Anomalous Dielectric Behavior of Nanoconfined Electrolytic Solutions

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We report an anomalous dielectric effect of electrolytes under cylindrical nanoconfinement. In bulk phase, the decrease in the water dielectric constant (ϵ) with increasing salt concentration is well known, and is due to dielectric saturation. From molecular dynamic simulations of confined water and NaCl solutions, we show a dielectric anisotropy and an unexpected increase in ϵ_{\perp} of NaCl solutions with respect to the confined pure liquid until a critical concentration is reached. We infer that this striking dielectric behavior results from the interplay between the effect of confinement and that of ions on the water hydrogen bonding network.

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There has been about one century in which the decrease in dielectric constant (ε) of water with an increasing electrolyte concentration has been experimentally observed [1–4]. During these 100 years, this effect has been profoundly investigated from theoretical and numerical perspectives, and has been interpreted in term of dielectric saturation [3,5]. Microscopically, the dielectric depletion has been attributed to the screening of solvent dipoles by ions, leading to a decrease in dipole-dipole correlations [6,7]. More generally, two competing phenomena are invoked in the bulk phase: the destructuration of the hydrogen bonding (HB) network, which increases the dielectric constant, and the dielectric saturation, decreasing ϵ . For electrolytes in aqueous solutions, the breaking down of the hydrogen bonding network and diminution of the void spaces lead to favourable entropy. This increases the dipolar fluctuations and the dielectric constant [5]. On the contrary, the dielectric saturation due to the orientation of water dipoles around the ions decreases their rotational degrees of freedom and reduces the dielectric constant. The infinite dielectric constant (ϵ_{∞}) is directly related to the electronic relaxation occurring at shorter time. Thus, to capture the atomistic reorientational motion of water, ϵ_0 is more suitable. Despite the huge amount of studies devoted to bulk electrolytes, the dielectric response of electrolyte solutions under nanoconfinement remains unknown fundamentally. Meanwhile, nanoscale processes such as nanofiltration or nanofluidics have found many applications during this last decade [8,9], and various physical and chemical properties critically depend on the dielectric function. When water is confined to channels that are only a few nanometers in dimension, it can have structural and dynamic properties that are remarkably different to bulk. These properties play a crucial role in biology, nanotechnology catalysis, and soil chemistry, as well as in biological processes such as protein folding or ionic transport in membranes. As an example, dielectric properties directly ruled the nanofiltration, reverse osmosis, and nanofluidic processes in seawater desalination. Thus, there is a fundamental interest in investigating the dielectric responses of nanoconfined water. The emerging questions are, (i) What is the dielectric response of water and electrolyte solutions under nanoconfinement? (ii) Does one observe an increase or a decrease in ϵ ? and (iii) What is the microscopic driving force of the evolution of ϵ ?

To address these issues, molecular dynamic (MD) simulations of water and NaCl solutions in a cylindrical hydrophilic silica nanopore (radius r = 12 Å) have been carried out by considering an infinite pore. The internal surface is covered by the hydroxyl group providing the hydrophilic character (see Fig. S1 of the Supplemental Material [10]). This inorganic framework has been frequently used as a model material to explore confinement effects [11]. Force field and the computational procedure are detailed in Sec. I of the Supplemental Material [10]. In Fig. 1, we report the ratio between the dielectric constant of NaCl solutions (in bulk and confined phases) of various concentrations and that of bulk water. The details of calculation of ϵ are



FIG. 1 (color online). Ratio of the dielectric constant of NaCl solutions in bulk phase (ϵ^{bs}) and the confined phase of various concentrations to the dielectric constant of water in bulk phase (ϵ^{bw}). In the confined phase, the dielectric constant is calculated from the average of the local component between r = 0 Å and r = 12 Å from the accounting of the dipolar relaxation of ions pairs (a) and considering water dipole only (b).

reported in Sec. II of the Supplemental Material [10]. Note that ϵ was computed from the dipolar moments of water molecules and the dipolar contribution of ion pairs. From the computation of the radial distribution function between Na⁺ and Cl⁻, we have determined a separated distance of 2.9 Å. Subsequently, this characteristic distance has been used to compute the whole of the ion pairs, and their dipolar relaxation was then accounted for in the dielectric constant calculation such that $\mathbf{M}(t) = \sum_{i}^{N_{water}} \mu_i(t) + \sum_{j}^{N_{pairs}} \mu_j(t)$, where **M** is the total dipole moment of the system given with respect to the individual molecular dipole moment of the *i*th water molecule and the *j*th ion pair.

