

## Field theory of structured liquid dielectrics

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We develop a field-theoretic approach for the treatment of both the nonlocal and the nonlinear response of structured liquid dielectrics. Our systems of interest are composed of dipolar solvent molecules and simple salt cations and anions. We describe them by two independent order parameters, the polarization field for the solvent and the charge-density field for the ions, including and treating the nonelectrostatic part of the interactions explicitly and consistently. We show how to derive functionals for the polarization and the electrostatic field of increasingly finer scales and solve the resulting mean-field saddle-point equations in the linear regime. We derive criteria for the character of their solutions that depend on the structural lengths and the polarity of the solvent. Our approach provides a systematic way to derive generalized polarization theories.

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### I. INTRODUCTION

Phenomenological functionals of polarization have featured prominently in the development of the electrostatic theory of structured dielectrics starting from the seminal contributions of Marcus in the 1950s on electron transfer theory based on local dielectric response theory [1,2]. Aqueous dielectrics, *de rigueur* in soft- and biomatter systems [3], pose another challenge as the dielectric response of water is strongly nonlocal and cannot be exhaustively described by a local dielectric approximation [4]. This has been the driving force behind the phenomenological nonlocal dielectric function methodology developed extensively by Kornyshev and collaborators [4–6] as well as the Landau-Ginzburg-type free-energy functionals describing the nonlocal dielectric response in spatially confined dielectrics [7–11], the two approaches being, of course, equivalent in bulk but differing in systems with boundaries.

While it would be, of course, desirable to have more microscopic theories, aqueous dielectrics have consistently eluded descriptions based on more detailed explicit molecular interactions. As a successful example of a microscopic nonlocal

dielectric theory, one can consider the statistical mechanical formulation of the nonlocal dielectric properties of ice by Onsager and Dupuis [12,13], later further elaborated and generalized by Gruen and Marčelja [14,15]. Of all the methodologies applied to nonlocal dielectrics, this is the first to be found in the literature that implements not only the nonlocal but also the nonlinear dielectric response of a system. It leads to *two coupled equations* for the electrostatic field and the dielectric polarization field and in general cannot be reduced to either the nonlocal dielectric function methodology or the local Landau-Ginzburg polarization functional. The coupling between the polarization and the electrostatic fields is provided by the structural interaction mediated by the Bjerrum structural defects in the ideal hydrogen bonded lattice of ice. In its absence the basic equations reduce to the standard dielectric response theory. Being based on the crystalline lattice and hydrogen-bonding defects, there is no simple way to use Onsager-Dupuis theory straightforwardly for a liquid aqueous dielectric.

An important area of application for the nonlocal dielectric response of structured dielectrics was and remains the theory of hydration forces [16,17], where the dielectric response of ice [18] as well as the nonlocal electrostatics of liquid water [6,19] were applied to water confined between substrate surfaces with the propensity for local ordering of vicinal water molecules. This type of water structural interaction modeling has been applied to solvation of phospholipid membranes [20], DNA molecules [21], linear polysaccharides [22], or to the solvation of proteins [23,24]. More recent approaches extend the ideas of nonlocal dielectric response of confined water [25] to the order-parameter description beyond the polarization [26], which are able to describe additional features of confined water structuring [27,28]. The order-parameter

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description can be arguably viewed as a generalization of the Landau-Ginzburg-type free-energy functionals beyond the polarization formulation [29], describing additional degrees of freedom pertinent to the complicated hydrogen-bond phenomenology [30]. The hydration force theory also sheds light on the fact that part of the water polarization is purely nonelectrostatic in nature, being a separate field, independent of the imposed electrostatic field. This is, in fact, one of the most important conclusions of the Onsager-Dupuis theory of the dielectric response of ice [13,14].

Motivated by the Onsager-Dupuis approach we develop a systematic field theory for the *nonlocal as well as the nonlinear dielectric response* of structured liquid dielectrics based on the electrostatic field and dielectric polarization as *separate order parameters*. From the outset, our approach decouples electrostatic and nonelectrostatic structural contributions to these order parameters, allowing for the consistent inclusion of the effects that could not be implemented in previous approaches. On the linear level, our theory reduces to two equations for the electrostatic and polarization potentials, which are coupled by the nonelectrostatic interaction potentials and assume a form completely consistent with the linearized Onsager-Dupuis theory of ice. We explicitly discuss three examples of linear models differing by the degree of structural detailed included and show how they relate to previously studied simplified models.

## II. ORDER PARAMETERS AND MICROSCOPIC INTERACTIONS

The systems we consider are composed of three components: A rigid rodlike solvent with a dipolar moment (N), positive simple salt ions (+), and negative simple salt ions (-). We first introduce two separate order parameters: Charge density and polarization (dipolar charge density). For the solvent (N) component, the order parameter is the *polarization field* defined as

$$\hat{P}(\mathbf{x}) \equiv \sum_{(N)} p \mathbf{n} \delta(\mathbf{x} - \mathbf{x}_n), \quad (1)$$

where  $p$  is the dipolar moment of the molecule, so that the bound charge-density field of the solvent material is

$$\hat{\rho}_{(N)}(\mathbf{x}) \equiv p \sum_N \mathbf{n} \cdot \nabla \delta(\mathbf{x} - \mathbf{x}_n) = \nabla \cdot \hat{P}(\mathbf{x}), \quad (2)$$

with dipoles considered to be pointlike. For the simple salt component we can define the total charge-density  $\hat{\rho}_{(\pm)}(\mathbf{x})$  as the sum of *cation* and *anion density fields*

$$\hat{\rho}_{(\pm)}(\mathbf{x}) \equiv e \sum_{N_+} \delta(\mathbf{x} - \mathbf{x}_n) - e \sum_{N_-} \delta(\mathbf{x} - \mathbf{x}_n), \quad (3)$$

where  $e$  is the elementary charge of the salt ions,  $N$  is the number of dipoles, while  $N_{\pm}$  are the numbers of positive and negative ions, respectively. The *total charge-density field* is then

$$\hat{\rho}(\mathbf{x}) = \hat{\rho}_{(\pm)}(\mathbf{x}) + \nabla \cdot \hat{P}(\mathbf{x}). \quad (4)$$

We will now first write the interactions in terms of these microscopic order parameters and then in the form of macroscopic collective coordinates in exactly the same way as

this is done for standard Coulomb fluids and/or for nematic Coulomb fluids [31]. The interactions in the system have the following components: The nonelectrostatic interactions in the harmonic approximation,

$$\mathcal{H}_{SR} = \frac{1}{2} \int_V d\mathbf{x} d\mathbf{x}' \hat{P}_i(\mathbf{x}) \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') \hat{P}_j(\mathbf{x}'), \quad (5)$$

where we assumed that the nonelectrostatic tensorial part  $\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}')$  is a *short-range, nonelectrostatic potential*; the electrostatic interactions are given by the standard Coulomb form

$$\mathcal{H}_C = \frac{1}{2} \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}(\mathbf{x}) u(\mathbf{x} - \mathbf{x}') \hat{\rho}(\mathbf{x}'), \quad (6)$$

with the proviso that we take the Coulomb potential with the nonconfigurational dielectric constant, or the high-frequency dielectric constant  $\varepsilon_{\infty}$  as in the Onsager-Dupuis model, i.e.,

$$u(\mathbf{x} - \mathbf{x}') = (1/4\pi \varepsilon_{\infty} \varepsilon_0) |\mathbf{x} - \mathbf{x}'|^{-1}, \quad (7)$$

where  $\varepsilon_{\infty}$  is associated with all the relaxation mechanisms apart from the dipolar one; further, we allow for nonelectrostatic interactions due to the hydration shell of the ions, which generalizes the role played by the ion-bound Bjerrum defects in the Onsager-Dupuis theory of ice [18]. This effect corresponds to the coupling between the ion density and  $\hat{\rho}_{(\pm)}(\mathbf{x})$  and  $\hat{P}_j(\mathbf{x})$ . To the lowest order this coupling can be written via the hydration energy of the form (for details, see Appendix B)

$$\mathcal{H}_{HY} = \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}(\mathbf{x}) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}'), \quad (8)$$

where the potential  $\tilde{u}(\mathbf{x} - \mathbf{x}')$  is again a *short-range, nonelectrostatic potential* for the hydration shell interactions. Here we assume for simplicity that the polarization in the hydration shell of anions and cations is—apart from its direction—the same.

The total interaction energy functional is thus composed of the standard electrostatic Coulomb interaction between all the charges in the system, but in a medium with high-frequency dielectric constant and the nonelectrostatic short-range polarization interactions and ion polarization interactions, and is written as

$$\mathcal{H} = \mathcal{H}_C[\hat{\rho}(\mathbf{x})] + \mathcal{H}_{SR}[\hat{P}(\mathbf{x})] + \mathcal{H}_{HY}[\hat{\rho}(\mathbf{x}), \hat{P}(\mathbf{x})], \quad (9)$$

so that the interaction Hamiltonian is  $\mathcal{H} \equiv \mathcal{H}[\hat{\rho}(\mathbf{x}), \hat{P}(\mathbf{x})]$ . We note that the interaction Hamiltonian need not be quadratic and our approach can easily incorporate higher-order interactions.

