Quadrupole terms in the Maxwell equations: Born energy, partial molar volume, and entropy of ions

Radomir I. Slavchov and Tzanko I. Ivanov

Articles you may be interested in

Quadrupole terms in the Maxwell equations: Debye-Hückel theory in quadrupolarizable solvent and self-salting-out of electrolytes
J. Chem. Phys. **140**, 164510 (2014); 10.1063/1.4871661

Statistical thermodynamics of fluids with both dipole and quadrupole moments
J. Chem. Phys. **134**, 234507 (2011); 10.1063/1.3599465

The origin of large overestimation of the magnetic entropy changes calculated directly by Maxwell relation
Appl. Phys. Lett. **96**, 222509 (2010); 10.1063/1.3446843

Soft sticky dipole-quadrupole-octupole potential energy function for liquid water: An approximate moment expansion
J. Chem. Phys. **124**, 134504 (2006); 10.1063/1.2161201

Dynamical aspects of mixing schemes in ethanol–water mixtures in terms of the excess partial molar activation free energy, enthalpy, and entropy of the dielectric relaxation process
J. Chem. Phys. **110**, 2508 (1999); 10.1063/1.477956

Quadrupole terms in the Maxwell equations: Born energy, partial molar volume, and entropy of ions

Radomir I. Slavchov[1,a)] and Tzanko I. Ivanov[2]

[1]*Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University, 1164 Sofia, Bulgaria*

[2]*Theoretical Physics Department, Faculty of Physics, Sofia University, 1164 Sofia, Bulgaria*

A new equation of state relating the macroscopic quadrupole moment density $\boldsymbol{Q}$ to the gradient of the field $\nabla \boldsymbol{E}$ in an isotropic fluid is derived: $\boldsymbol{Q} = \alpha_Q(\nabla \boldsymbol{E} - \mathbf{U}\nabla \cdot \boldsymbol{E}/3)$, where the quadrupolarizability α_Q is proportional to the squared molecular quadrupole moment. Using this equation of state, a generalized expression for the Born energy of an ion dissolved in quadrupolar solvent is obtained. It turns out that the potential and the energy of a point charge in a quadrupolar medium are finite. From the obtained Born energy, the partial molar volume and the partial molar entropy of a dissolved ion follow. Both are compared to experimental data for a large number of simple ions in aqueous solutions. From the comparison the value of the quadrupolar length L_Q is determined, $L_Q = (\alpha_Q/3\varepsilon)^{1/2} = $ 1-4 Å. Data for ion transfer from aqueous to polar oil solution are analyzed, which allowed for the determination of the quadrupolarizability of nitrobenzene. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4865878]

I. INTRODUCTION

The macroscopic Poisson equation of electrostatics combines the static macroscopic Coulomb and Ampere laws,

$$\nabla \cdot \boldsymbol{D} = \rho(\phi), \qquad (1)$$

$$\boldsymbol{E} = -\nabla\phi, \qquad (2)$$

with a linear dependence of the electric displacement field $\boldsymbol{D}$ on the electric field intensity $\boldsymbol{E}$:

$$\boldsymbol{D} \equiv \varepsilon_0\boldsymbol{E} + \boldsymbol{P} = \varepsilon_0\boldsymbol{E} + \alpha_P\boldsymbol{E} = \varepsilon\boldsymbol{E}. \qquad (3)$$

Here, ρ is the free charge number density; ϕ is the electrostatic potential; $\varepsilon \equiv \varepsilon_0 + \alpha_P = \varepsilon_0\varepsilon_r$ is the absolute dielectric permittivity, ε_0 is the vacuum permittivity, ε_r is the relative permittivity of the medium, α_P is the macroscopic polarizability of the medium. For a homogeneous medium ($\nabla\varepsilon = 0$) the Poisson equation for ϕ follows from Eqs (1)–(3):

$$-\varepsilon\nabla^2\phi = \rho(\phi). \qquad (4)$$

For conducting media, one must provide also an equation of state for the dependence $\rho(\phi)$. A common assumption is that the charges are distributed according to the Boltzmann distribution

$$\rho(\phi) = \sum e_i C_i \exp(-e_i\phi/k_B T), \qquad (5)$$

where $e_i = eZ_i$ is the absolute charge of the ith ion, e is the electron charge, Z_i is the relative ionic charge, $C_i = \nu_i C_{el}$ is the local concentration of the ith ion, ν_i stands for its stoichiometric number, C_{el} is the electrolyte concentration, T is the temperature, and k_B is the Boltzmann constant. Insert-

ing Eq. (5) into Eq. (4), one obtains the Poisson-Boltzmann equation, widely used in physical chemistry and colloid science. Numerous basic concepts such as Debye-Hückel double layer,[1,2] Gouy model for charged interface,[3,4] Davies adsorption model for ionic surfactant adsorption,[5,6] the electrostatic disjoining pressure in DLVO theory,[7–9] electrokinetic ζ-potential,[10] etc., are merely a consequence of Eqs. (4) and (5).

It has been early recognized that both Poisson and Boltzmann equations (4) and (5) have severe limitations. The derivation of Eq. (4) involves a multipole expansion of the local potential up to dipole terms, i.e., it neglects the quadrupole moment density.[11–13] Equation (3) is strictly valid for linear media.[14] The Boltzmann distribution (5) is only a first approximation valid for quasi-ideal solution;[15–17] other "external" potentials except $e_i\phi$ often arise.[18–20] In order to make Eqs. (3)–(5) applicable to real systems, numerous corrections have been proposed, to point a few: (i) Corrections to the Boltzmann distribution (5) by introduction of various additional interaction potentials, either for ion-ion non-electrostatic interaction[15,16] or various ion-surface interactions;[18–20] (ii) corrections for the macroscopic nature of the equation, involving explicit molecular treatment of the first neighbor interactions[21,14,22] or other discreteness effects;[23,24] (iii) correction for the dielectric saturation, i.e., the dependence of ε on the electric field intensity;[25,26,14] (iv) corrections related to the inhomogeneity of the medium ($\nabla\varepsilon \neq 0$; e.g., Refs. 27 and 28); (v) correlation effects[2,17] and non-local electrostatic effects,[29–32] etc. Every major correction of Eqs. (4) and (5) has been an impetus for reconsideration of the basic concepts following from the Poisson-Boltzmann equation.

