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Quantum theory of interfacial tension quantitatively predicts spontaneous charging of nonpolar aqueous interfaces

Ariel Fernández [a,b,*]

[a] Argentine Institute of Mathematics (I. A. M.), National Research Council (CONICET), Buenos Aires 1083, Argentina
[b] Collegium Basilea – Institute for Advanced Study, Basel CH4053, Switzerland

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ABSTRACT

The spontaneous negative charging of aqueous nonpolar interfaces has eluded quantitative first-principle prediction, possibly because it steadfastly challenges the classical Debye dielectric picture. In this work we show that quantitative prediction requires a substantive revision of Debye's linear dielectric *ansatz* to incorporate an anomalous polarization component yielding electrostatic energy stored as interfacial tension and detailed enough to account for the differences in electronic structure between water and its ionized states. The minimization of this interfacial tension is due to a quantum effect resulting in the reduction in hydrogen-bond frustration that takes place upon hydroxide ion adsorption. The quantitative predictions are validated vis-à-vis measurements of the free energy change associated with hydroxide adsorption obtained using sum-frequency vibrational spectroscopy.

1. Introduction

Interfacial water on a nonpolar surface remains a subject of intense scrutiny due to its relevance in delineating the molecular forces that steer protein folding [1] and molecular associations [2], and drive biotechnological innovation [2–6]. The spontaneous negative charging of such interfaces through transference of hydroxide ions (OH^-) from bulk water has been established [7–9], yet the topic still remains a subject of contention [5,7,9]. No first-principle inference of spontaneous interfacial charging has so far generated quantitative predictions amenable of experimental verification [8]. In this regard, the treatment of interfacial water through molecular dynamics (MD) appears to yield contradictory results, even predictions of acidic (proton donating) interfaces [7,10]. This controversy stimulates the fundamental approach taken in this work, which involves a substantive revision of Debye's dielectric ansatz [4]. The latter would predict no polarization-induced charge since there is no intrinsic electrostatic field to speak of. Thus, we may state that the spontaneous charging of an aqueous nonpolar interface poses a challenge to the standard dielectric picture, demanding a reworking of the Debye ansatz starting from first principles and the incorporation of quantum effects reflecting the differences in electronic structure between water and its ionized states.

In this work we argue that experimentally verifiable quantitative predictions of spontaneous negative charging of aqueous hydrophobic interfaces require a general treatment of interfacial water dielectrics that cannot be subject to the constraints imposed by Debye's ansatz regarding polarization alignment [1,11]. The conceptual departure is essential to include the anomalous polarization component that arises as a result of hydrogen-bond frustration at the contact region between the two bulk phases. This revision could not have been reasonably envisioned at the time Debye's linear dielectric ansatz was formulated since details on water hydrogen-bonding structure were unknown [4]. As shown subsequently, the non-Debye contribution generates interfacial tension that is stored as electrostatic energy, a tension shown in this work to be mitigated by the adsorption of hydroxide ions. By frustration in this context we refer to a hydrogen bonding opportunity that cannot materialize because the proton acceptor or nucleophilic group is not physically present, as it is the case with the water layer in contact with the nonpolar surface.

As previously noted, the departure from the Debye linear dielectric *ansatz* becomes imperative because no charge $\gamma = -\nabla.\mathbf{P}$ may be generated by water polarization ($\mathbf{P}$) if the latter is made proportional to the vanishing electrostatic field $\mathbf{E}$ at the nonpolar surface, as it is the case with the Debye assumption $\mathbf{P} = (\varepsilon - \varepsilon_o)\mathbf{E}$, where ε, ε_o denote dielectric and vacuum permittivity, respectively.

To predict quantitatively the spontaneous charging of the aqueous nonpolar interface, a more general dielectric scheme is re-

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[*] Correspondence to: Collegium Basilea – Institute for Advanced Study, Basel CH4053, Switzerland. Tel.: +54 11 4954 6781; fax: +54 11 4954 6782.
E-mail address: ariel@afinnovation.com.

