Electric double layer composed of an antagonistic salt in an aqueous mixture: 
Local charge separation and surface phase transition

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We examine an electric double layer containing an antagonistic salt in an aqueous mixture, where the cations are small and hydrophilic but the anions are large and hydrophobic. In this situation, a strong coupling arises between the charge density and the solvent composition. As a result, the anions are trapped in an oil-rich adsorption layer on a hydrophobic wall. We then vary the surface charge density $\sigma$ on the wall. For $\sigma > 0$ the anions remain accumulated, but for $\sigma < 0$ the cations are attracted to the wall with increasing $|\sigma|$. Furthermore, the electric potential drop $\Psi(\sigma)$ is nonmonotonic when the solvent interaction parameter $\chi(T)$ exceeds a critical value $\chi_c$ determined by the composition and the ion density in the bulk. This leads to a first order phase transition between two kinds of electric double layers with different $\sigma$ and common $\Psi$. In equilibrium such two layer regions can coexist. The steric effect due to finite ion sizes is crucial in these phenomena.

The electric double layer at a solid-liquid interface is one of the most important entities in physical chemistry \cite{1,2,3,4}. Its various aspects have long been studied mostly for one-component solvents with the mean-field Poisson-Boltzmann approach. However, in a mixture solvent, the ions interact with the two solvent components differently, leading to a coupling between the charge density and the solvent composition\cite{5,6,7,8,9}. This coupling is amplified in an aqueous mixture where the salt is composed of hydrophilic and hydrophobic ions (antagonistic salt)\cite{10,11,12,13,14,15,16,17,18,19,20,21,22,23}. In liquid water, small hydrophilic ions such as Na\textsuperscript{+} are surrounded by several water molecules due to the ion-dipole interaction\cite{1}. A notable example of hydrophobic ions is tetraphenylborate BPh\textsubscript{4}\textsuperscript{−}, which consists of four phenyl rings bonded to an ionized boron\cite{18}. Because of its large size, it largely deforms the surrounding hydrogen bonding\cite{19,20}. On the other hand, the ion solvation in nonaqueous solvent remains not well understood.

When hydrophilic and hydrophobic ions are added in an aqueous mixture, local charge separation occurs in the presence of compositional heterogeneity. Indeed, in a x-ray reflectivity experiment, Luo et al.\cite{21} observed such ion distributions around a water-nitrobenzene interface. The resultant double layer reduces the surface tension\cite{32,33,34,35,36,37,38,39,40}, as has been observed\cite{41}. Adding a small amount of NaBPh\textsubscript{4} in D\textsubscript{2}O-trimethylpyridine, Sadakane et al.\textsuperscript{42} found a mesophase near its criticality\cite{15,17} and multi-lamellar (onion) structures far from it\cite{16}.

The interactions of large hydrophobic ions with various soft matters are strong and sometimes dramatic\cite{2,42}. As an example, Calero et al.\cite{23} numerically studied accumulation of BPh\textsubscript{4}\textsuperscript{−} near a wall in pure water solvent to explain a charge inversion effect of colloidal particles. In the presence of a positive surface charge, they found that the BPh\textsubscript{4}\textsuperscript{−} density was peaked at a short distance of 2.5 Å for a hydrophobic wall, while it was broadly peaked at 3 nm for a hydrophilic wall.

In an aqueous mixture, hydrophilic (hydrophobic) ions are selectively adsorbed into a water-rich (oil-rich) adsorption layer\cite{12}. In this Letter, we further examine the distributions of hydrophobic anions (BPh\textsubscript{4}\textsuperscript{−}) and hydrophilic cations (Na\textsuperscript{+}) next to a hydrophobic wall varying the surface charge density $\sigma$. For $\sigma \geq 0$, the anions remain accumulated in the adsorption layer. However, for $\sigma < 0$, the cations are eventually attracted to the wall with increasing $|\sigma|$, where the composition profile also changes. We shall see that this changeover takes place as a first-order phase transition in some conditions of the parameters in our model. We treat large hydrophobic anions, so we should also account for the steric effect due to finite ion sizes. This effect has been studied in several papers in different situations\cite{32,30,31,32,33,34,35,36,37,38,39,40}.

