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► **To cite this version:**

R Blossey, R Podgornik. A comprehensive continuum theory of structured liquids. 2022. hal-03819365

HAL Id: hal-03819365

<https://hal.science/hal-03819365v1>

Preprint submitted on 18 Oct 2022

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A comprehensive continuum theory of structured liquids

R. Blossey¹ and R. Podgornik^{2,3,4*}

¹*University of Lille, Unité de Glycobiologie Structurale et Fonctionnelle (UGSF) CNRS UMR8576, 59000, Lille, France.

²School of Physical Sciences and Kavli Institute for Theoretical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China.

³CAS Key Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China and Wenzhou Institute of the University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325000, China.

⁴Also at: Department of physics, Faculty of mathematics and physics, University of Ljubljana, Ljubljana, Slovenia.

*Corresponding author(s). E-mail(s): podgornikrudolf@ucas.ac.cn;
Contributing authors: ralf.blossey@univ-lille.fr;

Abstract

We develop a comprehensive continuum model capable of treating both electrostatic and structural interactions in liquid dielectrics. Starting from a two-order parameter description in terms of charge density and polarization, we derive a field-theoretic model generalizing previous theories. Our theory explicitly includes electrostatic and structural interactions in the bulk of the liquid and allows for polarization charges within a Drude model. In particular, we develop a detailed description of the boundary conditions which include the charge regulation mechanism and surface polarization. The general features for solving the saddle-point equations of our model are elucidated and future applications to predict and validate experimental results are outlined.

Keywords: Poisson-Boltzmann theory, polarization, electrolyte

1 Introduction

The continuous development and improvement of modern experimental techniques is pushing the resolution limits in soft matter systems continuously further down towards atomistic regimes. As an example one can take the advances made with the application of different varieties of atomic-force microscopy (AFM) in liquids. Both conventional methods and the recently developed 3D-AFM technique [1–6] meanwhile allow access to unprecedented molecular and atomistic detail of liquids, notably aqueous ionic solutions, near hydrophilic and hydrophobic surfaces.

These successes, in turn, challenge theory. The parallel advances made in molecular computation, in addition in combination with machine learning approaches, seem to render purely theoretical approaches obsolete: theorists may want to lay down their original weapons and declare defeat. This view was recently expressed in the work of Mugele and collaborators. They notice that it is difficult or perhaps impossible to decouple the total monotonically decaying force into various well-defined separate contributions like DLVO and/or non-DLVO interactions, “because one cannot develop a universal Poisson-Boltzmann theory accounting for all nonelectrostatic effects (ionic chemical nature, size, charge, polarizability, and solvation)” [6].

In this paper we take up this challenge by developing a comprehensive field-theoretic continuum model extending standard Poisson-Boltzmann-type theories. The starting point of our analysis is our recently developed field theory of structured dielectrics [7], in which the bulk theory was developed based on a two-order parameter description in terms of charge density and polarization. In the development of this theory we were guided by the Onsager-Dupuis theory of the dielectric properties of ice [8–11]. For a recent perspective on how our work [7] can be placed in the context of earlier theories of polarization, see [12].

In order to bring this approach close to experiment, in this work we extend the basic theory in several respects. First, for the bulk system, we go beyond the previous formulation by explicit allowance for polarizability of the solvent, which we treat in terms of a Drude model. More importantly, we develop the formulation of the boundary conditions in detail, overall missing from previous endeavours, allowing for surface polarization as well as for charge regulation mechanisms. This part is the main new result of the present paper. Having formulated our general theory, we discuss how the saddle-point equations can be solved together with the boundary conditions. In closing we discuss experimental systems of interest to which our theory can be applied in the future.

2 A continuum model for a polarizable dipole-ion mixture

In our previous work we considered a structured liquid dielectric described by charge density and solvent polarization in a harmonic approximation and formulated the corresponding field theory for a bulk system [7]. Here, we first revisit the formulation of this theory by including the polarizability of the solvent dipoles, the non-electrostatic dipole-dipole interaction and the charge-dipole hydration coupling. In the subsequent

step, we derive a general expression for the surface free energy and the associated boundary conditions, which completes the development of our formalism and prepares our theory for applications to a variety of experimental systems.

2.1 Bulk equations

The physical components of the system we study are the solvent molecules and the electrolyte cations and anions. The polarizability of the constituents is implemented via harmonically connected Drude charges; this is fully described in Appendix A. Our approach begins with the identification of the appropriate *order parameters*; for a motivation, see, e.g., Ref. [13]. For the simple electrolyte component we can define the *cation* and *anion density fields*

$$\hat{\rho}_{(\pm)}(\mathbf{x}) \equiv \pm e \sum_{(\pm)} \delta(\mathbf{x} - \mathbf{x}_n) + q_I \sum_{(\pm)} \ell_i \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_i), \quad (1)$$

where e is the elementary charge of the salt ions and q_I (assumed to be the same for both types of ions) are the Drude charges, with a fluctuating separation ℓ_i exhibiting an average of $\langle \ell_i \rangle = 0$ and a variance of $\langle \ell_i^2 \rangle = \sigma_I^2$. The solvent molecule dipolar charge is now given as

$$\hat{\rho}_{(N)}(\mathbf{x}) = = q_D \sum_{(N)} \ell_i \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_i). \quad (2)$$

For the solvent molecules the fluctuating distance between the two Drude charges, ℓ_i , has an average of $\langle \ell_i \rangle = s$ and a variance of $\langle \ell_i^2 \rangle = \sigma_D^2$. Through we use the same symbol for the ionic and polarization Drude fluctuating separation, the context and properties are clearly different.

The *total charge density field* subject to Coulomb interactions is then given by the sum of the ionic charges and the divergence of the total polarization vector

$$\hat{\rho}(\mathbf{x}) = \pm e \sum_{(\pm)} \delta(\mathbf{x} - \mathbf{x}_i) + \nabla \cdot \hat{\mathbf{P}}(\mathbf{x}). \quad (3)$$

with the total polarization given by

$$\hat{\mathbf{P}}(\mathbf{x}) = q_D \sum_{(N)} \ell_i \delta(\mathbf{x} - \mathbf{x}_i) + q_I \sum_{(\pm)} \ell_i \delta(\mathbf{x} - \mathbf{x}_i), \quad (4)$$

where we reiterate that $\langle \ell_i \rangle = s$ for the solvent (N) and $\langle \ell_i \rangle = 0$ for ions (\pm).

The total Coulomb interaction energy has the standard form

$$\mathcal{H}_C = \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}(\mathbf{x}) u(\mathbf{x} - \mathbf{x}') \hat{\rho}(\mathbf{x}') \quad (5)$$

where the Coulomb kernel corresponds to the dielectric constant given solely by its non-configurational part, corresponding to the high-frequency dielectric constant,

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$\varepsilon_\infty = \varepsilon(\omega \rightarrow \infty)$, i.e.

$$u = \frac{1}{4\pi\varepsilon_\infty\varepsilon_0 |\mathbf{x} - \mathbf{x}'|}, \quad \text{with} \quad u^{-1} = -\varepsilon_\infty\varepsilon_0 \nabla^2 \delta(\mathbf{x} - \mathbf{x}'), \quad (6)$$

where ε_∞ accounts for all the relaxation mechanisms at higher relaxation frequencies. Clearly, while the Coulomb potential presents a non-local coupling, its inverse is a purely local operator.