While most studies in physical chemistry criticized mainly the Boltzmann part of Poisson-Boltzmann equation,

a)E-mail: fhri@chem.uni-sofia.bg

several studies of optical phenomena[33–36] attacked the Poisson part of it. It was demonstrated that the quadrupolar terms in the macroscopic Coulomb law (1) become quite significant in cases where high gradients of E are present. In such cases, quadrupolar term in the displacement field D need to be introduced:[36]

$$D = \varepsilon_0 E + P - \frac{1}{2} \nabla \cdot Q. \qquad (6)$$

Here, Q is the macroscopic density of the quadrupole moment tensor. Note that the numerical coefficient in front of $\nabla \cdot Q$ depends on the choice of definition of quadrupole moment (for convenience, a derivation of Eq. (6) and the definitions of the involved quantities are given in supplementary material A).[66] The substitution of Eq. (6) into Eq. (1) yields a generalization of the Poisson equation (4):

$$\nabla \cdot \left(\varepsilon E - \frac{1}{2} \nabla \cdot Q \right) = \rho, \qquad (7)$$

which opens a vast field for analysis of the effect of the quadrupole moments of the molecules composing a medium on the properties of charged particles in such medium. It has been recently demonstrated that quadrupole terms in D can play a role in solvent-solute interaction.[12,13] The correction for Q will be important if the solvent molecules possess large quadrupole moment – such is the case of water[37] and many others, including "non-polar" media of low dipole moment but high quadrupole moment such as liquid CO_2, fluorocarbons, etc.[13,38]

The purpose of our study is to analyze the consequences of the new term in Maxwell equation for several basic problems of physical chemistry of electrolyte solutions and colloid chemistry. Equation (7) is largely unknown to physical chemists and virtually has never been used in colloid science. There are three reasons for this neglect. First, Eq. (7) is useless without an equation of state for Q. There are several existing studies of this constitutive relation[39–42,12,13,36] but all are scarcely analyzed. Therefore, in Sec. II, we will derive a new equation of state as simple as possible, showing that Q is a linear function of $\nabla E - U \nabla \cdot E/3$, with a scalar coefficient of proportionality – the *quadrupolarizability*[33] α_Q (here U is the unit tensor). The second reason for Eq. (7) to be unknown in the colloid field is that it is a fourth-order equation with respect to ϕ, and requires the use of new boundary conditions. Seemingly, these new conditions have been derived only recently.[39,40] We will review this problem in Sec. III. Finally, the third obstacle to use Eq. (7) is that it involves a new parameter of unknown value – α_Q. We will give in this paper both theoretical estimation and values determined from 3 independent sets of experimental data for ions in water; we will consider also ions in polar oil solutions.

In Sec. IV, Eq. (7) is used to reinvestigate one basic concept in the physical chemistry of electrolyte solutions – Born energy. It will be shown that the "correction" Q in Eq. (7) in fact leads to results which have no counterpart in the frame of Poisson equation (4), notably, finite electrostatic potential and energy of a point charge in quadrupolarizable medium (similar result was obtained in Ref. 12). In Sec. IV, we compare our results for the Born energy in quadrupolar media to

experimental data, which allows us to determine the value of quadrupolarizability α_Q of water and nitrobenzene.

II. EQUATIONS OF STATE FOR THE QUADRUPOLE MOMENT DENSITY

The problem for the constitutive relation between Q and the field gradient ∇E has been addressed several times.[33,36,39–42,12,13] Using as a starting point the approach of Jeon and Kim,[13] we will be able to obtain a new simple equation of state which relates Q to the field gradient ∇E and the molecular properties of the solvent.

Consider an ideal gas consisting of molecules possessing a solid quadrupole moment tensor q_0 (for the sake of simplicity, the molecule is assumed non-polarizable and with no dipole moment). Since q_0 is symmetrical and traceless, by a suitable choice of the coordinate system it can be diagonalized[43] and in the general case, its diagonal form is

$$q_0 = \begin{pmatrix} q_{xx} & 0 & 0 \\ 0 & q_{yy} & 0 \\ 0 & 0 & q_{zz} \end{pmatrix} - \frac{q_{xx} + q_{yy} + q_{zz}}{3} U. \qquad (8)$$

The term $(q_{xx} + q_{yy} + q_{zz})/3 U$ ensures that the trace of q_0 is 0 and can be added because the field created by a quadrupole in vacuum is invariant with respect to the operation of exchanging the quadrupole strength q_0 with $q_0 + XU$, where X is any scalar.[11,44] The molecule is constantly rotating. An arbitrary rotation changes the quadrupole moment tensor from q_0 to q. For a rotation at arbitrary Eulerian angles ϕ, ψ, and θ, the Euler matrix $E^{\phi\psi\theta}$ is given by

$$E^{\varphi\psi\theta}$$

$$= \begin{pmatrix} \cos\varphi\cos\psi - & \sin\varphi\cos\psi + & \\ -\sin\varphi\sin\psi\cos\theta & +\cos\varphi\sin\psi\cos\theta & \sin\psi\sin\theta \\ & & \\ -\cos\varphi\sin\psi - & -\sin\varphi\sin\psi + & \\ -\sin\varphi\cos\psi\cos\theta & +\cos\varphi\cos\psi\cos\theta & \cos\psi\sin\theta \\ & & \\ \sin\varphi\sin\theta & -\cos\varphi\sin\theta & \cos\theta \end{pmatrix}. $$

$$\qquad (9)$$

The relation between the tensor q for a randomly oriented molecule and the tensor q_0 is

$$q_{ij}(\varphi, \psi, \theta) = E_{ik}^{\varphi\psi\theta} E_{jl}^{\varphi\psi\theta} q_{0kl}. \qquad (10)$$

In the absence of a gradient of the electric field the average value of q is 0. In an external electric field gradient ∇E, the molecule tends to orientate itself in order to minimize its electric energy, given by the expression (Eq 4.22 of Jackson, 3rd edition[11]):

$$u_{el} = -\frac{1}{2} q : \nabla E. \qquad (11)$$

Here, the double dot product symbol ":" denotes the operation $q : \nabla E = \Sigma\Sigma q_{ij} \partial E_i / \partial x_j$. The orientation of the molecule must follow the Boltzmann distribution which can be linearized in the case of $u_{el}/k_B T \ll 1$:

$$\rho_{\phi\psi\theta} = c_n \exp(-u_{el}/k_B T) \approx c_n(1 - u_{el}/k_B T). \qquad (12)$$

Here, c_n is a normalizing coefficient calculated as

$$c_n = 1 \Big/ \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (1 - u_{el}/k_B T) \sin\theta \, d\theta \, d\varphi \, d\psi = 1/8\pi^2. \tag{13}$$

The average quadrupole moment $\bar{\boldsymbol{q}}$ of a molecule can be calculated directly using Eqs. (8)–(13):

$$\bar{\boldsymbol{q}} = \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \boldsymbol{q} \rho_{\phi\psi\theta} \sin\theta \, d\theta \, d\varphi \, d\psi = \alpha_q (\nabla \boldsymbol{E} - \mathbf{U} \nabla \cdot \boldsymbol{E}/3). \tag{14}$$

Here, the molecular quadrupolarizability α_q was introduced, related to the diagonal components of $\boldsymbol{q}_0$ as follows:

$$\alpha_q = \boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T$$
$$= (q_{xx}^2 + q_{yy}^2 + q_{zz}^2 - q_{xx}q_{yy} - q_{xx}q_{zz} - q_{yy}q_{zz})/15 k_B T. \tag{15}$$

Equation (15) was obtained, e.g., in Ref. 13.