We also carried out the calculation with only the dipolar moments of water molecules. This allowed disentangling of the fundamental dielectric properties of water from ionic conductivity. Therefore, the static dielectric constants inferred from our simulations are not impacted by the dielectric divergence that occurs experimentally at zero frequency owing to ion conduction. Our results can be directly compared with the experimental observables accessible at low (but finite) frequencies. At zero frequency, we obtain the relative dielectric permittivity (static dielectric constant) $\epsilon(0)$; this is the usual way to describe the dielectric behavior of a liquid. In the case of a system with long-range interactions, treated by the Ewald method with conducting boundary conditions and nonpolarizable models, $\epsilon_{\infty} = 1$ [12,13]. Thus, the calculation of epsilon (r) will allow us to capture the dielectric discontinuity ruling process of nanofiltration. However, when the model is polarizable, a correction is needed [14] such that $\epsilon(0) = \epsilon_{\infty} +$ $\frac{4\pi(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2)}{3\epsilon_0 V k_B T} \text{ with } \boldsymbol{\epsilon}_{\infty} = \frac{4\pi \langle \sum_{j}^{N} \alpha_j \rangle}{3\epsilon_0 V k_B T} \text{ where } V \text{ is the sample volume, } \langle \dots \rangle \text{ denotes a statistical average over the differ$ ent configurations, k_B is the Boltzmann's constant, ϵ_0 is the vacuum permittivity, and α_i is the polarisability of the *i*th atoms.

As shown in Figs. 1 and 2, accounting of ion pairs in the calculation of the dielectric constant does not impact



FIG. 2 (color online). Profiles of ratio of ϵ_{\parallel} and ϵ_{\perp} of NaCl solutions in confined phase of various concentrations to the dielectric constant of water in bulk phase (ϵ^{bw}). (a) and (b): The water molecules and ion pair dipoles were considered in the calculation of ϵ . (c) and (d): Profiles were obtained by considering the water molecules dipoles only.

the tendencies of ϵ_{\perp} and ϵ_{\parallel} . Furthermore, the influence of the higher moments of water as quadrupole has also been investigated. In Sec. II of the Supplemental Material [10], the calculation of the quadrupolar contribution in the extraction of ϵ is detailed. We showed that the quadrupolar moments are negligible in the calculation of ϵ of water and the electrolytic solution under nanoconfinement. Additionally, the atoms of the silica material have not been accounted for in the calculation of ϵ . Indeed, experimentally the dielectric contribution of the material is subtracted to only capture the contribution of the confined fluid. Figure 1 shows that ϵ decreases with the increase of the salt concentration in the bulk phase. This result reproduces the experimental dependence [15], validating our numerical model. The comparison between the experiment at a low frequency and simulation is illustrated in Fig. S3 of the Supplemental Material [10]. This comparison was already attempted by A. Yu for two concentrations [16].

In the confined medium, the dielectric constant is deduced from the diagonal tensor (see Sec. II of the Supplemental Material [10]) with only two unique components parallel and perpendicular to the surface. In linear anisotropic media, it is a tensor of rank 2, and in nonhomogeneous media, it is a function of the position inside the medium. Thus, it is difficult to consider the overall dielectric constant under cylindrical confinement. The dielectric components in Fig. 1 are calculated from the volume-weighted average of the local dielectric constant between r = 0 Å and r = 12 Å. Details of calculations are reported in Sec. II of the Supplemental Material [10]. The error bars of the predicted dielectric tensor elements are ± 2 . The dielectric properties were evaluated into the canonical ensemble, and data analyses were carried out

for the last 30 ns of simulations after 2 ns of equilibration. As depicted from Figs. 1 and 2, three confinement effects are observed: (i) dielectric anisotropy; (ii) for pure water, a decrease in ϵ_{\perp} and an increase in ϵ_{\parallel} in confined phase with respect to the bulk phase; and (iii) for confined NaCl solutions, the axial component (ϵ_{\parallel}) decreases as a function of the NaCl concentration, following the bulk trend, whereas the radial term (ϵ_{\perp}) has two regimes with a maximum value around 0.5 M. It can be noted that similar results were obtained from simulations performed with a pore of finite length, i.e., considering explicit external solid-liquid interfaces (see Sec. V of the Supplemental Material [10]). The radial modulation and the different concentration dependence of the dielectric properties of confined electrolyte solutions with respect to the bulk phase suggest a different microscopic organization of water. Indeed, ϵ is linked to the dipolar fluctuations of water molecules, which are influenced by the possible formation and strength of a hydrogen bonding network.