## III. COLLECTIVE DESCRIPTION AND FIELD THEORY

From here we derive the partition function in terms of two order parameters and two auxiliary fields (for details, see Appendix A) as

$$\Xi \equiv \int \mathcal{D}[P_i(\mathbf{x})] \mathcal{D}[\mathcal{E}_i(\mathbf{x})] \int \mathcal{D}[\rho(\mathbf{x})] \mathcal{D}[\phi(\mathbf{x})] \times e^{-\beta \mathcal{H}[P_i(\mathbf{x}), \rho(\mathbf{x}), \mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]}. \quad (10)$$

This expression differs from the standard Coulomb fluid field-theoretical representation of the partition function [32,33]

by the presence of two additional independent fields  $P_i(\mathbf{x})$  and  $\mathcal{E}_i(\mathbf{x})$ . In what follows, we will not analyze the general features of the partition function but will limit ourselves immediately to its *saddle-point* evaluation, which is taken with respect to the auxiliary fields  $\mathcal{E}_i(\mathbf{x}) \rightarrow i\mathcal{E}_i^*(\mathbf{x})$  and  $\phi(\mathbf{x}) \rightarrow i\phi^*(\mathbf{x})$ . The partition function is then approxi-

mated by  $-\ln \Xi \rightarrow \beta\mathcal{H}[P_i(\mathbf{x}), \rho(\mathbf{x}); i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x})]$  where the effective-field Hamiltonian is obtained from the partial trace over coordinate and orientation degrees of freedom for the ions and dipoles in the partition function interacting via the interaction energy functional Eq. (9). It can be obtained in the form

$$\beta\mathcal{H}[P_i(\mathbf{x}), \rho(\mathbf{x}); i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x})] = \mathcal{H}[P_i(\mathbf{x}), \rho(\mathbf{x})] - \int_V d\mathbf{x} P_i(\mathbf{x})\mathcal{E}_i^*(\mathbf{x}) - \int_V d\mathbf{x} \rho(\mathbf{x})\phi^*(\mathbf{x}) - \int_V d^3\mathbf{x} v^*(\mathcal{E}_i^*(\mathbf{x}), \phi^*(\mathbf{x})), \quad (11)$$

where the first term is the interaction Hamiltonian, Eq. (9).

The expression for the effective-field interaction potential  $v^*(\mathcal{E}_i(\mathbf{x}), \phi^*(\mathbf{x})) = v(i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x}))$  depends crucially on the model used for the dipolar fluid. We specifically obtain its form for two models: the case of a *dipolar model* (DM) is obtained without any constraints on the summation [34], while in the case of the *dipolar Langevin model* (DLM) one assumes an underlying lattice of spacing  $a$  (roughly equal to the molecular size) [35], imposing the condition that each site of the lattice is occupied by only one of the species (incompressibility condition).

For the DM model the effective-field interaction potential can be written explicitly (see Appendix A) as

$$v_{DM}^*(\mathcal{E}_i^*(\mathbf{x}), \phi^*(\mathbf{x})) = \lambda \left( \frac{\sinh u}{u} + 2\tilde{\lambda}_s \cosh w \right), \quad (12)$$

where  $u = \beta p |\mathcal{E}^*(\mathbf{x}) - \nabla\phi^*(\mathbf{x})|$  and  $w = \beta e\phi^*(\mathbf{x})$ . The DM model implies no constraints on the local density of either ions or dipoles and thus exhibits a form of an ideal van't Hoff gas of ions and dipoles [34,36]. For the DLM model we have  $v_{DLM}^* = \frac{1}{a^3} \ln(v_{DM}^*/\lambda)$ .

An important new feature of both models is the dependence of the effective field interaction potential on the field difference  $\mathcal{E}^*(\mathbf{x}) - \nabla\phi^*(\mathbf{x})$ . The auxiliary field  $\mathcal{E}^*(\mathbf{x})$  here plays the role of a coupling field that quantifies the degree of nonelectrostatic coupling between polarization and electrostatic fields and is a *distinct feature* of our approach.

#### IV. MEAN-FIELD (SADDLE-POINT) EQUATIONS

The saddle-point equations can be obtained for all the variables, i.e., the order parameters as well as the auxiliary

fields. For the two order parameters we obtain

$$\begin{aligned} \mathcal{E}_i^*(\mathbf{x}) &= - \int_V d\mathbf{x}' \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') P_j(\mathbf{x}') \\ &\quad + \nabla_i \int_V d\mathbf{x}' \tilde{u}(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}'), \\ \phi^*(\mathbf{x}) &= \int_V d\mathbf{x}' u(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}') \\ &\quad + \int_V d\mathbf{x}' \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \mathbf{P}(\mathbf{x}'). \end{aligned} \quad (13)$$

Of the two saddle-point field equations, Eq. (13), the first one contains *only nonelectrostatic contributions* pertaining to the polarization  $\tilde{u}_{ij}$  and hydration  $\tilde{u}$  interaction potentials, corroborating our previous statement that the auxiliary field  $\mathcal{E}_i^*(\mathbf{x})$  quantifies the nonelectrostatic effects. The second equation contains the combined electrostatic  $u$  and nonelectrostatic  $\tilde{u}$  contributions, where the latter have their origin in the ion hydration shell.

After observing that the effective field interaction potential  $v^*[\mathcal{E}_i^*(\mathbf{x}), \phi^*(\mathbf{x})] = v^*[u, w]$ , the two coupled saddle-point equations for the auxiliary fields can be written as

$$\begin{aligned} P(\mathbf{x}) &= -(\beta p)^2 \left( \frac{1}{u} \frac{\partial v^*}{\partial u} \right) (\mathcal{E}^*(\mathbf{x}) - \nabla\phi^*(\mathbf{x})) \\ \rho(\mathbf{x}) - \nabla \cdot \mathbf{P}(\mathbf{x}) &= -(\beta e) \frac{\partial v^*}{\partial w}. \end{aligned} \quad (14)$$

Equation (14) together with Eq. (13) constitute the mean-field description of the structured dielectric.

In order to fully formulate our field equations, we need to define the structural potentials. For this we expand the nonelectrostatic potential in terms of its gradients and consider explicitly the local, second-order, and fourth-order forms,

$$\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') = \tilde{u}_P(0)(\delta_{ij}\delta(\mathbf{x} - \mathbf{x}') + \xi^2 \nabla'_j \nabla_i \delta(\mathbf{x} - \mathbf{x}') + \zeta^4 \nabla'_k \nabla'_j \nabla_k \nabla_i \delta(\mathbf{x} - \mathbf{x}')) + \dots \quad (15)$$

where  $\tilde{u}_P(0)$ ,  $\xi$ , and  $\zeta$  are the material constants in the constitutive relations. The length  $\xi$  corresponds to the solvent particle correlation length and  $\zeta$  to the solvent molecular size.

Equation (14) for  $\mathbf{P}(\mathbf{x})$  can be expressed for the DM and DLM-models as

$$\mathbf{P}(\mathbf{x}) = -\lambda_0(\beta p)^2 Q(u) (\mathcal{E}^*(\mathbf{x}) - \nabla\phi^*(\mathbf{x})), \quad (16)$$

where  $\lambda_0 \equiv \lambda$  for the DM and  $\lambda_0 \equiv 1/a^3$  for the dipolar Langevin model. Writing

$$\mathcal{E}^*(\mathbf{x}) = u_P(0)\mathbf{P}(\mathbf{x}) - \mathcal{F}(\nabla \cdot \mathbf{P}(\mathbf{x})) \quad (17)$$

we can express the polarization field as

$$\mathbf{P}(\mathbf{x}) = \frac{\lambda_0(\beta p)^2 Q(u)}{1 + \lambda_0 u_P(0)(\beta p)^2 Q(u)} (\nabla\phi^*(\mathbf{x}) + \mathcal{F}(\nabla \cdot \mathbf{P})). \quad (18)$$

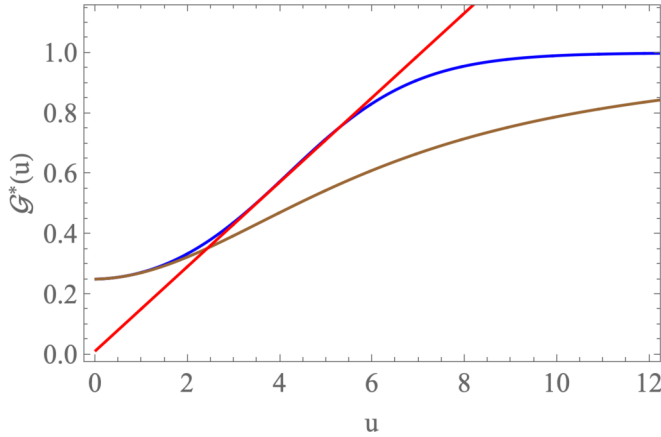


FIG. 1.  $\mathcal{G}^*(u)$  in the DM model (blue line) and the lowest-order nonlinear approximation to  $\mathcal{G}^*(u)$  in an expansion around the minimum (brown line); linear approximation to the central region of the function (red line)

The function  $Q(u)$  for the DM model can be written in the form

$$Q(u) = \mathcal{G}(u) \equiv \frac{1}{u} \frac{d}{du} \left( \frac{\sinh(u)}{u} \right) \quad (19)$$

while for the DLM model it reads as

$$Q(u) = \mathcal{H}(u) \equiv \frac{u}{\sinh(u)} \mathcal{G}(u). \quad (20)$$

The highly nonlinear dependence of the field equations on the polarization field and the electrostatic field via the function  $Q(u)$  is illustrated in Fig. 1 for the DM model. It shows the function

$$\mathcal{G}^*(u) = \frac{\lambda(\beta p)^2 G(u)}{1 + \lambda u_P(0)(\beta p)^2 G(u)} \quad (21)$$

together with the lowest-order nonlinear approximation from its Taylor-expansion around its minimum.

