Comment on Hydrophobic Surface Enhances Electrostatic Interaction in Water

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In inhomogeneous systems that contain interfaces, the water dielectric constant becomes anisotropic and position dependent [1–3]. In their letter, Sato *et al.* [4] extract perpendicular dielectric constant profiles $\varepsilon_\perp(z)$ from MD simulations of water at a planar hydrophobic surface using the expression

$$\frac{[\varepsilon_\perp(z) - 1][2\varepsilon_\perp(z) + 1]}{3\varepsilon_\perp(z)} = \frac{\langle \mu_{\perp,0}^2(z) \rangle - \langle \mu_{\perp,0}(z) \rangle^2}{4\pi\varepsilon_0 k_B T a^3}, \quad (1)$$

which is derived for infinite homogeneous systems [5], where $k_B T$ denotes thermal energy, ε_0 is the vacuum permittivity and $\mu_{\perp,0}(z)$ is the water dipole moment inside a probe sphere of radius a (subscript 0 denotes zero external field). The correct expression for $\varepsilon_\perp(z)$ in planar geometry looks very different [1],

$$\varepsilon_\perp^{-1}(z) = 1 - \frac{\langle m_{\perp,0}(z) M_{\perp,0} \rangle - \langle m_{\perp,0}(z) \rangle \langle M_{\perp,0} \rangle}{\varepsilon_0 k_B T + (\langle M_{\perp,0}^2 \rangle - \langle M_{\perp,0} \rangle^2)/V}, \quad (2)$$

where $m_{\perp,0}(z)$ is the local perpendicular polarization density, obtained from the local charge density profile $\rho_0(z)$ via $m_{\perp,0}(z) = -\int_0^z dz' \rho_0(z')$, and $M_{\perp,0}$ is the integral of $m_{\perp,0}(z)$ over the system volume V. To test these different expressions for $\varepsilon_\perp(z)$, we here compare the electric field profile induced by a finite constant displacement field $D_\perp$, extracted from simulations according to

$$\Delta E_\perp(z) = \varepsilon_0^{-1}[D_\perp - m_\perp(z) + m_{\perp,0}(z)], \quad (3)$$

with the linear response prediction

$$\Delta E_{\perp,\text{lin}}(z) = \varepsilon_0^{-1}\varepsilon_\perp^{-1}(z)D_\perp, \quad (4)$$

where $D_\perp = D'_\perp + (M_\perp - M_{\perp,0})/V$ contains the explicit displacement field $D'_\perp$ and the field due to periodic images [1, 5].

Similar to Ref. 4, we simulate water between two frozen neutral nonpolarizable planar hydrophobic graphene layers at a distance of $L = 3\,\text{nm}$. Long range electrostatics are handled using the smooth particle mesh Ewald (SPME) technique with tin-foil boundary conditions (see Ref. 6 for simulation details). In the finite-field simulations we apply an external field of $D'_\perp/\varepsilon_0 = 0.25\,\text{V nm}^{-1}$, which is well in the linear regime [2]. The field acts by exerting a supplemental force on all partial dcharges. The simulation time is $500\,\text{ns}$ with a time step of $2\,\text{fs}$ in the NVT ensemble. Without external field we obtain in the slab center a dielectric constant of $\varepsilon_\perp = 69 \pm 9$ consistent with bulk results [7]. Figure
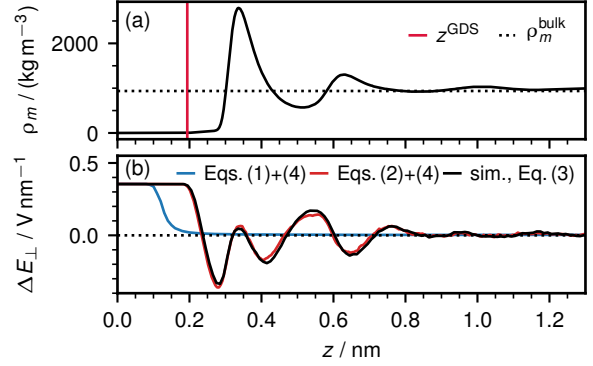

FIG. 1. (a) Water mass density profile at a graphene layer, the Gibbs dividing surface position is denoted by a red vertical line and the bulk density by a horizontal dotted line. (b) Perpendicular electric field profiles: The black line shows $\Delta E_\perp(z)$ directly extracted from a simulation for a finite applied displacement field of $D'_\perp/\varepsilon_0 = 0.25\,\text{V nm}^{-1}$, according to Eq. (3), the blue and red lines show the linear-response prediction according to Eq. (4) using Eq. (1) [4] and Eq. (2), respectively.

1(a) shows the water mass density profile $\rho_m(z)$, where $z = 0$ is the position of the charge neutral graphene layer, while Fig. 1(b) shows the perpendicular electric field profile $\Delta E_\perp(z)$ calculated using three different routes: The black line shows $\Delta E_\perp(z)$ according to Eq. (3) from simulations with an explicitly applied $D'_\perp$ field, while the linear-response predictions according to Eq. (4) in conjunction with the expressions for $\varepsilon_\perp(z)$ from Eqs. (1) and (2) are shown by blue and red lines, respectively. Clearly, the simulated electric field profile agrees perfectly with the predictions from Eq. (2) and shows oscillatory behavior, which is completely missed by the dielectric profile calculated according to Eq. (1). That a homogenous $D_\perp$ field induces locally a change of the electric field that has an opposite sign as the applied displacement field reflects the intricate layered water structure at interfaces. We conclude that Eq. (1) is not suitable to treat locally resolved electrostatic effects at interfaces.

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