Redefining the dielectric response of nanoconfined liquids: Insights from water

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Recent experiments show that the relative dielectric constant ϵ of water confined to a film of nanometric thickness reaches a strikingly low value of 2.1, barely above the bulk's 1.8 value for the purely electronic response. We argue that ϵ is not a well-defined measure for dielectric properties at subnanometer scales due to the ambiguous definition of confinement width. Instead, we propose the 2D polarizability $\alpha_\perp$ as the appropriate, well-defined response function whose magnitude can be directly obtained from both measurements and computations. Once the appropriate description is used, understanding the interplay between electronic and ionic contributions becomes critical, contrary to what is widely assumed. This highlights the importance of electronic degrees of freedom in interpreting the dielectric response of polar fluids under nanoconfinement conditions, as revealed by molecular dynamics simulations.

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I. INTRODUCTION

The relative dielectric constant $\epsilon_\perp$ across a nanometric thin film of water was recently measured to be as low as 2.1 for a width of 1 nm. This paper by Fumagalli *et al.* [1] attracted enormous attention for two main reasons: (i) it is a beautiful, impressive *tour de force* experiment and (ii) the mentioned value is strikingly low, barely above the water bulk's purely electronic response [2] $\epsilon^b = 1.8$. The first point is undisputed. It is the second one we want to qualify in this article.

A small value for $\epsilon_\perp$ is not a surprising result. Numerous simulations have already shown that values in the $\epsilon_\perp < 10$ range are to be expected for confined water geometries [3–7]. The explanation of the origin of such reduced value appearing in several works [8–10] after that of Fumagalli *et al.* [1], including high-quality calculations (see, e.g., Ref. [9]), agree, in essence, with the earlier literature, all based on a combination of a more rigid structure of the water layer close to the interface [3–6], and the dead-layer effect (capacitors in series) for the thickness dependence [7]. Alternatively, in a recent work, it was proposed that the dielectric permittivity reduction of water is not connected to the structural alignment of interfacial water molecules, and instead, it emerges from anisotropic long-range dipole correlations next to surfaces [11]. The reduction of the dielectric permittivity in other H-bonded and non-H-bonded solvents was discussed recently [12], highlighting the generality of the observed reduction of the dielectric permittivity under confinement conditions.

The impact of interfaces on the permittivity tensor of water has attracted significant attention, which has stimulated the use of the dielectric tensor as a local function explicitly quantifying its dependence on the distance to the interface using statistical mechanics fluctuation formulas [10,11,13,14]. These studies already showed that major changes in the dielectric response of water appear at distances <1 nm from a surface, demonstrating the anisotropy of the permittivity tensor, the relevance of the surface-water interactions in determining the permittivity, and the importance of interfacial layers in defining the dielectric response of interfacial water. Despite the intrinsic interest of calculating the spatial dependence of the dielectric permittivity profile, its interpretation in mesoscopic and molecular scales is not straightforward, as it requires an averaging process over molecular layers [9–11]. Furthermore, while most studies focused on the modification of molecular degrees of freedom such as dipole-dipole correlations or water orientation at surfaces, the impact of confinement on electronic degrees of freedom has escaped scrutiny. One aspect of particular importance, which we address in our work, is whether confinement influences the electronic polarizability of confined water relative to bulk conditions. This is an important question, especially considering the very low permittivity of confined water inferred from experiments and theory. The importance of confinement effects

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and of molecular degrees of freedom has been discussed more widely in the investigation of fluid flow at the nanoscale. Advances in this area are promising, particularly in the development of devices with enhanced properties, which rely to some extent on the breakdown of the macroscopic theories that assume a continuum framework [15]. We argue below that using macroscopically defined properties is also problematic when considering the electrostatic response of fluids under nanoconfinement conditions.

