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The polarized interface between quadrupolar insulators: Maxwell stress tensor, surface tension, and potential

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The quadrupolar Maxwell electrostatic equations predict several qualitatively different results compared to Poisson's classical equation in their description of the properties of a dielectric interface. All interfaces between dielectrics possess surface dipole moment which results in a measurable surface potential jump. The surface dipole moment is conjugated to the bulk quadrupole moment density (the quadrupolarization) similarly to Gauss's relation between surface charge and bulk polarization. However, the classical macroscopic Maxwell equations completely neglect the quadrupolarization of the medium. Therefore, the electrostatic potential distribution near an interface of intrinsic dipole moment can be correctly described only within the quadrupolar macroscopic equations of electrostatics. They predict that near the polarized interface a diffuse dipole layer exists, which bears many similarities to the diffuse charge layer near a charged surface, in agreement with existing molecular dynamics simulation data. It turns out that when the quadrupole terms are kept in the multipole expansion of the laws of electrostatics, the solutions for the potential and the electric field are continuous functions at the surface. A well-defined surface electric field exists, interacting with the adsorbed dipoles. This allows for a macroscopic description of the surface dipole-surface dipole and the surface dipole-bulk quadrupole interactions. They are shown to have considerable contribution to the interfacial tension—of the order of tens of mN/m! To evaluate it, the Maxwell stress tensor in quadrupolar medium is deduced, including the electric field gradient action on the quadrupoles, as well as quadrupolar image force and quadrupolar electrostriction. The dependence of the interfacial tension on the external normal electric field (the dielectrocapillary curve) is predicted and the dielectric susceptibility of the dipolar double layer is related to the quadrupolarizabilities of the bulk phases and the intrinsic polarization of the interface. The coefficient of the dielectro-Marangoni effect (surface flow due to gradient of the normal electric field) is found. A model of the Langevin type for the surface dipole moment and the intrinsic surface polarizability is presented. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4933370]

I. INTRODUCTION

The interface between any two insulators, say water (W) and oil (O), possesses specific surface dipole moment Γ_P, related to the preferential orientation of the molecules near the interface. This orientation results into a specific potential drop through the interface, $\Delta_W^O\phi = \phi_\infty^O - \phi_\infty^W$, where ϕ_∞^O and ϕ_∞^W are the respective bulk potentials (a list of symbols can be found in the supplementary material A[74]). The two quantities are related as[1,2]

$$\Gamma_P = \varepsilon_0 \Delta_W^O \phi, \tag{1}$$

where ε_0 is the permittivity of vacuum. The dipole moment Γ_P plays a role in a great variety of surface phenomena: light reflection,[3] capillary waves,[4] nucleation work of droplets on ions,[5] adsorption at solid surfaces;[6] it contributes to the potential of zero charge of the interface metal|electrolyte solution;[7] the long-ranged lateral interaction due to Γ_P results in beautiful structures observed in heterogeneous lipid monolayers,[8] etc. The surface dipole moment can be changed independently of the bulk properties, e.g., by spreading an insoluble monolayer on the interface. The respective change of $\Delta_W^O\phi$ can then be measured[9]—this is an important method for studying such monolayers.

Unlike the change of $\Delta_W^O\phi$, the *absolute* value of the potential drop is rather hard to measure; molecular simulations are also inconclusive. Even for the basic case of clean water surface, the experimental and theoretical estimations of $\Delta_W^O\phi$ vary by two orders of magnitude and even the sign is still disputed.[10,11] One reason for the discrepancy between the published simulation data for different models of water is the fact that the surface dipole moment depends strongly on the *quadrupole moment* $\boldsymbol{q}$ of the molecules in the bulk phase.[10,12] According to the theory of Stillinger and Ben-Naim,[13] for a clean aqueous surface, the force that orients the molecules in the interfacial region is the image potential related to water's quadrupole moment—an idea that can be traced back to Frenkel.[14] The importance of $\boldsymbol{q}$ of the solvent molecules for the value of the surface dipole moment Γ_P was later observed also in simulations.[10,15] Horváth *et al.* performed series of

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simulations with models of water of decreasing quadrupole moments to find that the higher quadrupole moment goes with higher polarization of the interface.[16] This relation is probably the reason why different models of water yield very different dipolar surface potentials (for water|gas, the classical SPC,[16] SPC/E, and TIP5P[18] give $\Delta_{\mathrm{W}}^{\mathrm{G}}\phi = \phi_{\infty}^{\mathrm{G}} - \phi_{\infty}^{\mathrm{W}}$ values of +41.5 mV, −260 mV, and −103 mV, respectively; quantum density functional theory yield either[18] −480 mV or[19] −18 mV; the "net potential" of Beck[20] is −430 V). Another example for the role of the quadrupoles is the finding of Wilson *et al.*[21] that the gradient of the field in the interfacial region is so high that the multipole expansion $\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P}$ of the displacement field is inadequate ($\boldsymbol{E}$—electric field intensity and $\boldsymbol{P}$—polarization).

A second reason for the confusion regarding the value of $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi$ is the definition of mean potential and more precisely, whether the potential contains the bulk Bethe potential[17,18] that stems from the non-zero trace of the quadrupole moment, Tr$\boldsymbol{q}$, of the molecules in the bulk phase. Tr$\boldsymbol{q}$ does not contribute to the multipole expansion of the electric field of a particle and to the long-range interactions between molecules and ions, respectively.[1,22] For this reason, with field-based macroscopic electrostatic equations, basic relation (1) excludes the Bethe potential. If potential-based electrostatic equations are used, a quadrupole term[23,20] arises in Eq. (1)—details are given in the supplementary material B.[74] The Bethe potential is essentially a bulk phenomenon that has nothing to do with the state of the surface. It originates mainly from the quadrupole moment of the system atomic nucleus-electronic cloud,[24] and the respective interactions are normally treated as the short-range steric potential. The contribution of the Bethe potential to the potential jump is experimentally attainable with techniques such as high energy electron holography and diffraction,[25,26] where the probe charge can overcome the steric repulsion. On the other hand, the classical electrochemical experiments concern the potential drop which is due to the state of the interface only—and we use the symbol $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi$ for this particular potential drop. It is often referred to as *the surface dipolar potential*,[16,27] and Eq. (1) must be considered its rigorous definition. Therefore, below only the zero-trace part[31] of the tensor $\boldsymbol{q}$ is considered, unless explicitly stated otherwise.

The molecular quadrupole moment was found to affect significantly not only the surface dipole moment but also the surface tension of the liquid.[12] This important finding has not received much attention in the literature. An aim of our work is to investigate further the nature of this relation.

Thus, enough evidence has been gathered that the quadrupole moments of the solvent molecules affect profoundly the properties of the interface between two dielectrics. On the other hand, the classical macroscopic Maxwell equations neglect the quadrupoles completely. They are approximated—they correspond to a multipole expansion[22,28] of the exact microscopic equations up to the dipole terms, while the quadrupole moments $\boldsymbol{q}$ and the quadrupolarizabilities α_q of the molecules constituting the medium are truncated. It is therefore concluded that the classical Maxwell equations and their corollaries (e.g., Poisson-Boltzmann equation) are inappropriate for modelling the polarized interfacial region. An example of that is the fact that Poisson's equation of electrostatics predicts that the surface dipole moment does not create electrostatic field. The charge distribution associated with Γ_P is equivalent to a condenser of zero thickness, and the field is constrained between the two plates of this condenser (supplementary material C[74]). Thus, contrary to what one expects,[29,30] according to the dipolar Maxwell equations, a molecule in the vicinity of a homogeneously polarized surface does not interact with it.

The second-order approximation of the macroscopic electrodynamics is given by the quadrupolar Maxwell equations, which account for the interaction of the quadrupoles with the field (or its gradient). For electrostatic problems, the correction[22,28] is reduced to addition of the divergence of the macroscopic density of quadrupole moment $\boldsymbol{Q}$ (the *quadrupolarization tensor*) in the electric displacement vector $\boldsymbol{D}$,

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P} - {}^1\!/_2\nabla\cdot\boldsymbol{Q}. \tag{2}$$

In this work, we are mainly concerned with flat symmetry and isotropic bulk phases, where Eq. (2) simplifies to

$$D_z = \varepsilon_0 E_z + P_z - {}^1\!/_2\mathrm{d}Q_{zz}/\mathrm{d}z. \tag{3}$$

Coulomb's macroscopic law reads[22,28]

$$\nabla\cdot\boldsymbol{D} = \mathrm{d}D_z/\mathrm{d}z = \rho, \tag{4}$$

where ρ is the free charge density. This form of Coulomb's law is valid for both dipolar and quadrupolar media, but in the latter case, the displacement field contains both dipole and quadrupole moment distributions $P_z(z)$ and $Q_{zz}(z)$. For the purpose of definition, let us emphasize that Eqs. (2)-(4) are field-based and the quadrupolarization $\boldsymbol{Q}$ in Eq. (2) is of zero trace.[31] This automatically excludes the Bethe potential from the potential of E_z (cf. supplementary material B[74]).

Eqs. (2) and (4) are general in the sense that they do not involve explicitly material characteristics. To make them specific to a given medium, equations of state relating $\boldsymbol{P}$ and $\boldsymbol{Q}$ to $\boldsymbol{E}$ and $\nabla\boldsymbol{E}$ are required. For a linear isotropic dielectric, the polarization is a linear function of $\boldsymbol{E}$, e.g., for water and oil,

$$\boldsymbol{P}^{\mathrm{W}} = \alpha_P^{\mathrm{W}}\boldsymbol{E}^{\mathrm{W}} = \mathbf{e}_z\left(\varepsilon^{\mathrm{W}} - \varepsilon_0\right)E_z^{\mathrm{W}},\ \boldsymbol{P}^{\mathrm{O}} = \mathbf{e}_z\left(\varepsilon^{\mathrm{O}} - \varepsilon_0\right)E_z^{\mathrm{O}}. \tag{5}$$

Here, ε^{W} and ε^{O} are the dielectric permittivities of water and oil (related to the respective macroscopic polarizabilities as $\varepsilon = \varepsilon_0 + \alpha_P$) and $\mathbf{e}_z$ is the Cartesian unit vector. The constitutive relation for $\boldsymbol{Q}$ of a linear isotropic quadrupolar medium was derived in Ref. 31; for flat symmetry, it reads

$$\boldsymbol{Q}^{\mathrm{W}} = \alpha_Q^{\mathrm{W}}\left(\nabla\boldsymbol{E}^{\mathrm{W}} - \mathbf{U}\nabla\cdot\boldsymbol{E}^{\mathrm{W}}/3\right) = \left(\mathbf{e}_z\mathbf{e}_z - \mathbf{U}/3\right)\alpha_Q^{\mathrm{W}}\frac{\mathrm{d}E_z^{\mathrm{W}}}{\mathrm{d}z} \tag{6}$$

and likewise for $\boldsymbol{Q}^{\mathrm{O}}$; here, $\mathbf{U}$ is the unit tensor and α_Q is the *macroscopic quadrupolarizability* (of water or oil). This characteristic is related to the molecular quadrupolarizabilities α_q and quadrupole moments $\boldsymbol{q}$ of the molecules[31,32]—the macroscopic α_Q is approximately proportional to $C(\alpha_q + \boldsymbol{q}:\boldsymbol{q}/10k_{\mathrm{B}}T)$, where C is the particle number density of the medium, k_B is the Boltzmann constant, T is temperature, and ":" denotes double scalar product, $\boldsymbol{A}:\boldsymbol{B} = A_{ij}B_{ji}$. The relation $\alpha_Q \propto C(\alpha_q + \boldsymbol{q}:\boldsymbol{q}/10k_{\mathrm{B}}T)$ can be compared to the linear Langevin-Debye formula[22,33] $\alpha_P \propto C(\alpha_p + \boldsymbol{p}\cdot\boldsymbol{p}/3k_{\mathrm{B}}T)$, where α_p and $\boldsymbol{p}$ are the average polarizability and the dipole moment of a solvent molecule.

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Substitution of Ampère's law ($\boldsymbol{E} = -\nabla\phi$ for electrostatics) and the constitutive relations (5) and (6) into Eqs. (3) and (4) leads to the explicit equations for the electrostatic potential ϕ in the two phases,

$$\frac{d^2\phi^W}{dz^2} - \left(L_Q^W\right)^2 \frac{d^4\phi^W}{dz^4} = -\frac{\rho^W}{\varepsilon^W}, \quad \frac{d^2\phi^O}{dz^2} - \left(L_Q^O\right)^2 \frac{d^4\phi^O}{dz^4} = -\frac{\rho^O}{\varepsilon^O}, \tag{7}$$

here, the *quadrupolar lengths* are defined as[31]

$$L_Q^W = \sqrt{\alpha_Q^W/3\varepsilon^W}, \quad L_Q^O = \sqrt{\alpha_Q^O/3\varepsilon^O}. \tag{8}$$

In the absence of quadrupoles, the length will be $L_Q = 0$ and Eqs. (7) simplify to Poisson's equation of electrostatics in dipolar medium.