As in Fig.1, we consider an electric double layer on a metal surface at $z = 0$. The z axis is perpendicular to the surface. The solvent consists of a waterlike component (called water) and a less polar component (called oil) with densities $n_w$ and $n_o$, respectively. For simplicity, they have the same molecular volume $v_0$, so their volume fractions are $\phi = v_0 n_w$ and $\phi' = v_0 n_o$. The cations and anions are monovalent with densities $n_1$ and $n_2$, respectively. Far from the wall, we have $n_1 \to n_0$, $n_2 \to n_0$, and $\phi \to \phi_\infty$. We set $n_0 = 4 \times 10^{-3} v_0^{-1}$ and vary $\phi_\infty$. Space is measured in units of $a \equiv v_0^{1/3} (\sim 3$ Å) and the Boltzmann constant is unity.

Introducing effective cation and anion volumes $v_1$ and $v_2$, we assume the total volume fraction is unity:

$$\phi + \phi' + v_1 n_1 + v_2 n_2 = 1,$$  \hspace{1cm} (1)

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which holds for very small compressibility. For polymer mixtures the space-filling condition in the same form has been assumed [33]. In our case we take $v_0$ as the inverse density in a one-component liquid of the first species at given $T$ and $p$ (for example, water at 300 K and 1 atm). Around this reference liquid we may define $v_i$ in the dilute limit of ions ($n_1 \to 0$ and $n_2 \to 0$ at $n_0 = 0$) as

$$\frac{v_i}{v_0} = \left( \frac{\partial n_i}{\partial n_w} \right)_{T,p,n}^{-1} \quad (i = 1, 2, j \neq i). \quad (2)$$

This ratio is also written as $(\partial p/\partial n_i)/(\partial p/\partial n_w)$, where $p$ depends on the densities and $T$. We assume that Eq.(1) is a good approximation even for not small $v_i/n_i$ (up to 0.2 in our analysis) at fixed $T$ and $p$ [34]. See Supplemental Information (SI) [35]. At present, we have no experimental data of $v_i$ from Eq.(2), so we set $v_1/v_0 = 0.5$ for small cations [36, 37] and $v_2/v_0 = 5$ for large anions [38].

The bulk free energy density is given by [3, 14]

$$f = \frac{T}{v_0} [\phi \ln \phi + \phi' \ln \phi' + \chi \phi \phi' + \frac{1}{2} C|\nabla \phi|^2]
+ \sum_{i=1,2} n_i [T \ln(n_i v_i) - T + \mu_{sol}^i(\phi)]
+ \frac{\epsilon(\phi)}{2} |E|^2, \quad (3)$$

where $\chi$ is the interaction parameter depending on $T$ and we set $C = T/a$ [38, 39]. The $\mu_{sol}^i$ is the solvation chemical potential, which is negative (positive) for hydrophilic (hydrophobic) ions. Its difference $\Delta \mu_{sol}^i$ between coexisting two phases is the Gibbs transfer free energy (per ion), whose size is large ($\gg T$) in aqueous mixtures in strong segregation [36] but is of order $T$ for water-alcohol in weak segregation [37]. Here, we assume the linear form,

$$\mu_{sol}^i(\phi) = -T g_i \phi, \quad (4)$$

with $g_1 = -g_2 = 10$. Then, $\Delta \mu_{sol}^i \sim \pm 10T$ for strong segregation [36]. The last term in $f$ is the electrostatic part, where $\epsilon$ is the dielectric constant and $E = -\nabla \psi$ is the electric field. We assume the linear form $\epsilon(\phi) = \epsilon_0 + \epsilon_1 \phi$ with $\epsilon_0 = \epsilon_1 = \epsilon^2/12\pi a T$. The Bjerrum length is then $3a/(1 + \phi)$. Most previous papers treated the simple case $v_1 = v_2 = v_0$ [3, 27–29], but some attempts were also made for the asymmetric case $v_1 \neq v_2$ [31, 32].

The surface free energy density at $z = 0$ is of the simple form $f_s = h_1 \phi$, where $h_1$ is the surface field arising from the solvent-wall interactions [41]. Minimizing the total free energy $F = \int_{z>0} df + \int_{z=0} dx dy f_s$, we find the boundary condition $\partial \phi/\partial z = h_1/2C$ at $z = 0$. Supposing a hydrophobic wall, we set $h_1 = 0.2T/a^2$ to obtain $\phi(z) = \phi(0) + 0.2z/a + \cdots$ for small $z$.

