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Abnormal in-plane permittivity and ferroelectricity of confined water: from sub-nanometer channels to bulk

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Dielectric properties of nano-confined water are important in several areas of science, i.e. it is relevant in dielectric double layer that exist in practically all heterogeneous fluid-based system. Molecular dynamics simulations are used to predict the in-plane dielectric properties of confined water in planar channels of width ranging from sub-nanometer to bulk. Because of suppressed rotational degrees of freedom near the confining walls the dipole of the water molecules tend to be aligned parallel to the walls which results in a strongly enhanced in-plane dielectric constant ($\varepsilon_{||}$) reaching values of about 120 for channels with height $8\text{\AA} < h < 10\text{\AA}$. With increasing width of the channel, we predict that $\varepsilon_{||}$ decreases nonlinearly and reaches the bulk value for $h > 70\text{\AA}$. A stratified continuum model is proposed that reproduces the $h > 10\text{\AA}$ dependence of $\varepsilon_{||}$. For sub-nanometer height channels an abnormal behaviour of $\varepsilon_{||}$ is found with two orders of magnitude reduction of $\varepsilon_{||}$ around $h \sim 7.5 \text{\AA}$ which is attributed to the formation of a particular ice phase which exhibits long-time ($\sim \mu$ s) stable ferroelectricity. This is of particular importance for the understanding of the influence of confined water on the functioning of biological systems.

INTRODUCTION

Adsorbed water in nanopores and its anomalous properties are a subject of recent theoretical and experimental interest, which is poorly understood. Several of its physical properties are strongly modified, e.g. its thermodynamics, mass transport, flow dynamics, heat transfer, melting and energy transport¹. The study of nanoconfined fluids (fluids confined in nanoscale geometries) has developed rapidly over the past few years. For example, the thermal conductivity of nanoconfined water was found to be anisotropic² and when the confining walls are made of graphene oxide membranes, nanoconfined water showed remarkable fast permeation^{3,4}. Recently, in a review paper Kavokine et al. discuss how basic equations that govern fluid behavior in the continuum limit break down and new properties emerge in molecular-scale confinement³. It was shown that a large number of analytical estimates and physical arguments are needed to organize various properties of confined water at channels with different heights⁵.

Determining the dielectric constant of nanoconfined water is a recent subject of research with conflicting predictions^{6,7}. Generally, the dielectric constant of a material has three main contributions^{8,9}: i) electronic, ii) ionic, and iii) dipolar. The dipolar contribution can be found using molecular dynamics simulations (MDS) or Monte Carlo simulations (MCS). In the past few years, MDS or MCS were used to examine water's unique properties employing a variety of classical force fields under both normal and critical conditions^{10–19}. For example, using MCS the variation of the dielectric constant of water with temperature and pressure were obtained by Aragones et al.²⁰ for both proton ordered and proton disordered structures of different ices using several water models. The dielectric constant of proton disordered ices (e.g. ice Ih at low temperatures) were perdicted to be larger than 100 while the proton ordered structures²⁰ have a much smaller dielectric constant of the order \sim 3-4. The latter is due to the decrease of the rotational degree of freedom and/or decrease of the number of H-bonds.

In the literature conflicting reports can be found on the value of the in-plane dielectric constant of confined water^{6,21–23}. For instance by applying a large external electric field $E_0 = 0.01$ V/Å, Itoh et al.⁶ found a nonlinear increase in the dielectric constant of confined water (for channels wider than 10Å) for both lateral and perpendicular fields. On the other hand, the in-plane dielectric constant of water as a function of the distance between hydrophobic confining surfaces (graphene) for nano-scale size channels was found to be fluctuating around the bulk dielectric constant when $h >> 10\text{\AA}$ and larger than the bulk value²² for $h \simeq$ 10Å, i.e. 105. Gekle et al.²¹ reported a small difference (up to 5%) between the in-plane dielectric constant of confined water in channels with size h=11, 31, and 61Å and bulk water. In addition, Ruiz-Barragan et al. [24] disclose stark dependences of the tensor profile for parallel dielectric response of confined water within planar graphene slit pores as a function of the confinement length.²⁴. Also, Schlaich et al. studied the dielectric constant of confined water in channels made of flexible polar head-groups of walls for channels with height $h>10\text{\AA}$ and found the bulk dielectric constant of water for channels with height $h > 10\text{\AA}$ and 85 for channel $h \sim 10$ Å. For channels smaller than h < 10Å there is no experimental data so far.