The quadrupolar equation for ϕ is of the fourth order and requires additional boundary conditions compared to Poisson's equation. One of these new boundary conditions was deduced by Graham and Raab[34,3] and by Batygin and Toptygin,[35] and it explicitly relates *the intrinsic surface normal dipole moment* P_z^S to the bulk quadrupole densities, $Q_{zz}^O(z=0) - Q_{zz}^W(z=0) = 2P_z^S$. Since it is of key importance for the theory of quadrupolar dielectrics, we will present shortly its derivation in Sec. I A. Neither Graham and Raab nor Batygin and Toptygin commented on the relation between the *intrinsic* surface dipole moment P_z^S and the *total* surface dipole moment Γ_P—as we will discuss in Sec. III, the two quantities are different. The other new boundary condition requires continuity of the normal component of the electric field at the surface.[36]

The mechanics of quadrupolar media in external field is discussed in Sec. II, where the respective Maxwell stress tensor is derived. In Sec. III, it is shown that the surface dipole moment creates a non-zero electrostatic field protruding the plates of the surface condenser. Using the quadrupolar Maxwell stress tensor, we derive the contribution of this field to the interfacial tension. In Sec. III B, we consider the interaction between the polarized interface and external field normal to the interface.

A. Boundary conditions

Following Graham and Raab,[34] we will derive the boundary conditions using the singular distribution approach developed by Albano, Bedeaux, and Vlieger.[37,38] We investigate the flat interface between two quadrupolar dielectrics; this interface has surface charge density ρ^S and intrinsic normal surface dipole moment density P_z^S. For definiteness, let the two dielectrics be water ($z < 0$) and oil ($z > 0$). The following singular distributions of the densities ρ, $\boldsymbol{P}$, and $\boldsymbol{Q}$ can be written for this system,

$$\rho = \eta^W\rho^W(z) + \eta^O\rho^O(z) + \delta\rho^S, \tag{9}$$

$$\begin{aligned} P_z &= \eta^W P_z^W(z) + \eta^O P_z^O(z) + \delta P_z^S \\ &= \eta^W\left(\varepsilon^W - \varepsilon_0\right)E_z^W + \eta^O\left(\varepsilon^O - \varepsilon_0\right)E_z^O + \delta P_z^S, \end{aligned} \tag{10}$$

$$Q_{zz} = \eta^W Q_{zz}^W(z) + \eta^O Q_{zz}^O(z). \tag{11}$$

Here, η is the Heaviside step function, $\eta^W \equiv \eta(-z)$, $\eta^O \equiv \eta(z)$, and $\delta \equiv \delta(z)$ is the Dirac delta function. The quadrupole density tensor components Q_{xx} and Q_{yy} are unimportant since they are independent of x and y and fall off from $\nabla\cdot\boldsymbol{Q}$ in Eq. (2); all other components of $\boldsymbol{Q}$ are zero. The *intrinsic surface quadrupole moment* Q_{zz}^S can be added as a δ-term in Eq. (11) (water, for example, is known for having surface of high quadrupole moment[15]), but it can be shown that in the macroscopic multipole expansion, the intrinsic surface quadrupole moment is at the same level of approximation as the bulk octupole moment density (if the bulk displacement vector $\boldsymbol{D}$ is truncated to the octupole terms, the singular distribution of Q_{zz} must be truncated at the δ-term and *vice versa*, otherwise the resulting electrostatic problem will be ill-defined). Since water is in the domain $z < 0$, the surface dipole moment is defined in direction towards oil or air—if water molecules at the surface are, on the average, pointing with the oxygen atom toward the hydrophobic phase, then P_z^S is negative. Note that P_z^S differs from the total surface dipole moment Γ_P—the total Gibbs excess of the polarization involves also a contribution from the adjacent bulk phases, as discussed in Sec. III. Similarly, although Q_{zz}^S is neglected, the surface still possesses an excess quadrupole moment.

Distributions (11) of P_z and Q_{zz} are substituted in Eq. (3) to obtain the singular distribution of D_z,

$$\begin{aligned} D_z = {} & \eta^W\left(\varepsilon^W E_z^W - \frac{1}{2}\frac{dQ_{zz}^W}{dz}\right) + \eta^O\left(\varepsilon^O E_z^O - \frac{1}{2}\frac{dQ_{zz}^O}{dz}\right) \\ & + \delta\left(P_z^S + \frac{1}{2}Q_{zz}^W(z) - \frac{1}{2}Q_{zz}^O(z)\right), \end{aligned} \tag{12}$$

where the relation $d\eta(\pm z)/dz = \pm\delta$ was used. The singular distributions (9) and (12) of D_z and ρ are then substituted into Coulomb's law (4) to obtain the singular expansion of the quadrupolar Maxwell electrostatic equation,

$$\begin{aligned} & \eta^W\left[\frac{d}{dz}\left(\varepsilon^W E_z^W - \frac{1}{2}\frac{dQ_{zz}^W}{dz}\right) - \rho^W\right] \\ & + \eta^O\left[\frac{d}{dz}\left(\varepsilon^O E_z^O - \frac{1}{2}\frac{dQ_{zz}^O}{dz}\right) - \rho^O\right] \\ & + \delta\left(-\varepsilon^W E_z^W + \frac{dQ_{zz}^W}{dz} + \varepsilon^O E_z^O - \frac{dQ_{zz}^O}{dz} - \rho^S\right) \\ & + \delta_1\left(P_z^S + \frac{1}{2}Q_{zz}^W(z) - \frac{1}{2}Q_{zz}^O(z)\right) = 0. \end{aligned} \tag{13}$$

Here, $\delta_1 = d\delta/dz$. Using further the relations $\delta f(z) = \delta f(0)$ and $\delta_1 f(z) = \delta_1 f(0) - \delta\,(df/dz)_{z=0}$, the above simplifies to

$$\begin{aligned} & \eta^W\left[\frac{d}{dz}\left(\varepsilon^W E_z^W - \frac{1}{2}\frac{dQ_{zz}^W}{dz}\right) - \rho^W\right] \\ & + \eta^O\left[\frac{d}{dz}\left(\varepsilon^O E_z^O - \frac{1}{2}\frac{dQ_{zz}^O}{dz}\right) - \rho^O\right] \\ & + \delta\left(-\varepsilon^W E_z^W + \frac{1}{2}\frac{dQ_{zz}^W}{dz} + \varepsilon^O E_z^O - \frac{1}{2}\frac{dQ_{zz}^O}{dz} - \rho^S\right)_{z=0} \\ & + \delta_1\left(P_z^S + \frac{1}{2}Q_{zz}^W - \frac{1}{2}Q_{zz}^O\right)_{z=0} = 0. \end{aligned} \tag{14}$$

Decomposition of Eq. (14) to its irreducible terms leads to the two bulk Maxwell equations, corresponding to the multipliers

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of η^{W} and η^{O}, valid in the respective bulk phases,

$$\begin{aligned} z<0: &\quad \frac{\mathrm{d}}{\mathrm{d}z}\left(\varepsilon^{\mathrm{W}}E_z^{\mathrm{W}}-\frac{1}{2}\frac{\mathrm{d}Q_{zz}^{\mathrm{W}}}{\mathrm{d}z}\right)=\rho^{\mathrm{W}},\\ z>0: &\quad \frac{\mathrm{d}}{\mathrm{d}z}\left(\varepsilon^{\mathrm{O}}E_z^{\mathrm{O}}-\frac{1}{2}\frac{\mathrm{d}Q_{zz}^{\mathrm{O}}}{\mathrm{d}z}\right)=\rho^{\mathrm{O}}, \end{aligned} \tag{15}$$

which, together with Eq. (6), yield the explicit Eqs. (7) for ϕ. Next, the multiplier of δ in Eq. (14) leads to the generalization of Gauss's law for the case where the bulk quadrupole moment contributes to the fixed surface charge density,

$$\left(\varepsilon^{\mathrm{O}}E_z^{\mathrm{O}}-\frac{1}{2}\frac{\mathrm{d}Q_{zz}^{\mathrm{O}}}{\mathrm{d}z}-\varepsilon^{\mathrm{W}}E_z^{\mathrm{W}}+\frac{1}{2}\frac{\mathrm{d}Q_{zz}^{\mathrm{W}}}{\mathrm{d}z}\right)_{z=0} = D_z^{\mathrm{O}}(0)-D_z^{\mathrm{W}}(0)=\rho^{\mathrm{S}}. \tag{16}$$

Thus, Gauss's law for the jump of D_z at a surface of charge ρ^{S} remains formally unchanged in quadrupolar solvents, except for the fact that D_z contains quadrupolar terms. Finally, the multiplier of δ_1 in Eq. (14) yields a new boundary condition, relating the intrinsic surface dipole moment P_z^{S} to the jump of the quadrupole moment,

$$\frac{1}{2}Q_{zz}^{\mathrm{O}}(0)-\frac{1}{2}Q_{zz}^{\mathrm{W}}(0)=P_z^{\mathrm{S}}. \tag{17}$$

This equation was derived with the classical methods by Batygin and Toptygin[35] (cf. also Eq. (65) of Shen and Hu[39]). We will refer to it as *multipolar (dipolar) condition for the jump of the electric field gradient*. The comparison with Eq. (12) shows that the δ term in the singular distribution of D_z is zero. The explicit forms of boundary conditions (16) and (17) are obtained by combining them with $\boldsymbol{E}=-\nabla\phi$ and Eq. (6) for $\boldsymbol{Q}$,

$$\varepsilon^{\mathrm{W}}\left[\frac{\mathrm{d}\phi^{\mathrm{W}}}{\mathrm{d}z}-\left(L_Q^{\mathrm{W}}\right)^2\frac{\mathrm{d}^3\phi^{\mathrm{W}}}{\mathrm{d}z^3}\right]_{z=0} -\varepsilon^{\mathrm{O}}\left[\frac{\mathrm{d}\phi^{\mathrm{O}}}{\mathrm{d}z}-\left(L_Q^{\mathrm{O}}\right)^2\frac{\mathrm{d}^3\phi^{\mathrm{O}}}{\mathrm{d}z^3}\right]_{z=0}=\rho^{\mathrm{S}}, \tag{18}$$

$$\varepsilon^{\mathrm{W}}\left(L_Q^{\mathrm{W}}\right)^2\left.\frac{\mathrm{d}^2\phi^{\mathrm{W}}}{\mathrm{d}z^2}\right|_{z=0}-\varepsilon^{\mathrm{O}}\left(L_Q^{\mathrm{O}}\right)^2\left.\frac{\mathrm{d}^2\phi^{\mathrm{O}}}{\mathrm{d}z^2}\right|_{z=0}=P_z^{\mathrm{S}}. \tag{19}$$

Two final boundary conditions are valid—the potential and the electric field must be continuous at $z=0$,

$$\begin{aligned} \phi^{\mathrm{W}}(0)&=\phi^{\mathrm{O}}(0) \quad (\equiv \phi^{\mathrm{S}}),\\ E_z^{\mathrm{W}}(0)&=E_z^{\mathrm{O}}(0) \quad (\equiv E_z^{\mathrm{S}}). \end{aligned} \tag{20}$$

Instead of continuous E_z, Chitanvis imposed continuity of the second normal derivative of the potential, "*... invoked on physical grounds, to ensure a higher-order continuity of the solution*"[40] (but the field itself remained discontinuous in his work). In Ref. 36, it was rigorously shown that the correct continuity condition is for the first derivative of ϕ, on the example of the problems for infinitely thin condenser and charged surface in quadrupolar medium. The derivation is given in the supplementary material C.[74]

Eqs. (7)-(20) define a unique solution for the electrostatic potential $\phi(z)$. Some simple consequences of it were investigated previously[36] and few examples are summarized in the supplementary material C.[74] Compared to the results of the classical dipolar electrostatics, two common features of the solutions of the quadrupolar electrostatic law can be pointed out: the *regularization of the potential* and the *damping of the field gradient*. A remarkable example of the first effect is the finding[31,40] that a point charge in quadrupolar medium has finite potential; in addition to this, the electric field at a charged surface is continuous, and the same is valid for the electrostatic potential of an infinitely thin condenser.[36]

II. MECHANICS AND THERMODYNAMICS OF NON-HOMOGENEOUS QUADRUPOLAR MEDIA

A. Quadrupolar ponderomotive forces and the Maxwell stress tensor

The classical expression for the free energy of the electric field in a linear, locally isotropic heterogeneous dielectric remains valid for a quadrupolarizable medium,

$$W_{\mathrm{el}}=\frac{1}{2}\int\rho\phi\mathrm{d}V=\frac{1}{2}\int\boldsymbol{D}\cdot\boldsymbol{E}\mathrm{d}V, \tag{21}$$

where the integration is over the volume of the dielectric; the equality of the two integrals follows[1,41] from $\nabla\cdot\boldsymbol{D}=\rho$. However, unlike the classical W_{el}, in quadrupolar media, the displacement field $\boldsymbol{D}$ contains $\boldsymbol{Q}$. Expression (21) is used in supplementary material D[74] for the derivation of the electric force density $\boldsymbol{f}_{\mathrm{el}}$ following the formalism of Tamm.[41] The final result is

$$\boldsymbol{f}_{\mathrm{el}}=\rho\boldsymbol{E}-\frac{1}{2}E^2\nabla\varepsilon-\frac{1}{4}\left[\nabla\boldsymbol{E}:\nabla\boldsymbol{E}-(\nabla\cdot\boldsymbol{E})^2/3\right]\nabla\alpha_Q +\frac{1}{2}\nabla\left(E^2C\frac{\partial\varepsilon}{\partial C}\right)+\frac{1}{4}\nabla\left\{\left[\nabla\boldsymbol{E}:\nabla\boldsymbol{E}-(\nabla\cdot\boldsymbol{E})^2/3\right]C\frac{\partial\alpha_Q}{\partial C}\right\}. \tag{22}$$

As seen, the ponderomotive force involves a *quadrupolar image force* ($\nabla\alpha_Q$) and *quadrupolar electrostriction* ($\partial\alpha_Q/\partial C$). The result is of importance for the flexoelecric phenomena in nanosized dielectrics[39] and lipid membranes.[42] If α_Q or $\nabla\boldsymbol{E}$ are negligible, the expression above reduces to the classical Helmholtz formula.[1,41] Let us mention that in our derivation of the ponderomotive force, we started with the variation of the free energy, hence, the derivatives $\partial\varepsilon/\partial C$ and $\partial\alpha_Q/\partial C$ in Eq. (22) are taken at constant temperature. If the variation of the internal energy is used instead, then expression (22) for the force would remain the same except for the derivatives, which would have to be understood as isoentropic.