The electric potential $\psi$ obeys the Poisson equation

$$\nabla \cdot \epsilon \nabla \psi = \epsilon n_2 - n_1 ,$$

where $\psi \to 0$ as $z \to \infty$. Then, $\Psi \equiv \psi(0)$ is the potential drop across the layer, which is independent of $(x, y)$ on a metal surface. In this Letter, we control the surface charge $Q = \int dxdy \sigma$, where $\sigma(x, y)$ is the charge density related to $\psi$ by

$$\sigma = -\epsilon \partial \psi/\partial z \quad (z = 0). \quad (5)$$

We calculated all the profiles assuming homogeneity of the chemical potentials $\mu_\phi = \delta F/\delta \phi$ and $\mu_i = \delta F/\delta n_i$ together with the Poisson equation for $z > 0$. Here, $\mu_\phi$ and $\mu_i$ are determined by $\phi_\infty$ and $n_0$ (see their explicit expressions in SI [35]).

We are not very close to the solvent criticality ($\chi = 2$ and $\phi_\infty = 0.5$) in the bulk. In its vicinity, a mesophase appears in the bulk with addition of an antagonistic salt [3, 12, 13]. We are also away from the solvent coexistence curve limiting ourselves to the case $\chi \leq 2$, so we do not discuss the wetting with ions [3, 8, 10]. In this situation, we first seek one-dimensional (1D) profiles fixing $\sigma$, where
all the quantities depend only on \( z \). For constant \( \mu_0 \) and \( \mu_1 \), we consider the grand potential density,

\[
\omega = \int_0^\infty \! dz \left[ \mu_0 \phi - \sum_i \mu_i n_i + p_\infty \right] + h_1 \phi(0). \tag{6}
\]

where \( p_\infty = \mu_0 \phi_\infty + \sum_i \mu_i n_i - f(\infty) \). We then find

\[
d\omega/d\sigma = \Psi, \tag{7}
\]

at fixed \( n_0 \) and \( \phi_\infty \) (see its derivation in SI [23]). Thus \( \Psi \) is the field variable conjugate to \( \sigma \). We require \( d\Psi/d\sigma > 0 \) for the thermodynamic stability.

For \( \sigma = 0 \), local charge separation occurs due to the presence of an oil-rich adsorption layer on a hydrophobic wall. In Fig.2, the anions accumulate for \( z < \ell_1 \sim 3a \), while the cations are richer in the next layer \( \ell_1 < z < \ell_2 \sim 7a \). In (a), and \( \sigma = 0 \), where the solvent is oil-rich at any \( z \). However, it is more amplified in (b) and (c). Indeed, the deviation \( \phi_\infty - \phi(z) \) is enlarged with \( \phi_\infty = 0.35 \) and \( \chi = 1.4 \) in (b), while the criticality is lower with \( \chi = 0.5 \) and \( \chi = 1.9 \) in (c). The normalized potential drop \( e\Psi/T \) is (a) \(-0.40\), (b) \(-2.31\), and (c) \(-1.16\). Furthermore, in (b) and (c), the deviations of \( \phi \), \( n_i \), and \( \psi \) are strongly coupled even in the bulk, leading to oscillatory decays (or a precursor of the mesophase) [4,13]. In addition, \( v_2n_2(0) \sim 0.1 \) in (b). Thus, to check relevance of the steric effect, we also calculated \( n_2(z) \) for \( v_1 = v_2 = 0 \) [12].

The resultant \( n_2(0) \) at \( z = 0 \) is twice larger than in (b) and (c), but is larger only by 20\% in (a). Notice that neutral colloidal particles in the same situation behave as negatively charged particles [25].

In Fig.3, we give profiles of \( n_1, \phi \), and \( \psi \) for (a) \( \sigma = 0.03 \) and (b) \( \sigma = -0.2 \), where \( \phi_\infty = 0.35 \) and \( \chi = 1.4 \) (see Fig.4(b) for the corresponding states). In (a), the anion accumulation is stronger than in Fig.2(a) (where \( n_2(0) \) is 3 times larger) and the cations are expelled from the wall. In (b), the surface charge density \(-0.2 \) is larger, which is needed to induce cation accumulation at the hydrophobic wall. In (b), we then find \( v_1n_1(0) \sim 0.15 \), where \( \phi(z) \) exceeds \( \phi_\infty \) at any \( z \). Here, \( e\Psi/T \) is equal to (a) 1.0 and (b) \(-1.0\).

