Neutron diffraction study of aqueous Laponite suspensions at the NIMROD diffractometer


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The process of dynamical arrest, leading to formation of different arrested states such as glasses and gels, along with the closely related process of aging, is central for both basic research and technology. Here we report on a study of the time-dependent structural evolution of two aqueous Laponite clay suspensions at different weight concentrations. Neutron diffraction experiments have been performed with the near and intermediate range order diffractometer (NIMROD) that allows studies of the structure of liquids and disordered materials over a continuous length scale ranging from 1 to 300 Å, i.e., from the atomistic to the mesoscopic scales.

NIMROD is presently a unique diffractometer, bridging the length scales traditionally investigated by small angle neutron scattering or small angle x-ray scattering with that accessible by traditional diffractometers for liquids. Interestingly, we have unveiled a signature of aging of both suspensions in the length scale region of NIMROD. This phenomenon, ascribed to sporadic contacts between Laponite platelets at long times, has been observed with the sample arrested as gel or as repulsive glass. Moreover, water molecules within the layers closest to Laponite platelets surface show orientational and translational order, which maps into the crystalline structure of Laponite.

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1. INTRODUCTION

The near and intermediate range order diffractometer (NIMROD) [1], installed at the ISIS second-target station, ISIS2 [2], has been designed to allow studies of the structure of liquids and disordered materials over a continuous length scale from 1 to 300 Å, i.e., from the atomistic to the mesoscopic lengths, in a single measurement. It is a state-of-the-art neutron diffractometer, bridging the length scale traditionally investigated by small angle neutron scattering (SANS) or small angle x-ray scattering (SAXS) with that accessible by traditional diffractometers for liquids. It is, therefore, the ideal instrument for structural investigation of soft matter, as it can probe, simultaneously, aggregation phenomena at the mesoscopic scale and their origin and consequences at the molecular and atomistic scale. Here we report a study of the structural evolution with time of two aqueous suspensions of Laponite at different weight concentrations.

Aqueous Laponite suspensions at ambient conditions display nontrivial aging dynamics. As a function of time they pass from a liquid phase to an arrested state whose nature depends on their weight concentration (Cw). In particular, the suspension at the lowest Laponite concentration investigated in the present study, Cw = 1.5%, becomes an equilibrium gel within a few months. The most concentrated suspension, Cw = 3.0%, arrests as a repulsive Wigner glass in a few days [3]. The Laponite interaction potential is characterized by attractive and repulsive competing terms whose balance depends on clay and salt concentrations: in salt-free water conditions, attractive and repulsive interactions are, respectively, dominant at low- and high-clay concentrations. The arrest phenomenology of these samples has been extensively studied by both dynamic light scattering (DLS) [4–7] and SAXS [7–9]. A wealth of information about its signatures is present at very small exchanged wave vectors (Q ≤ 0.04 Å⁻¹), characteristic of these techniques. In particular, it has been shown [7] that a freshly prepared (“young”) sample shows a broad diffraction peak at Q ≤ 0.02 Å⁻¹, due to the average distance between Laponite platelets in suspension. Conversely, an aged and arrested sample (“old”) is characterized by clearly distinct features, depending on Laponite concentration. In particular upon aging, low-concentration samples show a shift of the broad diffraction peak to higher Q values that corresponds to roughly contacting platelets in a T configuration (≤ 150 Å) and a strong increase of the intensity at low Q, consistent with the formation of a gel. At high concentration, only a small shift of the broad diffraction peak toward higher Q values is observed that corresponds to a distance of ≈ 400 Å, i.e., to platelets considerably far away from one another, consistent with the formation of a repulsive glass. A comparable knowledge on the structural evolution of these suspensions at length scales not accessible with DLS or SAXS is missing, although such studies could provide important information to improve the potential models currently employed to simulate the aging dynamics of colloidal systems [10–14]. The new diffractometer NIMROD, probing length scales ranging from atomic up to the mesoscopic scale, can shed light about the presence of structures of intermediate dimension between the single platelet and the fully connected gel structure, so complementing previous studies.