We report in Fig. 3(a) the radial profile of the density of hydrogen bonds for confined water. Hydrogen bonds have been defined through a geometric criterion (see Sec. IV of the Supplemental Material [10] for details). Figure 3(a) shows an increase in the density of hydrogen bonds under confinement with respect to the bulk phase. Additionally, the HB structure takes place radially (see Fig. S12 of the Supplemental Material [10]), which is the primal reason for the observed decrease of the dipolar radial fluctuations and ϵ_{\perp} in the pore center. Axially, and from the hydrogen bonding standpoint, the HB network is less cohesive than radially (see Fig. S12 of the Supplemental Material [10]). This loss of cohesion can lead to an increase in the rotational degree of freedom and then an increase of dipolar fluctuations. This could explain the rise of ϵ_{\parallel} under confinement with respect to the bulk phase. We further infer that the field induced by the confining matrix could additionally reduce the orientational freedom of water dipoles, acting in a similar way as the saturation effect. With regard to the interfacial layer, Fig. 3(b) shows an obvious correlation between the interfacial hydrogen bond depletion and



FIG. 3 (color online). (a) Radial profile of hydrogen bond density of confined water (solid line). The dashed line corresponds to the HB density of water in bulk phase. (b) Radial profile of the ratio between ϵ_{\parallel} of confined water and that of water in bulk phase (right axis and full circle symbols). Radial profile of the total number of hydrogen bonds per water molecule of nanoconfined water (dotted line and left axis).

the increase of the dielectric constant close to the solid surface. This interfacial dielectric increase was recently observed by Bonthuis and co-workers [17] for both hydrophilic and hydrophobic planar surfaces. The decrease in the number of hydrogen bonds close to the interface can be attributed to the formation of water-silanol hydrogen bonds. Indeed, as sketched in Fig. 4, the water molecules flip between the water-water and water-silanol HB networks, leading to a depletion zone such that dipolar fluctuations of water increase. This physical picture is corroborated by a decrease in the lifetime of hydrogen bonds ($\tau_{\rm HB} = 5.0$ ps for the depletion zone and 7.9 ps for the center of the pore), which is linked to a faster reorientational dynamic in this interfacial layer.

For pure water, the radial heterogeneous dielectric constant of the confined phase highlights the deep correlation that exists between the hydrogen bonding network and the dielectric properties. A kosmotropic effect of confinement is observed in the inner pore, leading to a strengthened HB structure with reduced dipolar mobility and dielectric constant. A chaotropic effect is induced at the interface, with the HB depletion zone increasing dipolar fluctuations and ϵ . The latter effect could also explain the interfacial increase in ϵ for a hydrophobic surface [17], as caused by a deficient HB network at the interface. The dielectric anisotropy of the confined water is supported by the recent dielectric measures carried out by Cui et al. on metal organic frameworks (MOFs) [18-20]. They provided a protocol able to measure ϵ_{\parallel} and ϵ_{\perp} of confined water in uniaxial channels. These MOFs have an anisotropy similar to our silica model, i.e., a radial confinement. These authors reported the dielectric behavior of guest water molecules in the channels of porous crystals. Thus, they showed that guest water molecules confined in channels



FIG. 4 (color online). Illustration of two hydrogen bonding networks (A = [<8 Å]; B = [8-10 Å]; C = [>10 Å]). The dashed and dotted bonds show the possibility of water molecules to form a hydrogen bond between two networks (water-water and water-SiOH).

exhibited anisotropy in a dielectric constant. They also provided a protocol to measure the orthogonal and axial component of ϵ in confined geometries. Thus, their results clearly corroborate our findings of an axial increase in ϵ_{\parallel} and a decrease in ϵ_{\perp} . In this Letter, we show that the local dielectric standpoint is in agreement with the linear dielectric response. However, in the Supplemental Material [10] we compare this with an overall calculation. This can be used for comparisons with experiments using the protocol proposed by Cui *et al.* [18–20]. Thus, given the cylindrical symmetry of our silica mesoporous material and the possibility to get ordered mesoporous silica samples, it is possible to measure ϵ_{\parallel} and ϵ_{\perp} .