The non-electrostatic short-range interactions (denoted by a tilde symbol) act between local solvent dipoles and can be written in a quadratic approximation as

$$\mathcal{H}_{SR} = \frac{1}{2} \int_V d\mathbf{x} d\mathbf{x}' \hat{\mathbf{P}}_i(\mathbf{x}) \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') \hat{\mathbf{P}}_j(\mathbf{x}'), \quad (7)$$

where $\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}')$ is a short-range, non-electrostatic interaction potential. A minimal model expression for this potential is the fourth order non-local derivative expression

$$\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') = \tilde{u}_P(0) \left(\delta_{ij} \delta(\mathbf{x} - \mathbf{x}') + \xi^2 \nabla'_j \nabla_i \delta(\mathbf{x} - \mathbf{x}') + \zeta^4 \nabla'_k \nabla'_j \nabla_k \nabla_i \delta(\mathbf{x} - \mathbf{x}') \right) + \dots \quad (8)$$

for the dipolar interactions, containing the correlation and the structural length of the solvent, implying the following form of the structural interaction free energy

$$\mathcal{H}_{SR} = \frac{1}{2} u_P(0) \int_V d\mathbf{x} \left(\hat{\mathbf{P}}^2(\mathbf{x}) + \xi^2 (\nabla \cdot \hat{\mathbf{P}}(\mathbf{x}))^2 + \zeta^4 (\nabla(\nabla \cdot \hat{\mathbf{P}}(\mathbf{x})))^2 \right). \quad (9)$$

There is no universality in the non-electrostatic interactions and they are invariably linked with different models of the liquid structure. Higher-order terms either in the polarization vector or its derivatives are also possible, e.g., close to an ordering transition of water dipoles where the polarization energy could be written in a Landau form consistent with presumed microscopic symmetries [14, 15].

Next we consider the hydration shell of the ions that corresponds to the coupling between the ion density and $\hat{\rho}_{(\pm)}(\mathbf{x})$ and $\hat{\mathbf{P}}(\mathbf{x})$. To the lowest order this coupling could be written as

$$\mathcal{H}_{HY} = \int_V \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}(\mathbf{x}) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{\mathbf{P}}(\mathbf{x}'), \quad (10)$$

where the potential $\tilde{u}(\mathbf{x} - \mathbf{x}')$ is again a short-range, non-electrostatic potential that can be modeled as

$$\tilde{u}(\mathbf{x} - \mathbf{x}') = \alpha \delta(\mathbf{x} - \mathbf{x}') + \dots \quad (11)$$

We assumed that the hydration polarization for anions and cations is - apart from the direction - identical for both. The implied hydration free energy then assumes the form

$$\mathcal{H}_{HY} = \alpha \int_V d\mathbf{x} \hat{\rho}(\mathbf{x}) \nabla \cdot \hat{\mathbf{P}}(\mathbf{x}). \quad (12)$$

The total interaction energy equals the sum of the above three contributions, *i.e.*,

$$\mathcal{H} = \mathcal{H}_C + \mathcal{H}_{SR} + \mathcal{H}_{HY}. \quad (13)$$

In the next step we introduce the two collective variables, $\rho(\mathbf{x})$ and $\mathbf{P}(\mathbf{x})$, which imply also two auxiliary fields, $\mathcal{E}(\mathbf{x})$, $\phi(\mathbf{x})$, which on the mean-field level turn out to be the non-electrostatic part of the polarization vector and the electrostatic potential scalar. On the saddle-point (mean-field level) the free energy can be cast into the form of a functional of the collective order parameters and auxiliary fields given by

$$\begin{aligned} \beta \mathcal{F}[\mathbf{P}(\mathbf{x}), \rho(\mathbf{x}); \mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] \equiv & \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' \mathbf{P}_i(\mathbf{x}) \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') \mathbf{P}_j(\mathbf{x}') + \\ & \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' \rho(\mathbf{x}) u(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}') + \int \int_V d\mathbf{x} d\mathbf{x}' \rho(\mathbf{x}) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \mathbf{P}(\mathbf{x}') \\ & - \int_V d\mathbf{x} \mathbf{P}_i(\mathbf{x}) \mathcal{E}_i(\mathbf{x}) - \int_V d\mathbf{x} \rho(\mathbf{x}) \phi(\mathbf{x}) - V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})], \end{aligned} \quad (14)$$

where $V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})]$ is the one-particle partition function of the system in an external field with the field Hamiltonian $\tilde{\mathcal{H}}^*$ of the form

$$\begin{aligned} \beta \tilde{\mathcal{H}}^*[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] = & \int_V d\mathbf{x} \hat{\mathbf{P}}(\mathbf{x}) \cdot \mathcal{E}(\mathbf{x}) + \int_V d\mathbf{x} \hat{\rho}(\mathbf{x}) \phi(\mathbf{x}) \\ = & q_D \sum_{(N)} \ell_i (\mathcal{E}(\mathbf{x}_i) - \nabla \phi(\mathbf{x}_i)) + q_I \sum_{(\pm)} \ell_i (\mathcal{E}(\mathbf{x}_i) - \nabla \phi(\mathbf{x}_i)) + \\ & + \sum_{(+)} e \phi(\mathbf{x}_i) - \sum_{(-)} e \phi(\mathbf{x}_i), \end{aligned} \quad (15)$$

with vector and scalar (external) auxiliary fields. The one particle partition function is then obtained by taking the trace over all the particle degrees of freedom, that is

$$e^{-V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})]} = \langle e^{-\beta \tilde{\mathcal{H}}^*} \rangle \quad (16)$$

where the symbolic average stands for the trace over the particle coordinates and internal degrees of freedom, *i.e.*, the extension ℓ_i and the orientation \mathbf{n} for the Drude model description. In addition this average can be taken either for a grand canonical ensemble or for a lattice gas ensemble, resulting in two different forms of the one-particle partition function $V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})]$. The one-particle partition function can be obtained explicitly for a mixture of a polarizable solvent - electrolyte solute by first defining

$$\begin{aligned} v(\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})) \equiv & e^{\mu_D} \frac{\sinh(\beta q_D s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|)}{q_D \beta s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|} e^{\frac{1}{2}(\beta \sigma q_D)^2 (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} + \\ & 2e^{\mu_{\pm}} \cosh \beta e \phi(\mathbf{x}) e^{\frac{1}{2}(\beta \sigma q_I)^2 (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2}. \end{aligned} \quad (17)$$

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Then we have in the grand canonical ensemble

$$V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] = \int d^3\mathbf{r} v(\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})), \quad (18)$$

while the lattice gas ensemble leads to

$$V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] = \frac{1}{a^3} \int d^3\mathbf{r} \ln v(\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})). \quad (19)$$

We assume that for a univalent electrolyte the chemical potentials satisfy $\mu_{\pm} = \mu_- = \mu_+$, while a^3 is the volume of a site in the lattice gas partition function. Apart from the contribution of the polarizability on the Drude model level, the expression matches the one derived before [7]. We also note that in the pure electrostatic case ($\mathcal{E} = 0$, see below) and with equal polarizability for the solvent and solute species, the polarizability terms decouple from the rest of the free energy.