The macroscopic density $\boldsymbol{Q}$ of the quadrupole moment in a gas acted upon by a field gradient $\nabla \boldsymbol{E}$ is the gas concentration C times $\bar{\boldsymbol{q}}$, Eq. (14):

$$\boldsymbol{Q} = \alpha_Q (\nabla \boldsymbol{E} - \mathbf{U} \nabla \cdot \boldsymbol{E}/3). \tag{16}$$

Here, the macroscopic quadrupolarizability α_Q is given by

$$\alpha_Q = C\alpha_q = C \boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T. \tag{17}$$

Our constitutive relation (16) is a direct consequence of the general form (8) of the molecular solid quadrupole and the linearized Boltzmann distribution (12). Note that according to Eq. (16) $\boldsymbol{Q}$ is traceless,[11] in contrast to Eq. 2.25 of Jeon and Kim.[13] References 42 and 45 contain some discussion in favor of their choice. However, in the supplementary material A,[66] we present arguments that the use of tensor $\boldsymbol{Q}$ with non-zero trace is incompatible with Eqs. (6) and (7). Equation 2.4 of Chitanvis[12] postulates an equation of state in which only the $\mathbf{U}\nabla \cdot \boldsymbol{E}$ term of our Eq. (16) is present, i.e., according to him, $\boldsymbol{Q}$ has only diagonal elements and a non-zero trace.

In general, $\boldsymbol{Q}$ depends not only on the field gradient but also on the field $\boldsymbol{E}$ itself, and, on the other hand, electric field gradient $\nabla \boldsymbol{E}$ can induce non-zero dipole moment.[39,36] For an ideal gas of solid dipoles within the linear approximation for $\rho_{\phi\psi\theta}$, this is not the case. This can be shown by a direct calculation analogous to the derivation of Eq. (16): if the molecule has dipole moment $\boldsymbol{p}_0$ and quadrupole moment $\boldsymbol{q}_0$, then in external field $\boldsymbol{E}$ and field gradient $\nabla \boldsymbol{E}$ its energy is[11]

$$u_{el} = -\boldsymbol{p} \cdot \boldsymbol{E} - \frac{1}{2} \boldsymbol{q} : \nabla \boldsymbol{E}. \tag{18}$$

Using this expression instead of Eq. (11), one can calculate the average dipole and quadrupole moments. This calculation yields for $\boldsymbol{Q}$ again Eq. (16), because the terms proportional to $\boldsymbol{E}$ cancel each other. Calculation of the macroscopic polarization $\boldsymbol{P}$ gives the classical result:[14]

$$\boldsymbol{P} = \alpha_P \boldsymbol{E}, \quad \alpha_P = C\alpha_p = C p_0^2 / 3 k_B T, \tag{19}$$

where α_p and α_P are the molecular and the macroscopic polarizabilities.

The derivation above is strictly valid for a gas of solid multipoles. It can be readily generalized to include molecular polarizabilities and quadrupolarizabilities.[13] This yields instead of Eq. (17) the expression

$$\alpha_q = \bar{\alpha}_{q0} + \boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T, \tag{20}$$

where $\bar{\alpha}_{q0}$ is the average intrinsic (atomic + electronic) molecular quadrupolarizability (Eq. 4.5 of Jeon and Kim[13]). Equation (20) can be compared to the well-known formula for the polarizability[14]

$$\alpha_p = \bar{\alpha}_{p0} + p_0^2 / 3 k_B T, \tag{21}$$

where $\bar{\alpha}_{p0}$ is the average intrinsic molecular polarizability. In addition, in the case of liquids one can introduce a Clausius-Mossotti type of relation for the local gradient $\nabla \boldsymbol{E}$ to the macroscopic quadrupole moment density $\boldsymbol{Q}$ and a reaction field (similar to the relation between local field and average macroscopic polarization[14] $\boldsymbol{P}$). The local field is investigated in Refs. 12 and 13. We shall not attempt such a generalization in our study and in what follows we will assume that the equation of state (16) is valid for isotropic fluids, provided that $\boldsymbol{E}$ and $\nabla \boldsymbol{E}$ are not too large (in order Eq. (12) to be applicable). For dense fluids, Eq. (17) for α_Q will be invalid but it still should give the correct order of magnitude of the quadrupolarizability.

Using the values of the quadrupole moment of water from Ref. 37: $q_{xx} = +5.85 \times 10^{-40}$ Cm^2, $q_{yy} = -5.56 \times 10^{-40}$ Cm^2, and $q_{zz} = -0.29 \times 10^{-40}$ Cm^2 (a factor of 2/3 for the different definitions of $\boldsymbol{q}_0$ used here and in Ref. 37 must be accounted for), we can calculate the value $\alpha_Q = 1 \times 10^{-30}$ Fm from Eq. (17). Both $\bar{\alpha}_{q0}$ and the Clausius-Mossotti effect increase α_Q. For comparison, the experimental value for the polarizability of water is $\alpha_P = \varepsilon - \varepsilon_0 = 6.8 \times 10^{-10}$ F/m, which is about 3 times higher than the one calculated through the estimation $\alpha_P = C p_0^2 / 3 k_B T$. By analogy, we can assume that α_Q is several times larger than the value following from Eq. (17).

Let us now estimate the pressure and temperature derivatives of α_Q. Assuming that the molecular quadrupolarizability α_q is independent on p, from Eq. (17) it follows that

$$\frac{1}{\alpha_Q} \left(\frac{\partial \alpha_Q}{\partial p} \right)_T \approx \frac{1}{C} \left(\frac{\partial C}{\partial p} \right)_T = \beta_T, \tag{22}$$

where β_T is the isothermal compressibility. Since Eq. (17) is approximate, the resulting equation (22) also gives only an estimate of $\partial \alpha_Q / \partial p$. For the temperature derivative of α_Q (suitably made dimensionless by a factor of T/α_Q), we use Eq. (20) for the dependence of the molecular quadrupolarizability on temperature and the relation $\alpha_Q = C\alpha_q$ to obtain

$$\frac{T}{\alpha_Q} \left(\frac{\partial \alpha_Q}{\partial T} \right)_p = \frac{T}{C} \left(\frac{\partial C}{\partial T} \right)_p + \frac{T}{\alpha_q} \left(\frac{\partial \alpha_q}{\partial T} \right)_p$$
$$= -T\alpha_p^v - \frac{\boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T}{\bar{\alpha}_{q0} + \boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T}. \tag{23}$$

Here, $\alpha_p^v = -C^{-1}(\partial C/\partial T)_p$ is the coefficient of thermal expansion. For water,[46] $T\alpha_p^v = 0.0763$. To estimate the second term, we assume that $\bar{\alpha}_{q0} \ll \boldsymbol{q}_0 : \boldsymbol{q}_0 / 10 k_B T$ (water has high quadrupole moment $\boldsymbol{q}_0$ and it is a "hard" molecule of low

intrinsic polarizability $\bar{\alpha}_{p0}$ and perhaps low $\bar{\alpha}_{q0}$). In this limit, the second term in Eq. (23) is about -1, much larger in absolute value than $T\alpha_p^v$. Therefore, we can write approximately that

$$\frac{T}{\alpha_Q}\frac{\partial \alpha_Q}{\partial T} = -1. \tag{24}$$

III. BOUNDARY CONDITIONS FOR THE GENERALIZED POISSON EQUATION

Within the quadrupolar approximation, the Coulomb-Ampere law (7) is of fourth order with respect to ϕ since upon substituting Eq. (16) in Eq. (7), one obtains

$$\nabla \cdot \left[\varepsilon \boldsymbol{E} - \frac{1}{2}\nabla \cdot \alpha_Q(\nabla \boldsymbol{E} - \mathbf{U}\nabla \cdot \boldsymbol{E}/3)\right] = \rho(\phi). \tag{25}$$