$\mathcal{G}^*(u)$  saturates at both small and large arguments and linearly interpolates between the two limiting values; see Fig. 1.

## V. LINEAR MODEL EQUATIONS

In view of the complexity of the fully nonlinear equations, we restrict our calculations in the following to the linear case, identical for the DM and DLM models, corresponding to the lowest-order term in Eq. (21). Truncating the nonelectrostatic structural interaction potentials Eq. (15) after the second-order and fourth-order derivative terms, respectively, we refer to the resulting expressions as *Models 1* and *2*. As the energy Eq. (8) is already first order in the derivatives, the simplest possible local interaction for the ion density-polarization coupling is

$$\tilde{u}(\mathbf{x} - \mathbf{x}') = \alpha \delta(\mathbf{x} - \mathbf{x}') + \dots \quad (22)$$

where  $\alpha$  can be interpreted as the strength of the hydration shell of the ions. Considering an ion with effective radius  $a$ , charge  $e$ , and polarization of the hydration shell  $P_n$  with a hydration (free) energy  $\mathcal{F}_{HY}$ , we are led to identify  $\alpha = \frac{1}{3} \mathcal{F}_{HY} a / (P_n e)$ . Including the ion density-polarization nonelectrostatic coupling given to the lowest order, we term this

expression *Model 3*. We now formulate the equations of these models explicitly.

*Model 1.* Stopping at the second-order derivative term in Eq. (15), we have from Eq. (13) for the structural part the relation

$$\mathcal{E}^*(\mathbf{x}) = u_P(0)(\mathbf{P}(\mathbf{x}) - \xi^2 \nabla(\nabla \cdot \mathbf{P}(\mathbf{x}))). \quad (23)$$

Employing the linearized saddle-point Eq. (14) with

$$v^*[\mathcal{E}^*(\mathbf{x}), \phi^*(\mathbf{x}), \nabla \phi^*(\mathbf{x})] = (\beta e)^2 \phi^*(\mathbf{x})^2 + \frac{\lambda(\beta p)^2}{6} u(\mathbf{x})^2,$$

we can eliminate the field  $\mathcal{E}^*(\mathbf{x})$  and find

$$u_P(0) \xi^2 \nabla(\nabla \cdot \mathbf{P}(\mathbf{x})) - \left( u_P(0) + \frac{3}{\lambda p^2} \right) \mathbf{P}(\mathbf{x}) = -\nabla \phi^*(\mathbf{x})$$

$$\nabla(\varepsilon_\infty \varepsilon_0 \nabla \phi^*(\mathbf{x}) + P(\mathbf{x})) = 2(\beta e)^2 \lambda_s \phi^*(\mathbf{x}). \quad (24)$$

The coupled equations for  $\phi^*(\mathbf{x})$  and  $\mathbf{P}(\mathbf{x})$  correspond to the equations derived in Ref. [37] with an opposite sign of the polarization field.

As in Refs. [14,37] we introduce the *polarization potential*  $\phi^\dagger(\mathbf{x})$  which can be defined via

$$\mathbf{P}(\mathbf{x}) = (\varepsilon - \varepsilon_\infty) \varepsilon_0 \nabla \phi^\dagger(\mathbf{x}), \quad (25)$$

making use of the identification

$$\varepsilon \varepsilon_0 \equiv \varepsilon_\infty \varepsilon_0 + \frac{\frac{1}{3} \lambda p^2}{1 + u_P(0) \frac{1}{3} \lambda p^2} \quad (26)$$

that relates the structural coupling  $u_P(0)$  to the dielectric constants and the strength of the water dipole. Integrating the equation for  $\mathbf{P}$ , using the definition Eq. (26) and defining

$$\widehat{\xi}^2 \equiv (\varepsilon - \varepsilon_\infty) \varepsilon_0 u_P(0) \xi^2, \quad (27)$$

the mean-field equations for our Model 1 read as

$$\nabla^2 \phi^\dagger(\mathbf{x}) = \widehat{\xi}^{-2} (\phi^\dagger(\mathbf{x}) - \phi^*(\mathbf{x})), \quad (28)$$

$$\begin{aligned} \nabla^2 \phi^*(\mathbf{x}) &= \frac{\varepsilon}{\varepsilon_\infty} \kappa_D^2 \phi^*(\mathbf{x}) \\ &+ \widehat{\xi}^{-2} \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) (\phi^*(\mathbf{x}) - \phi^\dagger(\mathbf{x})), \end{aligned} \quad (29)$$

in which the inverse square of the Debye length is defined by  $\kappa_D^2 \equiv 2(\beta e)^2 \lambda_s / \varepsilon \varepsilon_0$ . Except for the sign of  $\phi^\dagger$  these equations are the same as the Onsager-Dupuis equations [12].

*Model 2.* Keeping the terms up to the fourth order in derivatives in Eq. (15), we find, introducing a second redefined length  $\widehat{\zeta}_0$ ,

$$\widehat{\zeta}_0^4 \equiv (\varepsilon - \varepsilon_\infty) \varepsilon_0 u_P(0) \zeta^4 \quad (30)$$

the set of equations

$$\begin{aligned} \widehat{\zeta}_0^4 \nabla^2 \nabla^2 \phi^\dagger(\mathbf{x}) - \widehat{\xi}^2 \nabla^2 \phi^\dagger(\mathbf{x}) &= \phi^*(\mathbf{x}) - \phi^\dagger(\mathbf{x}), \\ \nabla^2 \phi^*(\mathbf{x}) + \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) \nabla^2 \phi^\dagger(\mathbf{x}) &= \frac{\varepsilon}{\varepsilon_\infty} \kappa_D^2 \phi^*(\mathbf{x}), \end{aligned} \quad (31)$$

which depend on three characteristic lengths,  $1/\kappa_D$ ,  $\xi$ , and  $\zeta_0$ .

*Model 3.* The ion density-polarization coupling is incorporated via the lowest-order expansion Eq. (22) and gives rise to



the following equations for the electrostatic and polarization potentials (for details on the derivation, see Appendix B),

$$\begin{aligned} \widehat{\zeta}^4 \nabla^4 \phi^\dagger(\mathbf{x}) - \widehat{\xi}^2 \nabla^2 \phi^\dagger(\mathbf{x}) + \widehat{\alpha}^2 \nabla^2 \phi^*(\mathbf{x}) \\ = \phi^*(\mathbf{x}) - \phi^\dagger(\mathbf{x}), \\ \left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right) [1 - \widehat{\alpha}^2 \nabla^2] \nabla^2 \phi^\dagger + \nabla^2 \phi^* \\ = \frac{\varepsilon}{\varepsilon_\infty} \kappa_D^2 \phi^* \end{aligned} \quad (32)$$

with the additional length  $\widehat{\zeta}$

$$\widehat{\zeta}^4 \equiv w(u_P(0)\zeta^4 - \alpha^2 \varepsilon_\infty \varepsilon_0)(\varepsilon - \varepsilon_\infty) \varepsilon_0 = \widehat{\zeta}_0^4 - \widehat{\alpha}^4 \left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right), \quad (33)$$

where the definition  $\widehat{\alpha}^2 \equiv \alpha \varepsilon_0 \varepsilon_\infty$  has been introduced. This model obviously depends on all four characteristic lengths that we consider in this model catalog.

Finally, we note that the linear saddle-point equations, coupling the electrostatic and polarization potentials, are generally of higher than the second order, entailing a nonlocal dielectric response of the bulk media, as has been observed already in the analysis of the seminal work of Onsager and Dupuis on the dielectric response of ice [14,15].

