When salts are added in small quantities to an aqueous solution, its surface tension increases [1, 2]. Wagner [3] was the first to connect this finding with the dielectric discontinuity at the air/water surface, suggesting dielectric image interactions as a possible explanation. This idea was implemented in the pioneering work of Onsager and Samaras (OS) that was built upon the work of Debye and Hückel [4]. In their model, OS found a universal limiting law for the dependence of the excess surface tension on the salt concentration [5]. However, the OS result implies an ionic-independent increase in the surface tension, which turned out to be violated in many physical realizations [6]. This led to numerous investigations of non-electrostatic ion-specific interactions between ions and surfaces [6, 7], and their role in modifying surface tension of electrolyte solutions [2]. Even nowadays a fundamental understanding of surface tension of electrolyte solutions is still missing.

On a broader scope, ion-specific effects date back to the late 19th century, when Hofmeister [8] measured the amount of protein precipitation from solution in presence of various salts. A universal (Hofmeister) series of ionic activity emerged. The same series is found in a large variety of chemical and biological systems [9–11], such as forces between mica or silica surfaces [12, 13], osmotic pressure in presence of biomacromolecules [14], and, most notably, the surface tension at the air/water interface [15, 16]. For simple monovalent salt, the latter depends strongly on the type of anion, while the dependence on the cation type is weak [17], and is consistent with the fact that anion concentration exceeds that of cations at the air/water interface. For halide ions, the lighter ones lead to a larger excess in surface tension in a sequence that is precisely the reverse of the Hofmeister series.

The OS treatment of electrolyte surface tension attracted much interest and generated a vast number of modifications to the original model. In particular, it is worth mentioning recent advances by Levin [18, 19], Dean and Horgan [20, 21] and Netz [22]. Levin and coworkers calculated the solvation free-energy of polarizable ions at air/water and water/oil interfaces. His model relies on three additional surface-ion terms that are added in an ad hoc way: image interaction with a Stern layer, ionic cavitation energy and ionic polarizability. While this model is not self-consistent, it allowed to fit the measured surface-tension dependence on ionic concentration for several monovalent salts. Quite separately, Dean and Horgan [21] calculated the ionic solution surface-tension to first order in a cumulant expansion, where the zeroth-order is equivalent to the Debye-Hückel approximation [4]. The surface-specific interactions were included via an ionic surface-exclusion layer in the vicinity of the dielectric interface. Concurrently, a surface cation-specific, short-range interaction was added [20], but the corresponding surface tension was not calculated. A different line of reasoning was initiated by Netz and coworkers [22], who calculated the surface tension for both charge and neutral surfaces by combing molecular dynamics (MD) with Poisson-Boltzmann (PB) theory. Their results fit well experiments conducted for hydrophobic and hydrophilic surfaces.

The inclusion of ion-specific effects into a self-consistent theory of electrolyte solutions is highly desirable but also quite difficult, or perhaps even impossible. We believe that one of the most promising lines of reasoning lies in a phenomenological approach [7] where short-range non-electrostatic interactions are added to the electrostatic free energy. This approach allows for a clearcut separation between various degrees of freedom. The additional free-energy terms describe specific electrolyte features that go beyond regular PB theory and depend on
the ion chemical nature, size, charge, polarizability, and the preferential ion-solvent interaction [7, 23–26].

In this Letter, we propose an approach that not only describes successfully the surface tension of electrolyte solutions, but also adds instructive insight into the corresponding surface interaction parameters. Our approach is self-consistent and extends the OS result in a direct and most natural way. Ionic specificity and its effect on the surface tension are taken into account by short-range ion-surface interactions characterized via a phenomenological adhesivity parameter, $\alpha$ [20, 27]. Our theoretical prediction fits well a variety of experimental interfacial tension data at the air/water and oil/water interfaces for several types of monovalent ions; the main advantage being that we are able to obtain an analytical expression for the surface tension in a systematic way.

In our model the water and air phases are taken as continuum media with uniform dielectric constant $\varepsilon_w$ and $\varepsilon_a$, respectively, with a sharp planar boundary between them at $z = 0$. The water volume $V = AL$ is modeled as a box of cross-section $A$ and an arbitrary large width, $L \rightarrow \infty$. We consider symmetric $(q^+_i q^-_j)$ salt, where $q$ is the ionic charge and the ions are taken to be point-like. Besides the usual Coulombic interaction $u(r, r') = 1/(4\pi \varepsilon_w |r - r'|)$, a short-range ion-surface interaction is added and modeled as a Dirac $\delta$-function, akin to the adhesivity introduced by Davies [28]. As it is experimentally known that anions are less hydrated than their cation counter-parts [17], the ion-surface interaction is considered only for anions, but our model can be easily implemented for more general setups. The model Hamiltonian is then:

$$H = \frac{1}{2} \sum_{i \neq j} q_i q_j u(r_i, r_j) + a \alpha \sum_{i \text{anions}} \delta (z_i),$$  

(1)

where $\alpha$ is expressed in units of $k_B T$ and the first term does not include the diverging ion self-energy. The minimal characteristic length, $a$, is associated with the ionic size, and the limit $a \rightarrow 0$ is appropriate for point-like ions.