In a homogeneous medium, this equation simplifies to

$$\nabla \cdot \boldsymbol{E} - \frac{\alpha_Q}{3\varepsilon}\nabla^2\nabla \cdot \boldsymbol{E} = -\nabla^2\phi + L_Q^2\nabla^4\phi = \frac{\rho(\phi)}{\varepsilon}. \tag{26}$$

Here, we have introduced the *quadrupolar length* L_Q defined with the relation

$$L_Q^2 = \alpha_Q/3\varepsilon. \tag{27}$$

From the estimation of α_Q in the end of Sec. II, we can say that $L_Q = (\alpha_Q/3\varepsilon)^{1/2} > 0.2$ Å, perhaps several times larger. Equations. (26) and (27) are of the same form as those of Chitanvis,[12] with the only difference of the obtained different numerical coefficient in Eq. (27). We are mainly concerned with spherical symmetry in this study, where Eq. (26) reads

$$\frac{1}{r^2}\frac{\mathrm{d}r^2 E_r}{\mathrm{d}r} - \frac{L_Q^2}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}}{\mathrm{d}r}\frac{1}{r^2}\frac{\mathrm{d}r^2 E_r}{\mathrm{d}r} = \frac{\rho(r)}{\varepsilon}. \tag{28}$$

We will need an explicit expression for $\boldsymbol{Q}$ and $\nabla \cdot \boldsymbol{Q}$; the gradient and the divergence of $\boldsymbol{E}$ in spherical coordinates are given by

$$\nabla \boldsymbol{E} = \begin{pmatrix} \mathrm{d}E_r/\mathrm{d}r & 0 & 0 \\ 0 & E_r/r & 0 \\ 0 & 0 & E_r/r \end{pmatrix}; \quad \nabla \cdot \boldsymbol{E} = \frac{\mathrm{d}E_r}{\mathrm{d}r} + \frac{2E_r}{r}. \tag{29}$$

Then from Eq. (16), one obtains

$$\boldsymbol{Q} = \frac{\alpha_Q}{3}\left(\frac{\mathrm{d}E_r}{\mathrm{d}r} - \frac{E_r}{r}\right)\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$\nabla \cdot \boldsymbol{Q} = \frac{2\alpha_Q}{3}\left(\frac{\mathrm{d}^2 E_r}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}E_r}{\mathrm{d}r} - \frac{2E_r}{r^2}\right)\mathbf{e}_r, \tag{30}$$

where $\mathbf{e}_r$ is a unit vector, collinear with the radius-vector.

The boundary conditions of Eq. (7) have been derived recently by Graham and Raab,[39] using the singular distributions approach of Bedeaux *et al.*[47,48] in the case of a flat boundary surface of an anisotropic medium with arbitrary equation of state; alternative derivation, again for flat boundary, was given in Ref. 40. Following the approach of Graham and Raab, we will deduce here the boundary conditions of Eq. (7) at a *spherical* surface dividing two isotropic phases. First, we write the singular distributions of $\varepsilon\boldsymbol{E}$, $\boldsymbol{Q}$, and ρ:

$$\varepsilon\boldsymbol{E} = \eta^+\varepsilon^+\boldsymbol{E}^+ + \eta^-\varepsilon^-\boldsymbol{E}^-,$$

$$\boldsymbol{Q} = \eta^+\boldsymbol{Q}^+ + \eta^-\boldsymbol{Q}^-,$$

$$\rho = \eta^+\rho^+ + \eta^-\rho^- + \delta\rho^{\mathrm{S}}. \tag{31}$$

Here, X^+ and X^- denote the corresponding physical quantities for the phase situated at $r > R$ and $r < R$, respectively; ρ^{S} is the surface charge density; the notations $\eta^{\pm}$ and δ stand for the Heaviside function η and the Dirac δ-function:

$$\eta^+ = \eta(r - R); \quad \eta^- = \eta(R - r); \quad \delta = \delta(r - R). \tag{32}$$

To obtain the necessary boundary conditions, we insert Eq. (31) into Eq. (7) and use the irreducibility of $\eta^{\pm}$, δ and its derivative $\delta_1 = \mathrm{d}\delta/\mathrm{d}r$. We need first to calculate $\nabla \cdot \varepsilon\boldsymbol{E}$ and $\nabla\nabla{:}\boldsymbol{Q}$, where $\varepsilon\boldsymbol{E}$ and $\boldsymbol{Q}$ are given by Eq. (31):

$$\nabla \cdot \varepsilon\boldsymbol{E} = \eta^+\nabla \cdot \varepsilon^+\boldsymbol{E}^+ + \eta^-\nabla \cdot \varepsilon^-\boldsymbol{E}^- + \delta\left(\varepsilon^+ E_r^+ - \varepsilon^- E_r^-\right),$$

$$\begin{aligned} \nabla\nabla{:}\boldsymbol{Q} = &\ \eta^+\nabla\nabla{:}\boldsymbol{Q}^+ + \delta\mathbf{e}_r \cdot (\nabla \cdot \boldsymbol{Q}^+) \\ &+ \delta\nabla \cdot (\mathbf{e}_r \cdot \boldsymbol{Q}^+) + \delta_1 Q_{rr}^+(r) \\ &+ \eta^-\nabla\nabla{:}\boldsymbol{Q}^- - \delta\mathbf{e}_r \cdot (\nabla \cdot \boldsymbol{Q}^-) - \delta\nabla \cdot (\mathbf{e}_r \cdot \boldsymbol{Q}^-) \\ &- \delta_1 Q_{rr}^-(r). \end{aligned} \tag{33}$$

Using Eqs. (33), we can write Eq. (7) in the form

$$\begin{aligned} & \eta^+\left[\nabla \cdot \left(\varepsilon^+\boldsymbol{E}^+ - \frac{1}{2}\nabla \cdot \boldsymbol{Q}^+\right) - \rho^+\right] \\ & + \eta^-\left[\nabla \cdot \left(\varepsilon^-\boldsymbol{E}^- - \frac{1}{2}\nabla \cdot \boldsymbol{Q}^-\right) - \rho^-\right] \\ & - \delta\left\{\begin{aligned} & \rho^{\mathrm{S}} - \left[\varepsilon^+ E_r^+ - \frac{1}{2}\mathbf{e}_r \cdot (\nabla \cdot \boldsymbol{Q}^+) - \frac{1}{2}\nabla \cdot (\mathbf{e}_r \cdot \boldsymbol{Q}^+) + \frac{1}{2}\frac{\mathrm{d}Q_{rr}^+}{\mathrm{d}r}\right] \\ & + \left[\varepsilon^- E_r^- - \frac{1}{2}\mathbf{e}_r \cdot (\nabla \cdot \boldsymbol{Q}^-) - \frac{1}{2}\nabla \cdot (\mathbf{e}_r \cdot \boldsymbol{Q}^-) + \frac{1}{2}\frac{\mathrm{d}Q_{rr}^-}{\mathrm{d}r}\right] \end{aligned}\right\}_{r=R} \\ & - \delta_1\frac{1}{2}\left(Q_{rr}^+(R) - Q_{rr}^-(R)\right) = 0. \end{aligned} \tag{34}$$