## VI. DECOUPLING AND SOLVING THE EQUATIONS

Since we will consider one-dimensional geometries like a slit geometry  $-L \leq z \leq L$  or a single-plate geometry  $0 \leq z < \infty$  we assume  $\mathbf{x} \equiv (0, 0, z)$  and the mean-field equations reduce to ordinary differential equations. The first step in solving these equations is then the decoupling of the electrostatic and polarization potentials,  $\phi^*$  and  $\phi^\dagger$ , respectively.

Solving the saddle-point equations in a slit or a single boundary geometries entails the knowledge of appropriate boundary conditions. Here one can follow two different approaches. First, since the key feature of our description is the decoupling of the degrees of freedom of the electrostatic field and the polarization field, this translates into the requirement of separate boundary conditions for both fields (see, e.g., Refs. [20,27,38]). Second, a more consistent approach would be to introduce also the appropriate boundary energy terms into the free energy (see, e.g., Refs. [11,27,39]) and then derive consistently also the saddle-point boundary conditions. Note, however, that since the free energy in general contains higher-order derivatives, this translates into additional higher derivative boundary conditions [40]. We will not pursue this approach in what follows but rather postulate a set of boundary conditions for all the fields.

### A. Model 1

In the case of *Model 1* the equations can be written in matrix form  $\frac{d^2}{dz^2} \Phi_1(z) = \mathcal{M}_1 \Phi_1(z)$  with the introduction of the composite field  $\Phi_1(z) \equiv (\phi^*(z), \phi^\dagger(z))$ . The coupling matrix  $\mathcal{M}_1$  is given by

$$\mathcal{M}_1 = \begin{pmatrix} \frac{\varepsilon}{\varepsilon_\infty} \kappa_D^2 + \left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right) \widehat{\xi}^{-2} & -\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right) \widehat{\xi}^{-2} \\ -\widehat{\xi}^{-2} & \widehat{\xi}^{-2} \end{pmatrix}.$$

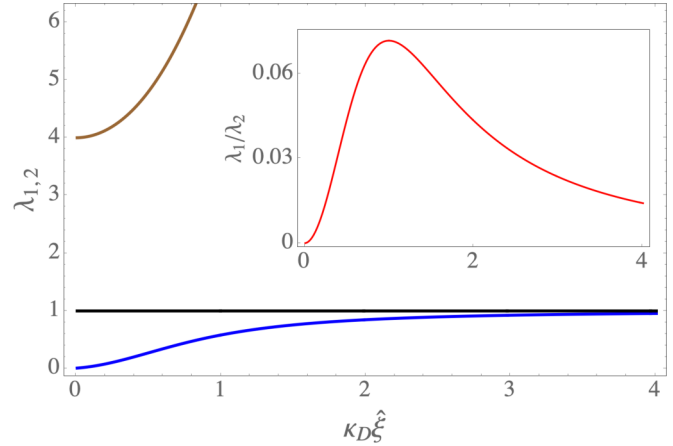


FIG. 2. The eigenvalues of the matrix  $\mathcal{M}_1$ , with  $\lambda_1 \leq 1$ , as a function of dimensionless parameter  $\kappa_D \widehat{\xi}$ . The horizontal line corresponds to  $\lambda = 1$ . Insert: The ratio of  $\lambda_1$  and  $\lambda_2$ .

Diagonalizing the matrix and rescaling the eigenvalues with  $\lambda \rightarrow \lambda/\widehat{\xi}^2$  lead to a quadratic eigenvalue equation given by

$$\lambda^2 - \lambda \frac{\varepsilon}{\varepsilon_\infty} (1 + (\kappa_D \widehat{\xi})^2) + \frac{\varepsilon}{\varepsilon_\infty} (\kappa_D \widehat{\xi})^2 = 0, \quad (34)$$

where  $\kappa^\pm = \sqrt{\lambda_\pm}$  are then the two inverse decay lengths corresponding to the two eigenvalues, which are both real and positive. They correspond to the decay lengths of the electrostatic and the polarization potentials, respectively, and coincide with the result of the linearized Onsager-Dupuis theory [15,37]. The decay lengths are shown in Fig. 2 as functions of  $\kappa_D \widehat{\xi}$  in accord with earlier results; see Ref. [38].

In order to solve the linear model equations in confined geometries, we also need to specify two separate boundary conditions for  $-\nabla \phi^* \cdot \mathbf{n}$  and  $\mathbf{P} \cdot \mathbf{n}$  at the bounding surface(s) with normal vector  $\mathbf{n}$ . Alternatively we can assume that the bounding surfaces carry “polarization charges”  $\sigma_P$

$$\nabla \cdot \mathbf{P}(\mathbf{x}) = \rho_P(\mathbf{x}) = \sigma_P \delta(z - z_0), \quad (35)$$

as well as the standard electric charges  $\sigma$

$$\varepsilon_\infty \varepsilon_0 \nabla \cdot \mathbf{E}(\mathbf{x}) = \rho(\mathbf{x}) = \sigma \delta(z - z_0), \quad (36)$$

where  $z$  is the coordinate perpendicular to the boundary. Figure 3 shows a solution of *Model 1* for the case of prescribed electric field and polarization at the boundary of a slit of width  $2L$ , i.e.,  $z_0 = \pm L$ . The solutions can be compared with the results derived in Ref. [38].

### B. Model 2

For *Model 2* (and later *Model 3*), we can proceed in a similar manner. In this case we first have to reduce the order of the equations from four to two by introducing an auxiliary potential  $\psi$  which in the one-dimensional geometry leads to

$$\frac{d^2 \phi^\dagger(z)}{dz^2} = \frac{1}{\widehat{\xi}^2} \psi(z). \quad (37)$$

In terms of the three-potential composite field  $\Phi_2(z) \equiv (\phi^*(z), \phi^\dagger(z), \psi(z))$  we now have the expression  $\frac{d^2}{dz^2} \Phi_2(z) =$

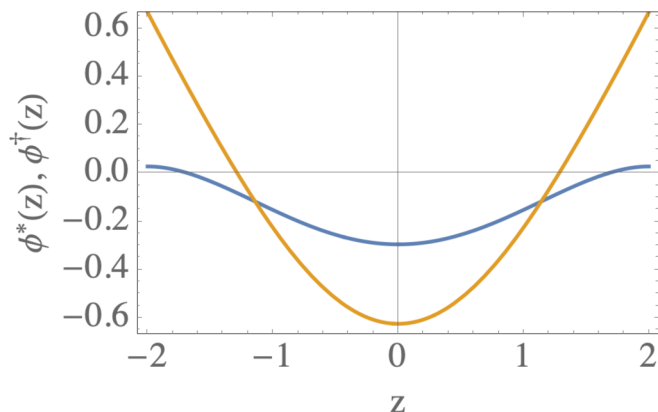


FIG. 3. Exemplary solutions of *Model 1* for  $\phi^*(z)$  (blue line) and  $\phi^\dagger(z)$  (yellow line). The boundary conditions are  $(\phi^*)'(-L) = -E_0$ ,  $(\phi^*)'(L) = E_0$ ,  $(\phi^\dagger)'(-L) = (\phi^\dagger)'(L) = 0$ .

$\mathcal{M}_2\Phi_2(z)$ , with the coupling matrix

$$\mathcal{M}_2 = \begin{pmatrix} \frac{\varepsilon}{\varepsilon_\infty} \kappa_D^2 & 0 & -\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right) \widehat{\xi}^{-2} \\ 0 & 0 & \widehat{\xi}^{-2} \\ \frac{\widehat{\xi}^2}{\zeta_0^4} & -\frac{\widehat{\xi}^2}{\zeta_0^4} & \frac{\widehat{\xi}^2}{\zeta_0^4} \end{pmatrix}. \quad (38)$$

The corresponding eigenvalue equations are thus of third order, depending on four parameters. One can scale out one of them, remaining with the ratios. For example, with the substitution  $\lambda \rightarrow \lambda/\widehat{\xi}^2$  the characteristic polynomial is given by an expression containing only the ratios of the model parameters

$$\lambda^3 - \lambda^2 \left[ \left(\frac{\widehat{\xi}}{\zeta_0}\right)^2 + \frac{\varepsilon}{\varepsilon_\infty} (\kappa_D \widehat{\xi})^2 \right] + \lambda \frac{\varepsilon}{\varepsilon_\infty} (1 + (\kappa_D \widehat{\xi})^2) - \frac{\varepsilon}{\varepsilon_\infty} (\kappa_D \widehat{\xi})^2 = 0. \quad (39)$$

In order to see the character of the roots we need to look at the discriminant  $\Delta$  of the cubic polynomial. Since both  $(\kappa_D \widehat{\xi})^2 \ll 1$  and  $(\kappa_D \widehat{\xi}_0)^2 \ll 1$ , the discriminant is approximately given by the expression

$$\Delta = \left(\frac{\varepsilon}{\varepsilon_\infty}\right)^2 \left( \left(\frac{\widehat{\xi}}{\zeta_0}\right)^4 - 4 \frac{\varepsilon}{\varepsilon_\infty} \right) \quad (40)$$

$$-4 \left(\frac{\widehat{\xi}}{\zeta_0}\right)^2 \left(\frac{\varepsilon}{\varepsilon_\infty}\right) \left( \left(\frac{\widehat{\xi}}{\zeta_0}\right)^4 - 4.5 \frac{\varepsilon}{\varepsilon_\infty} \right) (\kappa_D \widehat{\xi}_0)^2 - 27 \left(\frac{\varepsilon}{\varepsilon_\infty}\right)^2 (\kappa_D \widehat{\xi}_0)^4. \quad (41)$$

In the limit  $\kappa_D \widehat{\xi}_0 \rightarrow 0$  one sees that the sign of the discriminant depends on the difference  $\left(\frac{\widehat{\xi}}{\zeta_0}\right)^4 - 4 \frac{\varepsilon}{\varepsilon_\infty}$  i.e., in a highly nonlinear way on the length-ratio  $\widehat{\xi}/\zeta_0$  and the polarity of the solvent.