In Fig.4(a), we show \( \Psi \) vs \( \sigma \) for several \( \chi \) at \( \phi_\infty = 0.35 \). Here, \( \Psi \) has local maximum and minimum as a function of \( \sigma \) for \( \chi > \chi_c = -1.243 \). Generally, \( \chi_c \) depends on \( \phi_\infty \) and \( n_0 \). This indicates coexistence of two surface layers at \( \sigma = \sigma_1 \) and \( \sigma_2 \) with a common \( \Psi(\sigma_1) = \Psi(\sigma_2) \) for \( \chi > \chi_c \). Let the areas of these layers be \( S_1 \) and \( S_2 \), where \( S = S_1 + S_2 \) is the total wall area. At fixed charge

\[
Q = S_1\sigma_1 + S_2\sigma_2,
\]

we minimize the total grand potential,

\[
\Omega = S_1\omega(\sigma_1) + S_2\omega(\sigma_2) - \lambda(S_1\sigma_1 + S_2\sigma_2 - Q), \tag{8}
\]

with respect to \( \sigma_1 \), \( \sigma_2 \), and \( S_1 \). The \( \lambda \) is the Lagrange multiplier. With the aid of Eq.(7) we find \( \lambda = \Psi(\sigma_1) = \Psi(\sigma_2) \) and \( \omega(\sigma_1) = \sigma_1 = \omega(\sigma_2) = \lambda\sigma_2 \). These yield

\[
\omega(\sigma_2) - \omega(\sigma_1) = \int_{\sigma_1}^{\sigma_2} d\sigma \Psi(\sigma) = \Psi(\sigma_1)(\sigma_2 - \sigma_1). \tag{9}
\]

which is a Maxwell rule [42]. In (b), we then find \( \sigma_1 = -0.19 \) and \( \sigma_2 = -0.014 \) for \( \chi = 1.4 \). See SI for results in the range \( \sigma_1 < \chi < \sigma_2 \) [33].

In Fig.5, we display the coexistence curves in the \( \chi-\sigma \) and \( \chi-\Psi \) planes for several \( \phi_\infty \). For each \( \phi_\infty \), two layers coexist with \( \sigma = \sigma_1 \) and \( \sigma_2 \) inside the corresponding curve in (a), while \( \Psi \) is common in these layers in (b). Critical points are reached as \( \sigma_2 - \sigma_1 \to 0 \), which form a critical line on the coexistence surface in the \( \chi-\sigma-\phi_\infty \) (or
FIG. 5: (Color online) Coexistence curves in (a) σ-χ plane and (b) Ψ-χ plane. for φ∞ = 0.35, 0.4, 0.5, 0.55, and 0.65 at τ0 = 4 × 10^{-3}v_0. For each φ∞, two layers coexist inside the corresponding curve in (a), while Ψ is a field variable common in coexisting two layers. Critical points are marked (×).

χ-Ψ-φ∞) space (at fixed n0). These phase behaviors are sensitive to v_1, v_2, and h_1, though the transition itself exists even for v_1 = v_2 = 0.

We calculated 2D profiles from homogenous μφ and μi in the xx plane with χ = 2 and φ∞ = 0.35. For this φ∞, the phase transition behavior is not much changed in the range 1.4 ≤ χ ≤ 2 in Fig.5(a). In Fig.6, we show (a) φ(x,z) and (b) v_0(n_1 = n_2), where a stripe region with σ = σ_1 = -0.14 is embedded between regions with σ = σ_2 = 0.01 at Ψ = 0.32. Here, the mean surface charge density σ = Q/S is between σ_1 and σ_2. In (c), σ(x) from Eq.(5) is roughly equal to σ_1 or σ_2 except for the boundary regions. The fraction of the region with σ = σ_1 is nicely given by (σ_2 - σ)/|σ_2 - σ_1|. In (d), we plot ω(x) = ω(x) - Ψσ(x), where ω is defined in Eq.(6). From Eq.(9) it assumes a nearly common value ω_0 in the two regions. The integral of ω(x) dx across one of the boundary regions is the line tension τ [42], which is of order 0.17/a here. In (e) and (f), cross-sectional profiles of n_1 and n_2 at constant z are given, which exhibit small peaks at the boundaries slightly away from the wall. This is because of the Coulomb attraction between the cations and the anions which are locally separated across the boundaries. For the same reason, more marked peaks appear in the densities of antagonistic ion pairs near water-oil interfaces [3] [12] [21].

