

# Interaction between like-charged surfaces in water: does mean-field (Poisson Boltzmann) always apply for monovalent counterions?

## Simulations of Nanoseparated Charged Surfaces Reveal Charge-Induced Water Reorientation and Nonadditivity of Hydration and Mean-Field Electrostatic Repulsion

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Charged interfaces in water are widespread in industry and biology. The interactions of two like-charged interfaces, colloid/water/colloid[1, 2] or cell(vesicle)/water/cell(vesicle)[3] for example, received continuous attention since the start of the 20th. century[4]. It was early realized that several type of "interactions" are at work besides electrostatics, like van der Waals interactions, in the celebrated DLVO theory[4], or short range hydration forces (defined from neutral interfaces). In practice, for want of better options, those interactions are usually added up. The standard treatment of the electrostatic part uses the continuous Poisson–Boltzmann (P–B) theory, which is a mean-field theory. There are many, potentially important, corrections to the standard P–B treatment: non-electrostatic counterion–surface interactions, discreteness of the surface charge (both noted early[5]), non-uniform dielectric constant, correlations between counterions.\* The paper by Schlaich et al. combines chemically realistic Molecular Dynamics (MD) simulations and analytical theory (with the additional input of Monte Carlo (MC) for pure electrostatics) to address all these points and essentially solve the problem (for polar surfaces). It offers much more than suggested by the, unavoidably reductive, title. This comment presents some of Schlaich et al.'s results in relation to a posterior experimental paper on deposited bilayers[6] and a much older one on biliquid foams[7].

In continuous theories, the strength of electrostatics for a given solvent characterized by the Bjerrum length  $l_B = e^2/(4\pi\epsilon\epsilon_0k_B T)$  decreases with increasing dielectric constant  $\epsilon$ ,  $\epsilon_0$  being the permittivity of vacuum. Electrostatics of an isolated pair of elementary charges separated by more than  $l_B$  is overcome by thermal noise. The P–B theory adds a second length

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\*Reading, for exemple, the book by Verwey and Overbeek[4], it is clear that the community knew about the weaknesses of the Poisson-Boltzmann treatment for electrostatics, already by that time. But the success of DLVO steadily reported since, at least for monovalent counterions, is striking. At this point it is fair to say that in most experimental setups the conditions of the experiments are not easy to control and the parameters not always known with precision, or even fitted.

(the radius of curvature is sent to infinity), the Gouy-Chapman length  $\lambda = 1/(2\pi q l_B \sigma / e)$ , the typical width of the thermal fluctuation away from the charged surface with charge density  $\sigma$  for a counterion (of valency  $q$ , charge  $qe$ ), the direct interaction between counterions being ignored. Half of the counterions are located within the distance  $\lambda$  from the surface, beyond counterions are distributed according to a powerlaw concentration profile. In practice, even for moderate surface charges  $\lambda$  is pretty small and for larger valencies  $q$ , counterions form a strongly correlated quasi-2d liquid[8]. More recently considerable efforts were put to relax the approximations underlying the Poisson-Boltzmann theory by going beyond mean-field and (sometimes) introducing the excluded volume of ions. Correlations between counterions are due to their mutual interaction. Their pair interaction typically within the Gouy-Chapman layer and a mutual distance  $\lambda$  apart:  $\Xi k_B T = q^3 \sigma e^3 / (8\pi \epsilon^2 \epsilon_0^2 k_B T)$  defines the coupling parameter  $\Xi$  characterizing counterion – counterion correlations[9]. Counterion–counterion correlations are negligible for  $\Xi < 1$ , where P-B applies, but essential for  $\Xi > 1$ . In the strong coupling limit  $\Xi \gg 1$ , more easily reached for higher counterion valency, like-charged surfaces attract each other. It was often stressed that  $\Xi$  strongly increases with the valency of the counterion, but it also strongly decreases with  $\epsilon$ .<sup>†</sup>

Schlaich et al. perform chemically realistic MD simulations where the surfaces facing each other are bilayers of decanol based molecules with extra charges on their head groups and sodium counterions, mimicking soft polar charged surfaces encountered in biology. In the simulation the surface charge ranges from 0.11 e/nm<sup>2</sup> to 0.77 e/nm<sup>2</sup>, which corresponds to a nominal coupling parameter  $\Xi$  from weak to moderate ( $\lesssim 3$ ), if the dielectric constant  $\epsilon_b = 70$  of the model water is assumed. The authors assess every quantity of interest to evaluate the relevance of any effect within the model, a privilege of simulations. At moderate surface charge densities  $\sigma \approx 0.1$  e/nm<sup>2</sup>, the standard P–B counterion profile describes the data well at separations larger than 5 nm, but in the very vicinity of the surfaces. Further the hydration contribution, measured from a simulation with neutral surfaces, and electrostatic contribution to the pressure add up. A relief for many! Close to the surfaces or at somewhat smaller separations P–B becomes inaccurate but the modified P–B equation (MPB) taking into account a localized non-electrostatic counterion–surface interaction performs well. Other effects like the discreteness and the width normal to the surface of the surface charge distribution, the profile of dielectric constant are shown to be of lesser importance. At the highest (yet moderate) surface charge  $\sigma=0.77$  e/nm<sup>2</sup> the additivity of the hydration contribution and electrostatic contributions fails, which is attributed to the measured orientation of water molecules in the electrical field at the surfaces. At the same time MPB (drastically) overestimates the repulsion at small separations. This is attributed to markedly enhanced counterion–counterion correlations (larger  $\Xi$ ) induced by a lower ”local dielectric constant”. While P–B and its counterpart taking into account counterion–counterion correlations are generic (universal), additional effects like the affinity of the counterion for the surfaces *a priori* depend on chemistry and would need a fit or an independent measurement in experiments. The relative importance of those terms may depend on the system. For polar, usually negatively, charged soft surfaces and cationic counterions (their chemical nature is usually

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<sup>†</sup>In the context of the comment it is convenient to exclusively follow the line of Orland and Netz[9]. It is fair to also mention seminal work on fluctuations by Marcelja [10] and, in the extra strong limit ( $T = 0$ ), by Messina[11] (see also his broader review[12]) followed by a finite temperature expansion around the ground state by Šamaj and Trizac[13].

of lesser importance than for anions) we expect Schlaich et al.’s conclusions to hold quite generally.