Figure 4 shows the discriminant, Eq. (44), as a function of  $\widehat{\xi}/\zeta_0$  and  $\varepsilon/\varepsilon_\infty$ . The function is cut by the zero level such that for positive  $\Delta$  there are three real roots, while for negative  $\Delta$  there is one real and two complex conjugate roots. The discriminant of *Model 2* therefore signals a change in the

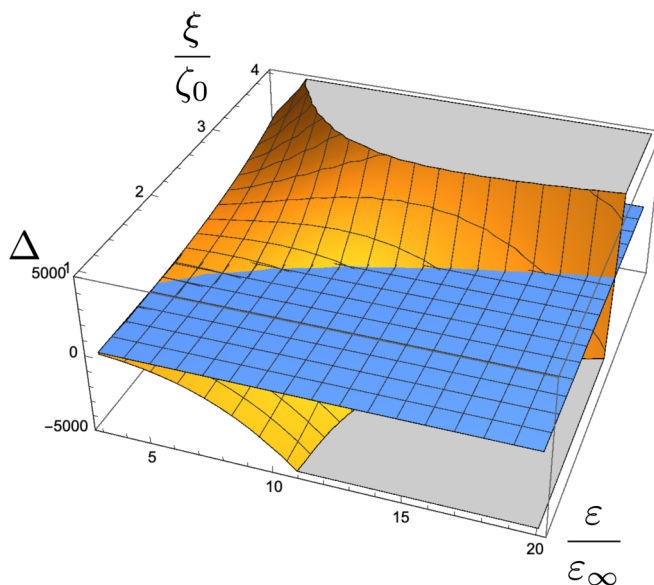


FIG. 4. The discriminant  $\Delta$  for *Model 2* as a function of  $\widehat{\xi}/\zeta_0$  and  $\varepsilon/\varepsilon_\infty$  in relevant parameter ranges;  $\kappa_D \widehat{\xi}_0 = 10^{-4}$ . For  $\Delta > 0$  there are three real roots of the eigenvalue equation, while for  $\Delta < 0$ , one real and two complex conjugate roots arise.

character of the solutions from exponential decay to damped oscillatory behavior.

Figure 5 displays the numerical solution of the equations of *Model 2* for the case of the plate geometry. The boundary conditions for the fields  $\phi^*$  and  $\phi^\dagger$  have been chosen in an antagonistic fashion, which show that both fields behave as separate entities near the wall. For distances  $z \gg 0$ , both fields merge into each other and fulfill the definition of the polarization field of Eq. (25) in the bulk.

Neglecting ionic screening altogether, i.e.,  $\kappa_D = 0$ , the equations for *Model 2* can be simplified further and reduced to a single fourth-order equation for the auxiliary field  $\psi(z)$  in

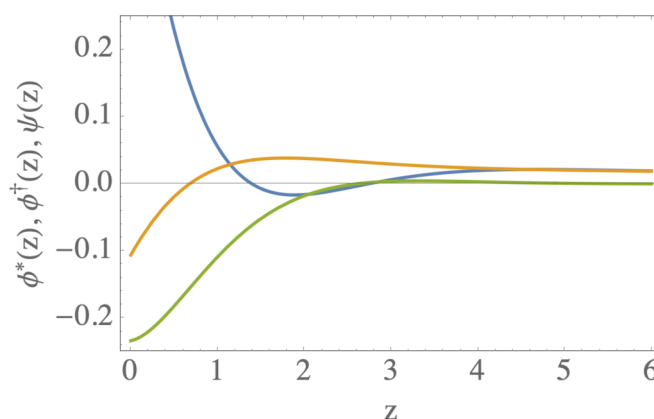


FIG. 5. Solutions to the equations of *Model 2*. Blue,  $\phi^*(z)$ ; brown,  $\phi^\dagger(z)$ ; green, auxiliary field  $\psi(z)$ . For  $z \gg 0$ , the solutions of  $\phi^*$  and  $\phi^\dagger$  merge, establishing the validity of the standard relation between the polarization and electric fields in the bulk.

the form

$$\widehat{\zeta}_0^4 \psi^{iv}(z) - \widehat{\xi}^2 \psi''(z) + \left(\frac{\varepsilon}{\varepsilon_\infty}\right) \psi(z) = 0. \quad (42)$$

Apart from the definition of the constants, the basic equation then reduces to the form introduced in Ref. [11]. We note that fourth-order equations can also be obtained by considering quadrupole coupling terms pertinent to the quadrupolarizable solvent models [41,42].

Making the substitution  $\kappa \rightarrow \kappa/\widehat{\zeta}_0$ , so that the decay length is in units of  $\widehat{\zeta}$ , the characteristic polynomial for the inverse decay length, Eq. (42), can be obtained in the simple form

$$\kappa^4 - \kappa^2 \left(\frac{\widehat{\xi}}{\widehat{\zeta}_0}\right)^2 + \frac{\varepsilon}{\varepsilon_\infty} = 0. \quad (43)$$

The solution for the eigenvalues are then of two types, real and complex, depending on the sign of the discriminant

$$\Delta = \left(\frac{\widehat{\xi}}{\widehat{\zeta}_0}\right)^4 - 4\frac{\varepsilon}{\varepsilon_\infty}, \quad (44)$$

which amounts to the identical dependence found in the discriminant  $\Delta$  of the full system of equations. In the case of  $\widehat{\xi}^2 > \sqrt{4\varepsilon/\varepsilon_\infty} \widehat{\zeta}_0^2$ , the eigenvalues are real and obtained as

$$\kappa_{1,2,3,4} = \pm \frac{1}{\sqrt{2}} \left( \left(\frac{\widehat{\xi}}{\widehat{\zeta}_0}\right)^2 \pm \delta^{1/2} \right)^{1/2}, \quad (45)$$

while for  $\widehat{\xi}^2 \leq \sqrt{4\varepsilon/\varepsilon_\infty} \widehat{\zeta}_0^2$ , the eigenvalues are complex conjugate pairs and given by

$$\kappa_{1,2,3,4} = \pm(\kappa_d \pm i\kappa_o), \quad (46)$$

where

$$\kappa_{d,o} = \frac{1}{2} \left( \left( \left(\frac{\widehat{\xi}}{\widehat{\zeta}_0}\right)^4 + (-\delta) \right)^{1/2} \pm \left(\frac{\widehat{\xi}}{\widehat{\zeta}_0}\right)^2 \right)^{1/2}. \quad (47)$$

This last case is also the one considered in Ref. [11]. Clearly, even with the fourth-order derivative polarization functional, the corresponding characteristic lengths can be real so that periodic solutions are not universal but depend on the sign of the discriminant Eq. (44). Since  $\zeta_0$  is comparable to the size of the molecule and  $\xi$  is the macroscopic correlation length, the periodic solutions are expected for sufficiently polar media  $4\varepsilon/\varepsilon_\infty \gg 1$ .

