Note: On the dielectric constant of nanoconfined water

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Investigations of dielectric properties of liquid water in nanoconfinement are highly relevant for the energy storage in electrochemical systems, mineral-fluid interactions in geochemistry and microfluid based devices in biomedical analysis. It has been reported that polarization shows a strong anisotropy at water interfaces and the dielectric constant of nanoconfined water is surprisingly low ($\epsilon_\perp \sim 10$). Here, using a simple capacitor model, we show that the low dielectric constant of nanoconfined water can be largely accounted by the so-called dielectric dead-layer effect known for ferroelectric nanocapacitors.

Before talking about the effect of nanoconfinement, one needs to realize that the first effect of having an interface corresponds to a switch in the electric boundary condition. From classical electrodynamics, we know that the electric field $E_z$ is discontinuous at a dielectric interface, that is the reason why it is convenient to use the electric displacement $D$ as the fundamental variable instead. In the latter case, the polarization of dielectrics $P_z$ is added into the electric field. This makes $D$ continuous in the direction perpendicular to an interface and leads to its definition $D = E_z + 4\pi P_z$.

When the electric boundary condition is switched from constant electric field $E$ to constant electric displacement $D$, the dielectric response will be different accordingly.

$$
P_\parallel = \chi_\parallel E, \epsilon_\parallel = 1 + 4\pi \chi_\parallel \quad (1)
$$

$$
P_\perp = \chi_\perp D, \epsilon_\perp = 1/(1 - 4\pi \chi_\perp) \quad (2)
$$

The difference in $\chi$ due to the electric boundary condition leads to differences in the fluctuation of polarization at zero field and in the corresponding relaxation time. This phenomenon is not limited to water in nanoconfinement where switching of electric boundary condition is enforced by introducing explicit interfaces but can also be realized in bulk liquid water by turning on the constant electric displacement simulation. For bulk liquid water, $\epsilon_\perp = \epsilon_\parallel$ even though $\chi_\perp$ is radically different from $\chi_\parallel$.

Now let us go back to the original question: What accounts for the low dielectric constant $\epsilon_\perp$ of water slab in nanoconfinement? Is water in nanoconfinement completely different from that in the bulk?

To answer this question, we applied the constant electric displacement simulation with $D = 0.6835V/\AA$ to a water slab confined between two hydrophobic walls at ambient conditions (Fig. 1). Interactions between water molecules is described by simple point charge/extended (SPC/E) model and the rigid hydrophobic walls are composed of atoms on a dense cubic lattice. All molecular dynamics (MD) simulations were performed with GROMACS 4 package and technical settings are the same as described in the previous work.

From the corresponding electrostatic potential profile $\varphi(z)$, we can extract the depolarization field $-4\pi P_\perp$ from the slope in the middle region of water slab (Fig. 1b). Inserting this value into Eq. 2 and knowing $D = 0.6835V/\AA$ as the control variable, one gets $\epsilon_\perp = 65$. This number is indeed quite close to that of the bulk liquid water at the same magnitude of $D$, see Ref[6]. In other words, water slab of about 30 Å thick can already recover the bulk dielectric response. Then, the question is why the reported dielectric constant $\epsilon_\perp$ can be as low as a single digit number?

One needs to realize that $\epsilon_\perp$ is the overall dielectric constant which includes both surface contribution and bulk contribution. Because the simulation system is under the constant electric displacement condition, there-

![FIG. 1. a) A snapshot of MD simulations of water slab confined between rigid walls under constant electric displacement $D = 0.6835V/\AA$. The separation distance between walls $L_w$ is 30.77Å in this case.; b) The corresponding electrostatic potential profile $\varphi(z)$ generated from the charge density. The slope gives the negative of the depolarization field $4\pi P_\perp$ in the bulk water region.](image-url)
fore surface region and bulk region can be regarded as capacitors connected in series. This was already pointed out in the study of ferroelectric nanocapacitor.

\[
\frac{1}{C_{\perp}} = \frac{1}{C_{\text{surf}}} + \frac{1}{C_{\text{bulk}}} \tag{3}
\]

where \(C_{\perp} = \epsilon_{\perp}/L_w\). \(C_{\text{surf}} = \epsilon_{\perp,\text{surf}}/L_{\text{surf}}\) and \(C_{\text{bulk}} = \epsilon_{\perp,\text{bulk}}/(L_w - L_{\text{surf}})\). \(L_w\) is the separation distance between walls and \(L_{\text{surf}}\) is the total width of two interfaces.

Because of this sum of inverses, the region which has a smaller dielectric constant will dominate. From Fig. 1, one can see there are two vacuum gaps between walls and confined water slab. Therefore, our simple capacitor model will just approximate the confined water as vacuum gaps (\(\epsilon_{\perp,\text{surf}} = 1\)) plus bulk water (\(\epsilon_{\perp,\text{bulk}} = 65\) at \(D = 0.6835\text{V}/\text{Å}\)).

Base on these considerations and Eq. 3, \(\epsilon_{\perp}\) can be rewritten as:

\[
\epsilon_{\perp} = \frac{L_w}{L_{\text{surf}} + (L_w - L_{\text{surf}})/\epsilon_{\perp,\text{bulk}}} \tag{4}
\]

Here, the only unknown parameter is \(L_{\text{surf}}\), which is the width of vacuum gaps in this capacitor model. Because \(L_{\text{surf}}\) depends on the van der Waals radius of wall atoms and interfacial water molecules, therefore, we approximate \(L_{\text{surf}}\) as \(\sigma_w + \sigma_{\text{corr}}\). \(\sigma_w\) is the interatomic distance when the underlying Lennard-Jones potential becomes zero and it roughly doubles the van der Waals radius of the corresponding wall atom. Because water in the nanoconfined geometry face two walls, therefore we consider \(\sigma_w\) as a first approximation of \(L_{\text{surf}}\). The remaining term \(\sigma_{\text{corr}}\) is a correction factor for the mixing effect, thus it should be small and can be obtained by fitting MD data.

Results of \(\epsilon_{\perp}\) as a function of \(L_w\) are shown in Fig. 2. Fitting MD data with Eq. 4 gives \(\sigma_{\text{corr}}\) as \(0.22\text{Å}\), which turns out to be small as supposed. Using this model, one can make a prediction regarding the relationship between the Lennard-Jones parameter \(\sigma_w\) of wall atoms and the dielectric constant of nanoconfined water \(\epsilon_{\perp}\). The agreement with MD simulations is encouragingly good (Fig. 2b). We conclude that this simple capacitor model successfully captures the main physical reason behind the low dielectric constant \(\epsilon_{\perp}\) of water in nanoconfinement. Nevertheless, one should be aware that the dielectric constant of the interface \(\epsilon_{\perp,\text{surf}}\) is (drastically) approximated to be 1 in Eq. 3 and future works should include the effect of the interfacial water (Fig. 1b).

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