For the derivation of Eqs. (33) and (34), we have used the properties of the singular functions: $\nabla \eta^+ = \mathbf{e}_r \delta$; $\nabla \eta^- = -\mathbf{e}_r \delta$; $\nabla \delta = \mathbf{e}_r \delta_1$; $\delta_1 Q_{rr}(r) = \delta_1 Q_{rr}(R) - \delta dQ_{rr}/dr|_{=R}$. Decomposition of Eq. (34) yields, first, the bulk equations for the two phases (the coefficients of $\eta^{\pm}$ in Eq. (34)):

$$\nabla \cdot \left(\varepsilon^+ \mathbf{E}^{\pm} - \frac{1}{2} \nabla \cdot \mathbf{Q}^{\pm} \right) = \rho^{\pm}. \tag{35}$$

Setting the factor multiplying δ in Eq. (34) to 0, we obtain a generalization of the Gauss law for the quadrupolar media:

$$\left[\varepsilon^+ E_r^+ - \frac{1}{2} \mathbf{e}_r \cdot (\nabla \cdot \mathbf{Q}^+) - \frac{1}{2} \nabla \cdot (\mathbf{e}_r \cdot \mathbf{Q}^+) + \frac{1}{2} \frac{dQ_{rr}^+}{dr} \right]_{r=R}$$
$$- \left[\varepsilon^- E_r^- - \frac{1}{2} \mathbf{e}_r \cdot (\nabla \cdot \mathbf{Q}^-) - \frac{1}{2} \nabla \cdot (\mathbf{e}_r \cdot \mathbf{Q}^-) + \frac{1}{2} \frac{dQ_{rr}^-}{dr} \right]_{r=R}$$
$$= \rho^{\mathrm{S}}. \tag{36}$$

The last term of Eq. (34), proportional to δ_1, results in a new boundary condition, which balances the quadrupole moment densities on the two sides of the spherical surface:

$$Q_{rr}^+(R) - Q_{rr}^-(R) = 0. \tag{37}$$

We now substitute Eqs. (30) into Eqs. (36) and (37) to obtain the explicit form of the boundary conditions. Equation (36) reads

$$\rho^{\mathrm{S}} = \left[\varepsilon^+ E_r^+ - \frac{\alpha_Q^+}{3} \left(\frac{d^2 E_r^+}{dr^2} + \frac{2}{r} \frac{dE_r^+}{dr} - \frac{2E_r^+}{r^2} \right) - \frac{\alpha_Q^+}{3} \frac{2}{r} \left(\frac{dE_r^+}{dr} - \frac{E_r^+}{r} \right) \right]_{r=R}$$
$$- \left[\varepsilon^- E_r^- - \frac{\alpha_Q^-}{3} \left(\frac{d^2 E_r^-}{dr^2} + \frac{2}{r} \frac{dE_r^-}{dr} - \frac{2E_r^-}{r^2} \right) - \frac{\alpha_Q^-}{3} \frac{2}{r} \left(\frac{dE_r^-}{dr} - \frac{E_r^-}{r} \right) \right]_{r=R}. \tag{38}$$

The explicit form of the new boundary condition (37) is

$$\alpha_Q^+ \left(\frac{dE_r^+}{dr} - \frac{E_r^+}{r} \right)_{r=R} - \alpha_Q^- \left(\frac{dE_r^-}{dr} - \frac{E_r^-}{r} \right)_{r=R} = 0. \tag{39}$$

Subtracting Eq. (38) and Eq. (39), we obtain the relation

$$D_r^+(R) - D_r^-(R) = \rho^{\mathrm{S}}, \tag{40}$$

which is formally equivalent to the classical Gauss law, but one must keep in mind that $\mathbf{D}$ involves higher derivatives of the field $\mathbf{E}$, cf. Eq. (6).

IV. EFFECT OF THE QUADRUPOLARIZABILITY OF A MEDIUM ON THE BORN ENERGIES, PARTIAL MOLAR VOLUMES, AND ENTROPIES OF DISSOLVED IONS

In this part of our study the general equation (28) of electrostatics in quadrupolar media at spherical symmetry and its boundary conditions (38) and (39) derived in Secs. I–III will be used to solve several basic electrostatic problems of high significance to the physical chemistry of electrolyte solutions.

A. Point charge in an insulator

We solve Eq. (28) with $\rho = e_i \delta(\mathbf{r})$. The general solution of the equation is

$$E = \frac{1}{r^2} \left[k_1 + k_2 \left(1 + \frac{r}{L_Q} \right) \exp \left(-\frac{r}{L_Q} \right) \right.$$
$$\left. + k_3 \left(1 - \frac{r}{L_Q} \right) \exp \left(\frac{r}{L_Q} \right) \right]. \tag{41}$$

In order to determine the three integration constants k_1, k_2, and k_3, we need to impose three conditions on E. The first one is to require E to tend to a finite value as $r \to \infty$ (this gives $k_3 = 0$). The second condition is that the asymptotic behavior of E at $r \to \infty$ is unaffected by the presence of quadrupoles, that is, the field of a point charge at $r \to \infty$ tends to $e_i/4\pi\varepsilon r^2$. This condition yields $k_1 = e_i/4\pi\varepsilon$ (the same result can be obtained by the Gauss law). There is one final condition needed to determine k_2. Our assumption is to require that E tends to something finite as $r \to 0$, i.e., there is no singularity of E at $r \to 0$, which yields $k_2 = -k_1$. Equation (28) has, thus, a *finite* solution, which is

$$E = \frac{e_i}{4\pi\varepsilon} \frac{1}{r^2} \left[1 - \left(1 + \frac{r}{L_Q} \right) \exp \left(-\frac{r}{L_Q} \right) \right]. \tag{42}$$

Integration of this result gives the following formula for the electrostatic potential:

$$\phi = \frac{e_i}{4\pi\varepsilon} \frac{1 - \exp(-r/L_Q)}{r}. \tag{43}$$

The potential in $r = 0$ is also finite, and its value at $r = 0$ is $\phi_0 = e_i/4\pi\varepsilon L_Q$. The ion has, therefore, a finite energy:

$$u_{\mathrm{el}} = e_i \phi_0 / 2 = e_i^2 / 8\pi\varepsilon L_Q. \tag{44}$$

This is in marked contrast to the case of ion in vacuum where the potential is diverging as $1/r$ and the electrostatic self-energy of a point charge is infinite (Fig. 1). For a point charge in water at $T = 25\,^{\circ}\mathrm{C}$, if $L_Q = 2$ Å, we obtain $\phi_0 = 92$ mV and $u_{\mathrm{el}} = 3.6 \times k_{\mathrm{B}}T$. Equation 2.8 of Chitanvis[12] has the same form as Eq. (43) (but his relation between L_Q and α_Q is different). Equation (43) can be compared also to Eq. 2.48 of
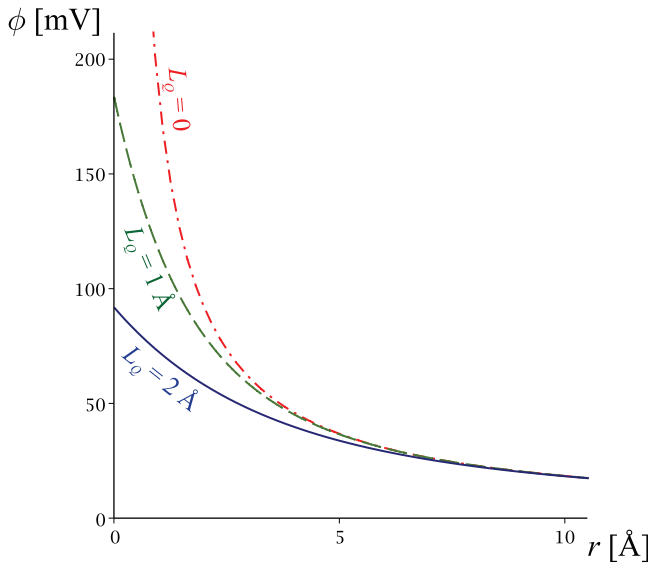
FIG. 1. Electrostatic potential ϕ of a point charge in a quadrupolar medium vs. the distance r from the point charge e in water, Eq. (43), for various quadrupolar lengths L_Q. In a quadrupolar medium, the point charge has finite potential at $r = 0$. Solid line: $L_Q = 2$ Å; dashed line: $L_Q = 1$ Å; dashed-dotted line: $L_Q = 0$ (the classical solution).