Using the standard Hubbard-Stratonovich transformation [29], the grand-partition function (up to a normalization factor) can be written as

$$\Xi = \left(\det[\beta^{-1} u(r, r')]\right)^{-1/2} \int D\phi e^{-S[\phi]},$$  

(2)

with $\beta = 1/k_B T$ being the inverse thermal energy and $S$ plays the role of a “field action”.

$$S = \int_V d^3 r \left( \frac{\beta \varepsilon_w}{8\pi} \nabla \phi(r)^2 - \lambda_+ e^{-\beta \phi(r)} - \lambda_- e^{\beta \phi(r)} \right) - a \lambda_- (e^{-\beta \alpha} - 1) \int_A d^2 r e^{\beta \phi(z=0)},$$  

(3)

where we define the fugacities via the chemical potentials $\mu_\pm$ as: $\lambda_\pm \equiv a^{-3} \exp \left[ \beta \mu_\pm - \frac{1}{2} \beta q^2 u(r, r') \right]$, where the self-energy $u(r, r')$ is subtracted. We then make use of the $\delta$-function property

$$e^{-\beta \alpha \delta(z)} = 1 + a \left( e^{-\beta \alpha} - 1 \right) \delta(z).$$  

(4)

By rescaling $S$ into a dimensionless form, we introduce the coupling constant $[30]$, $C = 2\pi \varepsilon_0 a \lambda_- (e^{-\beta \alpha} - 1)$. In the weak-coupling regime, $C \ll 1$, $S$ can be expanded around its mean-field (MF) solution $S_0$, yielding $S \simeq S_0 + S_1$, where $S_1$ is the one-loop correction [29]. The grand-potential can then be written to the one-loop order as [31]:

$$\Omega = \Omega_0 + \Omega_1 = k_B T S_0 + \frac{k_B T}{2} \text{Tr} \left( \beta^{-1} \int d^3 r'' \left( \delta^2 S \delta \phi(r') \delta \phi(r'') \right)_{10} \right),$$  

(5)

with $\delta^2 S_{\delta \phi(r') \delta \phi(r'')} |_{0}$ is the Hessian of $S$ evaluated at the mean field.

The MF solution corresponding to the stationary point of $S$ can be rewritten in a standard way by introducing $\psi = i \phi$. The electrostatic potential in the air ($z < 0$), $\psi_1(z)$, satisfies the Laplace equation, and the electrostatic potential in the aqueous phase ($z > 0$), $\psi_2(z)$, obeys the PB equation:

$$\psi_2''(z) = \frac{8\varepsilon_w q_{wa}}{\varepsilon_w} \sinh (\beta q \psi_2(z)).$$  

(6)

We used the electro-neutrality condition, $\sum_i \lambda_i q_i = 0$, which for symmetric electrolyte implies, $\lambda_+ = \lambda_- \equiv \lambda$, and $\lambda_\pm = n_\pm$. The boundary condition is $\varepsilon_w \psi_1'' |_{z=0} - \varepsilon_a \psi_2'' |_{z=0} = 4 \pi \sigma_\varepsilon$, where the effective surface charge $\sigma_\varepsilon$ is induced by the surface potential $\psi_0 \equiv \psi(z=0)$,

$$\sigma_\varepsilon(\psi_0) = \sigma_0 e^{\beta q \psi_0},$$  

(7)

and $\sigma_0 = a n_b q (e^{-\beta \alpha} - 1)$. In the weak-coupling regime, $C \ll 1$ implies that $\sigma_0$ is small and self-consistently the surface potential $\psi_0$ is weak. Therefore, $\beta q \psi(z) \ll 1$ and the above PB equation (6) can be linearized. Using the fact that the electrostatic field vanishes at $z \rightarrow \pm \infty$, $\psi_{1,2}$ become:

$$\psi_1 = \psi_0 = - \frac{4 \pi \sigma_0}{4 \pi q \sigma_0 \beta + \kappa_D \varepsilon_w},$$  

$$\psi_2 = - \frac{4 \pi \sigma_0}{4 \pi q \sigma_0 \beta + \kappa_D \varepsilon_w} e^{-\kappa_D z} = \psi_0 e^{-\kappa_D z},$$  

(8)

and $\kappa_D^{-1} = \sqrt{8 \pi q^2 n_b / (\varepsilon_w k_B T)}$ is the Debye length.