II. THEORETICAL FRAMEWORK

Our purpose here is not improving on the determination of $\epsilon_\perp$ but instead stating that it is an ill-defined quantity in the subnanometer regime, and that insisting on its quantification is misleading the discussion of the key variables determining the electrostatic screening of confined fluids. As noted above, a problem emerges when assigning a dielectric permittivity to a molecular layer. This calculation requires the definition of a layer thickness to integrate the local perpendicular dielectric permittivity. The minima of the water center-of-mass density profiles normal to the surface are often used to define such thickness. As discussed before [1,9], the actual value of the computed or measured $\epsilon_\perp$ is rather arbitrary, as the result depends on establishing an effective film width that cannot be uniquely defined. Hence, the definition of the film width becomes essentially the answer to an ill-posed question, which may have sensible answers but not observable ones. Think, e.g., asking what is the width of an isolated graphene sheet. In essence, this is a problem arising from carrying a macroscopic-theory language over to the subnanometer regime.

The dielectric constant, relating the polarization P to the applied electric field, quantifies the response of a material within the macroscopic framework of Maxwell's equations. It is P that is ill-defined due to the ambiguity in the width, as P is given by the dipole moment per unit volume. Instead, the corresponding characterization for a two-dimensional (2D) system is given by the dipole moment per unit area, $\mathcal{P}_{2D}$. We propose that for subnanometer thickness, the 2D description is the correct one to use, the crossover from the 3D description being determined by the ambiguity in $\epsilon_\perp$ becoming comparable with the value itself. The transverse dielectric response is then characterized by the 2D transverse polarizability

$$\alpha_\perp \equiv \frac{1}{\epsilon_0}\frac{\partial \mathcal{P}_{2D}}{\partial \;{}^{\rm ext}_{\perp}}, \quad (1)$$

as already proposed for 2D materials [16], instead of the conventional susceptibility in 3D. As done for the polarizability of molecules in the gas phase, referring to the externally applied electric field ${}^{\rm ext}_{\perp}$ is the obvious choice here, since it makes no sense to refer to the perpendicular field inside a 2D system. For solid-state thin film systems, a "macroscopically averaged" electrostatic potential can be defined as a function of the perpendicular component [17], which is routinely used in interface and heterostructure physics. It has also been used in soft matter thin films (e.g., soap/water interfaces [18]), but the difficulty remains when averaging the field over an ill-defined width.

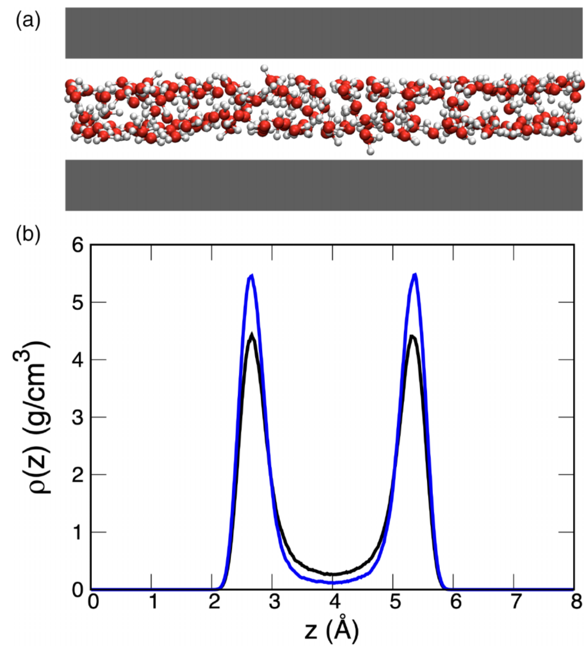

FIG. 1. (a) Schematic view of the simulation box, perpendicular to the confining plane. The gray-shaded regions represent the location of the confining soft potentials. Oxygen and hydrogen atoms in the water molecules are represented as red and white spheres, respectively. (b) Oxygen density profiles along the confining direction for 2D densities $\sigma = 0.177$ Å^{-2} (black) and 0.195 Å^{-2} (blue).