We note that the above expressions differs from the case of the fixed dipole-ion mixture analyzed by Abrashkin et al. [16?] and others as well as from the polarizable dipole-ion mixture analyzed by Buyukdagli et al. [18] and others, or indeed from the polarizable ion case as formulated by Demery et al. [19, 20] and others. There are, indeed, two crucial differences: the inclusion of the polarizability terms for the solvent molecules as well as the solute ions, and the dipolar orientational field, $\nabla\phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})$, which is given by the sum of the non-electrostatic component of polarization and the electrostatic field, *i.e.*, accounting for electrostatic as well as non-electrostatic orientational ordering, as we show explicitly in what follows.

Inserting the non-local potentials Eqs. (6), (8), (11) explicitly into the free energy allows us first to write down the equivalent mean-field form of the free energy, Eq. (14), as

$$\begin{aligned} \beta \mathcal{F}[\mathbf{P}(\mathbf{x}); \mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] \equiv & \frac{1}{2} u_P(0) \int_V d\mathbf{x} \left(\hat{\mathbf{P}}^2(\mathbf{x}) + \xi^2 (\nabla \cdot \hat{\mathbf{P}}(\mathbf{x}))^2 + \zeta^4 (\nabla(\nabla \cdot \hat{\mathbf{P}}(\mathbf{x})))^2 \right) \\ & - \frac{1}{2} \epsilon_{\infty} \epsilon_0 \int_V d\mathbf{x} \left(\nabla(\phi(\mathbf{x}) - \alpha(\nabla \cdot \mathbf{P}(\mathbf{x}))) \right)^2 - \int_V d\mathbf{x} \mathbf{P}_i(\mathbf{x}) \mathcal{E}_i(\mathbf{x}) - V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})]. \end{aligned} \quad (20)$$

The free energy is now cast into a completely local form and the corresponding form of the Euler-Lagrange equations are obtained straightforwardly. The transformation of the general non-local free energy Eq. (14) into a local form, *i.e.*, containing only local kernels, is important for our later analysis of the boundary conditions.

In deriving the Euler-Lagrange equations for the above free energy one needs to remember that for the free energy density dependent on the first derivatives of a field, $f_V(u, \nabla u)$, the Euler-Lagrange equations have the standard form

$$\frac{\partial f_V}{\partial u} - \nabla \left(\frac{\partial f_V}{\partial \nabla u} \right) = 0, \quad (21)$$

while for the free energy density dependent on the first and second derivatives of a field, $f_V(u, \nabla u, \nabla^2 u)$, the Euler-Lagrange equations then read as

$$\frac{\partial f_V}{\partial u} - \nabla \left(\frac{\partial f_V}{\partial \nabla u} \right) + \nabla^2 \left(\frac{\partial f_V}{\partial \nabla^2 u} \right) = 0. \quad (22)$$

With this in mind, the variation of the free energy with respect to polarization, $\delta \mathbf{P}(\mathbf{x})$, leads to the following equation for the polarization vector

$$u_P(0) \mathbf{P}(\mathbf{x}) - u_P(0) \xi^2 \nabla (\nabla \cdot \mathbf{P}(\mathbf{x})) + u_P(0) \zeta^4 \nabla^2 (\nabla \cdot \mathbf{P}(\mathbf{x})) + \alpha \varepsilon_\infty \varepsilon_0 \nabla^2 (\phi(\mathbf{x}) - \alpha (\nabla \cdot \mathbf{P}(\mathbf{x}))) - \mathcal{E}(\mathbf{x}) = 0. \quad (23)$$

From the above equation it follows straightforwardly that the auxiliary field \mathcal{E} is coupled exclusively with non-electrostatic dipolar and hydration interactions.

The variation with respect to the auxiliary polarization field, $\delta \mathcal{E}(\mathbf{x})$, leads to the modified non-linear Langevin-Poisson constitutive relation

$$-\mathbf{P}(\mathbf{x}) - \frac{\partial}{\partial \mathcal{E}(\mathbf{x})} v(\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})) = 0, \quad (24)$$

while the variation with respect to the auxiliary electrostatic potential, $\delta \phi(\mathbf{x})$, yields the modified non-linear Poisson-Boltzmann equation

$$-\varepsilon_\infty \varepsilon_0 \nabla^2 (\phi(\mathbf{x}) - \alpha (\nabla \cdot \mathbf{P}(\mathbf{x}))) - \left(\frac{\partial}{\partial \phi(\mathbf{x})} - \nabla \left(\frac{\partial}{\partial \nabla \phi(\mathbf{x})} \right) \right) v(\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})) = 0. \quad (25)$$

The three Euler-Lagrange equations, Eqs. (23), (24) and (25), then correspond to the definition of the non-electrostatic part of polarization auxiliary field, the polarization field constitutive equation, and the generalized Poisson-Boltzmann equation.

These are the final equations valid in the bulk of the system. We next analyze the boundary conditions.

2.2 Boundary terms and boundary conditions

In an inhomogeneous system, which is the standard in (bio)colloid science, the bulk is delimited by boundary surfaces. Often the surface is idealized to the extent that it presumably imposes some kind of *ad hoc* boundary conditions on the inhomogeneous mean-field solution. We believe these types of - otherwise easily implementable approaches - are insufficient to describe the intricacies of the solution-interface interactions. In fact boundary surfaces and their interactions with the vicinal solution ions as well as solvent molecules give no hint of universality, and a plethora of models exist to describe these surface-solution interactions.

The existence of surfaces implies boundary conditions for the order parameters and auxiliary fields that *have to be consistent* with the underlying free energies [21]. In order to derive these boundary conditions we need to include the variation of

the bulk fields as well as the surface fields into the Euler-Lagrange equations [22]. For a free energy that decouples into a volume part with density $f_V(u, \nabla u)$ and a surface part with density $f_S(u_S)$, index S denoting the surface value, the complete Euler-Lagrange equations Eq. (21) then also contains a surface part

$$\mathbf{n} \cdot \left(\frac{\partial f_V}{\partial \nabla u} \right)_S + \frac{\partial f_S}{\partial u_S} = 0 \quad (26)$$

where \mathbf{n} is the boundary surface normal. For the field which enters the free energy also with a second derivative, $f_V(u, \nabla u, \nabla^2 u)$, the surface part of the Euler-Lagrange equations Eq. (22) then reads

$$\mathbf{n} \cdot \left(\left(\frac{\partial f_V}{\partial \nabla u} \right) - \nabla \left(\frac{\partial f_V}{\partial \nabla^2 u} \right) \right)_S + \frac{\partial f_S}{\partial u_S} = 0. \quad (27)$$

In most of the existing literature one usually considers only the volume part because the surface-specific interactions are assumed to be absent. Nevertheless, the part played by the surface specific interactions has been recognized by several authors [15, 23, 24].