Jeon and Kim,[13] who obtained a divergent potential since they used another constitutive relation for **Q** and implied different conditions on their solutions to determine the integration constants. In order to corroborate our non-classical choice for the finite field condition, a different approach will be presented in Sec. IV B to derive the same result (43), by placing the charge into a spherical cavity of radius R (at $r = R$ the boundary conditions derived in Sec. III will be applied) and then taking the limit $R \to 0$ of the resulting potential.

B. Ion of finite size in an insulator

There are various models of an ion of finite size in a solution, which yield the same expression for the Born energy.[49,28,40] The simplest model assumes that the ion is a point charge e_i situated into a *cavity*, i.e., in an empty sphere of permittivity ε_0 and radius R_{cav}; the empty sphere is located in a medium of dielectric permittivity ε. This model neglects the detailed charge distribution in the ion and can be generalized in various ways.[12,13,17,21,22,27–32,50–52] Here, in order to keep the picture simple, we will hold on to the empty sphere model, only adding into account the quadrupolarizability α_Q of the medium. Similar problem (an entity of certain charge distribution placed into a cavity in a medium with intrinsic quadrupolarizability) was considered by Chitanvis[12] and Jeon and Kim[13] using different equations of state and a different set of boundary conditions.

We formulate the problem with the following equations:

(i) Inside the sphere (superscript "i"), at $r < R_{cav}$, there are no charges, bound or free, apart from the central ion of charge e_i:

$$\varepsilon_0 \nabla \cdot \boldsymbol{E}^{\mathrm{i}} = e_i \delta(\boldsymbol{r}). \qquad (45)$$

(ii) Outside the sphere (no superscript), at $r > R_{cav}$, Eq. (28) is valid with $\rho = 0$:

$$\frac{1}{r^2} \frac{\mathrm{d} r^2 E_r}{\mathrm{d} r} - \frac{L_Q^2}{r^2} \frac{\mathrm{d}}{\mathrm{d} r} r^2 \frac{\mathrm{d}}{\mathrm{d} r} \frac{1}{r^2} \frac{\mathrm{d} r^2 E_r}{\mathrm{d} r} = 0. \qquad (46)$$

(iii) The boundary conditions at $r = R_{cav}$ are given by Eqs. (38) and (39):

$$E_r - \frac{\varepsilon_0}{\varepsilon} E_r^{\mathrm{i}} - L_Q^2 \left(\frac{\mathrm{d}^2 E_r}{\mathrm{d} r^2} + \frac{2}{r} \frac{\mathrm{d} E_r}{\mathrm{d} r} - \frac{2 E_r}{r^2} \right) \Bigg|_{r = R_{cav}} = 0, \qquad (47)$$

$$\left(\frac{\mathrm{d} E_r}{\mathrm{d} r} - \frac{E_r}{r} \right)_{r = R_{cav}} = 0. \qquad (48)$$

The solution of Eqs. (45)–(48) in terms of the electrostatic potential is

$$\phi^{\mathrm{i}} = \frac{e_i}{4\pi \varepsilon_0} \frac{1}{r} - \frac{e_i}{4\pi R_{cav}}$$
$$\times \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon} \frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2} \right) \text{ at } r < R_{cav}, \qquad (49)$$

$$\phi = \frac{e_i}{4\pi \varepsilon} \frac{1}{r}$$
$$\times \left\{ 1 - \frac{3L_Q^2 \exp[-(r - R_{cav})/L_Q]}{R_{cav}^2 \left(1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2 \right)} \right\} \text{ at } r > R_{cav}, \qquad (50)$$

we used also the condition $\phi = \phi^{\mathrm{i}}$ at $r = R_{cav}$. As $R_{cav} \to 0$, Eq. (50) for ϕ simplifies to Eq. (43) for a point charge, which justifies the assumption for finite E and ϕ at $r \to 0$ which was used in Sec. IV A to derive Eq. (43) – that is, the results obtained in Sec. IV A can be obtained alternatively by taking the limit from Eq. (50) without making use of such a non-classical condition.

The self-energy u_{el} of the ion is determined by the potential $\Delta\phi^{\mathrm{i}} = \phi^{\mathrm{i}} - e_i/4\pi \varepsilon_0 r$, created by the polarized medium and acting upon the ion. It is obtained from Eq. (49) as

$$u_{el} = \frac{1}{2} e_i \Delta\phi^{\mathrm{i}}$$
$$= -\frac{e_i^2}{8\pi R_{cav}} \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon} \frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2} \right). \qquad (51)$$

It can be compared to Eq. 3.1 of Chitanvis,[12] who used instead of our equation (48) a condition for continuity of $\mathrm{d}E_r/\mathrm{d}r$ at $r = R_{cav}$, without discussion. Jeon and Kim[13] used another condition – for non-oscillatory solution, also with no good justification. When $L_Q \to 0$, Eq. (51) simplifies to the familiar expression for the Born energy:[49,50]

$$u_{Born} = -\frac{e_i^2}{8\pi R_{cav}} \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon} \right). \qquad (52)$$
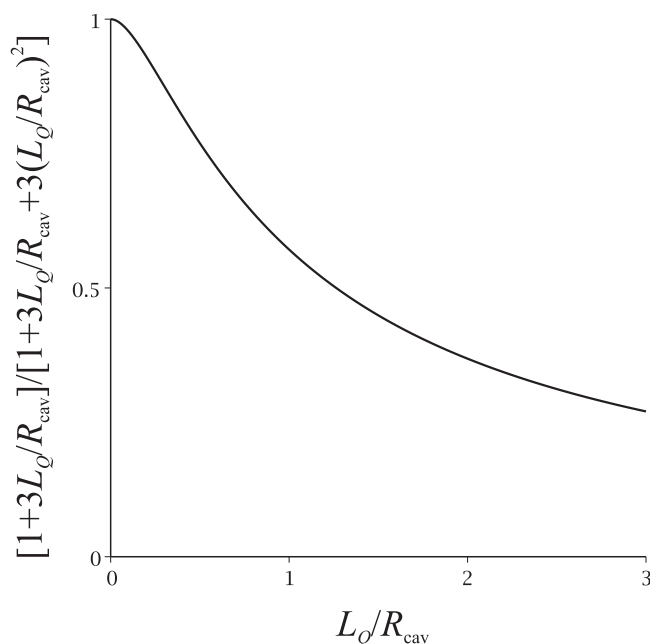
FIG. 2. Correction factor for the effect of the quadrupolarizability in the modified Born Eq. (51) as a function of L_Q/R_{cav}.

