorbed to the solid surface.

Once the local characteristic lengths δ_i are evaluated, a weighted mean δ can be computed on the solvent accessible surface as:

$$\delta = \frac{\sum_{i=1}^{N} \delta_i S_{loc,i}}{S_{tot}}, \tag{5}$$

where N is the total number of atoms forming the solid geometries, $S_{loc,i}$ the specific SAS of the i-th atom and $S_{tot} = \sum_{i=1}^{N} S_{loc,i}$ the overall SAS. Once the equilibrium configuration of the nanoconfined setup is known, both S_{tot} and $S_{loc,i}$ can be computed from short MD simulations; whereas δ is a characteristic quantity of the geometry (i.e. MD geometry) and nonbonded interactions (i.e. MD force field) of the solid–liquid interface. Since the solvent accessible surfaces obtained from MD trajectories show oscillations in time because of thermal fluctuations, standard deviations of δ can be also estimated for each considered geometry.

2.2. Molecular dynamics configurations

The dependence of δ on the particle size is here investigated for two classes of nanoscale geometries, namely carbon nanotubes and biomolecules. The variety of the considered sample allows to explore hydrophobic and hydrophilic surfaces, inorganic molecules and biomolecules as well as biomolecules with different biological functions, for a broader generalization of results.