We propose experiments in the above situation. Let σ be decreased slightly below σ_2 on a hydrophobic metal wall. Then, the oil-rich layer with hydrophobic anions becomes metastable against formation of small water-rich regions with hydrophilic cations. For a finite line tension τ, their shapes are circular with the critical radius [38]

\[ r_c = \frac{\tau}{[(d\Psi/d\sigma)(\sigma_2 - \sigma_1)(\sigma_2 - \sigma_1)]}, \]

where the derivative dΨ/da is taken at σ = σ_2. On the other hand, a hydrophilic metal wall will be covered with a water-rich layer for σ = 0, but small oil-rich regions will be nucleated with increasing σ > 0.

FIG. 6: (Color online) Coexistence of two layers with σ = 0.02 and -0.14 for φ∞ = 0.35 and χ = 2 (see Fig.5). (a) φ(x,z) and (b) v_0(n_1(x,z) - n_2(x,z)) on the xx plane. (c) σ(x)/a^2/e with \( \bar{\sigma} = Q/S \) being (A) -0.04 and (B) -0.07 in units of e/a^2. (d) [ω(x) - Ψσ(x)]a^2/T for (A) and (B). Cross-sectional profiles of (e) v_0n_1(x,a) and (f) v_0n_2(x,a) at z/a = 0, 1, 2, and 3, exhibiting small peaks at boundaries for z ≥ a.

In summary, we have found a first-order surface transition with antagonistic ion pairs having different sizes. In future, we should examine wetting near the solvent coexistence curve with an antagonistic salt. We will study behavior of colloidal particles (including Janus ones) in a mixture solvent with an antagonistic salt, where the ion distributions around them can be very complex.

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[27] For one-component fluids the chemical potential \(\mu = \frac{\partial f}{\partial n}\) depends on the density \(n\) at fixed \(T\) where \(f\) is the Helmholtz free energy density. When a gas with density \(n_g\) and a liquid with density \(n_l\) coexist, we have \(\int_{n_g}^{n_l} dn \mu(n) = \mu(n_g)(n_l - n_g)\) analogously to Eq.(9).
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Supplemental Information

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Local charge separation and surface phase transition

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Space-filling condition and chemical potentials

We introduce the ion volumes $v_1$ and $v_2$ using their definition in Eq.(2) in our Letter. The total volume fraction $\phi_{\text{tot}}$ is the sum of those of water, oil, cations, and anions:

$$\phi_{\text{tot}} = \phi + \phi' + v_1 n_1 + v_2 n_2. \quad (S.1)$$

where $v_0$, $v_1$, and $v_2$ depend on $T$ and $p$ but not on the mole fractions of the four components. We assume that $\phi_{\text{tot}}$ is very close to 1 even for not very small $v_1 n_1 + v_2 n_2$. Its deviation from 1 should yield an increase in the Helmholtz free energy $\Delta F = \int_{z>0} dr \Delta f$ with

$$\Delta f = \gamma (\phi_{\text{tot}} - 1)^2 / 2 v_0, \quad (S.2)$$

where $\gamma$ is a large coefficient ($\gg T$). If the fluid is homogeneous with volume $V$, the excess free energy is $\Delta F = \gamma (V - V_{\text{tot}}) / 2 V v_0$ with $V_{\text{tot}} = V \phi_{\text{tot}} = v_0 (N_w + N_o) + v_1 N_1 + v_2 N_2$, where $N_\alpha (\alpha = w, o, 1, 2)$ are the total particle numbers. Its differentiation with respect to $V$ at fixed $N_2$ gives the excess pressure,

$$\Delta p = \gamma (\phi_{\text{tot}} - 1) / v_0. \quad (S.3)$$

We treat physical states with $|\Delta p| \ll T / v_0$. If $\gamma \gg T$, the isothermal compressibility (at fixed molar fractions) is nearly equal to $v_0 / \gamma$. It is worth noting that the compressibility of ambient liquid water (300 K and 1 atm) is $4.5 \times 10^{-4} / \text{MPa} \sim 0.06 v_0 / T$ for $a = v_0^{1/3} = 3 \text{ Å}$.