Moreover, recently, by using electrostatic force detection with an atomic force microscope (AFM), unexpected variation in the out-of-plane permittivity of confined water between graphene and hexagonal boron nitride (h-BN) was observed⁷.

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The presence of a surface layer with vanishing small polarization is the reason for such small out-of-plane permittivity $\simeq 2$ for channels with size of h < 20Å. Beyond 20Å a nonlinear increase in the permittivity was observed. Despite several studies that determined the out-of-plane component of the dielectric constant of confined water, there is currently no experimental data for the in-plane component.

Up to now ferroelectricity in nanoconfined water is controversial and is expected to influence the functioning of biological systems. The timescale of proton vibration is beyond experimentally accessible timescales, thus observing proton ordering (ferroelectricity) in cubic and hexagonal ice XI is infeasible and controversial^{25,26}. In bulk water the hydrogen bonds screen the dipole-dipole coupling resulting in the suppression of ferroelectric order. However, in confined water ordering of molecular dipoles trapped in beryl crystal lattices was detected²⁷. A ferroelectric soft mode that causes a Curie-Weiss behaviour of the static permittivity was also observed²⁷. Nakamura et al.²⁸ reported spontaneous step-wise changes in the net polarization at the transition of immobile to mobile water when confined inside a carbon nanotube, which was understood as due to the transformation to single-domain ferroelectric water.

In this paper we performed extensive MDS to simulate water confined between graphene and h-BN layers. We calculate the in-plane component of the dielectric constant (dipolar part) of confined water as a function of the channel size *h*. Since the dielectric constant is a second rank tensor, the variation of $\varepsilon_{||} = (\varepsilon_{xx} + \varepsilon_{yy})/2$ with the slab size from h = 6.4Å to h = 100Å was obtained by calculating the fluctuation of the total dipole moment of water. We present a continuum model where we include some of the microscopic details of confined water which is able to reproduce like decreasing behaviors of $\varepsilon_{||}$ results for h>10Å. Furthermore, we predict long time stable ferroelectricity ($\simeq 1 \mu s$) of confined water in channels with $h = 7.4 \pm 0.5$ Å.

THE MOECULAR DYNAMICS SIMULATIONS

Equilibrium molecular dynamics simulations with the large scale atomic/molecular massively parallel simulator LAMMPS²⁹ was used to investigate the impact of the confining walls on the relative permittivity of water confined inside graphene (and hexagonal boron nitride) capillaries. Our simulated system (see Fig. 1(b)) contains two layers of graphene each with 680 carbon atoms, *i.e.* our configuration unit cell has a planar geometry with dimensions $A = l_x \times l_y = 42$ Å× 43 Å.

The confining walls were fixed at their *z*-positions. The SPC/E model was used to describe the water molecules³⁰. The number of water molecules inside channels have been chosen to provide bulk density, i.e. $\rho_B \simeq 1g.cm^{-3}$. For example the number of water molecules in the channel with heights of 6.5 and 10Å are 175 and 410, respectively. Other number of molecules for other channels can be found using $N = int[(Ah^{eff}\rho_B N_A)/m]$, where N_A is the Avogadros number, *m* is the mass of one water molecule and Ah^{eff} is the ef-



FIG. 1. (a) Continuum model and the atomistic model for confined water between two graphene or h-BN sheets (black balls) which are separated by distance h. In (a) the surface water layers and middle bulk water are shown by different colors and in (b) white (red) balls are hydrogen (oxygen) atoms.

fective volume that is introduced in next section. Notice that, the density of nanoconfined water might not be determined experimentally because different setups have different conditions such as size and confining walls and etc. Rather than the density, the chemical potential of water inside the channel should agree with the bulk value which can either be set by attached reservoir (as done in experiments) or by measuring the chemical potential $^{31-33}$. The driving force of water flow into graphene channel arises from lower chemical potential of nanoconfined water molecules to bulk water where the chemical potential difference is proportional to the logarithm of relative water density 31,34,35 . The water molecules interact with the graphene sheet via Lennard-Jones (LJ) pair potentials using $\varepsilon_{\rm C}$ =71.224 cal mol⁻¹, $\sigma_{\rm C}$ =3.41 Å and the cross LJ potential parameters were obtained using the Lorentz-Berthelot combining rules. The cut-off radius for the LJ potential was chosen at 10 Å. The NVT ensemble (Nose-Hoover thermostat) was used to keep the temperature at 300 K.

