

The structure of water near a charged crystalline surface



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ARTICLE INFO

Article history:

Received 26 May 2014

Received in revised form 4 August 2014

Available online 27 August 2014

Keywords:

Water;

Neutron spectroscopy;

Colloidal dispersions

ABSTRACT

The structure of water near a synthetic clay surface, Laponite, is probed experimentally by total neutron scattering, in both liquid and arrested states. It is shown that the crystalline structure of the Laponite platelets and their charge distribution determine polarization of the closest water layers, with a local density higher than that of bulk water. Interestingly these layers show long range order in the plane parallel to the Laponite surface, while no indication of strong hydrogen bonding between water and Laponite is found.

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1. Introduction

In many situations of interest to our life and our planet water is confined in volumes of linear dimensions ranging from microns to nanometers, within a cell, or a rock, or at the surface of a protein. Understanding how its properties are affected by confinement and interaction with the substrate is consequently an important issue of research. So far most experimental studies have been performed by confining water in emulsions [1–4] or amorphous solid substrates, such as silica [5–8]. Here we address the study of the structure of water under confinement at a charged crystalline surface, where recent simulations [9,10] have predicted interesting long range order effects. This condition is reproduced experimentally in aqueous Laponite suspensions where the nanometer-thick Laponite particles have diameters of the order of 25 nm and a known crystalline structure.

Aqueous Laponite suspensions exhibit a rich phase diagram [11]. When dispersed in water Laponite ages, passing with waiting time t_w from a liquid towards different arrested states, depending on Laponite weight concentration, C_w . At very low concentration ($C_w < 1.0\%$) a gel state is obtained after a few months from preparation: this lasts a few years and eventually separates into clay rich and clay poor phases. An equilibrium gel is instead obtained at $1.0\% \leq C_w < 2.0\%$ [12], while at $2.0\% \leq C_w \leq 3.0\%$ [13,14] the sample arrests as a Wigner glass in a few days. At higher concentrations ordered phases (liquid crystals) may also be observed [11]. Such complex behavior is ascribed to the anisotropy both in shape and in charge distribution of Laponite particles and to their mutual interactions. In coarse grained models Laponite platelets

are represented as disk shaped particles, exposing to the solvent negatively charged surfaces and positive rims. Their interaction is usually modeled in terms of a balance of attractive and repulsive forces between charged clay platelets, immersed in a continuum medium of constant dielectric properties and refractive index [15–19]. Laponite aqueous suspensions have been intensively studied both experimentally and theoretically [11]. In particular the experimental techniques employed are Static (SLS) [20] and Dynamic Light Scattering (DLS) [21–24], rheology [25–27] and, more recently, Small Angle X-ray Scattering (SAXS) [28,14,12,29] and X-ray Photon Correlation Spectroscopy (XPCS) [30–32]. These techniques are the best suited to follow the dynamic arrest process and to distinguish between different arrested states, as for instance a gel or a glass. Nevertheless these cannot probe the structure of water and its interaction with Laponite at the atomic scale.

Recently we have performed a neutron diffraction experiment, exploiting the isotope contrast variation [33] on water hydrogen atoms, aimed at investigating the structure of aqueous Laponite suspensions at the atomistic scale (at $C_w = 1.5\%$ and 3%) in both liquid and arrested states [34], over the wide range of exchanged momentum, Q , available at the Near and Intermediate Range Order Diffractometer (NIMROD) [35], installed at the ISIS second target station, ISIS2 [36]. This study has demonstrated that all structural properties of water and its interaction with Laponite do not depend on the age of the sample, at odds with the differences shown by the relative arrangement of the Laponite platelets in the liquid, gel or glassy states. It has also been shown that the structural evolution of the samples proceeds also after dynamical arrest, with signatures in the $0.1 \text{ \AA}^{-1} \leq Q \leq 1 \text{ \AA}^{-1}$ range of the neutron weighted Differential Cross Section (DCS).

In this paper we will focus our attention on the measured DCS at higher Q values ($0.5 \text{ \AA}^{-1} \leq Q \leq 50 \text{ \AA}^{-1}$), bringing information on the

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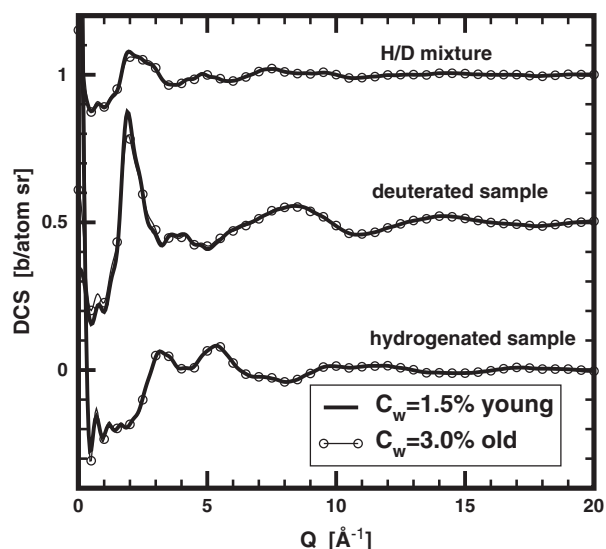


Fig. 1. Differential cross sections of the deuterated young $C_w = .5\%$ suspension (solid thick line) and of the arrested glass sample $C_w = 3.0\%$ (thin solid line with circles). No relevant differences in the Q range used within the EPSR Monte Carlo refinement is found: the data relative to the other two samples ($C_w = 1.5\%$ old and $C_w = 3.0\%$ young) do not deviate from the reported curves. Data for the deuterated and equimolar mixture have been offset for clarity.

microscopic structure of water and the relative arrangement of water molecules with respect to the Laponite platelet surface.