It can be shown that any other charge distribution of spherical symmetry and total charge e_i placed into the cavity will have the same Born energy (51) provided that this charge distribution is fixed (independent of the medium).[40] In supplementary material B,[66] we demonstrate this with another common Born model, where the ion is assumed to be a metal sphere of surface charge density $\rho^S = e_i/4\pi R_i^2$.

It follows from Eq. (51) that the Born energy of small ions is more strongly affected from the quadrupolarizability of the medium – this is illustrated in Fig. 2, where the factor multiplying $1/\varepsilon$ in Eq. (51) is plotted as a function of L_Q/R_{cav}. However, the effect of quadrupolarizability on the Born energy itself is negligibly small, at least for aqueous solutions: the $1/\varepsilon_0$ term is by far larger than the second term in the brackets of Eq. (51), which involves L_Q. For this reason, the obtained result (51) for the effect of L_Q on the self-energy u_{el} is not easy to test directly. In order to show the significance of the L_Q term in Eq. (51), we will eliminate the large term $1/\varepsilon_0$ using two different approaches: (i) By differentiating u_{el} either with respect to p or T in Secs. IV D and IV E, and comparing the results with experimental data for ionic partial molar volumes and entropies; (ii) By investigating in Sec. IV G the transfer energy of an ion from aqueous to polar oil solution (in this transfer energy, the $1/\varepsilon_0$ term cancels). This will allow us to give an estimate for the quadrupolar length L_Q and the quadrupolarizability α_Q of water and the polar oil. However, the correct assessment of L_Q requires the knowledge of the relation between the cavity radius R_{cav} and the crystallographic radius of the ion, R_i; this problem will be investigated in Sec. IV C.

C. Ion free energy of hydration

The standard molarity-based chemical potential μ_{0i} (corresponding to a standard concentration $C_0 = 1$ M) reflects the

state of a single ion in the solution, including the effect of the ion's field on the molecules of the solvent in the vicinity of the ion. For this energy one can write[2, 17, 22, 53]

$$\mu_{0i} = \mu_{intra}(T) + u_{el} + pv_0 + k_B T \ln C_0. \quad (53)$$

The first term in Eq. (53), μ_{intra}, is related to the intramolecular state of the ion itself. For simple ions, it is a common approximation that this term is the same in gaseous state and in any solvent. The second term, u_{el}, stands for the electrostatic ion-water interaction; we will use for u_{el} the generalized expression for the Born energy of the ion, Eq. (51), involving the quadrupolar length L_Q. The third term, pv_0, is the mechanic work for introducing an ion of radius R_i into a medium at pressure p. The fourth term, $k_B T \ln C_0$, originates from the choice of the standard state. The electrostatic term u_{el} is several orders of magnitude larger than the others in Eq. (53); however, we will see in Secs. IV D–IV E that the derivatives of μ_{0i} have non-negligible contributions from pv_0 and $k_B T \ln C_0$. Other contributions to the hydration energy, such as the energy for cavity formation[53] and various specific interactions,[51, 52] are here neglected for simplicity. This makes Eq. (53) and its derivatives inapplicable to large ions. Since the quadrupolar electrostatic effects we are investigating are significant for small ions only, this is not a drawback, but all data for molar hydration energies and partial molar volumes for ions larger than 3.2 Å will be neglected below. Hydrophobic effect is especially important for the partial molar entropy,[54] therefore, only entropy data for ions smaller than 2.3 Å will be taken into account. The full list of data-points is given in the supplementary material D.[66]

The standard free energy of hydration of an ion $\Delta\mu_{0i} = \mu_{0i} - \mu_{0i}^G$ is the energy for transfer of an ion from a hypothetical ideal gas at standard pressure p_0 to a hypothetical ideal 1M solution.[55] Neglecting the small contribution from pv_0, we can write

$$\Delta\mu_{0i} = k_B T \ln \frac{k_B T C_0}{p_0} - \frac{Z_i^2 e^2}{8\pi R_{cav}}$$
$$\times \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon} \frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2} \right). \quad (54)$$

The first term stands for the choice of standard states in the aqueous solution (hypothetical ideal solution with concentration $C_0 = 1$M $= 1000 \times N_A$ m^{-3}, N_A – Avogadro's number) and in the gas state (ideal gas of ions at standard pressure $p_0 = 101325$ Pa). Its value is rather small (7.9 kJ/mol) but still of the order of the contribution of the $1/\varepsilon$ term in the Born energy. The electrostatic energy in the gas (the $1/\varepsilon_0$ term in the brackets) is about 100 times larger than the respective energy in the solution (the term proportional to $1/\varepsilon$). Therefore, our expression (54) for $\Delta\mu_{0i}$ yields essentially the same results for the value of $\Delta\mu_{0i}$ as the one of Born who did not account for L_Q, i.e., the quadrupolarizability of the medium has virtually no effect on the hydration energy itself. We will discuss $\Delta\mu_{0i}$ here only in relation to our choice of model for the dielectric cavity radius R_{cav} in Eq. (51) and its relation to the crystallographic radius R_i of the ion. Latimer et al.[50] found that the experimental data for $\Delta\mu_{0i}$ agree well with the
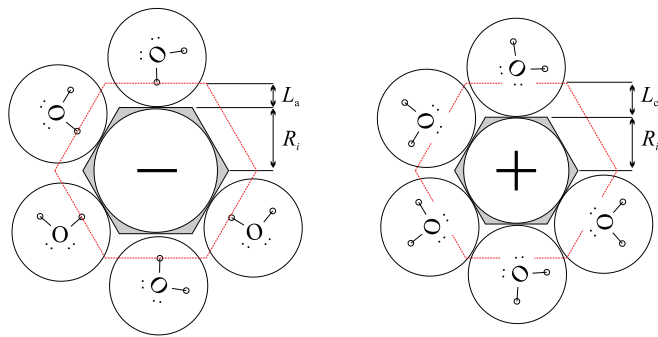
FIG. 3. Scheme of hydrated anion and cation. The lengths L_a and L_c reflect the distance between the ion and the precise position of the partial charges in the water molecule (water's hydrogen atom in the anion hydration shell or water's electron pair in the cation shell). The grey hexagons circumscribing the ions mark their partial molar volume v_0 in the absence of electrostriction (the difference between v_0 and $4/3 \, \pi R_i^3$ is accounted for by the packing factor g_V, cf. Eq. (60)). The outer hexagons mark the volume v_{cav} of the "dielectric" cavity.

assumption that

$$R_{cav,c} = R_i + L_c \quad \text{and} \quad R_{cav,a} = R_i + L_a \qquad (55)$$

for cations and anions, respectively. Latimer *et al.* obtained L_c = 0.85 Å and L_a = 0.1 Å, using data for the free energies for hydration $\Delta\mu_{0i}$ of several monovalent ions. Their interpretation of these values was that L_a reflects the distance between the anion and a proton from H_2O in its hydration shell, while L_c is the distance between a cation and the electron pair of an oxygen atom, cf. Fig. 3. Rashin and Honig[56] argued that R_i + L_c is, in fact, the covalent radius of the cation. Blum and Fawcett[57,58] related L_a and L_c to the dielectric constant of water using an estimation based on the so-called Wertheim equation. The length L_c was found to be the same for all cations, and L_a is the same for all anions.[50,56,58]