These suspensions are also challenging systems for experimental studies of water confined at a crystalline-charged surface. Such studies have been so far tackled only by computer simulations [15,16], which predict interesting long-range ordering induced on adjacent water molecules. Laponite powder, once dispersed in water, breaks into disk-shaped
platelets, exposing to the solvent negatively charged surfaces and positive rims and releasing Na⁺ ions in solution. Each platelet (diameter of the order of 250 Å and 10 Å thick) is seen by a single water molecule as an extended surface with a complex crystalline structure [16].

In this paper, we describe a neutron diffraction experiment with isotopic substitution (NDIS), performed at the NIMROD diffractometer [1], on both “young” and “old” aqueous Laponite suspensions, at ambient conditions and at the two mentioned concentrations (Cw = 1.5% and Cw = 3.0%). We have exploited the isotopic H-D substitution on the water hydrogen atoms [17], in order to extract the information on the microscopic structure of water and on its radial distribution functions relative to the Laponite surface. In the following sections we describe the experimental methods, including sample preparation, correction of systematic effects on the experimental data, and conversion to real space through the empirical potential structure refinement (EPSR) method [18]. Finally, we comment the results at both atomistic and nanoscopic scale.

II. MATERIALS AND METHODS

A. Sample preparation

Laponite is a synthetic clay, produced by Rockwood Additives Ltd, in the form of white powder that, when dispersed in water, creates a charged colloidal suspension of disk-shaped platelets. Each platelet contains 1500 replicas of the crystal elementary cell with chemical formula: Na₄₋₋₍₋₇₎(Si₈Mg₅₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋蹁-


B. NDIS data collection

Before the neutron diffraction experiment, DLS measurements [19] on all H-D substituted samples have been performed in order to investigate the dependence of the aging dynamics on the isotopic effect. This study has demonstrated that the aging phenomenology is independent on the isotopic state of water, albeit different times are needed to obtain a comparable dynamical behavior: deuterated samples require longer times to reach the same dynamical state of hydrogenated ones. This implies that, while at waiting time \( t_w = 0 \), all the isotopically substituted samples are identical ("young" samples); at longer \( t_w \), a time lag proportional to the sample deuterium concentration has to be taken into account. The "young" samples have been exposed to the beam immediately after filtration. Arrested samples ("old") have been measured at \( t_w = 3 \) days for \( C_w = 3.0\% \) and at \( t_w = 1 \) year for \( C_w = 1.5\% \). The experiment on the glass (\( C_w = 3.0\% \)) has been repeated also on a "very old" sample, i.e., 1 month after its preparation. A dataset every 30 min, over a total of 6 h, has been recorded at total proton charge delivered to the neutron target of about 20 \( \mu \text{Amp-h} \) for each sample. Data without signature of aging have been averaged. Measurements on the empty instrument, empty containers, vanadium standard sample, and pure water have been performed, in order to calibrate the suspension data on absolute scale and to test the correction routines for inelasticity and multiple scattering effects against pure water.

The raw differential cross-section (DCS) data of the \( C_w = 1.5\% \) "old" sample in D₂O, reported in Fig. 1 for selected angles, show systematic effects at low-\( Q \) values. While all data superimpose at \( Q \gtrsim 1 \text{Å}^{-1} \), as expected, at lower \( Q \) values the slope of the DCS increases with the diffraction angle and several peaks at different \( Q \) values, which depend on detector position, are clearly visible: these features are most likely due to the presence of inelasticity effects [20].