$\epsilon_0 \;{}^{\rm ext}_{\perp}$ in Eq. (1) equals to the electric displacement field $D_\perp$ to be used [19] when P is unambiguously defined. The defined $\alpha_\perp$ has units of length and is analogous to the conventionally defined molecular polarizability, which has units of volume. It can be called the dielectric thickness of the film. It is important to remember key differences when referring to the external field instead of the internal. For that, the definition in Eq. (1) can be extended to 3D as $\epsilon_0\alpha_{3D} \equiv \partial P/\partial \;{}^{\rm ext}$, using the conventional 3D polarization P. Both polarizabilities are related by $\alpha_{3D} = \alpha_\perp/$ in the context of this work [20], since $P = \mathcal{P}_{2D}/$. α_{3D} relates to the conventional relative dielectric constant as $\alpha_{3D} = 1 - \epsilon^{-1}$, which means that the range of 1 to for ϵ (from no response to complete screening of the internal field as in an ideal metal) becomes 0 to 1 for α_{3D}.

III. SIMULATION DETAILS

To illustrate the main ideas conveyed here, we present two sets of simulations for a bilayer liquid film of water confined along the z direction of the simulation box between two soft Lennard-Jones 9-3 separated by 8 Å between their respective origins (see Fig. 1). The parameters of the confining potential are set to mimic the interaction of water with solid paraffin [21]. This same system has been extensively studied in previous works [4,21–25]. The bilayer film thickness is at the lower end of the systems measured in Ref. [1]. For classical trajectories obtained using the empirical force field TIP4P/2005 [26] at $T = 300$ K under various values of an applied external field, we calculate $\alpha_\perp$ from the $\mathcal{P}_{2D}$ obtained from (i) the point charges of the TIP4P/2005 model and (ii) from the perpendicular dipole obtained with density functional theory (DFT)

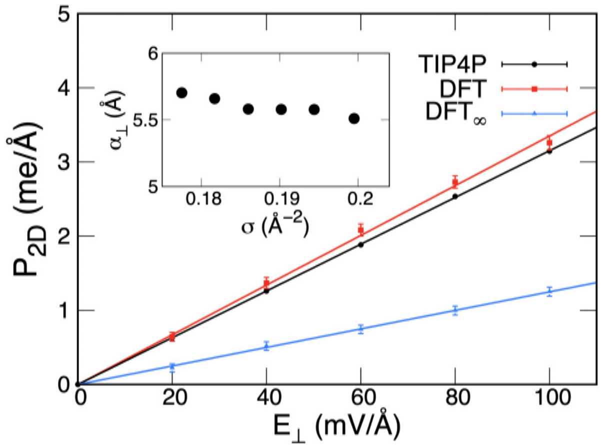

FIG. 2. 2D polarization $\mathcal{P}_{2D}$ vs external traverse electric field $_{\perp}^{\text{ext}}$ for TIP4P/2005 water classical trajectories (black) and for DFT calculations using the classical TIP4P/2005 under the same external field (red). In blue, we show the pure electronic response obtained from DFT as explained in the text. Inset: 2D density dependence of $\alpha_\perp$ obtained with the TIP4P/2005 classical simulations.

on a sample of snapshots of the classical trajectory, under the same external electrostatic field values. The TIP4P/2005 trajectories are generated within the NVT ensemble using the Nosé-Hoover thermostat involving 10 ns of equilibration time followed by 10 ns of production time. The simulation box, with dimensions 34.39 Å × 34.39 Å × 23.00 Å, contains between 210 and 236 water molecules. This corresponds to a 2D molecular density range of 0.177–0.200 Å^{-2}, where water is found to be in the liquid phase [27]. The periodic image interactions along the confining direction are effectively disabled by using the slab command in LAMMPS [28], with a `volf ctor` of 3.0. The DFT calculations were done with the SIESTA method [29] using the PBE density functional [30]. We use the TZP basis set for water described in Ref. [31]. To assess the accuracy of our simulation setup, we determine the polarizability of a water monomer. We obtain a polarizability of 1.6 Å^3 in Gaussian units (see the Supplemental Material [32] for calculation details), which is very close to the previously reported value of 1.59 Å^3 calculated using the same functional [33]. This result is also in reasonable agreement with the experimentally reported value of 1.45 Å^3 [34]. The remaining technical details for both kinds of calculations, classical and DFT, as well as a detailed description of the structural and other properties of the film as obtained in the simulations, can be found in Ref. [4].