As a consequence of the conservation of the momentum, electric force (22) can be presented in the form

$$\boldsymbol{f}_{\mathrm{el}}=\nabla\cdot\boldsymbol{T}_E, \tag{23}$$

where $\boldsymbol{T}_E$ is the stress tensor of the electric field (the Maxwell stress tensor). In order to define $\boldsymbol{T}_E$, all terms in Eq. (22) must be expressed as coordinate derivatives, which is done in supplementary material D.[74] There it is shown that $\boldsymbol{T}_E$ in Eq. (23) stands for

$$\boldsymbol{T}_E=\boldsymbol{D}\boldsymbol{E}+\frac{1}{2}\boldsymbol{Q}\cdot\nabla\boldsymbol{E}-\mathbf{U}\left\{\frac{1}{2}\left(\varepsilon-C\frac{\partial\varepsilon}{\partial C}\right)E^2 +\frac{1}{4}\left(\alpha_Q-C\frac{\partial\alpha_Q}{\partial C}\right)\left[\nabla\boldsymbol{E}:\nabla\boldsymbol{E}-\frac{1}{3}(\nabla\cdot\boldsymbol{E})^2\right]\right\}. \tag{24}$$

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This is the *generalized Maxwell stress tensor* in an isotropic quadrupolar medium. The quadrupolar terms in it correspond to the $\tau^{\mathrm{M}}_{ijm,m}$ tensor of Shen and Hu[39] (cf. also Ref. 43 in regard to the definition of $\boldsymbol{T}_E$).

Let us finally find the relation between the distributions of the total stress tensor $\boldsymbol{T}$ and the electric field E_z near a flat interface between two quadrupolar dielectrics. For the flat symmetry considered in this paper, Maxwell tensor (24) simplifies to

$$\boldsymbol{T}_E = \mathbf{e}_z\mathbf{e}_z\left\{\varepsilon E_z^2 + \frac{1}{3}\alpha_Q\left[(\partial_z E_z)^2 - E_z\partial_{zz}E_z\right]\right\} - \frac{1}{2}\mathbf{U}\left\{\left(\varepsilon - C\frac{\partial\varepsilon}{\partial C}\right)E_z^2 + \frac{1}{3}\left(\alpha_Q - C\frac{\partial\alpha_Q}{\partial C}\right)(\partial_z E_z)^2\right\}. \tag{25}$$

The balance between the mechanic and the ponderomotive forces requires that[43]

$$\nabla\cdot\boldsymbol{T} = \frac{\partial}{\partial z}\left(-p(z) + T_{E,zz}\right) = 0, \tag{26}$$

where the total stress tensor $\boldsymbol{T}$ is

$$\boldsymbol{T} = -p(z)\mathbf{U} + \boldsymbol{T}_E, \tag{27}$$

and p is the mechanical "plate pressure, P_{pl}" of Koenig.[44] The solution of Eq. (26) for $p(z)$ reads

$$p = p_0 + T_{E,zz}, \tag{28}$$

where p_0 is the pressure at $\boldsymbol{E} = 0$. Substituting this result back into Eq. (27) for $\boldsymbol{T}$, one obtains the sought relationship between the total stress $\boldsymbol{T}$ and $\boldsymbol{E}$,

$$\begin{aligned} T_{zz} &= -p + T_{E,zz} = -p_0,\\ T_{xx} &= -p + T_{E,xx} = -p_0 - \varepsilon\left\{E_z^2 + L_Q^2\left[(\partial_z E_z)^2 - E_z\partial_{zz}E_z\right]\right\}. \end{aligned} \tag{29}$$

The first formula states that for a system of flat symmetry in equilibrium, the stress tensor must have constant zz component. The second equation relates the tangential component of $\boldsymbol{T}$ (which depends on z) to the field distribution. Eq. (29) simplifies to a known result[5,45] if $L_Q = 0$.

The results above are valid for locally isotropic dielectric and are inapplicable to pyroelectric materials[1] where zero-field polarization $\boldsymbol{P}_0$ is present in the constitutive relation for $\boldsymbol{P}$. Although the polarized interface *is* a pyroelectric, cf. Sec. III, the $\boldsymbol{P}_0$ terms in the ponderomotive force are unimportant for the current work and for brevity are not considered here. In the excess surface stress tensor,[39] however, these terms will have a significant contribution.

B. Fundamental equations for a dielectric interface in external normal field

Consider the *heterogeneous insulating system* water|oil ($\rho = 0$) in the anisotropic *medium* illustrated in Fig. 1. The medium is a condenser of total surface charge e^{S} (which sets a constant displacement field D_z normal to the surface) and a thermostat; it has permeable walls (fixing the chemical potentials μ_i of all species) and is an anisotropic barostat (fixing the normal component T_{zz} of the stress tensor to $-p_0$

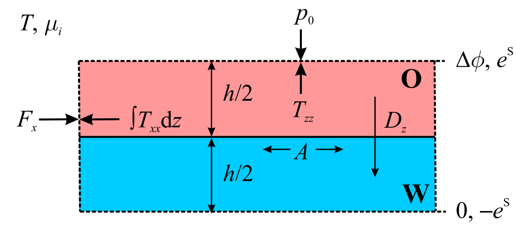

FIG. 1. The thermodynamic variables imposed by the external medium onto the two-phase system.

and the integral of the tangential component to a force per unit length F_x). The interface has area A; let for definiteness, the thickness of the two phases be $h/2$ and the position of the interface be $z = 0$.

The variation of the internal energy of the heterogeneous system is the sum of the heat $T\delta S$ transferred from the medium to the system, the mechanical work $-p_0 A\delta h - F_x\delta A$, the chemical work $\Sigma\mu_i\delta n_i$ and the work $\Delta\phi\delta e^{\mathrm{S}}$ for charging the condenser,

$$\delta U = T\delta S - p_0 A\delta h + \int_{-h/2}^{h/2} T_{xx}\mathrm{d}z\delta A + \sum\mu_i\delta n_i + \Delta\phi\delta e^{\mathrm{S}}. \tag{30}$$

The total surface charge is related to the electric displacement as $e^{\mathrm{S}} = \rho^{\mathrm{S}}A = -D_z A$. The potential difference between the plates of the condenser is related to the field in the system as $\Delta\phi = -\int E_z\mathrm{d}z$. This leads to a more useful form of Eq. (30),

$$\delta U = T\delta S - p_0 A\delta h + \int_{-h/2}^{h/2} T_{xx}(z)\mathrm{d}z\delta A + \sum\mu_i\delta n_i + \int_{-h/2}^{h/2} E_z(z)\mathrm{d}z\delta(AD_z) \tag{31}$$

compared with Eq. (3) of Koenig.[44] Following the Gibbs approach, we can now define an idealized system in which the two bulk phases are homogeneous, with respective fundamental equations,

$$\delta U^{\mathrm{W}} = T\delta S^{\mathrm{W}} - p_0 A\delta\frac{h}{2} + \int_{-h/2}^{0} T^{\mathrm{W}}_{xx\infty}\mathrm{d}z\delta A + \sum\mu_i\delta n_i^{\mathrm{W}} + \int_{-h/2}^{0} E^{\mathrm{W}}_{z\infty}\mathrm{d}z\delta AD_z$$

and

$$\delta U^{\mathrm{O}} = T\delta S^{\mathrm{O}} - p_0 A\delta\frac{h}{2} + \int_{0}^{h/2} T^{\mathrm{O}}_{xx\infty}\mathrm{d}z\delta A + \sum\mu_i\delta n_i^{\mathrm{O}} + \int_{0}^{h/2} E^{\mathrm{O}}_{z\infty}\mathrm{d}z\delta AD_z. \tag{32}$$

Here, $T_{xx\infty}$ and $E_{z\infty}$ are the values in the respective phases far from the interface and are independent of z (they are

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left under the integral for convenience). We can then write for the variation of the surface excess of the internal energy $U^{\mathrm{S}} = U - U^{\mathrm{W}} - U^{\mathrm{O}}$ the equation,

$$\delta U^{\mathrm{S}} = T\delta S^{\mathrm{S}} + \gamma\delta A + \sum \mu_i \delta n_i^{\mathrm{S}} - \Delta_{\mathrm{W}}^{\mathrm{O}}\phi\delta A D_z, \quad (33)$$

where S^{S} and n_i^{S} are the total surface entropy and the total adsorbed ith component, and the mechanical surface tension[5] γ and the surface potential drop stand for the surface excesses of T_{xx} and $-E_z$, i.e.,

$$\gamma = \int_{-h/2}^{0} \left(T_{xx} - T_{xx\infty}^{\mathrm{W}}\right) \mathrm{d}z + \int_{0}^{h/2} \left(T_{xx} - T_{xx\infty}^{\mathrm{O}}\right) \mathrm{d}z, \quad (34)$$

$$\Delta_{\mathrm{W}}^{\mathrm{O}}\phi = -\int_{-h/2}^{0} \left(E_z - E_{z\infty}^{\mathrm{W}}\right) \mathrm{d}z - \int_{0}^{h/2} \left(E_z - E_{z\infty}^{\mathrm{O}}\right) \mathrm{d}z. \quad (35)$$

The integration limits $\pm h/2$ can be substituted with $\pm\infty$ as long as $h \gg L_Q$. The Euler equation for Eq. (33) reads

$$U^{\mathrm{S}} = TS^{\mathrm{S}} + \gamma A + \sum \mu_i n_i^{\mathrm{S}} - \Delta_{\mathrm{W}}^{\mathrm{O}}\phi A D_z. \quad (36)$$

The substitution of Eq. (36) into (33) yields the Gibbs-Duhem equation of the surface

$$\delta\gamma = -s^{\mathrm{S}}\delta T - \sum \Gamma_i^{\mathrm{S}}\delta\mu_i + D_z\delta\Delta_{\mathrm{W}}^{\mathrm{O}}\phi, \quad (37)$$

where $s^{\mathrm{S}} = S^{\mathrm{S}}/A$ and $\Gamma_i^{\mathrm{S}} = n_i^{\mathrm{S}}/A$ are the surface entropy per unit area and the adsorption of the ith component. This is the equation of Rusanov and Kuni.[5] As remarked by them, in an external field, the mechanical and the thermodynamic definition of surface tension lead to different results—the thermodynamic tension is given by $\sigma = \gamma - D_z\Delta_{\mathrm{W}}^{\mathrm{O}}\phi$. Therefore, for the variation of σ, one finds from Eq. (37),

$$\delta\sigma = -s^{\mathrm{S}}\delta T - \sum \Gamma_i^{\mathrm{S}}\delta\mu_i - \Delta_{\mathrm{W}}^{\mathrm{O}}\phi\delta D_z. \quad (38)$$

For the surface tension defined with Eq. (34) (excess of the stress tensor), the correct Gibbs-Duhem relation is (37) (compared to Ref. 2). The thermodynamic surface tension (the surface omega potential) is instead the excess of the quantity $T_{xx} + E_z D_z$, or from Eq. (29), of $-p_0 - \alpha_Q(\partial_z E_z)^2/3$. A difference between the two tensions occurs also in the case of, e.g., curved interfaces[45] and surfaces of anisotropic solids.[46] Since γ and σ are related, an experiment determining one of them is also giving the other, and their use is a question of convenience. In statistical mechanics, σ is preferred.[5] Fundamental equation (38) of σ contains the more natural variable D_z. The thermodynamic interfacial tension controls "energetic" phenomena such as self-dispersion and nucleation. On the other hand, the expression for the generalized Laplace-Young law is simpler[5] in terms of γ, and it is more directly related to "mechanistic" phenomena such as capillary pressure and Marangoni effect.