The marked enhancement of correlation effects raises the question whether the electrostatic contribution can become attractive with monovalent counterions in a real system. It is commonly accepted that it cannot under usual experimental conditions, but what about surfaces at nanometric separations, a situation also relevant to biological systems? Two experiments[6, 7] suggest that it can.

In the experiment by Mukhina et al. the structure of two deposited bilayers is studied by neutron and X-ray reflectivity. The interpretation of the reflectivity data relies on a model composition profile whose ambiguities are here seriously limited by the joint use of both neutron reflectivity and high resolution X-ray (synchrotron) reflectivity, the former with different D<sub>2</sub>O/H<sub>2</sub>O solvents. In essence, the thickness of the water layer between bilayers is found smaller for like-charged bilayers than for zwitterionic ones, see Fig. 1. Already an indication for attraction induced by electrostatics. The setup and general idea of this experiment exploring sub nanometric separations is very similar to Schlaich et al.’s simulation but in the experiment the fully charged bilayers reach to higher surface charges ( and effective  $\Xi$ ) up to 1.5 e/nm<sup>2</sup>. Mukhina et al. further elaborate their very careful interpretation of the data and reach the conclusion that the effective dielectric constant may go down to  $\sim 10$ –30 ( $20 \leq \Xi \leq 300$ ,  $5 \leq d/\lambda \leq 30$ ).

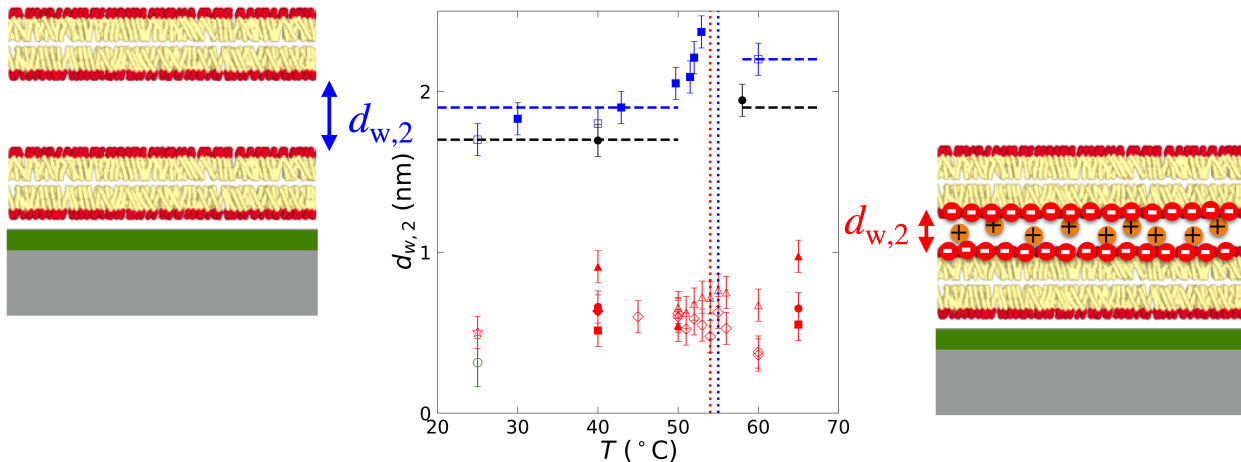


Figure 1: Schematics of the deposited double bilayer. For zwitterionic bilayers (left), charged bilayers (right). The water layer between bilayers is thinner for charged bilayers (center). (Figure courtesy of Mukhina et al.)

In their pioneering work, Sonneville-Aubrun et al. study biliquid foams obtained by centrifugation of an oil-in-water emulsion stabilized by SDS, where the continuous phase is almost completely eliminated<sup>‡</sup>. The thickness of the resulting black film between oil cells, measured by Small Angle Neutron Scattering, depends on the centrifugation pressure. In a very simplified view, two type of black films are evidenced, which differ in water thickness

<sup>‡</sup>Samples for various centrifugal pressures are obtained in one centrifugation run with a single extended cell.

and surfactant density: at moderate pressure, Common Black Films (CBF), whose thickness decreases with pressure, at high pressure Newton Black Films, whose thickness is  $\approx 1.3$  nm. While P-B with proper boundary conditions essentially explains the CBF, it fails to rationalize the transition to the thinner NBF. The authors cannot help but invoke an attraction between surfactant monolayers of electrostatic origin made plausible by the reduced dielectric constant. This is further supported by MC simulations of solid planar charged surfaces with idealized counterions. The proposed rationale settles for the dielectric constant  $\epsilon = 65$ , a moderate (conservative) reduction with respect to  $\epsilon_b = 78$ . Here the interpretation likely reaches its limits. An older work which deserves to be (re)discovered.

Schlaich et al.'s work offers analytical tools for a quantitative interpretation of experiments on (polar) like-charged surfaces with monovalent counterions in water, which deserve to be widely used in the future. Similar numerical work on surfaces that can afford a higher charge density should evidence attraction induced by electrostatics as detected in experiments[6, 7].

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