2. Material and methods

The colloidal dispersions have been prepared following the protocol described in Ref. [11], using synthetic Laponite from Rockwood Additives Ltd and pure, degassed, deionized D_2O , H_2O and an equimolar mixture of the two (hereafter labeled HDO). The aging zero time is defined as the time when the suspensions have been filtered and sealed into the quartz containers with internal dimensions $30 \times 30 \times 1 \text{ mm}^3$. The nominal weight concentrations, namely 1.5% and 3.0%, refer to the fully hydrogenated samples; the D_2O and HDO weight concentrations have been prepared in order to have three isotopic substituted suspensions of the

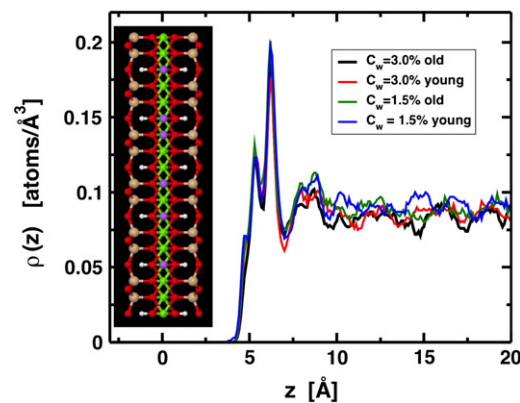


Fig. 3. Density profile of water oxygens along the direction normal to the Laponite surface for the four investigated samples, defined as: $\rho(z) = \frac{n(z, z + \Delta z)}{V(z, z + \Delta z)}$, where $V(z, z + \Delta z)$ is the volume of a slice of the simulation box of thickness Δz and containing n oxygen atoms. A fragment of simulated Laponite crystal is shown at the origin of the reference frame: different colors represent different atomic species (O red, H white, Si pink, Mg green, and Li violet).

same molar concentration. At these concentrations the samples evolve respectively towards a gel and a repulsive glass state.

The experiment has been performed at the NIMROD diffractometer [35], designed to allow studies of the structure of liquids and disordered materials over a continuous length scale from the atomistic to the mesoscopic ones, in a single measurement. Samples have been exposed to the neutron beam just after preparation (“young” sample) at waiting time $t_w = 0$ (liquid) and after dynamical arrest (“old” samples): respectively at $t_w = 3$ days for $C_w = 3.0\%$ (Wigner glass) and at $t_w = 1$ year for $C_w = 1.5\%$ (gel). The time lag between measurements of each isotopic composition has been set according to the scaling law reported in Ref. [37], where the modifications in the aging dynamics induced by isotopic substitution in the solvent have been investigated.

The details about the experiment, data reduction and analysis through the empirical potential structure refinement (EPSR) [38] method are thoroughly reported in Ref. [34]. We mention that the EPSR method is based on a Monte Carlo routine, which iteratively adjusts the interaction potential between individual atomic pairs, until a good fit of the experimental DCS is obtained and configurations

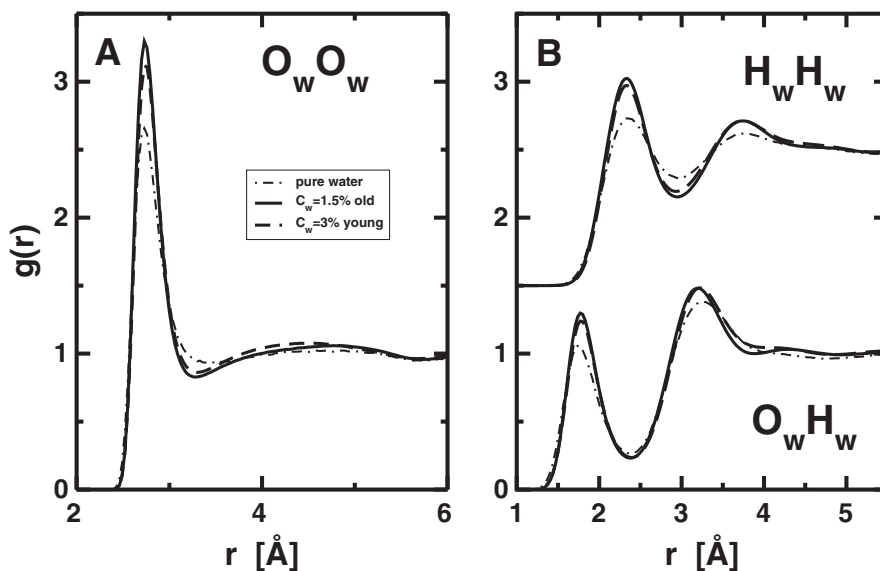


Fig. 2. A) $O_w O_w$ B) $O_w H_w$ and $H_w H_w$ radial distribution functions of two samples: old $C_w = 1.5\%$ (solid line) and young $C_w = 3.0\%$ (dashed line), compared with those of pure bulk water (dash-dotted line) [41]. The distribution functions of the two Laponite suspensions are almost identical and show only minor differences with respect to bulk water ones. The two samples shown here are different from those in Fig. 1, demonstrating that no aging and concentration effects on the structure of water at the atomistic level are visible.

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