If we allow small deviations of the space-filling condition (1), we should replace the total free energy $F = \int_{z>0} dr f + \int_{z=0} dx dy h_1 \phi$ by $F + \Delta F$. With the aid of Eqs.(3) and (4), the chemical potentials are defined by $\hat{\mu}_\alpha = \delta (F + \Delta F) / \delta n_\alpha (\alpha = w, o, 1, 2)$, where $F + \Delta F$ is treated as a functional of $n_w, n_o, n_1, n_2$ at fixed $T$ and surface charge $Q = \int dx dy \sigma$. To calculate these quantities we consider small variations $\delta \phi, \delta n_i, \delta \sigma$. Using $\delta (|E|^2) = -|E|^2 \delta \varepsilon + 2E \cdot \delta (E)$ and

$$\int_{z>0} dr E \cdot \delta (E) = \int_{z>0} dr \psi (\delta n_1 - \delta n_2) + \int_{z=0} dx dy \psi \delta (E_z), \quad (S.4)$$

we obtain the incremental change in $F + \Delta F$ as

$$\delta (F + \Delta F) = \int_{z>0} dr \sum_{\alpha = w, o, 1, 2} \hat{\mu}_\alpha \delta n_\alpha + \int_{z=0} dx dy \left[ (h_1 - C \partial \phi / \partial z) \delta \phi + \psi \delta (E_z) \right], \quad (S.5)$$

Then, since $\delta D_z = \delta \sigma$ and $C \partial \phi / \partial z = h_1$ at $z = 0$, the second term in Eq.(S.5) simply becomes $\Psi \delta Q$ on a metal surface with $\Psi = \psi(0)$ for $\phi(\infty) = 0$. Some calculations give

$$\hat{\mu}_w = T [\ln \phi + 1 + \chi \phi' - v_0 \sum_{i} g_i n_i - C v_0 \nabla^2 \phi - \frac{v_0 |E|^2}{2} + \frac{v_0 |E|^2}{2} + (\phi_T - 1)], \quad (S.6)$$

$$\hat{\mu}_o = T [\ln \phi' + 1 + \chi \phi] + \gamma (\phi_T - 1), \quad (S.7)$$

$$\hat{\mu}_1 = T [\ln (n_1 v_1) - g_1 \phi] + e \psi + \gamma (\phi_T - 1) v_1 / v_0, \quad (S.8)$$

$$\hat{\mu}_2 = T [\ln (n_2 v_2) - g_2 \phi] - e \psi + \gamma (\phi_T - 1) v_2 / v_0. \quad (S.9)$$

For equilibrium and metastable profiles, these chemical potentials are homogeneous constants. Using these profiles, we consider the grand potential defined by

$$\Omega = \int_{z>0} dr \left[ f + \Delta f + p \right] - \sum_\alpha \hat{\mu}_\alpha n_\alpha + \int_{z=0} dx dy h_1 \phi, \quad (S.10)$$
where $p_\infty$ is a constant chosen to make the integrand in the first term vanish for large $z$. Then, from $C\partial \phi / \partial z = h_1$ at $z = 0$ and Eq. (S.5), we obtain

$$\delta \Omega = \Psi \delta Q.$$  \hspace{1cm} (S.11)

If $\hat{\Omega}$ is treated as a function of $Q$, we obtain $d\hat{\Omega}/dQ = \Psi$ for each $\phi_\infty$, $n_0$, and $T$. As $\phi_{\text{tot}} \to 1$ in the one-dimensional case, $\Omega$ in Eq. (S.10) tends to $\delta \omega$, where $\omega$ is defined by Eq. (6) and $S$ is the surface area of the metal wall. Then, we find $d\omega / dz = \Phi$ in Eq. (7).

Below Eq. (5) of our Letter, we have introduced $\mu_\phi = \delta F / \delta \phi$ and $\mu_i = \delta F / \delta n_i$ starting with Eq. (1) ($\phi_{\text{tot}} = 1$), where $\phi'$ is eliminated and $F$ is a function of the three variables $\phi$, $n_1$, and $n_2$. For small $\phi_{\text{tot}} - 1$ and large $\gamma / T$, we can express $\mu_\phi$ and $\mu_i$ as

$$\mu_\phi = (\hat{\mu}_w - \hat{\mu}_\omega) / v_0, \quad \mu_i = \hat{\mu}_i - \hat{\mu}_\omega v_i / v_0 \quad (i = 1, 2),$$  \hspace{1cm} (S.12)

where the terms proportional to $\gamma(\phi_{\text{tot}} - 1)$ are eliminated.

