Supplementary Material

Anomalous Dielectric Response of Nanoconfined Water

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1. Derivation of the linear response equations

Here we provide derivations of Eqs. (2) and (3) (in the main text) from first principles. There are two different ways to derive these expressions- (i) directly from macroscopic electrostatics and (ii) by integrating microscopic formulae of grid-specific static dielectric constants. We show below that both approaches lead exactly to the same expression.

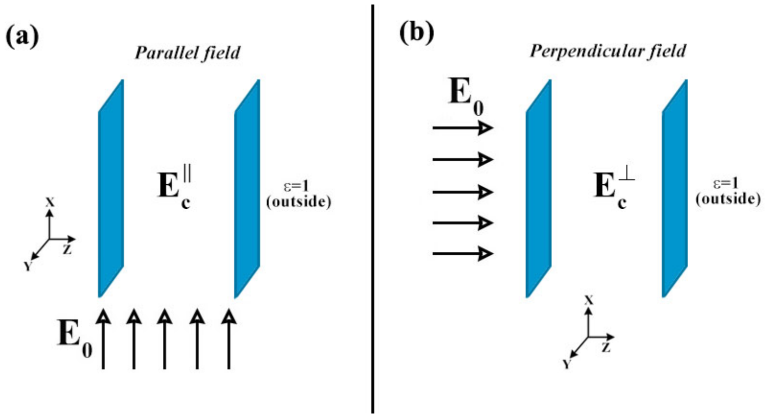

Figure S1. Schematic illustration of the placement of the slabs and the external fields to probe different components of the anisotropic dielectric tensor. The infinitely large slab is aligned along the XY plane and suspended in vacuum ($\varepsilon = 1$). (a) In case of the external field (E_0) parallel to the slabs, the cavity field becomes equal to E_0 as no dielectric boundaries are present. This gives us the parallel dielectric response. (b) For the perpendicular field (along the Z direction in the Cartesian frame), the cavity field gets modified. This provides the perpendicular (with respect to the slab plane) dielectric response.

For infinitely long slab confinement, the system is restricted (non-periodic) in one direction (Z) and open (periodic) along with the other two directions (X and Y). As a result, we obtain two unique eigenvalues of the dielectric tensor, namely, $\varepsilon_{\parallel}$ that is the same as $\varepsilon_x = \varepsilon_y$, and $\varepsilon_{\perp}$ that is the same as ε_z [Eq.(S1)].

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{\parallel} & 0 & 0 \\ 0 & \varepsilon_{\parallel} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix} \tag{S1}$$

In **Figure S1**, we schematically show the placement of the external probe field ($\mathbf{E}_0$) and the relative orientation of the system with respect to $\mathbf{E}_0$.

Here, due to the presence of a flat dielectric boundary in case of the perpendicular field, $\mathbf{E}_0$ gets screened by $\varepsilon_{\perp}$. That is, $\mathbf{E}_c^{\perp} = \mathbf{E}_0 / \varepsilon_{\perp}$. Hence, the relation becomes

$$\begin{gathered} \varepsilon_{\perp} = 1 + 4\pi \left(\frac{\mathbf{P}_{\perp}}{\mathbf{E}_c^{\perp}} \right) = 1 + 4\pi\varepsilon_{\perp} \left(\frac{\mathbf{P}_{\perp}}{\mathbf{E}_0} \right) \\ or,\ \frac{\varepsilon_{\perp} - 1}{\varepsilon_{\perp}} = 4\pi \left(\frac{\mathbf{P}_{\perp}}{\mathbf{E}_0} \right) \end{gathered} \tag{S2}$$

Now, we again apply LRT to obtain the expression for the perpendicular component of the dielectric constant [Eq.(S3)].

$$\varepsilon_{\perp}^{-1} = 1 - \frac{4\pi}{V k_B T} \left\langle \delta M_{\perp}^2 \right\rangle \tag{S3}$$

On the other hand, the cavity field along the parallel direction $\left(\mathbf{E}_c^{\parallel} \right)$ is exactly equal to the external field ($\mathbf{E}_0$). Hence, the relation $\varepsilon = 1 + 4\pi (P/E)$ remains intact and after the application of LRT we obtain Eq. (S4).

$$\varepsilon_{\parallel} = 1 + \frac{4\pi}{V k_B T} \left\langle \delta M_{\parallel}^2 \right\rangle \tag{S4}$$

Here $M_{\parallel}^2 = M_Z^2$ and $M_{\perp}^2 = \frac{1}{2}\left(M_X^2 + M_Y^2 \right)$ that are obtained from computer simulations of systems at equilibrium, as mentioned earlier.