This decoupling of the Euler-Lagrange equations is of course only possible if the free energy can be separated into the volume and surface parts and if it can be written as a purely local functional of the fields, which means that in Eq. (14) we need to integrate out the Coulomb non-local interactions leading to a local inverse Coulomb operator, which then finally yields a purely local functional Eq. (9).

Decoupling the local free energy functional into a volume and surface part allows us to derive not only the bulk Euler-Lagrange equations, but also their surface counterpart, see Ref. [13], *a.k.a.* the boundary conditions. We therefore start with

$$\beta \mathcal{F} = \beta \mathcal{F}_{bulk} + \oint_S d^2 \mathbf{x} f_S(P_S, \mathcal{E}_S, \phi_S), \quad (28)$$

with $\beta \mathcal{F}_{bulk}$ given by Eq. (9). We assume that the order parameters and the auxiliary fields have independent surface variations $\delta \phi_S$, $\delta \mathcal{E}_S = \delta(\mathcal{E} \cdot \mathbf{n})_S$ and $\delta P_S = \delta(\mathbf{P} \cdot \mathbf{n})_S$, where the index S refers to the surface values of the variables, we then end up with the following boundary equations: the surface variation of the electrostatic potential, $\delta \phi_S$, yields

$$\mathbf{n} \cdot \left(-\varepsilon_\infty \varepsilon_0 \nabla(\phi - \alpha(\nabla \cdot \mathbf{P})) - \frac{\partial v}{\partial \nabla \phi} \right)_S + \frac{\partial f_S}{\partial \phi_S} = 0, \quad (29)$$

where the subscript S in the first term signifies that the subscripted bulk quantity needs to be taken at the surface. Clearly this equation generalizes the boundary condition for the PB equation with surface interactions [25]; analogously the surface variation of the auxiliary field, $\delta \mathcal{E}_S$, yields a single surface terms of the form

$$\frac{\partial f_S}{\partial \mathcal{E}_S} = 0, \quad (30)$$

and finally the surface variation of the polarization field, δP_S , which can be deduced from the free energy Eq. (23) and leads to

$$u_P(0)\xi^2(\nabla \cdot \mathbf{P})_S - u_P(0)\zeta^4\nabla^2(\nabla \cdot \mathbf{P})_S + \varepsilon_\infty\varepsilon_0\alpha \mathbf{n} \cdot \nabla(\phi - \alpha(\nabla \cdot \mathbf{P}))_S + \frac{\partial f_S}{\partial P_S} = 0. \quad (31)$$

The last two boundary conditions are specific for our approach and embody the fact that electrostatic and polarization fields represent separate and independent degrees of freedom in this system.

The question now remains as to what is the surface free energy density that we refer to above. This issue has been detailed in Ref. [21] within the mean-field approximation and remains unchanged in the present formulation.

Since the description of the surface is much less universal and much more model dependent than the equivalent description of the bulk, we cannot aspire to the same level of generality as for the bulk. In fact, we need to make certain additional assumptions at this point in order to proceed.

We assume that there are surface specific polarization and charge interactions that contribute the analogous terms to the total surface free energy as in the volume case that we derived before. This leads us to the proposition

$$\begin{aligned} f_S(P_S, \mathcal{E}_S, \phi_S) &= \frac{1}{2}u_S P_S^2 - P_S \mathcal{E}_S - (P_0 P_S + \sigma_0 \phi_S) + \\ &+ \frac{k_B T}{b^2} \ln \left(\lambda_D \mathcal{P}(\beta q_D \mathcal{E}_S | \mathcal{E}_S - (\nabla \phi)_S) + \lambda_+ e^{(\beta e \phi_S - \alpha_+)} + \lambda_- e^{-(\beta e \phi_S + \alpha_-)} \right) \\ &= \frac{1}{2}u_S P_S^2 - P_S \mathcal{E}_S - (P_0 P_S + \sigma_0 \phi_S) + v_S(\mathcal{E}_S, \phi_S), \end{aligned} \quad (32)$$

with $\mathcal{P}(u) = \sinh u/u$. Eq. (32) is of course just one, but a fairly general one, assumed model to describe the bounding surfaces. Polarizability terms could be included if one deems the form of the free energy is still not complicated enough. Here, b is the size of the surface sites, which in general differs from the bulk lattice gas sites. The first two terms in the above expression quantify the surface specific, short-range polarization interactions, where P_0 is the surface density of polarization sources and σ_0 is the surface density of charge sources.

Inserting now this free energy into the boundary conditions we are left with the modified surface electrostatic boundary condition

$$\mathbf{n} \cdot \left(-\varepsilon_\infty\varepsilon_0 \nabla(\phi - \alpha(\nabla \cdot \mathbf{P})) - \frac{\partial v}{\partial \nabla \phi} \right)_S - \sigma_0 + \frac{\partial v_S}{\partial \phi_S} = 0, \quad (33)$$

(note the difference between v and v_S), the modified surface constitutive relation

$$-P_S + \frac{\partial v_S}{\partial \mathcal{E}_S} = 0, \quad (34)$$

and the modified surface polarization boundary condition

$$u_P(0)\xi^2(\nabla \cdot \mathbf{P})_S - u_P(0)\zeta^4\nabla^2(\nabla \cdot \mathbf{P})_S + \varepsilon_\infty\varepsilon_0\alpha\mathbf{n} \cdot \nabla(\phi - \alpha(\nabla \cdot \mathbf{P}))_S + u_S P_S - \mathcal{E}_S - P_0 = 0. \quad (35)$$

Clearly the derived boundary conditions, consistent with the form of the bulk as well as the surface free energies, are nowhere close to the assumption of constant surface fields. The electrostatic field boundary condition, Eq. (33), is closely related to the boundary conditions used in the charge regulation theory [21, 26, 27], while the polarization boundary condition, Eq. (35), is related to the boundary conditions used in the theory of hydration/structural forces [16, 23, 24].

Together with the bulk Euler-Lagrange equations these boundary conditions close the formulation of the non-homogeneous case. We next consider two illuminating limiting cases of the boundary condition obtained in the absence of hydration coupling, *i.e.*, $\alpha = 0$, that reduce to more familiar forms.