### C. Model 3

A similar, albeit approximate solution can be found for the case of *Model 3* when one neglects the solvent molecular length  $\zeta$  compared with the ion density-polarization coupling  $\alpha$ . We then have the coupling matrix for the composite potential  $\Phi_3(z) \equiv (\phi^*(z), \phi^\dagger(z), \psi(z))$  by the expression

$$\mathcal{M}_3 = \begin{pmatrix} \widehat{\alpha}^{-2} & -\widehat{\alpha}^{-2} & \widehat{\alpha}^{-2} \\ 0 & 0 & \widehat{\zeta}_0^{-2} \\ \frac{\widehat{\alpha}^{(m)2} - \frac{\varepsilon}{\varepsilon_\infty} (\kappa_D \widehat{\xi})^2}{(\frac{\varepsilon}{\varepsilon_\infty} - 1) \widehat{\alpha}^2} & -\frac{\widehat{\alpha}^{(m)2}}{(\frac{\varepsilon}{\varepsilon_\infty} - 1) \widehat{\alpha}^2} & \frac{\widehat{\alpha}^{(m)2} + (\frac{\varepsilon}{\varepsilon_\infty} - 1)}{(\frac{\varepsilon}{\varepsilon_\infty} - 1) \widehat{\alpha}^2} \end{pmatrix}. \quad (48)$$

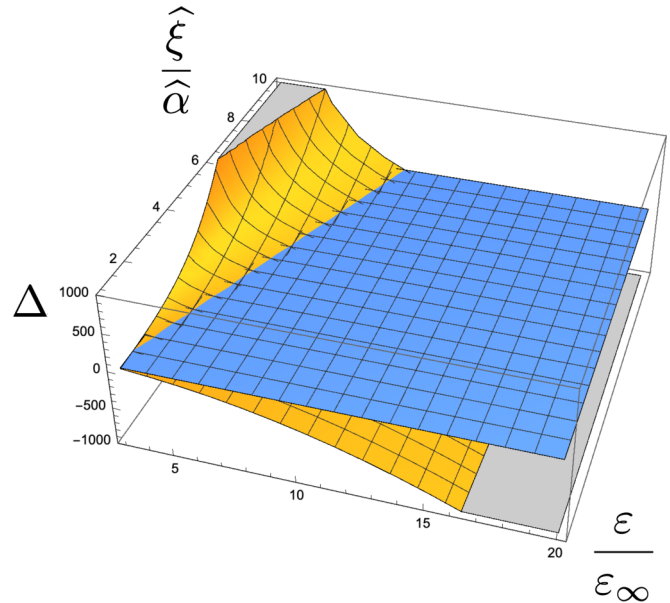


FIG. 6. The discriminant  $\Delta$  for *Model 3* as a function of  $\widehat{\xi}/\widehat{\alpha}$  and  $\varepsilon/\varepsilon_\infty$  in relevant parameter ranges;  $\kappa_D \widehat{\zeta} = 10^{-4}$ . For  $\Delta > 0$  there are three real roots of the eigenvalue equation, while for  $\Delta < 0$ , one real and two complex conjugate roots arise.

The corresponding characteristic polynomial is again of third order and contains four model parameters. Choosing one of them, e.g.,  $\widehat{\alpha}$ , and rescaling the roots by  $\lambda \rightarrow \lambda/\widehat{\alpha}^2$  the characteristic polynomial comes out as

$$\lambda^3 - \lambda^2 \left[ \frac{\left(\frac{\widehat{\xi}}{\widehat{\alpha}}\right)^2 + 2\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right)}{\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right)} \right] + \lambda \frac{\frac{\varepsilon}{\varepsilon_\infty} (1 + (\kappa_D \widehat{\xi})^2)}{\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right)} - \frac{\frac{\varepsilon}{\varepsilon_\infty} (\kappa_D \widehat{\alpha} 51)^2}{\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right)} = 0. \quad (49)$$

Comparing this expression with Eq. (39) we see that apart from the denominator  $(\frac{\varepsilon}{\varepsilon_\infty} - 1)$  there is an almost complete correspondence between the molecular length  $\zeta$  and the *secondary hydration* structural length  $\alpha$ . The discussion of the discriminant  $\Delta$  of the cubic polynomial for *Model 3*, therefore, shows the same characteristic behavior as for *Model 2*. The criterion for the change of the eigenvalue spectrum from real to real and complex conjugates is for this model replaced by the expression

$$\left(\frac{\widehat{\xi}}{\widehat{\alpha}}\right)^2 < 2 \left[ 1 - \frac{\varepsilon}{\varepsilon_\infty} \left( 1 - \left( 1 - \frac{\varepsilon_\infty}{\varepsilon} \right)^{1/2} \right) \right], \quad (50)$$

which in the limit  $\varepsilon \gg \varepsilon_\infty$  reduces to  $\widehat{\xi}^2/\widehat{\alpha}^2 < 1$ . Since by definition  $\widehat{\alpha}^2$  can be negative, in this case the eigenvalues are always real and complex conjugates; in the case  $\widehat{\alpha}^2 > 0$ , if the correlation length is larger than the ion-density polarization coupling, all eigenvalues are real. The plot of the discriminant for the case  $\widehat{\alpha}^2 > 0$  is shown in Fig. 6.

Profiting further from our insights from *Model 2*, we also consider the case of a vanishing Debye-screening length in

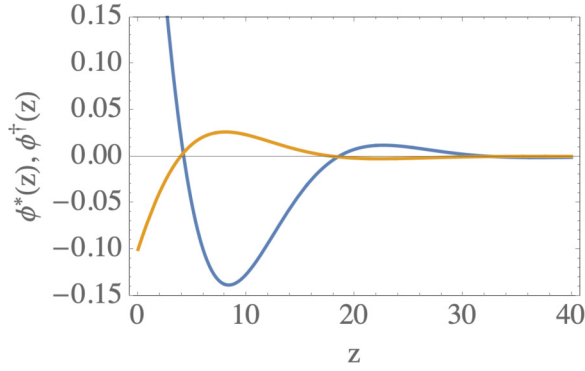


FIG. 7. Solutions of the equations of the reduced *Model 3*, Eq. (51);  $\phi^*(z)$  (blue line);  $\phi^\dagger(z)$  (brown line); see Appendix D for the analytic expressions for  $\phi^*(z)$  and  $\phi^\dagger(z)$ .

*Model 3.* We then find the expression

$$\widehat{\zeta}_0^4 (\phi^\dagger)^{iv} - \left( 2\widehat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \widehat{\xi}^2 \right) (\phi^\dagger)'' + \frac{\varepsilon}{\varepsilon_\infty} \phi^\dagger = 0. \quad (51)$$

Clearly the hydration coupling corresponds to secondary hydration effects with the square of the effective structural correlation length given by  $2\widehat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \widehat{\xi}^2$ . Making the substitution  $\kappa \rightarrow \kappa / \left( \left( \frac{\varepsilon_\infty}{\varepsilon} \right)^{1/4} \widehat{\zeta}_0 \right)$ , the characteristic polynomial of Eq. (58) can be obtained in the simple form

$$\kappa^4 - \kappa^2 \left( \frac{\varepsilon_\infty}{\varepsilon} \right)^{1/2} \left( 2 \left( \frac{\widehat{\alpha}}{\widehat{\zeta}_0} \right)^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \left( \frac{\widehat{\xi}}{\widehat{\zeta}_0} \right)^2 \right) + 1 = 0. \quad (52)$$

Equivalently, one can choose a different rescaling  $\kappa \rightarrow \kappa / \left( \left( \frac{\varepsilon_\infty}{\varepsilon} \right) (2\widehat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \widehat{\xi}^2) \right)^{1/2}$  which then leads to the characteristic equation

$$\left( \frac{\varepsilon_\infty}{\varepsilon} \right)^3 \widehat{\zeta}_0^4 \left( 2\widehat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \widehat{\xi}^2 \right)^2 \kappa^4 - \kappa^2 + 1 = 0. \quad (53)$$

The case  $\left( \frac{\varepsilon_\infty}{\varepsilon} \right)^3 \widehat{\zeta}_0^4 (2\widehat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \widehat{\xi}^2)^2 > 1/2$  has been discussed in Ref. [43] in the context of ionic liquids but is formally equivalent to the above case. The exact profile for the case of a planar charged surface  $0 \leq z < \infty$  is given in Appendix D. The corresponding profiles for  $\phi^*(z)$  and  $\phi^\dagger(z)$  are shown in Fig. 7.

## VII. DISCUSSION AND CONCLUSIONS

In this paper we have derived a field-theoretic description of structured liquid dielectrics, taking the Onsager-Dupuis theory of ice as a motivation. Starting from the introduction of *two separate order parameters* for the polarization field of the solvent and the charge density of the solvated ions, we provide a general formalism to introduce a family of models of different degrees of coarse-graining. Considering a harmonic approximation for the free energy of the polarization field and a DM for the solvent, we derive novel nonlinear equations that emerge from the present theory.

As a first application we discuss three models defined in the linear limit of the theory, which lead to coupled differential

equation systems for the electrostatic and polarization potentials. The generic behavior of the solutions is determined from a decoupling of these equations. The resulting discriminants of the eigenvalue equations define the solution behavior as functions of model structural lengths and solvent polarity. Since the model equations allow for independent boundary conditions for the electrostatic and polarization potentials, they have a high flexibility in the discussion of physical systems, which we illustrate for plate and slab geometries. In the case of the ion charge-density-solvent polarization coupling, our approach allowed us to describe the case of *secondary hydration* effects where the structural solvent correlation length has solvent *as well as* ion contributions.