![FIG. 1](image) (Color online) Differential cross-section of Laponite suspension in D₂O (\( C_w = 1.5\% \), "old" sample) measured at four different detector groups (diffraction angle increases with the detector group number, labeled as "no. xx") before correction of inelasticity effects and multiple scattering events. The arrows show structures in the raw data due to multiple scattering events. At odds with the genuine DCS structures, which are visible at \( Q \sim 1.9\text{Å}^{-1} \), \( \sim 4\text{Å}^{-1} \), and \( \sim 8\text{Å}^{-1} \) at all detector banks, structures due to multiple scattering events move in \( Q \) going from low- to high-diffraction angles. The slope of the data at low-\( Q \) contains an angle-dependent contribution, superimposed to the genuine low-\( Q \) features of the sample, due to the presence of inelasticity effects. Detector groups at the lowest diffraction angles extend over a shorter \( Q \) range, exhibiting lower inelasticity effects and higher noise.
and multiple scattering events. The routines currently used to correct these systematic effects on classical diffractometers, as for instance SANDALS [21,22], are not suitable in this case. Indeed, the low-$Q$ slope due to the inelasticity effects is superimposed on the genuine SANS signal characteristic of these samples, and there is no way to distinguish the two contributions in $Q$ space. Moreover, DCS data collected in light water suspensions show a distortion at high-$Q$ values (see Fig. 2), due to the vibrational degrees of freedom of the water molecules [20], which is usually not seen on SANDALS. Finally, the common routines for correction of multiple scattering effects are implemented for sample containers with essentially incoherent scattering cross-section (typically Ti-Zr alloy or V), giving a smooth multiple scattering contribution. On the contrary, the silica sample containers, used in the present experiment, scatter neutrons coherently, giving rise to a structured multiple scattering contribution, as evidenced by the arrows in Fig. 1. Given these difficulties, in order to establish a protocol for data correction, we have first analyzed the DCS of pure water, as measured on NIMROD, by using the same quartz glass containers used for Laponite aqueous suspensions. The procedure established for pure water and its extension to the correction of Laponite suspensions is described in the following subsection.

C. Correction of systematic effects on the DCS data

Data on pure water at ambient conditions have been collected by using the same silica sample containers employed for Laponite suspensions. DCS data (averaged over all detector groups), after subtraction of the silica sample container contribution, before correction for inelasticity and multiple scattering effects. We notice that the inelasticity effects increase with increasing H content and that, in particular, the data of the H$_2$O sample exhibit a spurious broad bump centered at about 20 Å$^{-1}$ and a slope at low $Q$. This spurious bump is less visible in the HDO sample and absent in the deuterated one. All datasets show the spurious structures due to multiple contributions at low-$Q$ values.

FIG. 2. (Color online) Differential cross-section of pure water (averaged over all detector groups), after subtraction of the silica sample container contribution, before correction for inelasticity and multiple scattering effects. We notice that the inelasticity effects increase with increasing H content and that, in particular, the data of the H$_2$O sample exhibit a spurious broad bump centered at about 20 Å$^{-1}$ and a slope at low $Q$. This spurious bump is less visible in the HDO sample and absent in the deuterated one. All datasets show the spurious structures due to multiple contributions at low-$Q$ values.

FIG. 3. (Color online) DCS data for heavy water at two selected diffraction angles (offset for clarity and labeled as “no. xx”), as a function of $Q$ (A) and as a function of $\lambda$ (B). The arrow indicates the contributions of multiple scattering events: these appear as broad peaks at low $Q$, in panel (a), and as a bump, centered at $\lambda \sim 4.7$ Å, in panel (b). The dashed lines are fits of the inelasticity contribution at each angle. The black solid line represents the average multiple scattering contribution. Data are reported as symbol plus errors (vertical bar).
diffraction angle. These observations suggest the strategy for data correction, which will be slightly different for the three isotopically substituted samples. In the case of D$_2$O, the multiple scattering is estimated by averaging the raw DCS data in the range $3 \, \text{Å} \leq \lambda \leq 10 \, \text{Å}$ over all detector banks. After subtraction of this contribution from the raw data, the inelastic scattering is estimated by linearly fitting the high-$\lambda$ region of the individual detector banks [magenta and green lines in Fig. 3(b)]. After subtraction of this latter contribution, data at all detector banks are compatible within the statistical accuracy and can be safely merged, to give the corrected DCS data shown in Figs. 4(a) and 4(d) (black curves) in comparison with the raw data (thin curves). In order to show the entire $Q$ range available and the goodness of the correction, data in Fig. 4(a) are reported in log scale. In Fig. 4(d) a zoom of the DCS shows that the corrections, in the high-$Q$ region, are very small for heavy water. The corrected DCS are almost flat at low $Q$ and show the known shape in the range $1 \, \text{Å}^{-1} \leq Q \leq 20 \, \text{Å}^{-1}$.

In the case of hydrogenated samples, H$_2$O and HDO, the inelastic contribution is larger than the multiple scattering one; for this reason we have performed the inelastic correction before the multiple-scattering ones. In these cases the inelastic contribution at high $\lambda$ has been estimated through a quadratic fit of the data on the individual detector banks. Then we have evaluated the average multiple-scattering contribution, as in the case of D$_2$O, and corrected and merged all detector banks data. The raw (thin curves) and corrected data (thick curves) are compared in Fig. 4 [panels (b) and (e) for HDO and panels (c) and (f) for H$_2$O]. Also in this case, the corrected DCS data show the characteristic shape of HDO and H$_2$O and a reasonable low-$Q$ behavior.