2.2.1 Limiting cases: inner Helmholtz layer - surface polarization

An interesting limiting case is obtained by ignoring any specific interactions of the ions with the surface, or actually ignoring ions altogether. In that case Eq. (32) simplifies to

$$f_S(P_S, \mathcal{E}_S, \phi_S) = \frac{1}{2}u_S P_S^2 - P_S \mathcal{E}_S - P_0 P_S + \frac{k_B T}{b^2} \ln \Xi(\mathcal{E}_S, (\nabla \phi)_S), \quad (36)$$

where now the surface partition function

$$\Xi(\mathcal{E}_S, (\nabla \phi)_S) = 1 + \lambda_D \mathcal{P}(\beta q_D s |\mathcal{E}_S - (\nabla \phi)_S|), \quad (37)$$

corresponds to the surface lattice gas of dipoles. In this case the relevant boundary conditions are obtained as

$$-\varepsilon_\infty\varepsilon_0(\mathbf{n} \cdot \nabla \phi)_S + P_S = 0 \quad \text{with} \quad P_S = \frac{k_B T}{b^2} \frac{\partial \ln \Xi}{\partial \mathcal{E}_S}, \quad (38)$$

for the surface constitutive relation connecting the electrostatic field and the polarization field, as well as

$$u_P(0)\xi^2(\nabla \cdot \mathbf{P})_S - u_P(0)\zeta^4\nabla^2(\nabla \cdot \mathbf{P})_S + u_S P_S - \mathcal{E}_S - P_0 = 0. \quad (39)$$

The solution of these boundary conditions gives us the surface polarization at the inner Helmholtz plane as a function of the surface electrostatic field. Because of the

In in Eq. (38) the surface polarization

$$P_S = \frac{\lambda_D q_{DS}}{b^2} \frac{\frac{\partial \mathcal{P}(u)}{u \partial u} (\mathcal{E}_S - (\nabla \phi)_S)}{1 + \mathcal{P}(\beta q_{DS} |\mathcal{E}_S - (\nabla \phi)_S|)}, \quad (40)$$

clearly shows a saturation behavior and cannot exceed the value of a fully oriented layer of surface solvent molecules.

2.2.2 Limiting cases: outer Helmholtz layer - charge regulation

We obtain another interesting limit of the above general model by first assuming that there are no polarization effects at the surface. In that case Eq. (32) becomes

$$f_S(P_S, \mathcal{E}_S, \phi_S) = -\sigma_0 \phi_S + \frac{k_B T}{b^2} \ln \Xi_S(\phi_S), \quad (41)$$

with the surface partition function

$$\Xi_S(\phi_S) = 1 + \lambda_+ e^{(\beta e \phi_S - \alpha_+)} + \lambda_- e^{-(\beta e \phi_S + \alpha_-)}, \quad (42)$$

that obviously corresponds to a surface lattice gas of adsorbed ions, or equivalently to a Langmuir isotherm. Of the different boundary conditions only Eq. (33) remains relevant and it can be recast in the form

$$-\varepsilon_\infty \varepsilon_0 (\mathbf{n} \cdot \nabla \phi)_S + P_S = \sigma_0 - \sigma(\phi_S), \quad (43)$$

where we introduced

$$\sigma(\phi_S) = \frac{\partial v_S}{\partial \phi_S} = \frac{\lambda_+ \beta e}{\Xi_S(\phi_S)} e^{(\beta e \phi_S - \alpha_+)} - \frac{\lambda_- \beta e}{\Xi_S(\phi_S)} e^{-(\beta e \phi_S + \alpha_-)}. \quad (44)$$

In the limit of adsorption for only a single type of ion, e.g. $\alpha_- \rightarrow \infty$, we get the boundary condition Eq. (43) in the simplified form

$$\varepsilon_\infty \varepsilon_0 E_S + P_S = \sigma_0 - 2\lambda_+ \beta e \left(1 + \tanh \frac{1}{2} (\beta e \phi_S - \alpha_+) \right), \quad (45)$$

corresponding exactly with the Langmuir adsorption isotherm charge regulation [21, 28]. The *Ansatz* for the surface free energy, Eq. (32), thus in general also incorporates charge regulation.

3 Solving the model equations

In our previous work we have discussed different versions of the bulk model in order to clarify the role the different bulk lengths play in the polarization interactions [7].

Specifically, we solved the linearized equations in a one-dimensional geometry with analytical and numerical methods.

The inclusion of further physical effects and, in particular, in the newly formulated boundary condition in this work renders the resulting theory extremely rich in physical variables and parameters. Not all of them will be of equal relevance for a specific experimental system, such that the determination of completely general parameter diagrams from the present theory will hardly be of general value. In this section we would therefore like to point out general characteristics of our theory which will be useful in later applications.

As in our previous work we consider the implementation of our theory for a 1D case, corresponding to a single or two planar surfaces perpendicular to the axis z , and in the latter case separated by the distance L .

In 1D the spatial dependence is a single coordinate z and all the vectorial variables only retain their z component, *i.e.*,

$$\mathbf{P} = (0, 0, P(z)), \quad \nabla\phi = (0, 0, \phi'(z)), \quad \boldsymbol{\mathcal{E}} = (0, 0, \mathcal{E}(z)). \quad (46)$$

We can write Eq. (9) as

$$\beta\mathcal{F} \equiv S \int_L dz f(P, P', P''; \phi, \phi'; \boldsymbol{\mathcal{E}}), \quad (47)$$

where S is the surface area. A useful general result is now available in the form of a first integral. In this case it can be obtained following the approach described in Ref. [?] as the expression

$$f - \phi' \frac{\partial f}{\partial \phi'} - P' \frac{\partial f}{\partial P'} - P'' \frac{\partial f}{\partial P''} + P' \left(\frac{\partial f}{\partial P''} \right)' = const. \quad (48)$$

The two last terms are a consequence of the higher-order derivative terms in the free energy density, see our previous discussion of the Euler-Lagrange equations in section II A. This relation is of general use in the integration of the saddle-point equations, albeit in the present complicated case this is not as easy as for the standard PB-equation for simple ions, where the electrostatic potential can be obtained by exact integration of the first integral. Eq. (48) holds for the fully nonlinear equations.

Of crucial interest is the role of the boundary conditions given for the general case by Eqs. (33), (34) and (35); we consider them for one surface only; we also set $\alpha = 0$. In the case of the two surfaces of the slit geometry, the discussion needs to be adapted accordingly.

The first important element is to notice the interdependence of the different surface variables expressed in these equations. The theory contains the six surface variables

$$\mathcal{E}_S, \phi_S, \phi'_S, P_S, P'_S, P'''_S,$$

whose relations are determined by the three boundary equations. Ultimately, this means that three values of the variables remain to be chosen.

Looking more closely, Eq.(33) expresses a relation between the field values \mathcal{E}_S , ϕ_S and ϕ'_S . We can thus, e.g., obtain \mathcal{E}_S as a function of ϕ_S and ϕ'_S , which together with Eq. (34) then defines a function $P_S = g_2(\phi_S, \phi'_S)$. Fixing the values for \mathcal{E}_S and P_S then allows to determine the corresponding values of ϕ_S and ϕ'_S . Further, Eq.(35) generally expresses a relationship between P_S , \mathcal{E}_S , ϕ'_S and the higher-order derivatives of P_S . In fact, one now has

$$u_P(0)(\xi^2 P_S'' - \zeta^4 P_S''') = g_3(\mathcal{E}_S, P_S, \phi'_S). \quad (49)$$

From the previous expressions the right-hand side of the last equation is now entirely fixed through the solution of the two previous equations. Thus, this relation fixes the relative difference between the two higher-order derivatives which remains as a final choice of boundary conditions. In this exemplary construction, the three values to choose are thus (\mathcal{E}_S, P_S) and the difference of the higher derivatives.