We believe that, beyond the introduction of our approach and first results in the linear regime, our theory is capable of addressing a wide class of continuum models for polarization phenomena in confined solvents, in particular phenomena pertinent to the nano-confined aqueous systems [25,26]. Recent experimental work has shown that the observed oscillatory behavior of electrostatic and hydration forces is largely determined by the bulk ion and polarization charges, while the solution pH essentially determines the boundary conditions [44]. Our work is straightforwardly amenable to further extensions, allowing for nonlinear polarization functionals in the bulk as well as the incorporation of surface polarization functionals.

## ACKNOWLEDGMENT

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## APPENDIX A: COLLECTIVE DESCRIPTION AND FIELD THEORY

To express the partition function in the form of a field theory, we take the same approach as with anisotropic Coulomb fluids [31], the outlines of which we briefly reiterate below.

We write the total energy with two collective variables, the polarization and the charge density, Eqs. (1) and (4), by introducing the decomposition of unity

$$1 \equiv \int \mathcal{D}[P_i(\mathbf{x})] \Pi_{\mathbf{x}} \delta(P_i(\mathbf{x}) - \hat{P}_i(\mathbf{x})) \times \int \mathcal{D}[\rho(\mathbf{x})] \Pi_{\mathbf{x}} \delta(\rho(\mathbf{x}) - \hat{\rho}(\mathbf{x})) \quad (A1)$$

together with the functional integral representation of the delta functions in terms of their respective auxiliary fields  $\mathcal{E}_i(x)$ ,  $\phi(x)$ :

$$\Pi_{\mathbf{x}} \delta(P_i(\mathbf{x}) - \hat{P}_i(\mathbf{x})) \longrightarrow \int \mathcal{D}[\mathcal{E}_i(\mathbf{x})] e^{-i\mathcal{E}_i(\mathbf{x})(P_i(\mathbf{x}) - \hat{P}_i(\mathbf{x}))}$$

$$\Pi_{\mathbf{x}} \delta(\rho(\mathbf{x}) - \hat{\rho}(\mathbf{x})) \longrightarrow \int \mathcal{D}[\phi(\mathbf{x})] e^{-i\phi(\mathbf{x})(\rho(\mathbf{x}) - \hat{\rho}(\mathbf{x}))}. \quad (A2)$$

Notably, we introduce the microscopic polarization as a separate order parameter, independently of the ion charge density. This will eventually lead to a two-order-parameter representation of the partition function.



Using these relations in the definition of the grand canonical partition function

$$\Xi \equiv \sum_N \frac{\lambda^N}{N!} \sum_{N_+} \sum_{N_-} \frac{\lambda_{(+)}^{N_+} \lambda_{(-)}^{N_-}}{N_+! N_-!} \times \int \mathcal{D}[\mathbf{x}_N] \mathcal{D}[\mathbf{n}_N] \int \mathcal{D}[\mathbf{x}_{N_{\pm}}] e^{-\beta \mathcal{H}[\mathbf{x}_N, \mathbf{x}_{N_{\pm}}]}, \quad (\text{A3})$$

with  $\lambda$  and  $\lambda_{(\pm)}$  as the absolute activities of the dipolar and ionic components, the introduction of collective variables  $P_i(\mathbf{x})$  and  $\rho(\mathbf{x})$  leads to the following field-representation of the partition function

$$\Xi = \int \mathcal{D}[P_i(\mathbf{x})] \mathcal{D}[\mathcal{E}_i(\mathbf{x})] \int \mathcal{D}[\rho(\mathbf{x})] \mathcal{D}[\phi(\mathbf{x})] \times e^{-\beta \tilde{\mathcal{H}}[P_i(\mathbf{x}), \rho(\mathbf{x}); \mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})] - V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]}. \quad (\text{A4})$$

The field action above decouples into two terms, of which the first one  $\beta \tilde{\mathcal{H}}[P_i(\mathbf{x}), \rho(\mathbf{x}); \mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})]$  depends on the collec-

tive order parameters  $P_i(\mathbf{x})$  and  $\rho(\mathbf{x})$  as well as the auxiliary fields

$$\begin{aligned} & \beta \tilde{\mathcal{H}}[P_i(\mathbf{x}), \rho(\mathbf{x}); \mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})] \\ &= \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' P_i(\mathbf{x}) \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') P_j(\mathbf{x}') \\ &+ \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' \rho(\mathbf{x}) u(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}') \\ &+ i \int_V d\mathbf{x} P_i(\mathbf{x}) \mathcal{E}_i(\mathbf{x}) + i \int_V d\mathbf{x} \rho(\mathbf{x}) \phi(\mathbf{x}) \end{aligned} \quad (\text{A5})$$

and is a sum of the interaction Hamiltonian for nonelectrostatic polarization interactions and Coulomb interactions between mobile and bound charges.

The second component, the effective field interaction potential, corresponding to the integration over the configurational variables  $\mathbf{x}_N$ ,  $\mathbf{n}_N$  and  $\mathbf{x}_{N_{\pm}}$  of the solvent dipoles and electrolyte ions, depends only on the auxiliary fields  $\mathcal{E}_i(\mathbf{x})$  and  $\phi(\mathbf{x})$  as

$$\begin{aligned} V[\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})] &\equiv \log \left( \sum_N \sum_{N_+} \sum_{N_-} \frac{\lambda^N \lambda_{(+)}^{N_+} \lambda_{(-)}^{N_-}}{N! N_+! N_-!} \int \mathcal{D}[\mathbf{x}_N] \mathcal{D}[\mathbf{n}_N] \int \mathcal{D}[\mathbf{x}_{N_{\pm}}] e^{-\beta \tilde{\mathcal{H}}^*[\mathcal{E}_i(\mathbf{x}_i), \phi(\mathbf{x}_i)]} \right) \\ &= \lambda \int_V d^3 \mathbf{x} \int_{\Omega} d\mathbf{n} e^{-i p \mathbf{n}_i \cdot (\mathcal{E}_i(\mathbf{x}) - \nabla_i \phi(\mathbf{x}))} + 2\lambda_s \int_V d^3 \mathbf{x} \cos \beta e \phi(\mathbf{x}) \\ &= \int_V d^3 \mathbf{x} \left( \lambda \int_{\Omega} \sin \theta d\theta e^{-i p \cos \theta |\mathcal{E}_i(\mathbf{x}) - \nabla_i \phi(\mathbf{x})|} + 2\lambda_s \cos \beta e \phi(\mathbf{x}) \right) \\ &= \lambda \int_V d^3 \mathbf{x} \left( \frac{\sin p |\mathcal{E}_i(\mathbf{x}) - \nabla_i \phi(\mathbf{x})|}{p |\mathcal{E}_i(\mathbf{x}) - \nabla_i \phi(\mathbf{x})|} + 2\tilde{\lambda}_s \cos \beta e \phi(\mathbf{x}) \right) = \int_V d^3 \mathbf{r} v(\mathcal{E}_i(\mathbf{x}), \phi(\mathbf{x})), \end{aligned} \quad (\text{A6})$$

where the single-particle configurational Hamiltonian is

$$\begin{aligned} \beta \tilde{\mathcal{H}}^*[\mathcal{E}_i(\mathbf{x}_i), \phi(\mathbf{x}_i)] &= -i p \sum_N \mathbf{n}_i \cdot (\mathcal{E}_i(\mathbf{x}_i) - \nabla_i \phi(\mathbf{x}_i)) - \\ &- i \sum_{N_+} \phi(\mathbf{x}_i) + i \sum_{N_-} \phi(\mathbf{x}_i). \end{aligned} \quad (\text{A7})$$

We have rescaled all the interaction energies in terms of the thermal energy and assumed that the salt ion activities are the same,  $\lambda_{(+)} = \lambda_{(-)} = \lambda_s$  [34,36]. Note that above we also redefined  $\lambda_s/\lambda \rightarrow \tilde{\lambda}_s$ .

Equation (A6) describes an ideal van't Hoff gas of ions and dipoles, corresponding to the DM. This expression differs from the standard Coulomb fluid field-theoretical representation of the partition function [32,33] by the presence of two additional independent fields  $P_i(\mathbf{x})$  and  $\mathcal{E}_i(\mathbf{x})$ . The saddle-point evaluation of the partition function is taken with respect to the auxiliary fields  $\mathcal{E}_i(\mathbf{x}) \rightarrow i\mathcal{E}_i^*(\mathbf{x})$  and  $\phi(\mathbf{x}) \rightarrow i\phi^*(\mathbf{x})$ . The partition function is then approximated by

$$- \ln \Xi \rightarrow \beta \mathcal{H}[P_i(\mathbf{x}), \rho(\mathbf{x}); i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x})], \quad (\text{A8})$$

where the effective-field Hamiltonian is obtained from the partial trace over coordinate and orientation degrees of freedom

for the ions and dipoles in the partition function interacting via the interaction energy functional Eq. (9).