Next, we derive the same equations from the grid-specific SDC expressions derived by Hansen, Netz and others in order to obtain spatially resolved dielectric profiles, $\varepsilon_{\perp}(z)$ and $\varepsilon_{\parallel}(z)$.[1-4] We directly provide these expressions in Eqs. (S5) and (S6).

$$\varepsilon_{\perp}^{-1}(z) = 1 - 4\pi\beta \left[\left\langle m_{\perp}(z) M_{\perp} \right\rangle_0 - \left\langle m_{\perp}(z) \right\rangle_0 \left\langle M_{\perp} \right\rangle_0 \right] \tag{S5}$$

$$\varepsilon_{\parallel}(z) = 1 + 4\pi\beta \left[\left\langle m_{\parallel}(z) M_{\parallel} \right\rangle_0 - \left\langle m_{\parallel}(z) \right\rangle_0 \left\langle M_{\parallel} \right\rangle_0 \right] \tag{S6}$$

Here β is $\left(k_B T\right)^{-1}$, *m(z)* is the dipole moment of a grid between *z* and *z+dz*, and M is the dipole moment of the whole system. The relation between M and m(**r**) is as follows,

$$M = \int_V d\mathbf{r}\, m(\mathbf{r}) \tag{S7}$$

We now need to integrate these two expressions with respect to volume element to obtain an average (or, effective) macroscopic expression,[5] that is,

$$\varepsilon_{eff} = \frac{1}{V}\int_0^d dV\, \varepsilon\left(z\right) \tag{S8}$$

where *V*=*A*×*d* or *dV*=*Adz* (A=area of each slab). Therefore, one can integrate Eq. (S5) as follows

$$\begin{aligned}
\varepsilon_\perp^{-1} &= \frac{1}{V}\int_0^d Adz - \frac{4\pi\beta}{V}\int_0^d Adz\left[\left\langle m_\perp\left(z\right)M_\perp\right\rangle_0 - \left\langle m_\perp\left(z\right)\right\rangle_0\left\langle M_\perp\right\rangle_0\right] \\
&= 1 - \frac{4\pi\beta}{V}\left[\left\langle M_\perp \int_0^d Adz\, m_\perp\left(z\right)\right\rangle_0 - \left\langle M_\perp\right\rangle_0 \int_0^d Adz\left\langle m_\perp\left(z\right)\right\rangle_0\right] \\
&= 1 - \frac{4\pi\beta}{V}\left[\left\langle M_\perp^2\right\rangle_0 - \left\langle M_\perp\right\rangle_0^2\right]
\end{aligned} \tag{S9}$$

Here the final expression is the same as Eq.(2) in the man text. Similarly, Eq. (S6) can be written as

$$\begin{aligned}
\varepsilon_\parallel &= \frac{1}{V}\int_0^d Adz + \frac{4\pi\beta}{V}\int_0^d Adz\left[\left\langle m_\parallel\left(z\right)M_\parallel\right\rangle_0 - \left\langle m_\parallel\left(z\right)\right\rangle_0\left\langle M_\parallel\right\rangle_0\right] \\
&= 1 + \frac{4\pi\beta}{V}\left[\left\langle M_\parallel \int_0^d Adz\, m_\parallel\left(z\right)\right\rangle_0 - \left\langle M_\parallel\right\rangle_0 \int_0^d Adz\left\langle m_\parallel\left(z\right)\right\rangle_0\right] \\
&= 1 + \frac{4\pi\beta}{V}\left[\left\langle M_\parallel^2\right\rangle_0 - \left\langle M_\parallel\right\rangle_0^2\right]
\end{aligned} \tag{S10}$$

The final expression of Eq. (S10) is the same as Eq.(3) in the main text. In the next section, we discuss another theoretical model to obtain the SDC of parallel slab confined liquids and its equivalence to the above fluctuation formulae.

2. Errors and convergence in the calculated values of the static dielectric constant

In this section we provide the standard deviations associated with the values of calculated static dielectric constants for slab and spherically confined systems in **Table S1**. In addition, we provide the time-evolution of $\varepsilon_{\perp}$ for nanoslabs with d= 1 to 5 nm in **Figure S2**.