III. THE INTERFACE WITH DIPOLE MOMENT

The dielectric properties of an interface are a question of high practical importance, especially in regard to the new nanodielectric materials,[47,48] and to diverse problems arising in biomembrane physics,[29,30] semiconductor surfaces,[49] nucleation[5] etc. There is a contrast between the importance of the field and the degree of development of its macroscopic theory, related to the fact that the dipolar macroscopic equations of Maxwell are somewhat unsuited for modelling dielectric surfaces.

Within the classical dipolar electrostatics, a flat surface of homogeneous dipole moment does not create electric field. A dipolar surface is an infinitely thin condenser; its electric field is confined between the walls of this condenser and is infinite,[41] i.e.,

$$\phi = \eta^{\mathrm{O}}\Delta_{\mathrm{W}}^{\mathrm{O}}\phi, \quad E_z = -\partial\phi/\partial z = -\delta\Delta_{\mathrm{W}}^{\mathrm{O}}\phi. \quad (39)$$

Hence, from Poisson's equation, it follows that the intensive characteristic $\boldsymbol{E}$ has a singular distribution. However, the conjugated extensive characteristic $\boldsymbol{P}$ also has a singularity, Eq. (10). This poses several problems which are hard to resolve within the macroscopic dipole expansion.

(i) A surface possessing dipole moment has infinite energy (surface dipoles in infinite local E_z).
(ii) If one allows the adsorbed dipoles to have polarizability, the singular surface field will induce infinite dipole moment.
(iii) The interaction of the infinitely thin condenser with an external field is hard to model within Poisson's equation, since the field jumps at the surface (which field acts on the dipoles, the one on the left or on the right hand side of the surface?).
(iv) The common case of a surface having both surface charge and dipole is also messy—the surface charge is situated at a point where the potential is discontinuous (which potential acts on the charges, the one on the left or on the right hand side of the surface?).
(v) According to classical formula (39), no electric field is present at any $z \neq 0$. This leads to the following curiosity: the electrostatic force acting on a positive ion situated above a surface of positive P_z^{S}, consisting of an infinite number of oriented dipoles is zero. The available data suggest that it is repulsion instead—the ion-surface dipole interaction is especially important in biophysical chemistry of membranes.[29,30] The attempts to resolve the problem gravitate around the discrete distribution of the adsorbed dipoles.[50–52] We find this approach unsatisfactory[53]—the discreteness effect is indeed significant, but the main hardship—the surface singularities—remains. In result, the field of a 2D lattice of dipoles at the interface is extremely sensitive to the position of the dipoles with respect to $z = 0$. Therefore, though a realistic model should account for the discrete distribution of P_z^{S}, discreteness alone cannot fix the problematic setup that macroscopic dipolar electrostatics offers for dielectric surfaces.

The question is further discussed in supplementary material C.[74] None of problems (i)-(v) are insurmountable within classical electrostatics. However, the combination of them results in models of the interface that are physically complicated and often involve many undefined parameters. As we will show below, the quadrupolar Maxwell equations give

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orderly and conceptually simpler description of the dielectric interface. Apart from these "fundamentalistic" reasons, the question for the role of the molecular quadrupoles for the structure of the interface is of high interest on its own,[12,16] regardless of the theoretical approach used to investigate it.

A. The contribution of the adsorbed dipoles to the interfacial tension

Let us start with the problem for the role of the surface dipole-bulk quadrupole interaction in the structure of the interface between insulators in the absence of external electric field. Croxton showed that this interaction has a significant effect on the interfacial tension value;[12] the surface dipole–surface dipole interaction energy is substantial as well.[52]

Consider the interface $z = 0$ between two dielectrics, e.g., an aqueous ($z < 0$) and an oil phase ($z > 0$), which are assumed insulators ($\rho^{\mathrm{W}} = \rho^{\mathrm{O}} = 0$). The surface is uncharged ($\rho^{\mathrm{S}} = 0$) but has dipole moment. We choose ϕ to be zero in the bulk of the water phase, $\phi^{\mathrm{W}}(-\infty) \equiv \phi^{\mathrm{W}}_{\infty} = 0$. The solution of quadrupolar electrostatic equations (7) that decays properly at $z = \pm\infty$ is

$$\phi^{\mathrm{W}}(z) = \Delta^{\mathrm{S}}_{\mathrm{W}}\phi \exp(z/L^{\mathrm{W}}_Q),\ \phi^{\mathrm{O}}(z) = \Delta^{\mathrm{S}}_{\mathrm{O}}\phi \exp(-z/L^{\mathrm{O}}_Q) + \Delta^{\mathrm{O}}_{\mathrm{W}}\phi. \tag{40}$$

This potential profile is similar to the dependence proposed by Madden *et al.*[54] and elucidates the nature of their empirical decaying length. In Eq. (40), $\Delta^{\mathrm{S}}_{\mathrm{W}}\phi \equiv \phi^{\mathrm{S}} - \phi^{\mathrm{W}}_{\infty}$ and $\Delta^{\mathrm{S}}_{\mathrm{O}}\phi \equiv \phi^{\mathrm{S}} - \phi^{\mathrm{O}}_{\infty}$ are the differences between the surface potential and bulk phase potentials. They are related to the potential difference[75] between the two bulk phases as $\Delta^{\mathrm{O}}_{\mathrm{W}}\phi = \phi^{\mathrm{O}}_{\infty} - \phi^{\mathrm{W}}_{\infty} = \Delta^{\mathrm{S}}_{\mathrm{W}}\phi - \Delta^{\mathrm{S}}_{\mathrm{O}}\phi$. These constants are determined by boundary conditions (19) and (20) (Gauss's law (18) is automatically fulfilled)—they yield

$$\Delta^{\mathrm{S}}_{\mathrm{W}}\phi = \frac{L^{\mathrm{W}}_Q}{\varepsilon^{\mathrm{W}}L^{\mathrm{W}}_Q + \varepsilon^{\mathrm{O}}L^{\mathrm{O}}_Q}P^{\mathrm{S}}_z,\ \Delta^{\mathrm{S}}_{\mathrm{O}}\phi = -\frac{L^{\mathrm{O}}_Q}{\varepsilon^{\mathrm{W}}L^{\mathrm{W}}_Q + \varepsilon^{\mathrm{O}}L^{\mathrm{O}}_Q}P^{\mathrm{S}}_z, \tag{41}$$

$$\Delta^{\mathrm{O}}_{\mathrm{W}}\phi = \frac{L^{\mathrm{W}}_Q + L^{\mathrm{O}}_Q}{\varepsilon^{\mathrm{W}}L^{\mathrm{W}}_Q + \varepsilon^{\mathrm{O}}L^{\mathrm{O}}_Q}P^{\mathrm{S}}_z. \tag{42}$$

Eq. (42) provides the relation between the surface potential drop due to the adsorbed dipoles and the intrinsic normal dipole moment density P^{S}_z of the interface. The potential $\Delta^{\mathrm{O}}_{\mathrm{W}}\phi$ has the same sign as P^{S}_z (this sign depend, of course, on the choice of direction of z). Eq. (42) can be compared with the often used Helmholtz formula

$$\Delta^{\mathrm{O}}_{\mathrm{W}}\phi = P^{\mathrm{S}}_z/\varepsilon^{\mathrm{S}}, \tag{43}$$

where ε^{S} is the dielectric permittivity of the hypothetical medium between the two charged surfaces and is a rather obscure quantity.[55,51] Comparison between (42) and (43) suggests that ε^{S} is an effective parameter equal to $(\varepsilon^{\mathrm{W}}L^{\mathrm{W}}_Q + \varepsilon^{\mathrm{O}}L^{\mathrm{O}}_Q)/(L^{\mathrm{W}}_Q + L^{\mathrm{O}}_Q)$ and thus it is, in fact, a bulk characteristic. If the hydrophobic phase is gas G of quadrupolar length $L^{\mathrm{G}}_Q \approx 0$, Eq. (42) simplifies to

$$\Delta^{\mathrm{G}}_{\mathrm{W}}\phi = P^{\mathrm{S}}_z/\varepsilon^{\mathrm{W}}. \tag{44}$$

Using the value[10,11,56,57] $\Delta^{\mathrm{G}}_{\mathrm{W}}\phi = -100$ mV for the dipolar potential and $\varepsilon^{\mathrm{W}} = 78 \times \varepsilon_0$, we find for the intrinsic dipole moment of the clean water surface $P^{\mathrm{S}}_z = -70 \times 10^{-12}$ C/m. The potential distribution corresponding to this value of P^{S}_z is illustrated in Fig. 2(a), according to Eqs. (40) and (41).

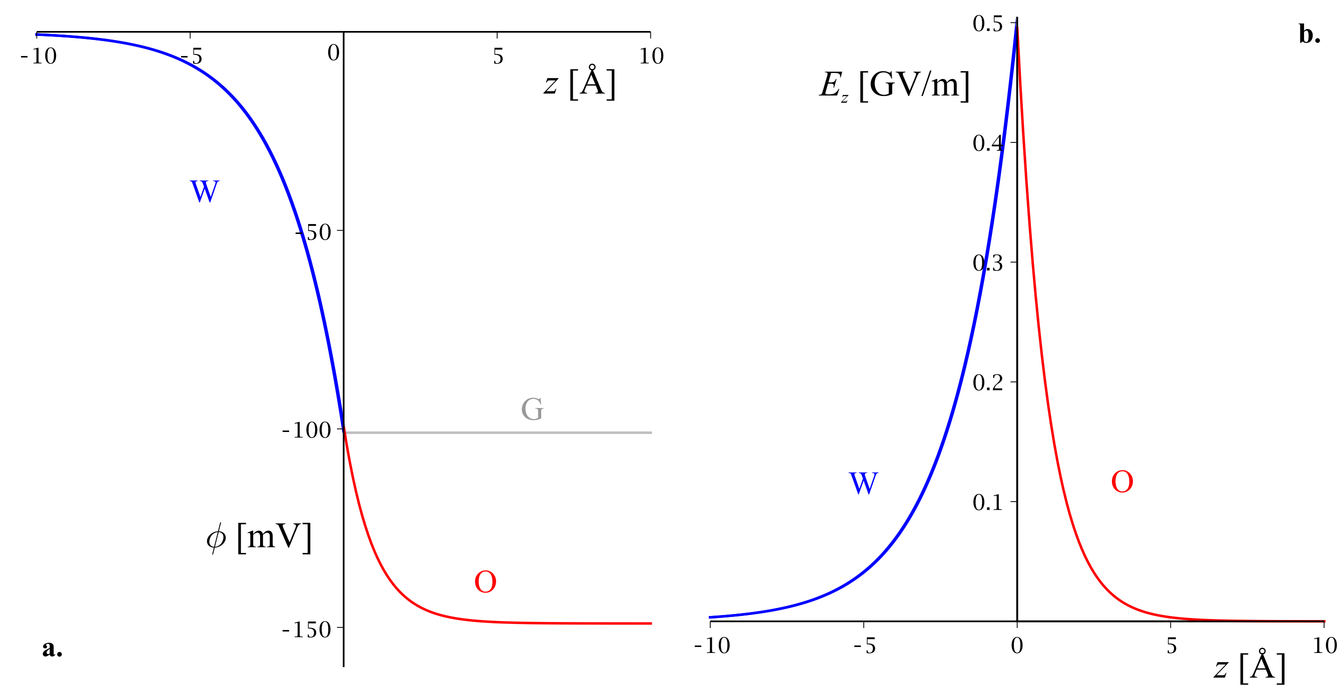

FIG. 2. (a) Distribution of the potential $\phi(z)$ and (b) the field $E_z(z)$ near the dipolar interface between two quadrupolar dielectrics in the absence of external field. Parameters: $P^{\mathrm{S}}_{z0} = -140 \times 10^{-12}$ C/m, $\alpha^{\mathrm{S}}_{zz}/\varepsilon_0 = 15$ nm, $\varepsilon^{\mathrm{W}} = 78 \times \varepsilon_0$, $L^{\mathrm{W}}_Q = 2$ Å, $\varepsilon^{\mathrm{O}} = 5 \times \varepsilon_0$, $L^{\mathrm{O}}_Q = 1$ Å. The case where the second phase is gas ($\varepsilon^{\mathrm{G}} = \varepsilon_0$, $L^{\mathrm{G}}_Q = 0$) is given for comparison.