Periodic boundary conditions are employed along all directions and the confinement was along the z-direction. The vacuum space between two periodic images in the z-direction is taken to be $l_z=100$ Å. This number is large enough to minimize the long range electrostatic interaction between periodic images along the z-axis. The particle-particle particle-mesh method was used to compute the long-range Coulomb interaction with a relative accuracy of 10^{-4} . Water bonds and angle were fixed by the SHAKE algorithm³⁶. This condition resulted in densities close to the bulk density when $h \ge 10$ Å and slightly larger than the bulk density for h < 10Å. A time step of 2 fs was taken. After relaxing the system for 1 ns, the thermodynamical sampling was done up to 16 ns to ensure that the permittivity was converged.

THE MICROSCOPIC MODEL

By defining parallel polarization correlation function as^{23,24,37,38}:

$$C_{\parallel}(z) = \langle m_{\parallel} M_{\parallel} \rangle - \langle m_{\parallel} \rangle \langle M_{\parallel} \rangle, \qquad (1)$$

where $m_{\parallel}(z)$ is the laterally averaged polarization density at position z. Also " $\langle \rangle$ " is the average over many uncorrelated realizations (MD snapshots) having equal z. Here, $M_{\parallel} = A \int m_{\parallel}(z)dz$ is the total in-plane polarization. Note that the symbol \parallel refers to either x or y directions. Using

the fluctuation-dissipation theorem the local in-plane dielectric constant is given by 23 :

$$\varepsilon_{||}(z) = 1 + \frac{C_{||}(z)}{\varepsilon_0 k_b T}.$$
(2)

In Fig. 2, as a typical case, we depict the variation of $\varepsilon_{||}(z)$ with *z*, for confined water between two graphene sheets which are separated by *h*=10Å. Our result is in good agreement with those reported in Ref. [24].

Next, by assuming an effective dielectric constant $\varepsilon_{||}^{eff}$ in a box with effective height h^{eff} and using Eq. (2)²³ one finds:

$$\varepsilon_{||}^{eff} = 1 + \frac{\left[\int_{-h/2}^{h/2} \varepsilon_{||}(z)dz\right] - h}{h^{eff}}.$$
(3)

Because of uniform charge distribution²³ in a plane located at height *z*, one can approximate Eq. (3) by²²:

$$\varepsilon_{||}^{eff} = 1 + \frac{\sigma_{||}^2}{\varepsilon_0 k_B T V^{eff}},\tag{4}$$

where the effective volume is $V^{eff} = Ah^{eff}$, $h^{eff} = (h - \sigma_{C-O})$, and $\sigma_{||}^2 = \langle M_{||}M_{||} \rangle - \langle M_{||} \rangle \langle M_{||} \rangle$. Here $\sigma_{C-O} = 3.2$ is subtracted from *h* in order to use the actual height of channels in the calculations, *i.e.* the excluded volume effect³¹. Notice that when the confining walls are h-BN layers the $h^{eff} = h - \frac{1}{2}(\sigma_{N-O} + \sigma_{B-O})$ where $\sigma_{N-O} = 3.26$ Å and $\sigma_{B-O} = 3.31$ Å³⁹.

To prove that the results of direct integration using Eq. (3) and that of Eq. (4) are equal, for channel with $h=10\text{\AA}$, we directly integrate over Eq. (2) and found $\varepsilon_{||}^{eff} \simeq 124.5$ which is an agreement with the number that we found by using Eq. (4), i.e. 120. Notice that the results for $\varepsilon_{||}^{eff}$ do not change remarkably by changing slightly the effective height of channel. Note that Eq. (4) can be reformatted²³ to have the usual form of the fluctuation dissipation theorem. Hereafter for simplicity, we use the $\varepsilon_{||}$ instead $\varepsilon_{||}^{eff}$. In fact, Eq. (4) has the linear response theory form with thermal averaging of the dipole of confined water when the external electric field is zero. This allows us to determine $\varepsilon_{||}$ using an equilibrium correlation function. By calculating Mx and My and corresponding variance using Eq. (4), we were able to compute $\varepsilon_{||} = (\varepsilon_{xx} + \varepsilon_{yy})/2$ as a function of h.