We finally illustrate this reasoning for the two limiting cases of surface polarization and charge regulation. In the case of example B.1, the surface polarization case which ignores the ions, since the boundary conditions do not depend on the electrostatic potential ϕ , Eqs. (38) result in a functional relationship between \mathcal{E}_S and P_S . In general, this equation can only be resolved numerically. If one expands both \mathcal{P} and the \ln for small arguments, \mathcal{E}_S turns out to be directly proportional to P_S . In this limit Eq.(35), the relative difference in the polarization derivatives at the wall, becomes a linear function of P_S , while the surface free energy becomes a quadratic function of P_S , as is well-known. In the second limiting example B.2, the charge regulation case neglecting all polarization effects, the value of P_S only remains as a parameter in Eq. (43) such that ultimately only the value of the electrostatic potential and its gradient, i.e. the electric field at the surface, remain coupled.

4 Discussion

In this work we have derived a comprehensive continuum theory of structured inhomogeneous liquid dielectrics. Starting from previous work for the bulk case [7], we develop a substantially extended version of our theory which explicitly includes the polarizability of the solvent molecules and the solvated ions species. In particular, we have carefully developed the theory of the surface free energy which includes surface polarization and charge regulation as two generic mechanisms. After formulating the bulk and surface free energies, we showed how to derive the corresponding saddle-point equations (nonlinear mean-field equations) together with the boundary equations. Being a fully formulated field theory, the application of the theory beyond mean-field theory is achieved by the computation of corrections in terms of a loop expansion.

We believe that our novel formulation of a comprehensive continuum theory of structured liquid dielectrics meets the challenge raised by Mugele et al. that we cited in the Introduction - it seems to be well possible to formulate a general Poisson-Boltzmann theory containing all non-electrostatic effects. We are careful to rather state ‘general’ than ‘universal’ here, since many of the included physical effects are indeed highly specific and thus a properly ‘universal’ theory cannot exist in principle.

The next step in the formulation of the theory will be the confrontation with experiment. Clearly, our comprehensive theory contains special cases for which such comparisons with experiment have already been undertaken; the challenge therefore rather is: how far can we go? As already discussed in the Introduction we think that the application to AFM measurements of structural forces are an evident first step to take. Previous work by Benaglia et al. [29] went already along this path employing density-functional theory (DFT). We think that the main advantage of the field-theoretic approach is its high transparency of the physical mechanisms explicitly built into the theory, in particular the flexibility of the treatment of the boundary conditions. This point of view is strengthened by the recent AFM-experiments of ionic solutions on silica and gibbsite surfaces. The experimentally observed oscillations in the force-distance curves are clearly due the ordering of bulk water molecules in the vicinity of the surface. The details of these curves are nevertheless dependent on pH and hence on charge regulation effects [6]. We believe that our approach will be flexible enough to disentangle and identify these different relevant effects on electrostatic and hydration forces at complex substrate surfaces.

Acknowledgments. RP wishes to acknowledge the support of the University of Chinese Academy of Sciences and funding from the NSFC under Grant No. 12034019.

Appendix A Drude model

The Drude model of polar and polarizable molecules [30] is based on two oppositely charged particles connected by a harmonic spring potential [18, 31]

$$U(\ell, \mathbf{n}) = \frac{1}{2} \frac{(\ell - \mathbf{s})^2}{\sigma^2} = \frac{1}{2} \frac{(\ell - \mathbf{s}\mathbf{n})^2}{\sigma^2}, \quad (\text{A1})$$

where $\mathbf{n} = \mathbf{s}/|\mathbf{s}| = \mathbf{s}/s$, yielding the separation distribution function $g(\ell)$ in the form

$$g(\ell) = (2\pi\sigma^2)^{-3/2} \int_{\Omega} \frac{d\mathbf{n}}{4\pi} \exp - \frac{(\ell - \mathbf{s})^2}{2\sigma^2} = (2\pi\sigma^2)^{-3/2} \int_{\Omega} \frac{d\mathbf{n}}{4\pi} e^{-U(\ell, \mathbf{n})} \quad (\text{A2})$$

with an average separation s and its variance σ^2 given by

$$\langle \ell \rangle = s, \quad \langle (\ell - s)^2 \rangle = \sigma^2, \quad (\text{A3})$$

where the average was defined as

$$\begin{aligned} \langle \dots \rangle &= \int d\ell g(\ell) = \\ &= (2\pi\sigma^2)^{-3/2} \int d\ell \int_{\Omega} \frac{d\mathbf{n}}{4\pi} (\dots) e^{-U(\ell, \mathbf{n})}. \end{aligned} \quad (\text{A4})$$

This is the model that we use to represent the aqueous solvent molecules as well as the solvated ions.

Appendix B One-body partition function

Here we derive the two expressions for the one-particle partition functions, $V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]$, in external fields which feature in the field-theoretic description of our system. The derivations follow Ref. [16] except for the inclusion of the polarizability terms. In addition, at the end because we work exclusively on the saddle-point level, we will need to make the transform $\phi \rightarrow i\phi$, $\mathcal{E} \rightarrow i\mathcal{E}$.

The one-body partition function in an external field, $V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]$, is defined as

$$\begin{aligned}
 e^{V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]} &\equiv \sum_N \sum_{N^+} \sum_{N^-} \frac{\lambda^N \lambda_{(+)}^{N^+} \lambda_{(-)}^{N^-}}{N! N^+! N^-!} \times \\
 &\times \int \mathcal{D}[\mathbf{x}_N] \mathcal{D}[\ell_N] \mathcal{D}[\mathbf{n}_N] e^{-\sum_N U(\ell_i, \mathbf{n}_i)} e^{-i\beta q_D \sum_N (\phi(\mathbf{x}_i) - \phi(\mathbf{x}_i + \ell_i)) - i q_D \sum_N \ell_i \cdot \mathcal{E}(\mathbf{x}_i)} \\
 &\times \int \mathcal{D}[\mathbf{x}_+] \mathcal{D}[\ell_+] e^{-\sum_{N^+} U(\ell_i, \mathbf{n}_i)} e^{-i\beta \sum_{N^+} \phi(\mathbf{x}_i) - i\beta q_l \sum_{N^+} (\phi(\mathbf{x}_i) - \phi(\mathbf{x}_i + \ell_i)) - i q_l \sum_{N^+} \ell_i \cdot \mathcal{E}(\mathbf{x}_i)} \\
 &\times \int \mathcal{D}[\mathbf{x}_-] \mathcal{D}[\ell_-] e^{-\sum_{N^-} U(\ell_i, \mathbf{n}_i)} e^{i\beta \sum_{N^-} \phi(\mathbf{x}_i) - i\beta q_l \sum_{N^-} (\phi(\mathbf{x}_i) - \phi(\mathbf{x}_i + \ell_i)) - i q_l \sum_{N^-} \ell_i \cdot \mathcal{E}(\mathbf{x}_i)}.
 \end{aligned} \tag{B1}$$