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The experimental or simulation data provide not the intrinsic, but the total dipole moment Γ_P of the interface (the total *adsorption of dipoles*). Γ_P has contributions from the two layers, aqueous and oil, adjacent to the interface, which are polarized by the field of P_z^{S}. The polarization of the water phase is given by $P_z^{\mathrm{W}} = -(\varepsilon^{\mathrm{W}} - \varepsilon_0)\mathrm{d}\phi/\mathrm{d}z$, and similarly for the oil; therefore, using solutions Eqs. (40)-(42) for ϕ, the respective dipole moments per unit area of the two surface layers can be written as follows:

$$\Gamma_P^{\mathrm{W}} = \int_{-\infty}^{0} P_z^{\mathrm{W}}\mathrm{d}z = -\frac{(\varepsilon^{\mathrm{W}} - \varepsilon_0)\, L_Q^{\mathrm{W}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} = -(\varepsilon^{\mathrm{W}} - \varepsilon_0)\, \Delta_{\mathrm{W}}^{\mathrm{S}}\phi$$

and

$$\Gamma_P^{\mathrm{O}} = \int_{0}^{\infty} P_z^{\mathrm{O}}\mathrm{d}z = -\frac{(\varepsilon^{\mathrm{O}} - \varepsilon_0)\, L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} = (\varepsilon^{\mathrm{O}} - \varepsilon_0)\, \Delta_{\mathrm{O}}^{\mathrm{S}}\phi. \quad (45)$$

Hence, according to Eqs. (10), (42), and (45) and the Gibbs definition of a surface excess, the total adsorbed dipole moment per unit area Γ_P is

$$\Gamma_P = P_z^{\mathrm{S}} + \Gamma_P^{\mathrm{W}} + \Gamma_P^{\mathrm{O}} = \frac{\varepsilon_0 \left(L_Q^{\mathrm{W}} + L_Q^{\mathrm{O}}\right)}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} = \varepsilon_0 \Delta_{\mathrm{W}}^{\mathrm{O}}\phi. \quad (46)$$

General relation (1) is fulfilled (regarding the Bethe Tr$\boldsymbol{Q}$ contribution[23,20] to $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi$, cf. supplementary material B[74]). For water|gas, the value $\Delta_{\mathrm{W}}^{\mathrm{G}}\phi = -100$ mV corresponds to total dipole moment $\Gamma_P = -0.9 \times 10^{-12}$ C/m. Thus, within the quadrupolar macroscopic model we are using, the dipole moment of the water|oil interface is distributed in three layers. The first one is of zero thickness (or better said, of thickness $h^{\mathrm{S}} \ll L_Q$) and of moment P_z^{S}, large and negative towards the oil. The second layer (situated between say $z = -3L_Q^{\mathrm{W}}$ and 0) consists of bulk water molecules oriented oppositely due to the interaction with the specifically "adsorbed" P_z^{S}; their total dipole moment is only slightly less than $-P_z^{\mathrm{S}}$. The third layer is situated between $z = 0$ and, e.g., $z = 3L_Q^{\mathrm{O}}$ and possesses total moment of about $-P_z^{\mathrm{S}}(\varepsilon^{\mathrm{O}} - \varepsilon_0)L_Q^{\mathrm{O}}/\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}}$. The two bulk layers compensate to a large extent the intrinsic dipole moment of the surface (Γ_P is always smaller than P_z^{S}—cf. Eqs. (46) and (42)). This picture corresponds to a structure similar to an electric double layer, but instead of diffuse free charge neutralizing the intrinsic surface charge ρ^{S}, one has a diffuse dipole distribution compensating partially the intrinsic surface dipole moment P_z^{S}. We will call this structure the *dipolar double layer*. In Sec. IV, the analogy between the electric and the dipolar double layer will be pushed further.

The two orientational layers have been observed in classical MD simulations of water surface[16] and also at solid surfaces, e.g., Fig. 5 in Ref. 6. The SPC model predicts dipolar potential of $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi = +40$ mV and $\Gamma_P = +0.4 \times 10^{-12}$ C/m—the sign corresponds to the opposite orientation of the water molecules compared to the experimental negative sign, but the values are of the correct order of magnitude (cf. supplementary material E[74]). We used the data of Horváth *et al.*[16] to estimate also the order of magnitude of the intrinsic dipole moment density of SCP water—our estimate gives[74] $P_z^{\mathrm{S}} = +2.4 \times 10^{-12}$ C/m. In agreement with our predictions, this is indeed much higher than the value of the total dipole moment Γ_P; yet the value of P_z^{S} is lower than the one following from Eq. (44). The reason seems to be the neglected overlapping. As the analysis in supplementary material E[74] shows, the thickness h^{S} of the surface layer of dipoles is of the same order of magnitude as L_Q—since h^{S} is a characteristic of the length of action of the specific interactions that orient the molecules (image forces, hydrogen bonds, van der Waals, steric forces), it can be even larger than L_Q. Therefore, overlapping effect similar to the one observed in the electric double layer at high electrolyte concentrations[57,58] is inevitable. The bimodal distribution of the orientation of water molecules near the surface observed in simulations[15,16] corresponds, in the language of our work, to overlapping surface layer of moment P_z^{S} and oppositely oriented bulk layer with moment Γ_P^{W}.

It is also worth noting that, although the interface possesses no *intrinsic* quadrupole moment (cf. Eq. (11)), adsorbed quadrupole is present

$$\boldsymbol{\Gamma_Q} = \int_{-\infty}^{0} \boldsymbol{Q}^{\mathrm{W}}\mathrm{d}z + \int_{0}^{\infty} \boldsymbol{Q}^{\mathrm{O}}\mathrm{d}z$$

$$= (3\mathbf{e}_z\mathbf{e}_z - \mathbf{U})\, \frac{\varepsilon^{\mathrm{O}}\left(L_Q^{\mathrm{O}}\right)^2 - \varepsilon^{\mathrm{W}}\left(L_Q^{\mathrm{W}}\right)^2}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}}. \quad (47)$$

For water|gas, using the values above and the quadrupolar length[31,59] $L_Q^{\mathrm{W}} = 2$ Å, we obtain $\Gamma_{Q,zz} = -2\Gamma_{Q,xx} = -L_Q^{\mathrm{W}} P_z^{\mathrm{S}} = 1.4 \times 10^{-20}$ C.

Let us now consider the field distribution in the interfacial region. Within the quadrupolar equations of electrostatics, where Eq. (20) holds, the electric field is a continuous function at the interface and a well-defined surface electric field exists

$$E_z^{\mathrm{S}} = -\frac{1}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}}. \quad (48)$$

The distribution of the electric field that follows from Eq. (40) can be therefore written as

$$E_z^{\mathrm{W}} = E_z^{\mathrm{S}} \exp(z/L_Q^{\mathrm{W}}), \quad E_z^{\mathrm{O}} = E_z^{\mathrm{S}} \exp(-z/L_Q^{\mathrm{O}}). \quad (49)$$

This distribution is illustrated in Fig. 2(b). It is functionally similar with the potential in an electric double layer, but instead of the Debye length, the diffuse dipole layer thickness is controlled by L_Q. In Sec. IV, the analogy between the electric and the dipolar double layer will be further investigated.

In contrast to Eq. (48), the classical dipolar electrostatics predicts different values of E_z at $z = \pm 0$, so E_z^{S} is undefined (except if one assumes that $E_z^{\mathrm{S}} = -P_z^{\mathrm{S}}/\varepsilon^{\mathrm{S}} h^{\mathrm{S}}$, where h^{S} is the thickness of the surface condenser, another ill-defined quantity). If the hydrophobic phase is gas and $L_Q^{\mathrm{G}} \approx 0$, then, according to Eq. (48), the surface electric field[76] is equal to $E_z^{\mathrm{S}} = -P_z^{\mathrm{S}}/\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}}$. Using the values of the parameters above, we find $E_z^{\mathrm{S}} = 5 \times 10^8$ V/m. This result can be compared with simulation data. However, simulations lead almost always to surface dipolar potential that differs from the experimental one (e.g., Kathmann *et al.*[19] obtained a rather small potential of $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi = -18$ mV—probably due to the small size of the

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simulated system). As far as we expect $E_z^S \propto \Delta_W^O \phi$, the direct comparison of the E_z^S values is inappropriate. We compare instead the ratio $-\Delta_W^O \phi / E_z^S = 2$ Å obtained from our numbers with the one stemming from the values of Kathmann *et al.*[19]—the two ratios are equal. The physical meaning of this ratio can be understood by comparing Eqs. (44) and (48)—they suggest that $-\Delta_W^O \phi / E_z^S$ must be of the order of L_Q^W.

The surface field $\boldsymbol{E}^S$ is extremely high and its direction is the opposite to the one of $\boldsymbol{P}^S$, hence, it is able to depolarize the surface (such an effect was discussed, e.g., in Refs. 5 and 60). Assuming linear response, we can write the *constitutive relation* for the surface dipole moment,

$$P_z^S = P_{z0}^S + \alpha_{zz}^S E_z^S. \tag{50}$$

This is the constitutive relation for the polarization of a pyroelectric[1]—the anizotropic surface layer has a symmetry which allows for zero-field dipole moment P_{z0}^S. The coefficient α_{zz}^S is the *normal component of the intrinsic surface polarizability tensor*. The tangential component α_{xx}^S was investigated previously[49]—for InP surface, we found $\alpha_{xx}^S/\varepsilon_0 \sim 10$ nm, of the order of the bulk dielectric constant of InP times the thickness of the surface layer. The expected order of magnitude of $\alpha_{zz}^S/\varepsilon_0$ of water is, by analogy, ~5-50 nm (ε^W times several ångstroms). If $P_z^S = -70 \times 10^{-12}$ C/m and $E_z^S = 5 \times 10^8$ V/m, Eq. (50) yields for P_{z0}^S a value between -90×10^{-12} and -300×10^{-12} C/m. For the illustrative calculations below, we will use $\alpha_{zz}^S/\varepsilon_0 = 15$ nm and $P_{z0}^S = -140 \times 10^{-12}$ C/m.

In order to elucidate the physical nature of the quantities P_{z0}^S and α_{zz}^S, let us develop a model of the Langevin type for the pyroelectric interface. Consider a molecule of dipole moment $\boldsymbol{p}$ at the surface ($|\boldsymbol{p}| = 6.2 \times 10^{-30}$ Cm for water molecule; for simplicity, we neglect its polarizability α_p). Let Γ such molecules be subjects to an orientating potential—image force,[13] hydrogen bonding,[15] van der Waals and steric forces[16]—for which one can write in linear approximation $u_{or} = -k_{or} \cos\theta$. Here, θ is the angle between the dipole $\boldsymbol{p}$ and the z-axis. If the energy is minimal when the partial positive charge is pointing toward the aqueous phase ($z < 0$), then the coefficient k_{or} must be negative. The dipoles interact also with a local surface electric field E_z^S, which may be due to the dipoles themselves or may be external, as discussed in the following Sec. III B. The total potential energy of a molecule is

$$u(\theta) = -(k_{or} + |\boldsymbol{p}| E_z^S) \cos\theta. \tag{51}$$

The average macroscopic dipole moment P_z^S corresponding to potential (51) is then given by Langevin's function,[33]

$$P_z^S = \Gamma\, |\boldsymbol{p}| \left(\coth X - 1/X\right), \tag{52}$$

where X stands for

$$X = (k_{or} + |\boldsymbol{p}/E_z^S)/k_B T. \tag{53}$$

The expansion in series of Eq. (52) for small X yields constitutive relation (50) of the pyroelectric interface, where P_{z0}^S and α_{zz}^S are given by

$$P_{z0}^S = \Gamma\, |\boldsymbol{p}|\, k_{or}/3k_B T, \quad \alpha_{zz}^S = \Gamma |\boldsymbol{p}|^2/3k_B T. \tag{54}$$

Assuming that Γ is of the order of the bulk concentration of water C times 1 or 2 water diameters ($\Gamma \sim 0.033$ Å$^{-3} \times$ 1-2 $\times$ 2.8 Å, i.e., one water molecule per 5-10 Å^2 is subject to u_{or}), we obtain for $\alpha_{zz}^S/\varepsilon_0$ the value 3-6 nm. The Langevin theory underestimates the macroscopic polarizabilities of bulk dielectrics and of water especially[33] and it is likely that the same is valid for our pyroelectric surface. Therefore, $\alpha_{zz}^S/\varepsilon_0$ will probably be few times larger than what follows from Eq. (54). This is in agreement with the simpler estimation above. As for the zero-field polarization, a value $k_{or} = -5 \times k_B T$ (of the order of the energy of a weak hydrogen bond) results in P_{z0}^S between -100 and -200×10^{-12} C/m, which is reasonable. These values suggest, however, that the linearization of Eq. (52) is not an adequate approximation and a non-linear dependence of P_z^S on both k_{or} and E_z^S must be expected. In addition, the order of magnitude of the electric field found above, $E_z^S = 5 \times 10^8$ V/m, suggests that hyperpolarizabilities will affect also the bulk polarization.[61] The non-linear problem is, however, beyond the scope of the current work.