In addition, one can find $\sigma_{||}^2$

$$\sigma_{||}^2(h) = \lambda(h)k_BT, \qquad (5)$$

where $\lambda(h) = (\frac{2d}{h}(\varepsilon_{||} - \varepsilon_b) - (\varepsilon_b - 1))\varepsilon_0 V$. This equation relates the macroscopic parameters of confined water to a microscopic parameter ($\sigma_{||}^2$) which has the usual form of the fluctuation dissipation theorem⁴⁰.

DENSITY PROFILE

The number of water molecules across the channels significantly influences the physical properties of confined water. The variation of local mass density $\rho(z)$ was depicted in



FIG. 2. The variation of in-plane dielectric constant (Eq. (2)) versus z which is perpendicular to the graphene sheets for h=10Å.

Z(Å)

h=10 Å

400

300

100

0

 $\hat{\vec{s}}_{200}$



FIG. 3. The variation of local mass density of confined water versus z which is perpendicular to the graphene sheets.

Fig. 2 versus *z*-direction across the channel for four different *h*, i.e., h = 6.5, 10, 12 and 15Å. There is a dense layer of water in the channel with height h = 6.5Å which is almost four times larger than the density of bulk water. The two layers of water (with smaller peaks and an almost empty middle part) are formed by increasing the height of the channel up to h = 10Å. These two sharp peaks remain constant at the layer closest to the surface for h > 10Å and correspond to the interaction between water molecules and confining walls⁶. For the larger channels (h = 15Å) other smaller density peaks appear between the two layers. Note that by increasing the channel height, the local mass density between these layers approaches to bulk value $1gr.cm^{-3}$.

CHANNELS WITH HEIGHT SMALLER THAN 10Å

It is seen from Fig. 4 that for channels with size smaller than 6.7Å the total in-plane dielectric constant $(\varepsilon_{\parallel}^T)$ is larger than 120, and for channels with height within the range 6.7Å < h < 8Å there is a deep minimum at h=7.4Å with $\varepsilon_{\parallel}^T \approx 1.93$. The latter is about a factor 40 smaller than the bulk value. This is





FIG. 4. The variation of the in-plane dielectric constant $\varepsilon_{||}$ with height of the channel for confined water between graphene sheets for channels with size $h \leq 10$ Å. The inset shows the corresponding results for confined water between two h-BN sheets.

due to the formation of an unusual amorphous ice structure of confined water⁴¹ between the two confining walls when they are separated by $h \simeq 7.4 \pm 0.5$ Å. Because of the obtained structure, one can categorize this as a proton-disordered ice phase of water. Previously it was found that the proton-disorder phase of ice (e.g. ice Ih) can have a dielectric constant of 100 and larger^{42,43}.

The radial distribution function (RDF) of the oxygen atoms confirms the mentioned ordered structure of confined water (see Fig. 5). The two dimensional RDF (RDF_{||}) of systems with size h=6.5Å and h=7.4Å are shown in Fig. 5 where the horizontal axis is $r = \sqrt{x^2 + y^2}$. In these RDFs significant second and third peaks appear only for h=7-8Å. On the one hand, the results for h=7.4Å and h=6.5Å indicate a very different planar microscopic structure of confined water.