IV. RESULTS AND DISCUSSION

Figure 2 shows $\mathcal{P}_{2D}$ versus $_{\perp}^{\text{ext}}$ for a 2D molecular density of $\sigma = 0.177$ Å^{-2}, for both TIP4P/2005 and DFT calculations. Regarding the orientation of the molecular dipole moment predicted by the TIP4P/2005 model along the confining direction, two preferential orientations are observed in each water layer (see the Supplemental Material [32]). This agrees with the structure reported in previous calculations using first-principles accuracy neural network potentials [9]. The 2D polarization for the DFT calculations is slightly larger,

TABLE I. Two-dimensional normal polarizability of the water film in Å. The experimental value $\alpha_\perp^{\text{exp}}$ is obtained from the values of $\epsilon_\perp$ and reported in Ref. [1]. TIP4P/2005 values ($\alpha_\perp^{\text{TIP}}$) were obtained from TIP4P/2005 trajectories under various values of the normal electric field. DFT results correspond to calculations under the same field values on a sample of snapshots of the corresponding TIP4P/2005 classical trajectories ($\alpha_\perp^{\text{DFT}}$), or snapshots of classical trajectories for TIP4P/2005 under zero field conditions ($\alpha_\perp^{\text{DFT}}$). $(\alpha_\perp \;\; /\alpha_\perp)^{\text{exp}}_{\text{bulk}}$ corresponds to the ratio of polarizabilities as obtained from $\epsilon = 78$ and $\epsilon \;\; = 1.8$ for bulk water.

$\alpha_\perp^{\text{exp}}$	$\alpha_\perp^{\text{TIP4P}}$	$\alpha_\perp^{\text{DFT}}$	$\alpha_\perp^{\text{DFT}}$	$(\alpha_\perp \;\; /\alpha_\perp)^{\text{DFT}}_{\text{film}}$	$(\alpha_\perp \;\; /\alpha_\perp)^{\text{exp}}_{\text{bulk}}$
4.5–7.9	5.7	6.1	2.3	0.37	0.45

consistent with the deformation of the electronic cloud. The resulting values of $\alpha_\perp$ are shown in Table I, and compared with the results of experiment [1]. For the latter, there is an ambiguity since the actual values of capacitance, $\mathcal{P}_{2D}$, or $\alpha_\perp$ were not reported, but $\epsilon_\perp = 2.1$ was given for a range of water film thickness between 8.5 and 15 Å.

The $\alpha_\perp$ interval appearing in Table I corresponds to that range of film thicknesses. Both theoretical values of $\alpha_\perp$ (TIP4P/2005, DFT) fall within the range inferred from experiments ($\alpha_\perp^{\text{exp}}$). The inset of Fig. 2 also shows the dependence of $\alpha_\perp$ on the 2D density of water molecules obtained from the analysis of TIP4P/2005 classical trajectories. These results address the experimental difficulty in ascertaining the experimental pressure conditions [1]. Our results (see Fig. 2) show that $\alpha_\perp$ features a very small dependence on the 2D density.