**Changeover of layer profiles**

In our Letter, we have presented numerical results for $\phi_\infty = 0.35$ and $n_0 = 4 \times 10^{-3} v_0^{-1}$ at $\chi = 1.4$ on a hydrophobic wall in Figs. 2-4. Here, adopting these parameter values, we give 1D profiles of (a) $n_1(z)$, (b) $n_2(z)$, (c) $\phi(z)$, and (d) $\psi(z)$ in dimensionless units in Fig. S1. We set $\sigma$ equal to (A) 0, (B) $-0.04$, (C) $-0.08$, (D) $-0.12$, and (E) $-0.16$ in units of $e/\alpha^2$, where $v_0 = a^3$. These quantities largely change with decreasing $\sigma$. In (a), the cations are expelled from the wall for $\sigma = 0$, but they abruptly accumulate near the wall for $\sigma \lesssim -0.08$ because of their small size $v_1 = 0.5v_0$. In (b), the anions are accumulated near the wall with $n_2(0) \approx 0.05$ for $\sigma = 0$, but are expelled from the wall for $\sigma \gtrsim -0.08$. The anions accumulate more weakly than the cations because of their large size ratio $v_2 / v_1 = 10$. In (c), the water volume fraction $\phi(z)$ is less than $\phi_\infty$ near the wall for $\sigma = 0$ and -0.04, but is increased above $\phi_\infty$ for the lower $\sigma$ values. In (d), the potential drop $\Psi = \psi(0)$ remains negative, but $\psi(z)$ gradually increases near the wall. For $\sigma \lesssim -0.08$, $\psi(z)$ exhibits a maximum at an intermediate $z_m \sim 1.5a$, so the electric field $E_z = -d\psi / dz$ is positive for $z < z_m$ and negative for $z > z_m$.

For the parameter values in Fig. S1, a first order phase transition occurs between two surface charge densities given by $\sigma_1 = -0.19$ and $\sigma_2 = -0.014$ from Fig. 4(b). In Fig. S2(a), the grand potential density $\omega(\sigma)$ in Eq. (6) is plotted, where its tangential line at $\sigma = \sigma_1$ and that at $\sigma = \sigma_2$ coincide from Eq. (9) with a common slope equal to the potential drop $\Psi$. Thus, the state (A) is stable where $\sigma > \sigma_2$. However, the states (B)-(E) are metastable or unstable because their $\sigma$ values are between $\sigma_1$ and $\sigma_2$. In (b) and (c), we plot the excess adsorbates $\Gamma_w$, $\Gamma_1$, and $\Gamma_2$ for water molecules, cations, and anions, respectively. In our semi-infinite case they are defined by

$$\Gamma_w = v_0^{-1} \int_0^\infty dz [\phi(z) - \phi_\infty], \quad \Gamma_i = \int_0^\infty dz [n_i(z) - n_0] \quad (i = 1, 2).$$  \hspace{1cm} (S.13)

With decreasing $\sigma$, $\Gamma_w$ and $\Gamma_1$ increase, while $\Gamma_2$ decreases to zero, which confirms the strong coupling between the composition and the ion densities.

![Image](https://example.com/image.png)

**FIG. S7:** (Color online) Changeover of profiles of (a) $v_0n_1(z)$, (b) $v_0n_2(z)$, (c) $\phi(z)$, and (d) $e\psi(z)/T$ for five values of $\sigma$, where $\chi = 1.4$, $\phi_\infty = 0.35$, and $n_0 = 4 \times 10^{-3} v_0^{-1}$.
$\phi_\infty = 0.35, \chi = 1.4$

FIG. S8: (Color online) (a) $\omega a^2/T$, (b) $\Gamma_w a^2$, and (c) $\Gamma_i a^2$ ($i = 1, 2$) as functions of $\sigma$ (in units of $e/a^2$). First order phase transition occurs between two states at $\sigma = \sigma_1 = -0.19$ and $\sigma = \sigma_2 = -0.014$. In (a) points A, B, ..., and E correspond to those in Fig.S1. In (b) and (c) these points are marked by $\times$. The other parameter values are the same as those in Fig.S1.