When evaluating the time series of the total dipole moment, we discovered that confined water in channels with size $h = 7.4 \pm 0.5$ Å exhibits ferroelectricity. In Fig. 6(a), we depict the time evolution of $P_{x,y,z}$ for water in a channel with height *h*=7.4Å. Notice that $P_z = 0$ while $P_x \neq 0$ and $P_y \neq 0$ for very long time simulation (we ran the simulation up to $\sim 1 \mu s$ and found P_{v} is nonzero), i.e. non-zero net macroscopic electrical polarization. We found that when we repeat our simulations with new seed points, P_x and P_y showed other patterns but still $P_x \neq 0$ and $P_y \neq 0$. This led us to conclude that confined water in channels with height $h = 7.4 \pm 0.5$ Å exhibits ferroelectricity. This effect profoundly influence water permittivity and transport inside either one dimensional or twodimensional channels^{28,31}. For other values of *h* we did not find any net dipole moment. To gain more insights, we calculated the time average of the polarization vectors ($\langle M_{x,y} \rangle$) of confined water for channels h < 10 Å. The results are shown

FIG. 5. Planar radial distribution function $(RDF_{||})$ for confined water in channels with h=6.5Å, and 7.4Å. The inset shows corresponding structure of confined water.

in Fig. 5(b). It is seen that the confined water in channels $h = 7.4\pm0.5$ Å exhibits ferroelectricity. The latter is due to the particular local ordered structure of confined water at these channels. Note that $\langle M_z \rangle$ almost equal zero for all channel heights.

CHANNEL WITH HEIGHT LARGER THAN 10Å

By increasing the channel height further $\varepsilon_{||}$ approaches the bulk value $\simeq 75$, see Fig. 7. Notice that the scattering in the data of $\varepsilon_{||}$ for confined water between two h-BN sheets (the inset of Fig. 7) is due to the ionic nature of the h-BN sheet, i.e. the N and B atoms have local charges of -0.3e and 0.3e, respectively. In other words, in addition to the vdW interactions between water molecules and N and B atoms, the Coulomb interaction is also involved in the simulations. The latter causes a competition between thermal motion of the water molecules and the Coulomb (and vdW) interaction resulting in an enhanced variance of the dipoles of water i.e. $\sigma_{||}^2$. The results for h-BN were obtained by using the water-h-BN potential introduced by Wu et al.⁴⁴. Therefore we conclude that independent of the strength of the interaction between the water and the confining walls, there is a universal behavior in $\varepsilon_{||}$ with *h* in case of hydrophobic confining walls.

THE CONTINUUM MODEL

The capacitors-in-series model can explain the channel size dependence of the out-of-plane dielectric constant. It was first proposed by Zhang [49]. Here, we extend this idea and to find the in-plane dielectric constant of nanoconfined water. It has



FIG. 6. a)Time series of the three different components of the dipole moment of confined water in a channel with h=7.4Å. b) The variation of polarization vs *h*.

also been used to explain experimental results in Ref. [7].

Confined water can be considered as a continuum media consisting of three regions⁷, i.e. two surface water layers (SL) and bulk water (b) between them (see Fig. 1(a)). One naturally expects, because of the isotropy in the (x, y)-plane in the absence of external field, that the net in-plane polarization of the system is zero. For a given channel with height h, the boundary conditions on the in-plane components of the electric field $(E_{||})$ at the interfaces of the aforementioned regions are $E_{||}^{SL} = E_{||}^{b}$ where || refers to the planar component. Moreover, the total in-plane dipole moment $P_{||}^{T}$ of the system is given by

$$P_{||}^{T} = 2P_{||}^{SL} + P_{||}^{b}, \qquad (6)$$

where $P_{||}^{SL}$ and $P_{||}^b$ are the dipole moments at the SL and bulk region of the system (see the small box in Fig. 1(a) which indicates the interface between bulk and SL regions). The factor 2 in Eq. 6 is added because there are two SLs at the top and bottom of the system (see Fig. 1(a)). Here, $P_{||}^{SL,b} = \varepsilon_0(\varepsilon_{||}^{SL,b} - 1)E_{||}^{SL,b} \times V^{SL,b}$ where $V^{SL} = dA$ and $V^b = (h - 2d)A$ are the volume of SL and bulk region, respectively. Also, *A* is the area of the interface and h(d) is the height of the channel (SL). Notice, $\varepsilon_{||}^{SL}$ and $\varepsilon_{||}^b (= \varepsilon_{\perp}^b = \varepsilon^b)$ are the parallel (in-plane) component of the dielectric constant of SL and bulk water, respectively. Substituting the polarization in Eq. 6, one finds the following in-plane component of dielectric constant