As in Langevin's linear problem, the free energy per dipole is $-k_B T X^2/6$, so the total free energy σ_P^S per unit area of Γ dipoles is

$$\sigma_P^S = -\Gamma k_B T X^2/6 = -\left(P_{z0}^S + \alpha_{zz}^S E_z^S\right)^2/2\alpha_{zz}^S = -\left(P_z^S\right)^2/2\alpha_{zz}^S, \tag{55}$$

where Eqs. (54) and (50) were used. Within the quadrupolar electrostatics, the potential ϕ is a continuous functions at $z = 0$. Since no jump of ϕ occurs at $z = 0$ (so $\Delta_{-0}^{+0}\phi \equiv \phi(+0) - \phi(-0) = 0$), then, according to the relation $\sigma_P^S = \gamma_P^S - D_z \Delta_{-0}^{+0}\phi$, for the surface layer of dipoles, there is no difference between the thermodynamic and the mechanical tension.

Eqs. (48) and (50) are two linear equations for E_z^S and P_z^S and their solution is

$$\begin{aligned} E_z^S &= -\frac{1}{\varepsilon^W L_Q^W + \varepsilon^O L_Q^O + \alpha_{zz}^S} P_{z0}^S, \\ P_z^S &= \frac{\varepsilon^W L_Q^W + \varepsilon^O L_Q^O}{\varepsilon^W L_Q^W + \varepsilon^O L_Q^O + \alpha_{zz}^S} P_{z0}^S. \end{aligned} \tag{56}$$

According to it, the intrinsic dipole moment P_z^S of the interface is smaller than P_{z0}^S, because of the depolarizing field E_z^S (acting in the opposite direction of P_z^S). If the surface polarizability is low ($\alpha_{zz}^S \ll \varepsilon^W L_Q^W + \varepsilon^O L_Q^O$), the dipole moment P_z^S is equal to P_{z0}^S, i.e., the dipole is solid. On the other hand, if the quadrupolar lengths tend to zero, E_z^S reaches the limiting value $-P_{z0}^S/\alpha_{zz}^S$, which corresponds to complete depolarization of the interface and $P_z^S = 0$, cf. Eq. (50). This limit does not correspond to a real physical situation, but it accentuates the role of the interaction of the bulk quadrupoles with the surface dipoles for the correct description of the properties of the polarized interface.

The contribution of the bulk electric field to the mechanical interfacial tension γ can be calculated as the surface excess of T_{xx}. Using results (29) for T_{xx} and T_{zz} and the formula of Bakker,[62,45] we obtain

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$$\gamma_P^{\mathrm{W}} = \int_0^{\infty} (T_{xx}^{\mathrm{W}} - T_{zz}^{\mathrm{W}})\,\mathrm{d}z = -\varepsilon^{\mathrm{W}} \int_0^{\infty} \left\{ \left(E_z^{\mathrm{W}}\right)^2 + \left(L_Q^{\mathrm{W}}\right)^2 \left[\left(\frac{\mathrm{d}E_z^{\mathrm{W}}}{\mathrm{d}z}\right)^2 - E_z^{\mathrm{W}} \frac{\mathrm{d}^2 E_z^{\mathrm{W}}}{\mathrm{d}z^2} \right] \right\} \mathrm{d}z,$$
$$\gamma_P^{\mathrm{O}} = \int_{-\infty}^{0} (T_{xx}^{\mathrm{O}} - T_{zz}^{\mathrm{O}})\,\mathrm{d}z = -\varepsilon^{\mathrm{O}} \int_{-\infty}^{0} \left\{ \left(E_z^{\mathrm{O}}\right)^2 + \left(L_Q^{\mathrm{O}}\right)^2 \left[\left(\frac{\mathrm{d}E_z^{\mathrm{O}}}{\mathrm{d}z}\right)^2 - E_z^{\mathrm{O}} \frac{\mathrm{d}^2 E_z^{\mathrm{O}}}{\mathrm{d}z^2} \right] \right\} \mathrm{d}z. \tag{57}$$

Substituting here field (48) and (49) following from the quadrupolar Maxwell equations, one finds the contribution to γ of the electric field created by the surface dipoles in the two bulk phases, W and O,

$$\gamma_P^{\mathrm{W}} = -\frac{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}}}{\left(\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}\right)^2} \frac{(P_z^{\mathrm{S}})^2}{2},$$
$$\gamma_P^{\mathrm{O}} = -\frac{\varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}}{\left(\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}\right)^2} \frac{(P_z^{\mathrm{S}})^2}{2}. \tag{58}$$

The total contribution γ_P of the adsorbed dipoles to the mechanic surface tension of the interface is the sum of Eqs. (55) and (58),

$$\gamma_P = -\frac{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}} + \alpha_{zz}^{\mathrm{S}}} \frac{\left(P_{z0}^{\mathrm{S}}\right)^2}{2\alpha_{zz}^{\mathrm{S}}}, \tag{59}$$

where we used also Eq. (56). In the absence of external field, γ_P coincides with the thermodynamic tension $\sigma_P = \gamma_P - D_z \Delta_{\mathrm{W}}^{\mathrm{O}}\phi$ (since the displacement field D_z is zero). For water|gas surface of $P_z^{\mathrm{S}} = -7 \times 10^{-11}$ C/m, $L_Q^{\mathrm{W}} = 2$ Å, and $\alpha_{zz}^{\mathrm{S}}/\varepsilon_0 = 5$ or 50 nm, we find that the surface dipole moment has a very significant contribution to the surface tension of water: $\sigma_P = -73$ or -23 mN/m, respectively. This order of magnitude is comparable with the results in Refs. 63, 12, and 52. Eq. (59) can be written as $\sigma_P = -(P_{z0}^{\mathrm{S}})^2/2\alpha_{zz}^{\mathrm{S}} - P_{z0}^{\mathrm{S}} E_z^{\mathrm{S}}/2$, where $-(P_{z0}^{\mathrm{S}})^2/2\alpha_{zz}^{\mathrm{S}} = -\Gamma k_{\mathrm{or}}^2/6k_{\mathrm{B}}T$ is the energy gain due to the orientation potential u_{or} and $-P_{z0}^{\mathrm{S}} E_z^{\mathrm{S}}/2$ is the positive electrical energy which opposes the orientation. The contribution σ_P is very sensitive to the quadrupolar moment and the quadrupolarizability of the water molecules through the quadrupolar length L_Q (at $L_Q \to 0$, σ_P approaches 0).

B. The interaction of normal electric field with the interface and the dielectrocapillary curve

We now investigate a more general setup, where besides surface dipole-induced surface electric field (48), an external field acts on the interface. The interaction between a static field and an interface between insulators (where the interface is an entity on its own, with its intrinsic electrical and mechanical properties) has been investigated by Rusanov and Kuni[5] in regard to its effect on nucleation. Warshavsky and Zeng further investigated the role of the bulk quadrupoles in this problem, using density functional theory.[64] Bedeaux and Vlieger[38] and Graham and Raab[3] investigated the interaction of a dielectric interface with light. Apart from the applications mentioned in the Introduction, the problem may be of practical importance for, e.g., the electrospinning process.[65] The effects investigated in this section will have significant contribution also to the image force acting on an ion (the ion polarizes not only the bulk phases but also the surface).

Consider an electrostatic field $\boldsymbol{E} = \mathbf{e}_z E_{z\infty}^{\mathrm{W}}$ acting on the aqueous phase and penetrating the oil as $\mathbf{e}_z E_{z\infty}^{\mathrm{O}}$. The interface is also subject to this field and, in addition, to a significant field gradient due to the swift change of E_z from $E_{z\infty}^{\mathrm{W}}$ to $E_{z\infty}^{\mathrm{O}}$ in a dipolar double layer that is several Å thick. Within the classical macroscopic dipolar equations of electrostatics, E_z experience a discontinuity at $z = 0$, while within the quadrupolar ones, E_z is continuous, Eq. (20).

For this problem, it is convenient to choose the zero of the potential at $z = 0$ (i.e., $\phi(0) = 0$). The solution of Eqs. (7) that has the proper asymptotic behaviour at $z \to \pm\infty$ is

$$\phi^{\mathrm{W}} = \Delta_{\mathrm{W}}^{\mathrm{S}}\phi \left[\exp(z/L_Q^{\mathrm{W}}) - 1\right] - E_{z\infty}^{\mathrm{W}} z,$$
$$\phi^{\mathrm{O}} = \Delta_{\mathrm{O}}^{\mathrm{S}}\phi \left[\exp(-z/L_Q^{\mathrm{O}}) - 1\right] - E_{z\infty}^{\mathrm{O}} z. \tag{60}$$

Here, $\Delta_{\mathrm{W}}^{\mathrm{S}}\phi$ and $\Delta_{\mathrm{O}}^{\mathrm{S}}\phi$ are integration constants, and together with $E_{z\infty}^{\mathrm{O}}$, they are determined by boundary conditions (18)-(20). Gauss's law (18) leads to the trivial result

$$\varepsilon^{\mathrm{W}} E_{z\infty}^{\mathrm{W}} = \varepsilon^{\mathrm{O}} E_{z\infty}^{\mathrm{O}} \quad (= D_z). \tag{61}$$

In the absence of free charges, the displacement field D_z is independent of z. For $\Delta_{\mathrm{W}}^{\mathrm{S}}\phi$ and $\Delta_{\mathrm{O}}^{\mathrm{S}}\phi$, we obtain

$$\Delta_{\mathrm{W}}^{\mathrm{S}}\phi = \frac{L_Q^{\mathrm{W}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} - \frac{\left(\varepsilon^{\mathrm{W}} - \varepsilon^{\mathrm{O}}\right) L_Q^{\mathrm{W}} L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} E_{z\infty}^{\mathrm{W}},$$
$$\Delta_{\mathrm{O}}^{\mathrm{S}}\phi = -\frac{L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} - \frac{\left(\varepsilon^{\mathrm{W}} - \varepsilon^{\mathrm{O}}\right) L_Q^{\mathrm{W}} L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} E_{z\infty}^{\mathrm{O}} \tag{62}$$

compared to Eqs. (41). Potential (60) is illustrated in Fig. 3(a).

From Eqs. (60)-(62), we find that the surface electric field $E_z^{\mathrm{S}} = -\mathrm{d}\phi/\mathrm{d}z|_{z=0}$ is

$$E_z^{\mathrm{S}} = -\frac{1}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} P_z^{\mathrm{S}} + \frac{L_Q^{\mathrm{W}} + L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}}} D_z. \tag{63}$$

Except for the *self-field* of the dipoles, Eq. (63) contains a second term over Eq. (48), standing for the contribution of the external field D_z. Eq. (63) is similar to Eq. (12) of Onsager,[66] used for his famous model for dipolar fluids. The first term in Eq. (63) is the surface analogue of Onsager's *reaction field* and the second one is similar to his *cavity field*.[66] The molecules at the surface are subject to the total field E_z^{S} ("*local internal field*"). Eqs. (63) and (50) are two linear equations for E_z^{S} and P_z^{S} (compare to Eqs. (4) and (12) of Onsager[66]) and their

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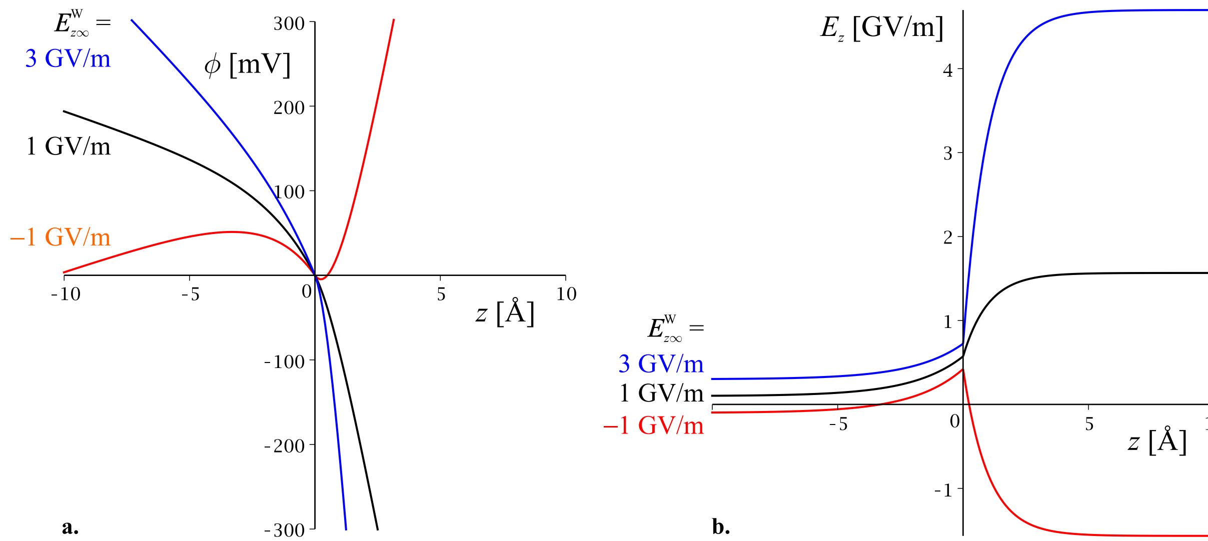

FIG. 3. (a) Distribution of the potential $\phi(z)$ and (b) the field $E_z(z)$ near a polarized interface in external field $E^{W}_{z\infty} = D_z/\varepsilon^{W}$. Material parameters as in Fig. 2. The external field value 1 GV/m is close to the point of zero surface dipole of this interface.

solution is

$$E^{S}_{z} = -\frac{1}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}P^{S}_{z0} + \frac{L^{W}_{Q} + L^{O}_{Q}}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}D_z, \tag{64}$$

$$P^{S}_{z} = \frac{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q}}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}P^{S}_{z0} + \frac{\left(L^{W}_{Q} + L^{O}_{Q}\right)\alpha^{S}_{zz}}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}D_z. \tag{65}$$

Note that P^{S}_{z0} is the dipole moment in the absence of *local internal* field and not in the absence of *external* field. Even when D_z is absent, the local field is not zero due to the reaction field; the inherent dipole moment and field of the interface, Eqs. (56), are obtained from Eq. (65) by setting $D_z = 0$.