Using the definition of the average over the harmonic Drude degrees of freedom, Eq. (A4), for polar solvent molecules (with $\langle \ell \rangle = s$ and $\langle (\ell - s)^2 \rangle = \sigma_D^2$) and ionic charges (with $\langle \ell \rangle = 0$ and $\langle \ell^2 \rangle = \sigma_l^2$) we end up with

$$\begin{aligned}
 &\int \mathcal{D}[\ell_N] \mathcal{D}[\mathbf{n}_N] e^{-\sum_N U(\ell_i, \mathbf{n}_i)} e^{-i\beta q_D \sum_N (\phi(\mathbf{x}_i) - \phi(\mathbf{x}_i + \ell_i)) - i q_D \sum_N \ell_i \cdot \mathcal{E}(\mathbf{x}_i)} = \\
 &= \left(\frac{\sin(\beta q_D s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|)}{\beta q_D s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|} e^{-\frac{1}{2}(\beta \sigma_{qD})^2 (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} \right)^N \\
 &\int \mathcal{D}[\mathbf{x}_+] e^{-i\beta \sum_{N^+} \phi(\mathbf{x}_i)} = \left(\int d^3 \mathbf{x} e^{-i\beta \phi(\mathbf{x})} e^{-\frac{1}{2}(\beta \sigma_{q_l})^2 (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} \right)^{N^+} \\
 &\int \mathcal{D}[\mathbf{x}_-] e^{i\beta \sum_{N^-} \phi(\mathbf{x}_i)} = \left(\int d^3 \mathbf{x} e^{i\beta \phi(\mathbf{x})} e^{-\frac{1}{2}(\beta \sigma_{q_l})^2 (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} \right)^{N^-}. \tag{B2}
 \end{aligned}$$

Clearly all the sums in Eq. (B1) can be evaluated explicitly so that we finally remain with

$$\begin{aligned}
 V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] &= \int_V d^3 \mathbf{x} \left(\lambda_D \frac{\sin(\beta q_D s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|)}{\beta s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|} e^{-\frac{(\beta \sigma_{qD})^2}{2} (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} + \right. \\
 &\quad \left. + 2\lambda_s \cos \beta e \phi(\mathbf{x}) e^{-\frac{(\beta \sigma_{q_l})^2}{2} (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} \right).
 \end{aligned}$$

(B3)

We now one repeat the procedure for the lattice gas case. The only difference is in how one treats the sum over particles which now has to be performed over discrete sites of the lattice. Introducing the occupation of sites by electrolyte ions and Drude ions, which will be taken as occupying a single cell, we assign to each cell j , located at \mathbf{x}_j , a spin-like variable s_j that can have one of three values: $s_j = 0$ if the cell is occupied by a Drude dipole, and $s_j = \pm 1$ according to the sign of the electrolyte ion.

Defining a new variable that depends on the spin-like variable s_j , $u(s_j)$, as

$$\begin{aligned} u(s_j) = & i\beta e s_j \phi(\mathbf{x}_j) + i\beta q_I s_j^2 (\phi(\mathbf{x}_j) - \phi(\mathbf{x}_j + \ell_j)) \\ & - i\beta q_I s_j^2 (\ell_j \cdot \mathcal{E}(\mathbf{x}_j)) + \mu_j s_j^2 + \\ & + i\beta q_D (1 - s_j^2) (\phi(\mathbf{x}_j) - \phi(\mathbf{x}_j + \ell_j)) - \\ & - i\beta q_D (1 - s_j^2) (\ell_j \cdot \mathcal{E}(\mathbf{x}_j)) + \mu_j (1 - s_j^2), \end{aligned} \quad (\text{B4})$$

it then follows specifically for $s_i = \pm 1, 0$ that

$$\begin{aligned} u(s_j = +1) = & i\beta e \phi(\mathbf{x}_j) + i\beta q_I (\phi(\mathbf{x}_j) - \phi(\mathbf{x}_j + \ell_j)) + \\ & - i\beta q_I (\ell_j \cdot \mathcal{E}(\mathbf{x}_j)) + \mu_+ \\ u(s_j = -1) = & -i\beta e \phi(\mathbf{x}_j) + i\beta q_I (\phi(\mathbf{x}_j) - \phi(\mathbf{x}_j + \ell_j)) + \\ & - i\beta q_I (\ell_j \cdot \mathcal{E}(\mathbf{x}_j)) + \mu_- \\ u(s_j = 0) = & i\beta q_D (\phi(\mathbf{x}_j) - \phi(\mathbf{x}_j + \ell_j)) - \\ & - i\beta q_D (\ell_j \cdot \mathcal{E}(\mathbf{x}_j)) + \mu_D. \end{aligned} \quad (\text{B5})$$

The one particle partition function can then be written as

$$e^{V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]} \equiv \prod_j \left(\sum_{s_j} e^{u(s_j)} \right) = \prod_j \left(e^{u(s_j=+1)} + e^{u(s_j=-1)} + e^{u(s_j=0)} \right). \quad (\text{B6})$$

From here it follows furthermore that

$$\begin{aligned} V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] = & \sum_j \ln \left(\lambda_D \frac{\sin(\beta q_D s_j |\nabla \phi(\mathbf{x}_j) - \mathcal{E}(\mathbf{x}_j)|)}{\beta_S |\nabla \phi(\mathbf{x}_j) - \mathcal{E}(\mathbf{x}_j)|} e^{-\frac{(\beta \sigma q_D)^2}{2} (\nabla \phi(\mathbf{x}_j) - \mathcal{E}(\mathbf{x}_j))^2} \right. \\ & \left. + 2\lambda_S \cos \beta e \phi(\mathbf{x}_j) e^{-\frac{(\beta \sigma q_I)^2}{2} (\nabla \phi(\mathbf{x}_j) - \mathcal{E}(\mathbf{x}_j))^2} \right). \end{aligned} \quad (\text{B7})$$

Here $\lambda_D = e^{\mu_D}$ and $\lambda_S = e^{\mu_{\pm}}$ for an asymmetric electrolyte. Going to the continuum limit from here and assuming that all the sites have the same volume a^3 then the continuum limit of the above result is given by

$$V[\mathcal{E}(\mathbf{x}), \phi(\mathbf{x})] = \frac{1}{a^3} \int d^3 \mathbf{r} \ln \left(\lambda_D \frac{\sin(\beta q_D s |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|)}{\beta_S |\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x})|} e^{-\frac{(\beta \sigma q_D)^2}{2} (\nabla \phi(\mathbf{x}) - \mathcal{E}(\mathbf{x}))^2} \right)$$

$$+ 2\lambda_s \cos \beta e \phi(\mathbf{x}) e^{-\frac{(\beta \sigma q)^2}{2} (\nabla \phi(\mathbf{x}) - \boldsymbol{\varepsilon}(\mathbf{x}))^2}. \quad (\text{B8})$$

These are the one body partition functions in the case of a mixture of the Drude oscillators and Drude electrolyte ions. Without the dipolar contribution the two expressions above reduce to the well known Poisson-Boltzmann theory and the Poisson-Boltzmann lattice gas theory.