In addition to directly calculable, the proposed 2D polarizability $\alpha_\perp$ can be directly obtained from experiment, in particular from capacitance measurements using $l - \alpha_\perp = \epsilon_0/C$, where C is the capacitance per unit area and l is the effective distance between the capacitor plates. This distance is, in principle, ill-defined at the nanoscale, as the effective width of a plate capacitor depends on the charge distribution around its surface planes [35]. Differential capacitance measurements can be used to avoid the dependence on l, as done in Ref. [1]. In particular, by measuring the capacitance per unit area with and without dielectric (water), C and C_0, respectively,

$$\alpha_\perp = \epsilon_0\big(C_0^{-1} - C^{-1}\big). \tag{2}$$

If a change in the interplate distance $\;\; l$ is measured when the capacitor is filled with water (as in Ref. [1]), it simply needs to be added to Eq. (2): $\alpha_\perp = \;\; l + \epsilon_0(C_0^{-1} - C^{-1})$. Note that $\;\; l$ is independent of the choice of the reference position of each plate, as it directly quantifies the displacement that occurs between the plates before and after filling with water. Additionally, the measurements of C and C_0 are enough to define an "effective" dielectric constant, $\epsilon_\perp^{\text{eff}} = \frac{C}{C_0}$, without the need to estimate the effective distance l. $\epsilon_\perp^{\text{eff}}$ represents the overall dielectric behavior of the plate capacitor's interior [36,37], and it is not the dielectric constant of the water film. It can be used to partition the system into layers and evaluate the total capacitance as a model of capacitors in series. But such partitions, particularly the surface ones, are still ill-defined and arbitrary. We illustrate here the extreme sensitivity of $\epsilon_\perp$ if insisting on defining a water film width $\;\;$, in spite

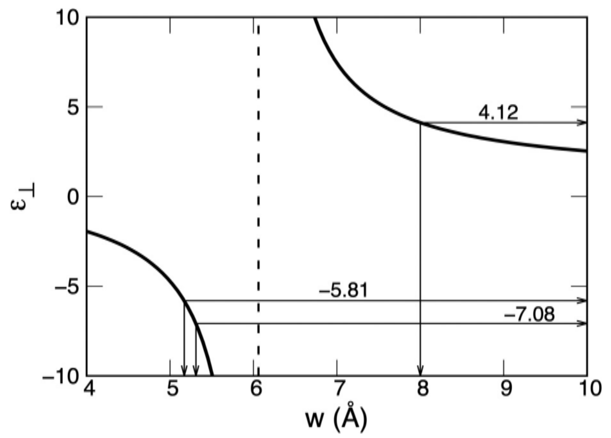

FIG. 3. Dielectric constant across a water thin film as a function of the defined width of the film for a given value of the 2D polarizability $\alpha_\perp = 6.06$ Å, as obtained with DFT simulations described in the text. Values of $\epsilon_\perp$ are highlighted for three values of for the same film: (i) the distance between the origins of the confining potentials $= 8$ Å, (ii) $= 5.17$ Å, the accessible perpendicular space as defined by Kumar *et al.* [21], for this bilayer film, and (iii) $= 5.31$ Å, obtained from normalising the 2D density of the film with the 3D density of bulk water. Negative values for $\epsilon_\perp$ indicate overscreening, a larger polarization than what is needed to screen the field completely.

of the acknowledged arbitrariness of such a choice [9]. The macroscopic formalism is thereby recovered, with $\alpha_\perp$ relating to $\epsilon_\perp$ through [19]

$$\epsilon_\perp = \left(1 - \frac{\alpha_\perp}{}\right)^{-1}. \tag{3}$$

$\epsilon_\perp$ diverges when $= \alpha_\perp$, which nicely points to the physical meaning of the length $\alpha_\perp$: The width of an ideal metal film that would respond with the same polarizability as the one being measured. The divergence is also responsible for the high sensitivity of the value of $\epsilon_\perp$ to the chosen . Figure 3 illustrates the variability for the DFT simulations described above, showing that a given value of $\alpha_\perp$ offers dramatically different values of $\epsilon_\perp$ for different sensible choices of .