$\Omega_0$ is obtained by substituting Eq. (8) into Eq. (5), while the fluctuation contribution $\Omega_1$ around the MF can be obtained rather straightforwardly by using the argument principle [31]. The discrete sum of the Hessian operator eigenvalues is then expressed in terms of its secular determinant, $D_\nu$. This yields

$$\Omega_1 = \frac{A k_B T}{8 \pi^2} \int d^2 k \ln \left( \frac{D_{\nu=1}(k)}{D_{\nu=0}(k)} \right),$$  

(9)
and the integral is over the transverse wave vector \( k = (k_x, k_y) \). The index \( \nu \) refers to the eigenvalue equation of the form
\[
\rho''(z) - k^2 \rho(z) = \nu \kappa_D^3 \cosh(\beta \psi_0 e^{-\kappa_D z}) \rho(z),
\]
with the boundary condition at \( z \to 0 \)
\[
\varepsilon_w \rho'(0^+) - \varepsilon_a \rho'(0^-) = -\Delta \rho(0),
\]
and \( \rho(z) \to 0 \) as \( L \to \pm \infty \), where \( \Delta \rho = \nu \) for \( 4\pi \sigma_B \beta q \). The secular determinant, \( D_\nu \), is then obtained from the boundary condition equations. In the weak-coupling regime, the RHS of Eq. (10) can be linearized, yielding
\[
f'_\nu(0^+) - \varepsilon_a f''(0^-) = -\Delta \rho(0),
\]
and \( \rho(\pm L) \to 0 \), giving our primary result
\[
\Delta \rho = \frac{k_B T}{8\pi} \int_0^L dk k \ln \left[ \frac{\varepsilon_w \varepsilon_a k - \Delta}{\varepsilon_w + \varepsilon_a} \right],
\]
with \( \Delta = \Delta_\nu = 1 \), and expressing \( \kappa_D \) in terms of the fugacity.

In order to calculate the surface tension, we need to find the Helmholtz free energy \( F \). A useful simplification is to replace the fugacities, \( \Lambda \), by the bulk densities, \( n_{B}^{(b)} \). This simplification is exact to the one-loop order for symmetric electrolytes [30]. Taking explicitly the \( \Lambda \to \infty \) only in the first term of Eq. (12), we obtain:
\[
F = \Omega_1 + 2k_BTV n_b \ln(n_B a^3) - \frac{k_B T}{12\pi} \kappa_D^3
+ \frac{k_B T}{4\pi} \int_0^L dk k \ln \left[ \varepsilon_w \varepsilon_a k - \Delta \right].
\]
The excess surface tension for the air/water interface is defined as
\[
\Delta \gamma = \left[ F - F^{(B)}(L) - F^{(air)}(L) \right]/\Lambda,
\]
with \( F^{(B)} \) being the free energy of a slab containing aqueous solution of width \( L \), and \( F^{(air)} \) is the free-energy of a slab of air [32].

The excess surface tension to one-loop order can now be written as a sum of two terms, \( \Delta \gamma = \Delta \gamma_0 + \Delta \gamma_1 \), giving our primary result
\[
\Delta \gamma_0 = -k_B T \left[ \frac{\sigma_e}{q} + 8\pi n_B \kappa_D^3 \left( 1 + \frac{q \psi_0}{2k_B T} \right) \right],
\]
\[
\Delta \gamma_1 = \frac{k_B T}{8\pi} \int_0^L dk k \ln \left[ \frac{\varepsilon_w \varepsilon_a k - \Delta}{\varepsilon_w + \varepsilon_a} \right].
\]
where \( \Delta \gamma_0 \) is the MF excess [27] and \( \Delta \gamma_1 \) is the fluctuation term containing a correction to the OS result [5, 21, 29]. The integral in Eq. (15) can be evaluated numerically for any value of \( \Lambda \), and has a leading asymptotic behavior in the \( \Lambda \to \infty \) limit,
\[
\Delta \gamma_1 \approx \frac{k_B T}{8\pi} \left[ \frac{1}{\varepsilon_w - \varepsilon_a} \right] \ln \left( \frac{\kappa_D^2}{\Lambda^2} \right).
\]
Writing \( \Delta \gamma_1 = \Delta \gamma_{11} + \Delta \gamma_{12} \), we note that \( \Delta \gamma_{11} \) is the well-known OS result [5, 21, 29], that is dominant for \( \alpha \to 0 \) limit. Interestingly, for \( \alpha > 0 \) and as long as the weak-coupling expansion is valid, the \( \Delta \gamma_1 \) will dominate over the MF term, \( \Delta \gamma_0 \).