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quired. The hydrogen-bond frustration of interfacial water, described by the scalar field $\phi = \phi(\mathbf{r})$, with $\phi(\mathbf{r})$ = expected number of unfulfilled hydrogen bonds for a water molecule at position $\mathbf{r}$, generates a non-Debye polarization component $\mathbf{P}^{\#} = \mathbf{P} - (\mathbf{P}.\mathbf{e})\mathbf{e}$ ($\mathbf{e} = \mathbf{E}/\|\mathbf{E}\|$). In turn, this "orthogonal" polarization induces a net charge $\gamma^{\#} = -\nabla.\mathbf{P}^{\#}$. In previous work [1,11] we showed that distortions from bulk structure cause $\mathbf{P}^{\#}$ to be proportional to the frustration gradient, according to the equilibrium relation

$$\mathbf{P}^{\#} = -\xi \nabla \phi, \tag{1}$$

where $\xi = (\lambda \varepsilon_o)^{1/2}$ and $\lambda = 9.0$ mJ/m at 298 K [1]. The generation of net charge, and thereby of polarization, arises from the hydrogen-bond frustration at the interface (Eq. (1)) that leaves partial charges on the water atoms untitrated. The lack of interfacial charge neutralization implies that interfacial tension, which by definition arises from hydrogen-bond frustration, is also stored electrostatically in the anomalous polarization [1,4], as mathematically shown in this work. Eq. (1) will be subsequently corroborated in the context of this study. From Eq. (1), the net charge $\gamma^{\#}$ induced by $\mathbf{P}^{\#}$ becomes $\gamma^{\#} = \xi \nabla^2 \phi$. By making interfacial tension proportional to electrostatic energy, the non-Debye treatment enables the computation of the net charge induced by the frustration at the water layer in contact with the nonpolar surface, and hence becomes adequate to predict quantitatively the spontaneous charging of the interface.

This effect prompts us to further adapt the non-Debye approach to include adsorption of ionic species (OH^-, H_3O^+) that have an electronic structure different from water. The novelty of this study relative to previous reformulations of the Debye ansatz [1,2,4] resides in the fact that we now delineate and assess the impact of quantum effects related to the adsorption chemical heterogeneity on the interfacial tension and polarization electrostatics.

2. Methods

For simplicity, we consider water in contact with a featureless slab on nonpolar nonpolarizable material typically realized by fully hydrogenated graphene, a quintessential hydrophobic material [9]. The frustration or net loss of hydrogen bonding opportunities at the hydrophobic interface generates interfacial tension quantifying the disruption of the bulk-like tetrahedral hydrogen-bond coordination of water [1,2,11]. While the number of hydrogen-bond coordinations for water and hydroxide ion are the same in bulk ($g = 4$, with three proton-accepting lone electron pairs in OH^- and two in water), the extent of frustration of a water molecule at a liquid/solid interface is expected to be higher than that of a hydroxide ion (OH^-). This is so since the donated proton in the latter chemical species is expected to have a lower electrophilicity than the water proton, and therefore is expected to be less prone to form hydrogen bonds with a nearby nucleophile [9]. This conjecture will be corroborated in this work and is based on the fact that the hydroxide oxygen is less electrophilic than the water oxygen, since the former gained an electron while the latter shares an electron pair with a hydrogen atom. The argument leads us to postulate that the interfacial tension is lowered by adsorption of hydroxide ions or, in other words, the spontaneous negative charging of the nonpolar interface is expected to result from the relief of interfacial tension.

Given the above-noted observations, a quantum parameter, ζ, will be subsumed into the MD computations scaling a term accounting for interfacial energy in order to quantify the degree of frustration of interfacial hydroxide relative to interfacial water. The relative hydrogen bond frustration is given by the quotient $\zeta = \zeta(OH^-/H_2O) = F_h/F_w = 0.021/0.179 = 0.117$ (± 0.017), where F_h, F_w are the expected net quantum electrostatic fields (in e/Å^2 units) at the position or probe site of a putative hydrogen-bonding nucleophile (lone electron pair) that acts as putative acceptor of the proton donated by OH^- and H^2O, respectively [9]. The fields were obtained by molecular projection of the delocalized quantum charges in the aqueous condensed phase [12] along the direction of proton donation for hydrogen bonding [9]. The authors in Ref. [9] implemented a Car–Parrinello molecular dynamics scheme in a Wannier representation of the condensed phase [12], thus generating a unique set of maximally localized Wannier functions that realized the solid-state equivalent of localized molecular orbitals.