The expression for the effective field interaction potential  $V^*[\mathcal{E}_i(\mathbf{x}), \phi^*(\mathbf{x})] = V[i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x})]$  depends crucially on the model used for the dipolar fluid; see the main text. The saddle-point form of the DM effective field interaction potential  $V^*[i\mathcal{E}_i^*(\mathbf{x}), i\phi^*(\mathbf{x})]$  can be finally written explicitly in the form of Eq. (A6) but with  $\sin \beta p |\mathcal{E}_i^*(\mathbf{x}) - \nabla \phi^*(\mathbf{x})| \rightarrow \sinh \beta p |\mathcal{E}_i^*(\mathbf{x}) - \nabla \phi^*(\mathbf{x})|$  and  $\cos \beta e \phi^*(\mathbf{x}) \rightarrow \cosh \beta e \phi^*(\mathbf{x})$ .

## APPENDIX B: HYDRATION SHELL COUPLING AND THE DERIVATION OF Model 3

Since it couples the ion density and polarization, the microscopic hydration energy of Model 3 is actually of the form

$$\mathcal{H}_{HY} = \frac{1}{2} \int \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}_{(\pm)}(\mathbf{x}) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}'), \quad (\text{B1})$$

where the potential  $\tilde{u}(\mathbf{x} - \mathbf{x}')$  is a short-range, nonelectrostatic potential describing the hydration shell interactions. We assumed that the hydration polarization for anions and cations is—apart from the direction—the same. This could be of

course elaborated further. Notice, however, that the hydration energy can be recast as

$$\mathcal{H}_{HY} = \frac{1}{2} \int_V d\mathbf{x} d\mathbf{x}' (\hat{\rho}(\mathbf{x}) - \nabla \cdot \hat{P}(\mathbf{x})) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}'), \quad (\text{B2})$$

so that the last term would just rescale the potential  $\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}')$  in Eq. (5)

$$\tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') \longrightarrow \tilde{u}_{ij}(\mathbf{x} - \mathbf{x}') + \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla_i \nabla'_j, \quad (\text{B3})$$

and if we take the nonelectrostatic potential to the second order in derivatives this simply means a rescaling of the corresponding constants, which is irrelevant. The hydration energy can thus be simply taken as

$$\int \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}(\mathbf{x}) \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}'), \quad (\text{B4})$$

which is what we use in the main text, Eq. (8). If the hydration shell of anions and cations differ, the proper *Ansatz* would then be

$$\int \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}_{(+)}(\mathbf{x}) \tilde{u}_{+}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}') + \int \int_V d\mathbf{x} d\mathbf{x}' \hat{\rho}_{(-)}(\mathbf{x}) \tilde{u}_{-}(\mathbf{x} - \mathbf{x}') \nabla \cdot \hat{P}(\mathbf{x}'), \quad (\text{B5})$$

where the  $\tilde{u}$ 's are now the nonelectrostatic hydration shell potentials, different for different types of ions.

In the case of the mean-field approximation, the *Model 3* saddle-point equations are reduced to

$$\phi^*(\mathbf{x}) = \int_V d\mathbf{x}' u(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}') + \quad (\text{B6})$$

$$\int_V d\mathbf{x}' \tilde{u}(\mathbf{x} - \mathbf{x}') \nabla \cdot P(\mathbf{x}') \quad (\text{B7})$$

and

$$\mathcal{E}^*(\mathbf{x}) = -\alpha \nabla \rho(\mathbf{x}) + u_P(0) \mathbf{P}(\mathbf{x}) - \mathcal{F}(\nabla \cdot \mathbf{P}(\mathbf{x})), \quad (\text{B8})$$

where  $\mathcal{F}$  is considered up to fourth order. With

$$\tilde{u}(\mathbf{x} - \mathbf{x}') = \alpha \delta(\mathbf{x} - \mathbf{x}') + \dots \quad (\text{B9})$$

the expression for  $\phi^*(\mathbf{x})$  simplifies to

$$\phi^*(\mathbf{x}) = \int_V d\mathbf{x}' u(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}') + \alpha \nabla \cdot P(\mathbf{x}). \quad (\text{B10})$$

Applying the Laplacian on the last equation yields

$$\rho(\mathbf{x}) = \alpha \varepsilon_\infty \varepsilon_0 \nabla^2 \nabla \cdot P(\mathbf{x}) - \varepsilon_\infty \varepsilon_0 \nabla^2 \phi^*(\mathbf{x}). \quad (\text{B11})$$

Combining everything together into the final set of saddle-point equations for the ion density polarization coupling case we remain with

$$\mathcal{E}^*(\mathbf{x}) = u_P(0) - \mathcal{F}(\nabla \cdot \mathbf{P}(\mathbf{x})) \quad (\text{B12})$$

$$-\alpha^2 \varepsilon_\infty \varepsilon_0 \nabla^2 \nabla (\nabla \cdot \mathbf{P}(\mathbf{x})) + \alpha \varepsilon_\infty \varepsilon_0 \nabla^2 (\nabla \phi^*(\mathbf{x})). \quad (\text{B13})$$

The  $\alpha$ -coupling therefore modifies the fourth-order coefficient of the expansion of the nonelectrostatic potential.

TABLE I. Model parameters

Symbol	Meaning	Value
$1/\kappa_D$	Debye length	$\sim 10$ nm
$\xi$	Bulk water correlation length	1–10 nm
$\zeta$	Water molecular size	0.3 nm
$\varepsilon$	Bulk dielectric constant	5–80
$\varepsilon_\infty$	Dielectric constant first dispersion	4–10
$\alpha$	Ion density-polarization coupling	$\pm 0.5$ –5 nm

### APPENDIX C: MODEL PARAMETRIZATION

For numerical calculations of the solutions shown in the paper, we employ parameters chosen according to the ranges indicated in Table I. The coupling parameter of the structural interactions,  $u_P(0)\varepsilon_0$ , can be obtained from Eq. (26) in the main text, slightly rewritten in order to make the dimensional dependencies explicit. It then reads as

$$\left( \frac{\varepsilon}{\varepsilon_0} - \frac{\varepsilon_\infty}{\varepsilon_0} \right) = \frac{\frac{\lambda p^2}{3\varepsilon_0}}{1 + u_P(0)\varepsilon_0 \frac{\lambda p^2}{3\varepsilon_0}}, \quad (\text{C1})$$

where  $\lambda$  is the fugacity and  $p$  the dipole moment in the DM. The form of this relation would remain unchanged if one considers the dipolar Langevin model, but the values of the constants would have a different meaning. We consider these differences as irrelevant at this stage, since we are mainly interested here in qualitative features of the theory. By dimensional analysis, one has

$$[\lambda] = J^{-1} m^{-3}, \quad [p] = Cm, \quad [\varepsilon_0] = \frac{C^2}{Jm}. \quad (\text{C2})$$

In order to connect the value for  $u_P(0)\varepsilon_0$  with a measurable macroscopic property, we invoke an additional relation

$$1 + \frac{\lambda p^2}{3\varepsilon_0} = \frac{\varepsilon}{\varepsilon_0}, \quad (\text{C3})$$

which has been used [36]. For the standard values for water,  $\varepsilon = 80$ ,  $\varepsilon_\infty = 4$ , we have  $u_P(0)\varepsilon_0 = 5 \cdot 10^{-4}$ . The hatted parameters can then be computed from the bare lengths by multiplication with a factor  $\approx 0.038$ .

### APPENDIX D: THE ANALYTIC SOLUTION FOR THE REDUCED *Model 3* IN THE PLATE GEOMETRY

The analytic solution for the reduced *Model 3* in the slab geometry can be obtained by making recourse to the SI of Ref. [43]. Defining

$$\delta_c^2 \equiv \left( \frac{\varepsilon_\infty}{\varepsilon} \right)^3 \hat{\zeta}_0^4 \left( 2\hat{\alpha}^2 \left( \frac{\varepsilon}{\varepsilon_\infty} - 1 \right) + \hat{\xi}^2 \right)^2, \quad (\text{D1})$$

one has, for  $\delta_c > 1/2$ , the exact solution in the slab geometry given by

$$\phi^\dagger(z) = P_c e^{-\kappa_1 z} [\cos(\kappa_2 z) + A \sin(\kappa_2 z)] \quad (\text{D2})$$

with

$$\kappa_1 = \frac{\sqrt{2\delta_c + 1}}{2\delta_c}, \quad \kappa_2 = \frac{\sqrt{2\delta_c - 1}}{2\delta_c} \quad (\text{D3})$$

and

$$A = -\frac{\sqrt{2\delta_c + 1}(\delta_c - 1)}{\sqrt{2\delta_c - 1}(\delta_c + 1)}. \quad (\text{D4})$$

From this solution,  $\phi^*(z)$  follows via the expression

$$\phi^*(z) = -\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right)\left(1 - \widehat{\alpha}^2 \gamma \frac{d^2}{dz^2}\right)\phi^\dagger(z) \quad (\text{D5})$$

with

$$\gamma \equiv \left(2\widehat{\alpha}^2\left(\frac{\varepsilon}{\varepsilon_\infty} - 1\right) + \widehat{\zeta}^2\right)^{-1}. \quad (\text{D6})$$

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