The form of these equations used in the main text, *i.e.* Eqs. (17), is obtained by inserting the saddle point form (imaginary value) of the auxiliary field variables, which eventually converts the trigonometric into hyperbolic functions and changes the sign of the Gaussian factors.

References

- [1] Fukuma, T., Ueda, Y., Yoshioka, S., Asakawa, H.: Atomic-scale distribution of water molecules at the mica-water interface visualized by three-dimensional scanning force microscopy. *Phys. Rev. Lett.* 104, 016101 (2010)
- [2] Kimura, K., Ido, S., Oyabu, N., Kobayashi, K., Hirata, Y., Imai, T., Yamada, H.: Visualizing water molecule distribution by atomic force microscopy. *The Journal of Chemical Physics* 132(19), 194705 (2010)
- [3] Herruzo, E.T., Asakawa, H., Fukuma, T., Garcia, R.: Three-dimensional quantitative force maps in liquid with 10 piconewton, angstrom and sub-minute resolutions. *Nanoscale* 5, 2678-2685 (2013)
- [4] Fukuma, T., Garcia, R.: Atomic- and molecular-resolution mapping of solid-liquid interfaces by 3d atomic force microscopy. *ACS Nano* 12(12), 11785-11797 (2018)
- [5] van Lin, S.R., Grotz, K.K., Siretanu, I., Schwierz, N., Mugele, F.: Ion-specific and ph-dependent hydration of mica-electrolyte interfaces. *Langmuir* 35(17), 5737-5745 (2019)
- [6] Klaassen, A., Liu, F., Mugele, F., Siretanu, I.: Correlation between electrostatic and hydration forces on silica and gibbsite surfaces: An atomic force microscopy study. *Langmuir* 38(3), 914-926 (2022)
- [7] Blossey, R., Podgornik, R.: Field theory of structured liquid dielectrics. *Phys. Rev. Research* 4, 023033 (2022)
- [8] Onsager, L., Dupuis, M.: The electrical properties of ice. In: *Rend.Sc.Int.Fis. "Enrico Fermi"*, Corso X Varenna 1959, pp. 294-315. N. Zanichelli, Bologna (1960)
- [9] Onsager, L., Dupuis, M.: The electrical properties of ice. In: *Pesce, B. (ed.) Electrolytes*, pp. 27-46. Pergamon, Oxford (1962)

- [10] Gruen, D.W.R., Marčelja, S.: Spatially varying polarization in ice. *J. Chem. Soc. Faraday Trans. 2* 79, 211-223 (1983)
- [11] Gruen, D.W.R., Marčelja, S.: Spatially varying polarization in water. A model for the electric double layer and the hydration force. *J. Chem. Soc. Faraday Trans. 2* 79, 225-242 (1983)
- [12] Blossey, R., Podgornik, R.: Continuum theories of structured dielectrics, <https://arxiv.org/abs/2206.01789> (2022)
- [13] Podgornik, R.: Theory of inhomogeneous rod-like Coulomb fluids. *Symmetry* 13(2) (2021)
- [14] Maggs, A.C., Everaers, R.: Simulating nanoscale dielectric response. *Phys. Rev. Lett.* 96, 230603 (2006)
- [15] Monet, G., Bresme, F., Kornyshev, A., Berthoumieux, H.: Nonlocal dielectric response of water in nanoconfinement. *Phys. Rev. Lett.* 126, 216001 (2021)
- [16] Abrashkin, A., Andelman, D., Orland, H.: Dipolar Poisson-Boltzmann equation: Ions and dipoles close to charge interfaces. *Phys. Rev. Lett.* 99, 077801 (2007)
- [17] Gongadze, E., Velikonja, A., Šarka Perutkova, Kramar, P., Mačcek-Lebar, A., Kralj-Iglič, V., Iglič, A.: Ions and water molecules in an electrolyte solution in contact with charged and dipolar surfaces. *Electrochimica Acta* 126, 42-60 (2014)
- [18] Buyukdagli, S., Ala-Nissila, T.: Microscopic formulation of nonlocal electrostatics in polar liquids embedding polarizable ions. *Phys. Rev. E* 87, 063201 (2013)
- [19] Netz, R.R.: Static van der Waals interactions in electrolytes. *The European Physical Journal E* 5(2), 189-205 (2001)
- [20] Démary, V., Dean, D.S., Podgornik, R.: Electrostatic interactions mediated by polarizable counterions: Weak and strong coupling limits. *The Journal of Chemical Physics* 137(17), 174903 (2012)
- [21] Podgornik, R.: General theory of charge regulation and surface differential capacitance. *The Journal of Chemical Physics* 149(10), 104701 (2018)
- [22] Avni, Y., Andelman, D., Podgornik, R.: Charge regulation with fixed and mobile charged macromolecules. *Current Opinion in Electrochemistry* 13, 70-77 (2019)
- [23] Cevc, G., Podgornik, R., Zeks, B.: The free energy, enthalpy and entropy of hydration of phospholipid bilayer membranes and their difference on the

- interfacial separation. *Chemical Physics Letters* 91(3), 193-196 (1982)
- [24] Kanduč, M., Schlaich, A., Schneck, E., Netz, R.R.: Hydration repulsion between membranes and polar surfaces: simulation approaches versus continuum theories. *Adv. Colloid Interface Sci* 208, 142-152 (2014)
- [25] Podgornik, R.: Electrostatic correlation forces between surfaces with surface specific ionic interactions. *The Journal of Chemical Physics* 91(9), 5840-5849 (1989)
- [26] Podgornik, R., Zeks, B.: Hydration force and hydration regulation. *Studia Biophysica* 111(2-3), 135-142 (1986)
- [27] Markovich, T., Andelman, D., Podgornik, R.: *Handbook of Lipid Membranes: Molecular, Functional, and Materials Aspects*. CRC Press, Boca Raton, Florida, U.S. (2021)
- [28] Ninham, B.W., Parsegian, V.A.: Electrostatic potential between surfaces bearing ionizable groups in ionic equilibrium with physiologic saline solution. *Journal of Theoretical Biology* 31(3), 405-428 (1971)
- [29] Benaglia, S., Uhlig, M.R., Hernández-Munoz, J., Chacón, E., Tarazona, P., Garcia, R.: Tip charge dependence of three-dimensional AFM mapping of concentrated ionic solutions. *Phys. Rev. Lett.* 127, 196101 (2021)
- [30] Bordin, J.R., Podgornik, R., Holm, C.: Static polarizability effects on counterion distributions near charged dielectric surfaces: A coarse-grained molecular dynamics study employing the drude model. *The European Physical Journal Special Topics* 225(8), 1693-1705 (2016)
- [31] Budkov, Y.A.: Statistical field theory of ion-molecular solutions. *Phys. Chem. Chem. Phys.* 22, 14756-14772 (2020)