The following form follows for the electric field distribution in the interfacial region from (60)-(63),

$$\begin{aligned} E^{W}_{z} &= (E^{S}_{z} - E^{W}_{z\infty})\exp(z/L^{W}_{Q}) + E^{W}_{z\infty},\\ E^{O}_{z} &= (E^{S}_{z} - E^{O}_{z\infty})\exp(-z/L^{O}_{Q}) + E^{O}_{z\infty}. \end{aligned} \tag{66}$$

The field profile is illustrated in Fig. 3(b). Note the functional similarity of this field distribution to Overbeek's *potential* distribution near a charged surface between two electrolyte solutions that build up a Galvani potential[67]—this is another example for the analogy between diffuse charge and diffuse dipole layers.

Let us now calculate the Gibbs excess of the dipole moment—we substitute Eqs. (65) and (66) into the definition of Γ_P,

$$\begin{aligned} \Gamma_P &= P^{S}_{z} + \int_{-\infty}^{0}(P^{W}_{z} - P^{W}_{z\infty})\,\mathrm{d}z + \int_{0}^{\infty}(P^{O}_{z} - P^{O}_{z\infty})\,\mathrm{d}z\\ &= \frac{\varepsilon_0\left(L^{W}_{Q} + L^{O}_{Q}\right)}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}P^{S}_{z0} + \chi^{S}D_z, \end{aligned} \tag{67}$$

where the *dielectric susceptibility of the dipolar double layer* χ^{S} stands for

$$\begin{aligned} \chi^{S} &= \frac{\partial\Gamma_P}{\partial D_z}\\ &= \frac{\varepsilon_0}{\varepsilon^{W}\varepsilon^{O}}\frac{(\varepsilon^{W} - \varepsilon^{O})^2L^{W}_{Q}L^{O}_{Q} + \left(\varepsilon^{W}L^{O}_{Q} + \varepsilon^{O}L^{W}_{Q}\right)\alpha^{S}_{zz}}{\varepsilon^{W}L^{W}_{Q} + \varepsilon^{O}L^{O}_{Q} + \alpha^{S}_{zz}}. \end{aligned} \tag{68}$$

Relations (67) and (68) set the basic theory of the coefficients in the constitutive relation of $\Gamma_P(D_z)$ (compare to those in Ref. 5). A feature of Eq. (67) is that the total dipole moment of the interface becomes zero at a certain *displacement field of zero dipole*,

$$D_{z,P=0} = -\frac{\varepsilon^{W}\varepsilon^{O}\left(L^{W}_{Q} + L^{O}_{Q}\right)}{(\varepsilon^{W} - \varepsilon^{O})^2L^{W}_{Q}L^{O}_{Q} + \left(\varepsilon^{W}L^{O}_{Q} + \varepsilon^{O}L^{W}_{Q}\right)\alpha^{S}_{zz}}P^{S}_{z0}. \tag{69}$$

In the limit where both quadrupolar lengths tend to zero, this field becomes undefined (another weakness of the classical Maxwell equations).

One can substitute field (66) in definition (35) of the potential drop in the surface condenser due to the surface dipole moment to show that $\Delta^{O}_{W}\phi = \Gamma_P/\varepsilon_0$ with Γ_P given by Eq. (67). Therefore, the basic Eq. (1) is fulfilled also in the case of external field acting on an interface between quadrupolar media (Eq. (3.8) in Ref. 2).

The electric energy of the adsorbed dipoles per unit area ($\sigma^{S}_{P} = \gamma^{S}_{P}$) in the local field E^{S}_{z} is still given by Eq. (55), but the surface dipole P^{S}_{z} is altered by the external field according to Eq. (65). The total energy of the dipoles involves also the contribution of the electric field in the bulk. In case that external field is present in the bulk phases, the bulk stress tensors are anisotropic, i.e., $T^{W}_{xx\infty} \neq T^{W}_{zz}$ and $T^{O}_{xx\infty} \neq T^{W}_{zz}$. The T_{zz} component is constant equal to $-p_0$ and the respective values of $T^{W}_{xx\infty}$ and $T^{O}_{xx\infty}$ follow from Eq. (29) at $z \to \pm\infty$ (where $\boldsymbol{Q}$ is zero):

$$T^{W}_{xx\infty} = -p_0 - \varepsilon^{W}(E^{W}_{z\infty})^2, \quad T^{O}_{xx\infty} = -p_0 - \varepsilon^{O}(E^{O}_{z\infty})^2. \tag{70}$$

In such case, Bakker's formula is invalid and instead of it one should use directly definition (34) of γ—it yields

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$$\gamma_P^{\mathrm{W}} = \int_0^\infty (T_{xx}^{\mathrm{W}} - T_{xx\infty}^{\mathrm{W}})\,\mathrm{d}z = -\varepsilon^{\mathrm{W}} \int_0^\infty \left\{ (E_z^{\mathrm{W}})^2 - (E_{z\infty}^{\mathrm{W}})^2 + \left(L_Q^{\mathrm{W}}\right)^2 \left[\left(\frac{\mathrm{d}E_z^{\mathrm{W}}}{\mathrm{d}z}\right)^2 - E_z^{\mathrm{W}} \frac{\mathrm{d}^2 E_z^{\mathrm{W}}}{\mathrm{d}z^2} \right] \right\} \mathrm{d}z,$$
$$\gamma_P^{\mathrm{O}} = \int_{-\infty}^0 (T_{xx}^{\mathrm{O}} - T_{xx\infty}^{\mathrm{O}})\,\mathrm{d}z = -\varepsilon^{\mathrm{O}} \int_{-\infty}^0 \left\{ (E_z^{\mathrm{O}})^2 - (E_{z\infty}^{\mathrm{O}})^2 + \left(L_Q^{\mathrm{O}}\right)^2 \left[\left(\frac{\mathrm{d}E_z^{\mathrm{O}}}{\mathrm{d}z}\right)^2 - E_z^{\mathrm{O}} \frac{\mathrm{d}^2 E_z^{\mathrm{O}}}{\mathrm{d}z^2} \right] \right\} \mathrm{d}z, \tag{71}$$

compared to Eqs. (57). Substituting here solutions (64) and (66) for the field and summing with σ_P^{S} from Eq. (55) with P_z^{S} from Eq. (65), we obtain for the mechanical interfacial tension of the interface in external field,

$$\gamma_P = \sigma_P^{\mathrm{S}} + \gamma_P^{\mathrm{W}} + \gamma_P^{\mathrm{O}} = \gamma_P(D_z = 0) + \chi^{\mathrm{S}} D_z^2/2\varepsilon_0, \tag{72}$$

where the contribution of the adsorbed dipoles to the mechanical interfacial tension in the absence of external field is given by Eq. (59) and the susceptibility χ^{S}—by Eq. (68). From this result, it follows that γ increases in normal external field, cf. the blue curve in Fig. 4 (where the non-electrostatic contribution to γ is added to γ_P by substituting $\gamma_P(D_z = 0)$ with $\sigma_0 = 72$ mN/m). The curve $\gamma(E_{z\infty}^{\mathrm{W}})$ is symmetrical with respect to $E_{z\infty}^{\mathrm{W}} = 0$, so the direction of the field is unimportant for γ. A field of strength $E_{z\infty}^{\mathrm{W}} = \pm 5 \times 10^6$ V/m applied to a water|gas surface will result in increase of γ of the order of 0.001 mN/m, which is enough to cause a significant Marangoni flow. Thus, in case that tangential gradient of E_z exists along the surface, it will draw liquid from the low-field region to the high-field region (which can be called *dielectro-Marangoni effect*—compared to the electro-Marangoni effect[68] driven by tangential gradient of ϕ). The effect will have a first order

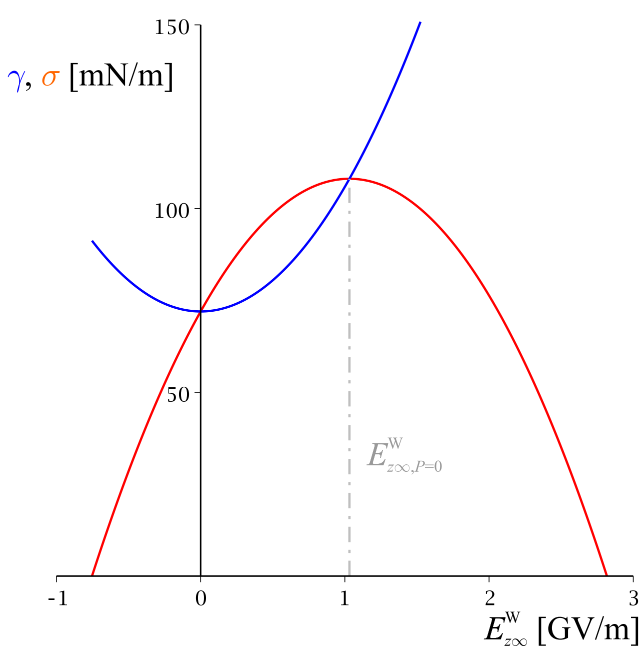

FIG. 4. Dependence of the mechanical surface tension $\gamma(E_{z\infty}^{\mathrm{W}})$ (blue line) and the thermodynamic surface tension $\sigma(E_{z\infty}^{\mathrm{W}})$ (red line) on the normal electric field in the aqueous phase and for water|gas, Eqs. (72) and (73). The field of zero surface dipole is marked with dashed-dotted line.

contribution to all surface properties considered in Ref. 39 (and to Eq. (12) in particular).

The thermodynamic tension is obtained as $\sigma_P = \gamma_P - D_z \Delta_{\mathrm{W}}^{\mathrm{O}} \phi$ from Eqs. (1), (67), and (72),

$$\sigma = \sigma_0 - \frac{L_Q^{\mathrm{W}} + L_Q^{\mathrm{O}}}{\varepsilon^{\mathrm{W}} L_Q^{\mathrm{W}} + \varepsilon^{\mathrm{O}} L_Q^{\mathrm{O}} + \alpha_{zz}^{\mathrm{S}}} P_{z0}^{\mathrm{S}} D_z - \frac{\chi^{\mathrm{S}}}{2\varepsilon_0} D_z^2, \tag{73}$$

the non-electrostatic contributions to σ has been added and σ_0 is the *total* surface tension in the absence of field ($\gamma_P(D_z = 0)$ is different from σ_0; this equation follows strictly from Eqs. (1), (38), and (67)). The function $\sigma(D_z)$ is asymmetric, Fig. 4. If D_z is of the same sign as P_{z0}^{S}, the thermodynamic surface tension decreases. For D_z in the opposite direction of the adsorbed dipoles, σ first increases and then passes through a maximal value located at $D_z = D_{z,P=0}$. According to Rusanov and Kuni,[5] this asymmetry explains why water droplets nucleate preferentially on negative charges. Eq. (73) predicts the existence of one negative value and one positive value of the external field that nullify σ, causing self-dispersion. It is seen that the thermodynamic surface tension becomes zero at two values of the external displacement field, namely,

$$D_{z,\sigma=0} = D_{z,P=0} \pm \sqrt{D_{z,P=0}^2 + 2\varepsilon_0 \sigma_0/\chi^{\mathrm{S}}}. \tag{74}$$

For water|gas surface, using $L_Q^{\mathrm{W}} = 2$ Å, $\alpha_{zz}^{\mathrm{S}}/\varepsilon_0 = 15$ nm, $P_{z0}^{\mathrm{S}} = -140 \times 10^{-12}$ C/m, and $\sigma_0 = 72.2$ mN/m, we obtain from Eqs. (68), (69), and (74), (i) susceptibility of the dipolar double layer $\chi^{\mathrm{S}} = 1.3 \times 10^{-12}$ m; (ii) field of zero dipole $E_{z\infty,P=0}^{\mathrm{W}} = D_{z,P=0}/\varepsilon^{\mathrm{W}} = +1.0 \times 10^9$ V/m; and (iii) field of self dispersion $E_{z\infty,\sigma=0}^{\mathrm{W}} = D_{z,\sigma=0}/\varepsilon^{\mathrm{W}} = +2.8 \times 10^9$ and -7.5×10^8 V/m. These fields are so high that linear relationships (5) between $\boldsymbol{P}$ and $\boldsymbol{E}$ are no longer valid.[61] Instead, for a quantitatively correct theory, a non-linear dependence of the Langevin type or at least quadratic $\boldsymbol{P}(\boldsymbol{E})$ dependence should be used, as already discussed. Our results above correspond to a linear dipolar double layer theory. They are probably as far from truth as the linear Gouy-Chapman theory of the electric double layer differs from the non-linear one.[69,70] Nevertheless, we expect the qualitative features of our theory to be correct. The numerical estimations for the parameters from Sec. III, however rough, are summarized in Table I for the surfaces of the two dielectrics for which both L_Q and $\Delta_{\mathrm{L}}^{\mathrm{G}}\phi$ have been estimated from experimental data:[10,31,53,71] water and methanol.