We now compare our result for the surface tension, Eq. (15), to experimental values [33] for four different ionic solutions (with Na\(^+\) as their cation) at the air/water interface. Treating \( \alpha \) and \( \kappa \) as two independent parameters, we are able to fit experimental data perfectly. For the larger anions Br\(^-\) and I\(^-\) the fit agrees well for the entire concentration range up to \( \sim 1 \) M, while for the smaller anions, F\(^-\) and Cl\(^-\), deviations at larger concentrations \( \gtrsim 0.8 \) M are noticed. The other parameter values used in the fit are \( T = 300 \) K, \( \varepsilon_a = 1 \) for air and \( \varepsilon_w = 80 \) for water.

The fitted values of the ionic radii are in agreement with previous results for ionic size, such as those obtained in Ref. [34]: \( a_F = 1.36 \) Å; \( a_{Cl} = 1.81 \) Å; \( a_{Br} = 1.95 \) Å; \( a_I = 2.16 \) Å, implying a consistency check of our formulation. We note that the values for \( \alpha \) do not change significantly for various ions at the air/water interface. Hence, in this case it is appropriate to consider \( \alpha \) as independent.
of \( \alpha \).

Our model can be successfully applied to other types of liquid interfaces such as oil/water. In Fig. 2(a), we present a fit with experiments for air/water, and in 2(b) for dodecane/water. The fits are done for a series of three different salts having in common the K\(^+\) cation. For the dodecane dielectric constant we use \( \varepsilon_d = 2 \), while maintaining all other parameters as in Fig. 1. The fitted values of the ionic size \( a \) have been extracted from the data at the air/water and are carried over to the dodecane/water, while \( \alpha \), being a property of the interface, was fitted in (a) and (b) separately. The fitting for both interfaces is in excellent agreement with experiments, beside perhaps the KI case at the dodecane/water interface. The latter shows a very small \( \Delta\gamma \) that is almost independent of the salt concentration and, hence, is harder to fit. Comparing the \( \alpha \) and \( \alpha \) values for seven different salts at the air/water interface as presented in Figs. 1 and 2(a), we see that \( \alpha \approx -0.1 k_B T \) and does not change much, while \( \alpha \) varies from 1.35 Å to about 2.9 Å, in agreement with known ionic sizes. Also, at the dodecane/water interface [Fig. 2(b)] the interaction strength \( \alpha \) increases as compared with its fitted value for the air/water interface [2(a)]. These larger values of \( \alpha \) at the dodecane/water interface can be explained by an additional attraction of ions to the interface driven by the surface orientation of water molecules as was suggested for silica/water interface [12]. We note that the fitted values of \( \alpha \) agree well with known ionic radii. Although the interaction strength \( \alpha \) cannot be measured directly, our fitted values of \( \alpha \) agrees reasonably with the spatial average of the surface potential as reported in Fig. 1 of Ref. [19]. This spatial average gives \( \alpha \approx -0.1 \) \( k_B T \).

The present work offers several important advantages over previous ones. It is a self-consistent theory that extends the OS result, and can be used quite generally for a wide variety of interfaces and surface interactions, all taken on a common and unified ground. The model predicts analytically the dependence of the excess surface tension of different electrolytes at the air/water as well as at the oil/water interface. The obtained fits agree well with experiments and show clearly the reversed Hofmeister series (\( F^- > Cl^- > Br^- > I^- \)) at both interfaces. It is of importance to remark that within the range of validity of our theory, fluctuations dominate over the MF contribution to the computed surface tension. Finally, it will be of interest to generalize our model to calculate surface tension at the interface between two immiscible electrolyte solutions, where the ions are present in both solutions.

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\[ F(B) \] is obtained from Eq. (13) by replacing the air phase at \( z < 0 \) with an aqueous solution, \( \varepsilon_a \rightarrow \varepsilon_w \). Because there is no interface at \( z = 0 \), the ion-surface interaction vanishes leading to \( \Delta = 0 \). The only changes needed in order to obtain \( F(B) \) are to replace \( D_1(k)/D_0(k) \) by \( p/k \) and insert \( \Omega_0 = -2n_s \), where for the latter we use the MF solution of \( \psi = 0 \) for bulk solvent. Because there are no ions in the air phase, \( F_{\text{air}} = 0 \).