In Fig. 5 the comparison between raw DCS data of an “old” Laponite suspension at $C_w=1.5\%$ in D$_2$O with those of pure D$_2$O at the same detector bank is shown. The multiple-scattering features appear at the same low-$Q$ values and with the same intensity for both samples. The slope at low $Q$ measured for the suspension is instead much higher, due to the genuine low-$Q$ signal from aged Laponite suspensions [7–9,24]. The same features are observed for the other four suspensions in heavy water. This suggests that the multiple scattering is mainly due to double silica-water or silica-silica scattering events. Similarly, we are confident that the inelastic contribution is almost totally due to the presence of water deuterium atoms, being that all other nuclei of the suspension are much heavier than these. Moreover, we have already observed that the systematic distortions of the data at $Q$ values higher than $1 \, \text{Å}^{-1}$ are negligible in the case of D$_2$O. Therefore, we have corrected Laponite-D$_2$O data by subtracting at each detector bank the raw data of pure D$_2$O for $Q \leq 1 \, \text{Å}^{-1}$ and finally merging all detector groups. The same procedure has been applied for all data relative to suspensions in D$_2$O and H$_2$O: raw and corrected data are compared in Figs. 6 and 7 for one sample of each isotopic composition.

In Fig. 6 the comparison between raw (dashed line) and corrected (solid line) DCS data in the case of the “old” $C_w=1.5\%$ Laponite suspension in D$_2$O.
D. EPSR simulation

This section briefly describes the Monte Carlo (MC) routine (EPSR) used for analyzing the experimental data, for \( Q \) values larger than 0.25 Å\(^{-1}\), in terms of molecular configurations. In this range the corrected NDIS data are expressed in terms of interference differential cross-sections, as

\[
F(Q) = \sum_\alpha \sum_\beta w_{\alpha\beta} [S_{\alpha\beta}(Q) - 1],
\]

where \( \alpha \) and \( \beta \) label the atomic sites, and the functions \( S_{\alpha\beta}(Q) = 4\pi \rho \int_0^\infty r^2 [g_{\alpha\beta}(r) - 1] \frac{\sin Qr}{Qr} dr \)

called partial structure factors (PSF), are the Fourier transforms of the individual site-site radial distribution functions (RDF) \( g_{\alpha\beta}(r) \). The weighting coefficients are defined as \( w_{\alpha\beta} = c_\alpha c_\beta b_\alpha b_\beta (2 - \delta_{\alpha\beta}) \), where \( c_\alpha, c_\beta \) are the atomic concentrations of the \( \alpha \) and \( \beta \) nuclei, and \( b_\alpha, b_\beta \) are their neutron scattering lengths, \([23]\) respectively. For each sample, i.e., at each concentration and “age,” we have recorded three \( F(Q) \) functions (for the deuterated, hydrogenated, and equimolar mixture).

Thanks to the large difference between the scattering lengths of deuterium and hydrogen, these differ one from each other for the weighting coefficients and can be consequently considered as independent information on the structure of the sample. On the other hand, this is not enough to solve the system defined in Eq. (1) and to extract the whole structural information on the samples. This can be achieved by using the EPSR \([18]\) code, similar in principle to the methods routinely used in crystallography, which refines the molecular configurations that best fit the experimental data. The MC simulation is performed with a simulation box of dimensions, density, and chemical composition determined by the known physical and chemical properties of the real sample. By assuming that the sample components interact via a pairwise additive potential model suitable to reproduce as many as possible sample properties (reference potential), after equilibration of the system, the procedure accumulates the first molecular configurations from which the neutron \( F(Q) \) functions are then calculated. The differences with the experimental data are used as a feedback to make corrections to the reference potential (empirical potential). This loop is repeated until a satisfactory fit of the experimental data is obtained: at this point the corrected potential (reference plus empirical) is used to run a MC simulation, which allows us to record configurations compatible with the NDIS data. All structural characteristics of the sample can be finally calculated from the recorded molecular configurations.