Let us now consider the situation of confined NaCl solutions. On the one hand, the dielectric properties of the contact layer are slightly perturbed by the addition of electrolytes. This is consistent with the fact that Cl⁻ ions are located in this thin region (see Fig. S14 of the Supplemental Material [10]). A striking increase of ϵ_{\perp} is obtained for concentrations up to 0.5 M (see Fig. 2). Based on the structural aspects developed previously, the modifications of this dielectric component of confined NaCl solutions in the low-concentration regime (c < 0.5 M) can be attributed to two concomitant effects. The addition of ions perturbs the water hydrogen bond network that was initially enhanced by confinement for pure water. This is in favor of an increase of rotational motion. Moreover, the water-matrix electrostatic interaction that acts as a saturation field for pure water is gradually screened by the electrolytes. Both mechanisms contribute to an increase of ϵ_{\perp} and drive the dielectric properties of the confined phase toward the bulk values. It is noteworthy that in this regime of low concentration, there are few ions aggregated (see Fig. S13 in the Supplemental Material [10]) that would be required for an effective breaking of HB. Indeed, below a critical ion concentration, water molecules can reorganize themselves around ionic species so as to maintain a saturated hydrogen bonding network. This is borne out by the fact that the number of HBs per water molecule for a solution at 0.1 M is similar to water in the confined phase (Table I). This phenomenon is in line with the solvating mechanism of small hydrophobic species

TABLE I. HB lifetime $(\tau_{\rm HB})$, water dipolar relaxation time $(\tau_{\rm M})$, and number of HB bonds per water molecule $(n_{\rm HB})$ for confined water and NaCl solutions.

	$ au_{ m HB}$ (ps)	$ au_{ m M}$ (ps)	n _{HB}
		Bulk phase	
Water	7.9	5.1	1.9
NaCl(0.1M)	10.2	12.7	1.9
		Confined phase	
Water	7.9	20.2	1.9
NaCl(0.1M)	7.1	18.1	1.9
NaCl(1M)	8.9	29.4	1.6

described by Chandler [21]. Therefore, it is more likely that in this low-concentration range, the preservation of the HB network proceeds through a dynamical reorganization of water molecules around ions. This reorganization leads to a reorientational gain increasing dipolar fluctuation, which results in the observed increase in ϵ_{\perp} below the critical concentration. The decrease of τ_{HB} of NaCl solution at 0.1 M in the confined phase with respect to the bulk ones (Table I) confirms this hypothesis of a reorientational gain under confinement.

At higher concentrations, the ion-water interaction is dominant and the HB network is profoundly affected. The contribution of dielectric saturation prevails, and it is no more possible for the adjacent water molecules to maintain a complete HB network with the surrounding liquid. An increasing fraction of the HB possibilities are thus lost close to the pairs of ions (which are not observed at low concentrations). This loss of HB is balanced by a favoured orientation of water dipoles around ion clusters. This dominant saturation effect explains the bulk-like decrease in ϵ_{\perp} at higher ion concentrations and the fact that the dielectric function gradually looses its anisotropic character, initially induced by unidirectional confinement. This microscopic point of view is confirmed by the calculation of the HB lifetime (τ_{HB}) and dipolar relaxation time $(\tau_{\rm M})$ for various NaCl concentrations. Indeed, we show in Table I that $\tau_{\rm HB}$ and $\tau_{\rm M}$ are weaker in a 0.1 M NaCl-confined solution than in the pure liquid, suggesting a faster reorientational dynamics. In contrast, at 1 M, we observe an increase in the characteristic times, signifying a slowdown of the orientational dynamics.

Dipolar fluctuations of nanoconfined water and NaCl solutions have been investigated from MD simulations. We have highlighted an anomalous salt effect on dielectric properties of confined water. Below a critical salt concentration level (around 0.5 M), we have shown an increase in ϵ_{\perp} and a decrease of ϵ_{\parallel} with increasing salt concentration. This increase has been correlated to the reorganization of water molecules to keep their unperturbed HB network. In addition, we showed that the electrolytes balance the effect of confinement on ϵ of liquid water. Future work will focus on the effect of the pore size and surface properties on the dielectric properties of confined water.

Summary of supplemental material.—The supplemental material provides a model and computational procedure as well as details the calculation of dielectric constants, relaxation times, hydrogen bond density, and hydrogen bond lifetime. We also provide complementary information about the dielectric and structural analysis of water in bulk and confined phases.

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- [10] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.109.107801 for a model and computational procedure as well as details the calculation of dielectric constants, relaxation times, hydrogen bond density, and hydrogen bond lifetime.

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