Based on the estimation of the quantum parameter ζ given above, we may assert that *the extent of frustration due to an unfulfilled hydrogen bond in the hydroxide ion at a nonpolar interface is 11.7% of the hydrogen-bond frustration of water with a dangling OH group*. Conversely, $\zeta(H_3O^+/H_2O) = 1.922$ (± 0.102) (cf. [9]), implying that hydronium adsorption would entail almost twice as much frustration than water at the interface. To summarize, mitigation of interfacial tension dictates that hydroxide ion – and not hydronium – must be preferentially adsorbed.

The spontaneous interface charging is studied via molecular dynamics computations [1], monitoring water local structure defined by the frustration ϕ and frustration gradient $\nabla\phi$ at each water spatial location and computing both interfacial tension $\Delta u = \Delta u_\zeta$ and non-Debye electrostatic energy density $\Delta u^{\#}$ as functionals of the water-discretized structural scalar field (ϕ) and vector field ($\nabla\phi$): $\Delta u = -(1/2)c(\lambda/\varepsilon_o)^{1/2} \int \gamma \phi^2 dr$, $\Delta u^{\#} = (1/2)\lambda \int \|\nabla\phi\|^2 d\mathbf{r} = (1/2)\varepsilon_o^{-1} \int P^{\#2} d\mathbf{r}$ (cf. [1]). To ensure smoothness (differentiability) of the water structure descriptors, the time-averaged number of hydrogen bonds of a water molecule at position $\mathbf{r}$ is computed while it visits a sphere of radius r = 4 Å centered at position $\mathbf{r}$ for a timespan $\tau = 1$ ps.

The spatial cell is partitioned by a regular periodic array containing the maximum number of balls of radius 4 Å with disjoint interiors, and all balls are probed simultaneously at 1-ps intervals. The system has reflection symmetry relative to the hydrogenated graphene slab. The $g(\mathbf{r})$-value is computed as the time-averaged number of hydrogen bonds involving a water molecule while its center of mass is inside the ball of radius 4 Å centered at $\mathbf{r}$. The hydrogen bond O_d–H–O_a (d = donor, a = acceptor) is detected with the geometric constraints subject to the standard parametrization: distance $(O_d, O_a) < 3.6$ Å, $120° \leq$ in-plane-angle $(O_dH, HO_a) \leq 180°$. The frustration scalar field $\phi(\mathbf{r}) = 4 - g(\mathbf{r})$ vanishes beyond the third water layer, precisely at distances $x > 9$ Å to the hydrogenated graphene slab ([1], Fig. 2b), and the gradient also vanishes for distances $x > 9$ Å since the slope of ϕ is zero at the point of contact with the x-axis. Thus, the choice of integration domain Ω becomes inconsequential in regards to the numerical value of the integrals in Eqs. (2), (3) provided Ω contains at least three water layers enveloping the slab.

We generated 10 MD 24-ps trajectories for water dynamics within an isobaric/isothermal ensemble (1 atm, 298 K) with 10,160 water molecules and a total of 160 ions, with 80 OH^- and 80 H^+ ($[OH^-] = 0.4$ M) packed against a featureless layer of fully hydrogenated graphene (6×6 supercell, 72C, 72H) representing a hydrophobic material [9]. The MD 24-ps trajectories for water dynamics are generated as described in [1] except for the incorporation in the potential energy of an interfacial term to account for hydrogen bond frustration at the nonpolar region of contact. The solvent bath provides at least four water layers of solvent envelope with water molecules extending 18 Å from the hydrogenated graphene surface. The evaluation of the interfacial tension-generating frustration incorporates a quantum mechanical parameter ζ describing the relative electrophilicity of the donated hydroxide proton relative to the water proton, a measure of the hydrogen bonding propensity of the dangling O–H bond in hydroxide relative to water. Thus, the assigned frustration at the interface is $\phi = 1$ for