This method is now routinely used for analyzing NDIS data from liquids \([17,25,26]\) and has been recently upgraded to allow simulating complex inhomogeneous samples, as for instance, emulsions \([27]\), or the present one, where noncubic simulation boxes are required. At the time of this analysis the simulation box could only contain a maximum of 3 \( \times \) \( 10^4 \) atoms and 40 different atomic species. As a consequence, we could not build either a suspension of Laponite platelets in water or a complete single Laponite platelet. Thus, our simulation box contains only a portion of a Laponite platelet, built from 15 (out of the 1500) replicas of the elementary cell,
over a rhombohedral symmetry. This crystal sits in the middle of the simulation box and determines its transverse dimensions ($26 \times 27 \, \text{Å}^2$). The box’s longitudinal dimension (234 Å and 395 Å for the high and low concentration, respectively), along with the number of water molecules at each side of the Laponite fragment, are determined by the constraint on the maximum number of atoms supported by the simulation routine and by the sample density (0.1 atoms/Å$^3$). Finally, 15 Na$^+$ ions (one per each elementary cell of the Laponite crystal) are solvated in the simulation box in order to simulate the real relative composition of the sample and balance the net negative charge of the platelet.

We have used the simple point charge/extended (SPC/E) model [28] as reference potential for water, and the model proposed in Ref. [16] for Laponite. The interaction between different atomic species is evaluated by applying the Lorentz-Bethelot rules. An example of the comparison of the experimental data and the fit is reported in Fig. 9.

As a consequence of the above-quoted numerical limitations, the EPSR routine can be used to fit the experimental data for $Q > 0.25 \, \text{Å}^{-1}$. Therefore, all three isotopic substituted samples, reliable at these high-$Q$ values, can be used to constrain the fit. However, in this $Q$ range the EPSR will give information at the atomistic level only, and there is no possibility to reproduce the large-scale arrangement of platelets in the real sample, and as a consequence could not provide information on the aging state of each sample.

III. THE DCS AND THE AGING PHENOMENON

The signatures of the aging phenomenon are visible at both concentrations in the region $0.02 \leq Q \leq 1 \, \text{Å}^{-1}$ (Fig. 10), well beyond that investigated so far by SAXS [7–9,24]. At higher $Q$ values, no differences in the DCS data due to Laponite concentration and aging are visible.

The aging effects, which cannot be reproduced by the EPSR (as commented in the previous section), will be discussed by looking at the fully deuterated samples, where the coherent signal is higher and the inelasticity and multiple scattering corrections (performed by direct subtraction of the systematic contribution estimated for pure water) are more reliable.

At $Q < 0.1 \, \text{Å}^{-1}$ the slope of the DCS is due to the tail of the $S(Q)$ broad peak centered at around 0.02 Å$^{-1}$ (observed in the SAS data for the “young” samples) and its evolution with aging is consistent with previous evidences [3]. In the range $0.1 \, \text{Å}^{-1} \leq Q \leq 1 \, \text{Å}^{-1}$ a signature of aging, never detected so far, is observed at both concentrations. In particular, at $C_w = 1.5\%$ in the gel state (1-year- “old” sample) the DCS is more intense than that measured in the liquid state (“young” sample) (Fig. 10). At $C_w = 3.0\%$, the “young” and 3-days- “old” (glassy) samples look identical, while the intensity of the DCS of the “very old” glassy sample (measured 1 month after arrest) is clearly higher (Fig. 10).

This behavior might be ascribed to sporadic contacts between few platelets, since the $Q$ range considered corresponds to lengths of the 6 to 60 Å range, which are intermediate between the thickness and the diameter of a platelet. These occur in both suspensions at delay time long enough that Laponite particles not involved in the gel network (in one case), or particles forming the repulsive glass (in the other case), can be brought into contact by attractive interactions. This finding is not surprising in the low-concentration sample, where the attractive interaction drives the arrest process (gelification). On the other hand, it is not obvious to find such contacts also in the glassy sample, where the arrest dynamics at short waiting times is determined by the repulsive interaction. This underlines the important role of attractive interactions even in
high-concentration repulsive glass as suggested in Ref. [8] and very recently demonstrated in Ref. [29], where the intervening long-time attraction strengthens the glass.