The 2D polarizability $\alpha_\perp$ as defined here is an intensive property in the plane (per unit area), but extensive out of plane, and it depends on the amount of substance per unit area and the 2D density σ. When it is normalized by the experimental density ρ of bulk water at ambient conditions, it gives another effective thickness $= \sigma/\rho$, which converges to the film thickness in the macroscopic limit.

In our simulations, we obtain $= 5.31$ Å for the molecular 2D density $\sigma = 0.177$ Å^{-2} and $T = 300$ K. We include this thickness in the analysis shown in Fig. 3.

Finally, we address the striking experimental result that the reported dielectric response of the film $\epsilon_\perp = 2.1$ is only marginally larger than the electronic dielectric constant of bulk water $\epsilon^b \ = 1.8$.

We calculate the electronic 2D polarizability $\alpha_\perp^{\rm DFT}$ of the film by running DFT calculations under different values of $_\perp^{\rm ext}$ on a sample of snapshots from the zero-field TIP4P/2005 trajectory. The results are shown in Fig. 2, giving the value of $\alpha_\perp^{\rm DFT} = 2.3$ Å (Table I), which corresponds to a ratio of $\alpha_\perp^{\rm DFT}/\alpha_\perp^{\rm DFT}$ of 0.37 for the film. This ratio represents the percentage of electronic to total out-of-plane polarizability in the film. It can also be estimated for bulk water from experiments as

$$\left(\alpha^{3D}/\alpha^{3D}\right)^{\rm exp}_{\rm bulk} = \left(1 - \epsilon^{-1}\right)/(1 - \epsilon^{-1}). \tag{4}$$

Using $\epsilon^b \ = 1.8$ and $\epsilon^b = 78$ the ratio is 0.45, a 40% increase with respect to the thin film. If insisting on keeping the 3D language to discuss the film properties, our result indicates that if $\epsilon_\perp = 2.1$ as reported in previous experiments, then $\epsilon_\perp \ = 1.24$ instead of the bulk accepted value 1.8. However, that comparison relies on the experimentally reported value for $\epsilon_\perp = 2.1$, which was obtained assuming that the film thickness is well defined. A more appropriate description of the reduction in electronic response can be established by considering the (electronic) molecular polarizability. For the film, it is given by normalizing $\alpha_\perp^{\rm DFT}$ with the 2D molecular density $\sigma = 0.177$ Å^{-2}. We obtain a value of 1.01 Å^3 in Gaussian units, which is significantly lower than the molecular polarizability of water in the bulk phase: 30% smaller than the 1.45 Å^3 inferred from experiments [38] and 42% smaller than the 1.75 Å^3 obtained from DFT calculations using the same exchange-correlation functional as in this work [33].

The indications obtained in this work point to a reduction of the electronic response of the film. While this provides a plausible explanation for the striking experimental result reported, further investigation would be desirable to confirm and quantify this effect more precisely. In particular, *ab initio* molecular dynamics simulations could offer valuable insight. In this sense, our observations agree with the comment of Ref. [11] that the reduction in $\epsilon_\perp$ is not necessarily connected to interfacial water alignment. Our results suggest instead that it may be related to changes in electronic polarizability, a point that has not been considered or addressed in previous works.

V. CONCLUSIONS

That reduction becomes the intriguing result now. The directional dependence of the electronic polarizability tensor of the water molecule [33] is too small to support the hypothesis of the electronic response reduction being due to prevalent molecular orientations in the film.

Nonetheless, the thickness dependence observed for $\epsilon_\perp$ remains nicely explained by the capacitors-in-series, dead-layer picture. The point that it is $\alpha_\perp$ what is suitable for observation, both experimental and computational, does not invalidate a good phenomenological theory for analysis, but care should be exercised when attempting to interpret the experimental behavior in terms of ill-defined experimental observables.

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DATA AVAILABILITY

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

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