Table S1. Effective static dielectric constants with errors for (a) water under planer nanoconfinement and (b) water under spherical nanoconfinement.

(a) Planer Confinement			
d (nm)	**d_{eff} (nm)**	$\varepsilon_{\|\|}$	$\varepsilon_{\perp}$
1.0	0.816	75.4 ± 1.01	2.27 ± 0.017
2.0	1.876	69.9 ± 0.62	2.12 ± 0.015
3.0	2.856	73.3 ± 0.50	2.13 ± 0.014
4.0	3.856	64.0 ± 0.56	2.18 ± 0.019
5.0	4.866	65.2 ± 0.42	2.14 ± 0.012
7.0	6.876	69.0 ± 0.41	10.0 ± 0.016
10.0	9.896	70.8 ± 0.46	37.7 ± 0.018

(b) Spherical Confinement		
R_c (nm)	**R_{eff} (nm)**	ε_s
1.0	0.93	17.2 ± 1.1
1.5	1.44	20.7 ± 1.2
2.0	1.93	27.3 ± 1.5
2.5	2.44	34.2 ± 1.7
3.0	2.90	43.4 ± 1.8
4.0	3.92	55.7 ± 2.3

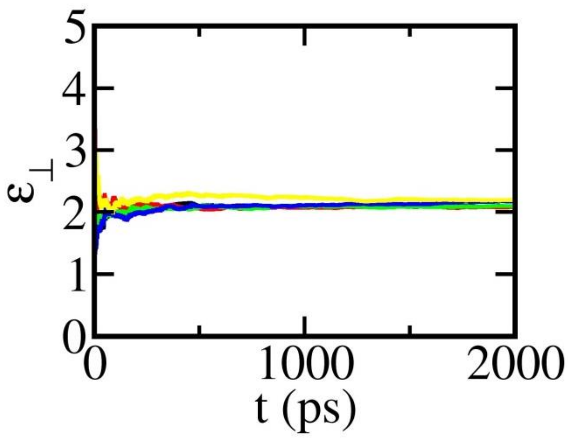

Figure S2. Cumulative time evolution of the perpendicular component of the effective dielectric constants for water in between parallel graphene sheets of d=1 to 5 nm. The values seem to converge well within ~2 ns.

3. Grid-wise <δ$M_{||}^2$> and <δ$M_\perp^2$> for slab-system, and <δM_R^2> for spherical system

Here we show the grid-wise mean squared dipole moment fluctuations for one nanoslab (d=3.0 nm) and one nanospherical (r=1.5 nm) systems. Because of the anisotropy, we decompose **<δM^2>** into **<δ$M_{||}^2$>** and **<δ$M_\perp^2$>** for slabs [**Figure S3(a)**]. On the other hand, for the spherical system we have one unique radial component **<δM_R^2>** [**Figure S3(b)**].

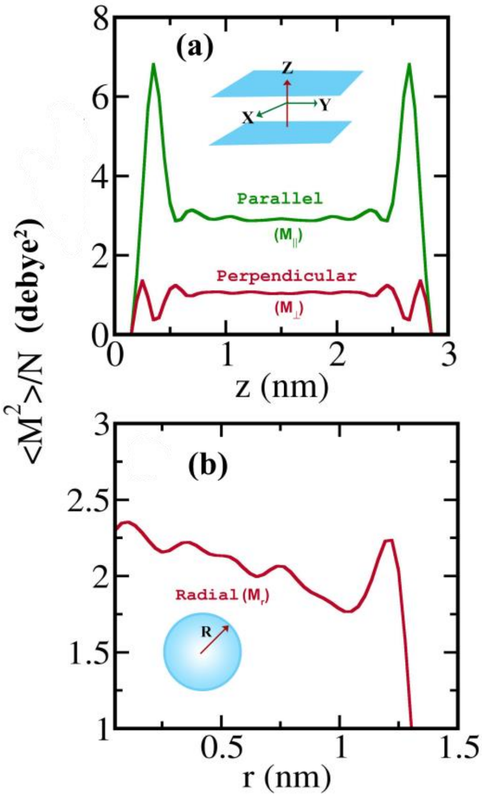

Figure S3. Polarisation profiles of nanoconfined water inside (a) parallel slabs with d=3 nm, and (b) spherical system with r=1.5 nm. For systems with different sizes, similar spatial profiles are obtained.

References

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