At $Q > 0.5 \, \text{Å}^{-1}$, we notice [Fig. 9(b)] that the first diffraction peak of the deuterated samples is sharper than found in pure water, suggesting that in these Laponite suspensions water is more ordered than in the pure liquid. In this $Q$ range, aging gives little or no differences among the DCS functions, as already stated.

IV. DENSITY PROFILES OF WATER AND IONS

The atomic configurations recorded by the EPRS code can be used to evaluate the density profiles of individual sample components, $\rho_i(z)$, along the $z$ direction, perpendicular to the Laponite surface:

$$\rho_i(z) = \frac{n_i(z, z + \Delta z)}{V(z, z + \Delta z)},$$

(3)

where $V(z, z + \Delta z)$ is the volume of a slice of the simulation box of thickness $\Delta z$ and containing $n_i$ atoms of species $i$. These are reported in Fig. 11 for water components in the case of $C_w = 1.5\%$ “old” sample; the profiles are similar at all concentrations and ages. In particular, for water atoms, as already found under confinement within a solid matrix [16,26,30,31] or in the vicinity of a solid surface [15,32,33], the profiles are not homogeneous, and show the presence of a first dense wetting layer, with thickness of $\sim 2 \, \text{Å}$. Notably the density of the wetting layer is almost twice the density of bulk water. The Na$^+$ ions are instead homogeneously distributed within the simulation box, contrarily to that found in previous simulation work [16]. This difference is likely due to the different concentration of Laponite and box dimensions considered in Ref. [16], where 1200 water molecules and 24 ions were confined between two Laponite crystals $\sim 34 \, \text{Å}$ apart.

V. RADIAL DISTRIBUTION FUNCTIONS

The interaction of water with the Laponite surface determines the particular shape of the radial distribution functions of water atoms (O$_w$ and H$_w$) and, for instance, Laponite oxygens

FIG. 11. (Color online) Density profile of water atoms (oxygens, black squares; hydrogens, red circles) along the direction normal to the Laponite surface, for the $C_w = 1.5\%$ “old” sample. The profiles for all other samples are similar.

FIG. 12. (Color online) Radial distribution function of the O$_w$-H$_w$ and O$_s$-O$_w$ pairs, for samples at different Laponite concentration and age. No differences can be appreciated due to Laponite concentration and age. Interestingly, the $g_{O_s,O_w}(r)$ functions show a clear periodicity, due to the interaction of water with the crystalline surface of Laponite platelets. Conversely, the $g_{O_s,H_w}(r)$ functions suggest that the arrangement of the hydrogen sites is orientationally disordered and that water does not form H bonds with Laponite (unless very weak ones). Notice also that the O$_s$-H$_w$ minimum approach distance ($\sim 2.7 \, \text{Å}$) is shorter than that of the O$_w$-O$_w$ pairs ($\sim 3.2 \, \text{Å}$).

(labeled O$_s$), as shown in Fig. 12 for two samples out of the five. We observe that the minimum approach distance between H$_w$ atoms and O$_s$ ones is of the order of 1.5 Å, i.e., about 1.2 Å shorter than that of the O$_w$-O$_w$ pairs. Moreover, the $g_{O_s,H_w}(r)$ function has a broad, asymmetric first neighbor peak at $\sim 2.7 \, \text{Å}$, while the first peak of the $g_{O_s,O_w}(r)$ function is sharp and centered at $\sim 3.2 \, \text{Å}$. This means that the water molecules of the wetting layer orient their hydrogens mainly toward the Laponite surface, as shown by the snapshot of the simulation box reported in Fig. 13(a).

FIG. 13. (Color online) (a) A snapshot of the central part of the EPRS simulation box, showing the laponite crystal in the middle (O$_s$ atoms in red) and the first layers of water molecules (O$_w$ in red, H$_w$ in white). Notice that all water molecules in the Laponite first-neighbor layer orient their hydrogens toward the Laponite surface. (b) The red circles represent the O$_s$ spatial arrangement on the Laponite surface; the regions where the probability of finding a water molecule exceeds the 20% are highlighted in gray.

Nevertheless, there is no evidence for strong H bonds with the O$_s$ atoms, because the
The $O_s$-$H_w$ average distance is relatively large and the first peak of the radial distribution function quite broad. Interestingly, the $g_{O_sO_s}(r)$ function shows very sharp peaks and a clear periodicity, which is reminiscent of the crystalline structure of the Laponite surface.