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TABLE I. Estimated dielectric, pyroelectric, and mechanistic characteristics of the water and methanol surfaces.

	$\Delta_L^G\phi$ potential drop at the surface (mV)	ε dielectric constant	L_Q quadrupolar length (Å)	P_z^S intrinsic surface dipole, Eq. (44) (C/m)	Γ_P total surface dipole moment, Eq. (1) (C/m)
Water|gas	-100[10,11,56,57]	$78 \times \varepsilon_0$	2[31,53]	-70×10^{-12}	$+0.9 \times 10^{-12}$
Methanol|gas	$+180$[71]	$33 \times \varepsilon_0$	1[53]	$+50 \times 10^{-12}$	$+1.6 \times 10^{-12}$

	E_z^S surface field, Eq. (48) (V/m)	$\alpha_{zz}^S/\varepsilon_0$ surface polarizability[a] (nm)	P_{z0}^S zero-field polarization[a] (C/m)	σ_P contribution of P_z^S to σ, Eq. (59) (mN/m)	σ_0 surface tension of the clean surface (mN/m)
Water|gas	0.5×10^9	15	-140×10^{-12}	-36	72
Methanol|gas	-1.3×10^9	3.3	$+100 \times 10^{-12}$	-85	23

	χ^S surface susceptibility, Eq. (68) (m)	$E^W_{z\infty,P=0}$ field of zero dipole, Eq. (69) (V/m)	$E^W_{z\infty,\sigma=0}$ field of self-dispersion, Eq. (74) (V/m) Lower	$E^W_{z\infty,\sigma=0}$ field of self-dispersion, Eq. (74) (V/m) Higher	$\sigma_{P=0}$ maximal value of the surface tension (at $D_{z,P=0}$), Eq. (73) (mN/m)
Water|gas	1.3×10^{-12}	$+1 \times 10^9$	-0.8×10^9	$+3 \times 10^9$	110
Methanol|gas	1.5×10^{-12}	-3.4×10^9	-7×10^9	$+0.4 \times 10^9$	110

[a]The values are chosen for illustrative purposes only; they correspond to $\alpha_{zz}^S = \varepsilon L_Q$ and $P_{z0}^S = 2P_z^S$.

TABLE II. Comparison between electric double layer and dipolar double layer.

Diffuse charge layer	Diffuse dipole layer
The specifically adsorbed surface charge density ρ^S is compensated by a diffusely distributed bulk free charge. The total charge of the surface is zero	The intrinsic surface dipole moment P_z^S is *partially* compensated by bulk dipoles of diffuse distribution. The total surface dipole Γ_P is smaller than P_z^S
In linear approximation (small ϕ^S), the bulk potential decays exponentially with characteristic length $L_D = (\varepsilon k_B T/2e^2C_{el})^{1/2}$ (the Debye length), where $2C_{el}$ is the concentration of free charges	The potential decays exponentially with characteristic length $L_Q = (\alpha_Q/3\varepsilon)^{1/2}$ (the quadrupolar length)
L_D^2 is approximately proportional to $\boldsymbol{p}\cdot\boldsymbol{p}C/e^2C_{el}$ ($\varepsilon \sim \boldsymbol{p}\cdot\boldsymbol{p}C/T$). L_D is nearly independent of T	L_Q^2 is approximately proportional to $\boldsymbol{q}:\boldsymbol{q}C/\boldsymbol{p}\cdot\boldsymbol{p}C$ ($\alpha_Q \sim \boldsymbol{q}:\boldsymbol{q}C/T$). L_Q is nearly independent of T
Its structure determines the shape of the electrocapillary $\sigma(\phi)$ curves, according to Lipmann's equation. A feature of this curve is a maximum at the potential of zero charge	Its structure determines the shape of the dielectrocapillary curves $\sigma(D_z)$, according to Rusanov-Kuni equation (37). This curve has a maximum at field (69) of zero surface dipole
Gouy's equation relates ϕ^S and ρ^S; it follows from Gauss's law[69]	Eq. (63) relates E_z^S and P_z^S. It follows from Graham-Raab multipolar condition (17)
The diffuse charge layer due to the Galvani potential at the interface between two electrolyte solutions has potential profile given by Overbeek's formula[67]	The diffuse dipole layer due to the external field at the interface between two insulators has electric field profile given by Eq. (66)

IV. CONCLUSIONS

(i) The work presents a full set of boundary conditions (Eqs. (16), (17), and (20)) at a flat interface between two isotropic media for the quadrupolar equation of electrostatics. Their corollaries were investigated on the example of several problems. Compared to the classical results that follow from Poisson's equation, the quadrupolar electrostatics leads to regularization of the potential (continuous ϕ and E at an interface possessing surface charge and surface dipole moment).

(ii) The quadrupolar electrostatic equations predict that near a polarized interface, a *diffuse dipole layer* is formed. Strong analogy exists between diffuse charge layer near a charged surface and diffuse dipole layer near a polarized surface—these are summarized in Table II. The main difference is that the electric double layer is electroneutral at equilibrium, while the dipolar double layer has an equilibrium non-zero total dipole moment Γ_P.

(iii) The Maxwell stress tensor and the electric force density in a linear isotropic quadrupolar medium are derived, Eqs. (22) and (24). The ponderomotive force has contribution from the action of the electric field gradient on the bulk quadrupoles, as well as from the quadrupolar image force and the quadrupolar electrostriction.

(iv) Significant effects from the bulk quadrupolarizability on several properties of the dielectric interface are found, among them the surface field, the electrostatic contribution to the interfacial tension, the double layer susceptibility, etc., cf. Table I.

(v) The dependences of the mechanical and the thermodynamic interfacial tensions on the external electrostatic field normal to the surface are predicted (the *dielectrocapillary curves*, Fig. 4). The relation of the susceptibility of the dipolar layer ($\chi^S = \mathrm{d}\Gamma_P/\mathrm{d}D_z$), the field of zero surface dipole and the dielectro-Marangoni coefficient $\mathrm{d}\gamma/\mathrm{d}(D_z^2)$ to the surface and bulk dielectric properties is analyzed.

The presented macroscopic description of the interfacial structure within the macroscopic quadrupole expansion is natural and straightforward. The presented model is, however, of quite limited applicability. Let us summarize the main limitations and the route for their elimination.

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(i) The surface electric field is very high, close to the point of dielectric saturation, and non-linear dependence of $\boldsymbol{P}$ vs. $\boldsymbol{E}$ must be expected. The linearization of Eq. (52) is also hardly a good approximation. This problem was realized also by Rusanov and Kuni,[5] who accounted for hyperpolarizability in their model of P_z^{S}.

(ii) The assumption that the surface layer where the intrinsic dipole P_z^{S} is situated is thinner than the quadrupolar length L_Q is far from truth. Overlapping between the adsorbed layer and the diffuse dipole layer will be present, which must be dealt with similarly to the overlapping between the diffuse and the adsorbed electric layers near the charged surface of a concentrated electrolyte solution.[57]

(iii) We present a macroscopic theory for a nano-object few ångstroms thick. Strong structural effects must be expected, which can be resolved by introducing levels of microscopic description.[59,72] The results for discrete dipole distribution at the interface are an example for such an approach.[50–53]

(iv) Most parameter values used for the examples are quite uncertain. The value $L_Q^{\mathrm{W}} = 2$ Å is probably overestimated,[31,59] $\Delta_{\mathrm{W}}^{\mathrm{O}}\phi$ is disputed,[10,11] and the values of P_{z0}^{S} and α_{zz}^{S} are nothing more than rough estimations.

The above limitations unfortunately make the predictive power of our model questionable. The calculated values in Table I should be therefore considered estimations of the order of magnitude.

We deliberately have not considered the nature of the orientation potential $u_{\mathrm{or}} = -k_{\mathrm{or}} \cos\theta$ in Eq. (51), for the sake of generality and simplicity. Note that this potential is also most probably closely connected to the quadrupolar electrostatics. For example, the image forces[13] will obviously depend on L_Q, P_z^{S}, and α_{zz}^{S}, as well on the tangential polarizability of the interface[49] α_{xx}^{S}. This is a problem that we will hopefully consider in the near future.

Precise mechanistic model of the $\boldsymbol{P}^{\mathrm{S}}(\boldsymbol{E})$ dependence is another requirement for the successful application of the quadrupolar theory. Langevin's model (51)-(54) is a first step which neglects numerous features of the interface. One such feature is that the quantities α_{xx}^{S} and α_{zz}^{S} must involve, in principle, a contribution due to the profile of the dielectric permittivity tensor (cf., e.g., Refs. 5 and 73)—in a sense, α_{xx}^{S} and α_{zz}^{S} are the surface excesses of the tangential and the normal component of the ε tensor.

An important conclusion from our macroscopic model of the interface is the tight relation between surface dipole and the bulk quadrupole moments. It elucidates the high sensitivity of the surface potential obtained by various models and simulations to the quadrupole moment of water.[10,15,13,12,16] Such sensitivity is evident already from multipolar condition (17) at the interface. It states that the quadrupole terms in the macroscopic multipole expansion in the bulk phases are of the same order of approximation as the surface dipole moment. To put it simply, from Eq. (17), it follows that in a simulation, if the implemented molecular quadrupole moments and quadrupolarizabilities are inaccurate, then the surface dipole moment and the surface potential drop obtained will be exactly as inaccurate as them.

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[74]See supplementary material at http://dx.doi.org/10.1063/1.4933370 for (A) list of symbols. (B) The trace of the quadropolarization tensor, the average potential, the average field, and its potential. (C) Field of a condenser, a dipolar, and a charged surface in quadrupolar medium: derivation of the continuity of $\boldsymbol{E}$. (D) Derivation of the electric force density and the generalized Maxwell stress tensor in quadrupolar medium. (E) Estimation of the intrinsic surface dipole moment from simulation data.
[75]We adopt the following terminology: (i) Surface dipolar potential is a surface characteristic related to the surface excess of the polarization through Eq. (1); it corresponds to the potential difference at two points z^{W} and z^{O} such that $L_Q^{\mathrm{W}} \ll |z^{\mathrm{W}}| \ll L_{\mathrm{D}}^{\mathrm{W}}$ and $L_Q^{\mathrm{O}} \ll |z^{\mathrm{O}}| \ll L_{\mathrm{D}}^{\mathrm{O}}$, where L_{D} are the Debye lengths in the respective phases; (ii) Galvani potential difference is a thermodynamic bulk quantity related to bulk partitioning equilibria of all electrolytes present in the system; (iii) A third, double layer potential (a surface characteristic) stemming from the adsorption of charged species can be rigorously defined through the free charge surface moment (the integral of $z\rho$). The latter two will be discussed in detail from the viewpoint of the linear quadrupolar electrostatics in a following paper. (iv) The potential stemming from Tr$\boldsymbol{Q}$ (Bethe potential) is resulting in a fourth potential drop across the interface, which is a bulk quantity of little importance for electrochemical systems.[74]
[76]Note that in case that $L_Q^{\mathrm{O}} \to 0$, $E_z(z)$ has discontinuity at $z = 0$. Therefore, the problem for water|gas surface is easier to analyze by taking the limit $L_Q^{\mathrm{O}} \to 0$ of the results for water|oil rather than solving it directly.

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