FIG. 7. The variation of in-plane dielectric constant $\mathcal{E}_{||}$ with channel height for confined water between graphene sheets. The inset shows the corresponding results for confined water between two h-BN sheets. The solid curves are the results of Eq. 7 and dashed lines are bulk value from SPC/E model, i.e. 72.

as a function of *h*:

$$\boldsymbol{\varepsilon}_{||}^{T}(h) = \frac{2d(\boldsymbol{\varepsilon}_{||}^{SL} - \boldsymbol{\varepsilon}_{||}^{b})}{h} + \boldsymbol{\varepsilon}_{||}^{b}.$$
(7)

The water molecules in SLs are weakly bound to the graphene walls due to the van der Waals interaction between the water molecules and graphene, therefore, they are less mobile as compared to the water molecules in the bulk region. In order to determine $\varepsilon_{||}^{T}(h)$ one needs to know d, $\varepsilon_{||}^{SL}$ and $\varepsilon_{||}^{b}$. It is known that in bulk water $\varepsilon_{||}^{b} = \varepsilon_{\perp}^{b} = \varepsilon^{b} \cong 80$. Moreover, in Ref. [6], it was found that the SLs have: i) an effective width of about $d \simeq 5 \cdot 10$ Å, ii) an amorphous ice structure, and iii) small out-of-plane dielectric constant⁷ $\varepsilon_{\perp}^{SL} \sim 2 - 3$. From our MD simulations we found that $\varepsilon_{\perp}^{SL} \ll \varepsilon_{||}^{SL}$ which results in a nonlinear decrease in $\varepsilon_{||}^{T}$ versus h, i.e. $d\varepsilon_{||}^{T}/dh < 0$. In addition, Eq. (4) is a capacitors based model as previously introduced by Zhang for determining the out-of-plane dielectric constant of nanoconfined water [49].

The solid curve in Fig. 7 and corresponding inset figure are the results of Eq. 7. With $d = 5\text{\AA}$, $\varepsilon_{||}^{SL} = 115$ and $\varepsilon_{||}^{b} = \varepsilon^{b} = 72$ (the bulk value as obtained from the SPC/E model). For h-BN walls we used $d = 6\text{\AA}$. In fact, there is a weak van der Waals adhesion between the graphene (and h-BN) walls and the water molecules resulting in a weak bonding of water to the walls. A typical length scale of this attraction is 5Å for SLs near graphene and 6Å for that near h-BN. Notice that this simplest model is able to describe the $h > 10\text{\AA}$ behavior of $\varepsilon_{||}$ very well.

CONCLUSION

In summary, we performed extensive atomistic simulations

to determine the in-plane component of the dielectric constant of confined water in two regimes, i.e. h < 10Å and $h \ge 10$ Å. The atomically smooth graphene and h-BN interfaces were used as confining walls. The correlation between the height of the channels and the physical properties of the trapped water was studied. We constructed continuum model that is able to fit our atomistic simulations for channels with h > 10Å where there is a strong enhancement of ε_{\parallel} . Our results verify the final conclusions of the review paper by Kavokine et al.⁵ about different theoretical approach that one needs to study confined water at slits with size smaller or larger than 10Å. For channels with $h = 7.4 \pm 0.5$ Å we obtained values for $\mathcal{E}_{||}$ ($\mathcal{E}_{||}(\infty)$) up to almost two orders of magnitude smaller (the same order of magnitude) as compared to the bulk value $\sim 80 \ (\sim 3)^{45}$. This was explained as due to the formation of a crystalline phase of water. Furthermore, we predict ferroelectricity in the experimentally accessible timescales $(1\mu s)$ and temperature (300 K) in water confined in channels with height $h = 7.4 \pm 0.5$ Å. We found that while the diffusion coefficient reaches its bulk value for channels of h > 15Å (i.e. diffusion is governed by short range effects), the effects of graphene (or h-BN) sheets on the fluctuation of $M_{x,y}$ is long range, i.e. channels with height of 50Å have still suppressed fluctuations of $M_{x,y}$. The abnormal decrease in the dielectric constant of confined water in channels with height $h = 7.4 \pm 0.5$ Å is related to the emergence of ferroelectricity. Our results provide insights into the dielectric properties of nanoconfined water gives a consistent physical picture of $\varepsilon_{||}$ as function of the water layer thickness.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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