The $O_s$ atoms on the surface of the platelets sit at the vertices of hexagons [see the red points in Fig. 13(b)] and we notice that the peak positions (3.1 Å) and periodicity of the $g_{O_sO_s}(r)$ radial distribution function suggest that the $O_w$ atoms sit on top of the center of these hexagons. This is confirmed by the regions within the first layer of water, where the probability of finding a water oxygen exceeds the 20%, evidenced in gray in Fig. 13(b). The water molecules first neighbors of the $O_s$ atoms likely point their hydrogens toward two opposite hexagons vertices (≈3.96 Å apart one from each other). The broadness of the first peak of the $g_{O_sH_w}(r)$ is due to the orientational disorder and tilting of the water molecules around their axes. In this hypothesis, the structured second and subsequent peaks of the $g_{O_sO_s}(r)$ functions can be interpreted as due to the superposition of two correlation functions. Namely, that between the $O_w$ atoms of the wetting layer and the $O_s$ atoms belonging to the neighboring hexagons on the Laponite surface (sharp feature of each peak), and that between the $O_s$ atoms, and the $O_w$ atoms far from the Laponite surface (broad shoulder at the right-hand side of each peak).

The water-water radial distribution functions look the same at all concentrations and age (Fig. 14) as expected by inspection of the DCS functions at $Q \geq 0.5$ Å. All of them show sharper and more intense peaks than the radial distribution functions of pure water. Notably, this cannot be due only to the wetting water layer, since the volume of water in our suspensions is so large that the number of water molecules at the surface is negligible, compared to the bulk ones. Therefore, the sensible difference between water-water correlations in pure water and in Laponite suspensions suggests that the presence of a relatively ordered water phase at the interface with Laponite platelets imposes a constraint also on water molecules in the next layers.

VI. CONCLUSIONS

We have reported a detailed analysis of the NDIS data on Laponite aqueous suspensions at two weight concentrations and different ages collected at the new diffractometer NIMROD. All the steps necessary to achieve correction for systematic errors, when the isotopic H-D substitution is applied and the sample container has a nonnegligible coherent contribution, as in the case of the silica containers used in the present instance, are described. The samples have been studied in both the liquid and the arrested states.

In the very low-$Q$ range, the data confirm previous results: in particular the slope of the NIMROD data at $Q \leq 0.1$ Å$^{-1}$ is in agreement with the changes of intensity and position of the diffraction peak observed through SAXS experiments [7–9].

More importantly, present data have unveiled a new aging phenomenology, visible in the region $0.1$ Å$^{-1} \leq Q \leq 1$ Å$^{-1}$: that is precisely the region of momentum transfer uniquely accessible by NIMROD. Indeed, we observe an increase of intensity of the DCS in this range in the arrested gel state (1 year after preparation) and in the so-called “very old” glassy sample (namely after 1 month from its preparation). As a matter of fact, although the dynamical arrest occurs within a few days in the latter case, the enhancement of intensity cannot be observed in the just-arrested samples (named “old” throughout this paper), but only after longer waiting times. This phenomenon can be ascribed to the attractive forces between Laponite platelets, which have effects on the aging dynamics of the suspensions at longer times compared to the repulsive ones. Indeed, when the repulsive forces are predominant, the dynamical arrest is reached in a few hours or days (high-concentration samples), while the attractive interactions are dominant in the low-concentration samples, which take a time of the order of weeks or months to reach the gel-arrested state. Our data show that, when the high concentration samples are left undisturbed for a sufficiently long time after dynamical arrest, the effect of the attractive forces becomes visible and suggests the occurrence of pair contact between Laponite platelets. This demonstrates the importance of attractive forces also for high-concentration samples at long time after dynamical arrest.

The high-$Q$ data have been analyzed in terms of molecular configurations by running an EPSR simulation, which reproduces the data for $Q \geq 0.25$ Å, thus allowing us to investigate the structure of water in the suspension. This seems to have very weak or no dependence on the Laponite concentration and age, although showing a greater degree of order compared to pure bulk water. In particular we have found that the spatial arrangement of water molecules within the layers closest to the Laponite platelets surface shows orientational and translational order, which is reminiscent of the crystalline structure of the Laponite.

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