We assume a slightly different model of the cavity size which accounts for the packing factor g_V of the water molecules in the first hydration shell of the ion[††]. This packing factor is standing for the fact that the real volume occupied by the ion is not a sphere (of volume $4/3 \, \pi R_i^3$) but rather a polyhedron (cf. Fig. 3). The water molecules in the pure liquid have a packing factor of $g_{V,w}$ = 2.7 (the molecular volume v_w = 29.9 Å³ following from the density of liquid water divided by the volume 11.2 Å³ of a single H_2O molecule with radius R_w = 1.39 Å); this is close to the packing factor of a diamond crystal structure, due to the tetrahedral structure of the first neighbors shell in both cases. It can be expected that the molecules in the hydration shell of an ion will be packed more densely, so that g_V will be of the order of the packing factor corresponding to hexagonal lattice, g_V = 1.35, or body-centered cubic, 1.47. The packing factor probably decreases with the ion radius, but we will assume for simplicity that g_V is approximately independent of R_i and it has the same value of about 1.35 for all ions studied. The volume of the cavity around an ion, instead of being $v_{cav,c} = 4/3\pi(R_i + L_c)^3$ and $v_{cav,a} = 4/3\pi(R_i + L_a)^3$ as in the model of Latimer-Pitzer-Slansky, must be corrected for the packing factor:

$$v_{cav,c} = 4/3\pi g_V(R_i + L_c)^3 \quad \text{and} \quad v_{cav,a} = 4/3\pi g_V(R_i + L_a)^3 \qquad (56)$$

(outer hexagons in Fig. 3). These values of v_{cav} correspond to the following effective radii of a sphere of the same volume:

$$R_{cav,c} = g_V^{1/3}(R_i + L_c) \quad \text{and} \quad R_{cav,a} = g_V^{1/3}(R_i + L_a) \qquad (57)$$

for anions and cations, respectively. Equations (57) yield slightly better agreement with the experiment than Eqs. (55), and more importantly, they allow the cavity radius to have certain compressibility through g_V, cf. Sec. IV D.

We tested both Latimer *et al.*'s model, Eq. (55), and our equation (57) by fitting the data for $\Delta\mu_{0i}$ taken from Refs. 55 and 53. We were, thus, able to determine the values of L_c and L_a. Data-points for large ions as well as certain ions of high polarizability or dipole moments were neglected (cf. supplementary material D[66] for the list). The merit function, measuring the mean square difference between the theoretical and experimental hydration energies, is defined as

$$\sigma_{\Delta\mu}^2(L_c, L_a)$$

$$= \frac{\sum\limits_{Z=1}^{4} \sum\limits_{i} [\Delta\mu_{0i,th}(Z, R_i; L_c, L_a) - \Delta\mu_{0i,exp}(Z, R_i)]^2}{N - f}, \qquad (58)$$

where $\Delta\mu_{0i,th}$ is the predicted value according to Eq. (54) of an ion of valence Z and bare radius R_i; $\Delta\mu_{0i,exp}$ is the respective experimental value; N = 86 is the number of data points, and f is the number of free parameters used in the optimization procedure. For R_{cav} we used either Eq. (55) or (57); in the second case, we assumed that g_V = 1.35 (as a first approximation; cf. Sec. IV F for a direct determination of g_V) and L_Q = 1 Å. The merit function is almost independent on L_Q, so the second value is unimportant for the result for L_c and L_a.

The results from the minimization of $\sigma_{\Delta\mu}$ with respect to L_c, L_a are given in Table I. There, the performance of Latimer *et al.* formula (55) (row a) is compared with our equation (57) accounting for the packing factor (row b). The two models have almost identical deviations from the experimental hydration energies (151.0 vs. 149.6 kJ/mol). The use of the new Eq. (57) leads to smaller values of L_c and L_a. The obtained value of L_c in row b compares well with the distance between a cation and an electron pair of the oxygen atom (cf. Fig. 3): using R_w = 1.39 Å for the effective radius of a water molecule and 0.7 Å for the distance between the oxygen atom in the water molecule and its electron pair (according to the TIP5P model[59]), one obtains L_c = 0.69 Å, coinciding with the value L_c = 0.69 ± 0.05 Å obtained from the fit with our model for $R_{cav,c}$. The value of L_a that follows from TIP5P model of water is L_a = 1.39–0.96 = 0.43 Å (where 0.96 Å is the length of the OH bond[59]), while the fit with both models suggests that L_a is zero, within the error (±0.15 Å). Most probably, this difference is due to the neglected contribution of van der Waals energy to $\Delta\mu_{0i}$: anions have higher polarizabilities and the dispersion ion-solvent interactions lead to a significant decrease of their free energy in water,[51,52] which is partly compensated in the model we use by the lower value of L_a.

The comparison between the experimental data and the predictions of Eq. (54) with R_{cav} obtained from Eq. (57) is

TABLE I. Values of L_c, L_a, L_Q, g_V, $\partial g_V/\partial p$, and $\partial g_V/\partial T$ obtained from the fit of the experimental data for the hydration energies, partial molar volumes, and the hydration entropies of various ions with the theoretical expressions, Eqs. (54), (64) and (68).

(a) Standard molar hydration energies, model of Latimer, Pitzer, and Slansky, Eqs. (54) and (55)						
f	L_c (Å)	L_a (Å)	L_Q (Å)			$\sigma_{\Delta\mu}$ (kJ/mol)
2	0.83	0.14	0^a			151.0
(b) Standard molar hydration energies, R_{cav} corrected for the packing factor g_V, Eqs. (54) and (57)						
f	L_c (Å)	L_a (Å)	L_Q (Å)	g_V		$\sigma_{\Delta\mu}$ (kJ/mol)
2	0.69	~ 0	1^a	1.35^a		149.6
(c) Ionic partial molar volumes at infinite dilution, Eq. (64)						
f	L_c (Å)	L_a (Å)	L_Q (Å)	g_V	$1/g_V \times \partial g_V/\partial p$ (1/Pa)$\times 10^{10}$	σ_v (ml/mol)
2	0.69*	0^a	1.8	1.35^a	−0.37	12.5
(d) Standard molar hydration entropies, Eq. (72)						
f	L_c (Å)	L_a (Å)	L_Q (Å)	g_V	$T/g_V \times \partial g_V/\partial T$	σ_s (J/Kmol)
2	0.69^a	0^a	1.3	1.35^a	0.082	53.1
(e) Simultaneous minimization of σ_μ, σ_v, and σ_s, Eq. (75)						
f	L_c (Å)	L_a (Å)	L_Q (Å)	g_V	$1/g_V \times \partial g_V/\partial p$ (1/Pa) $\times 10^{10}$	$T/g_V \times \partial g_V/\partial T$
6	0.68	~ 0	2.5	1.39	−0.40	0.092
					$\sigma_{\Delta\mu} = 150.4$ kJ/mol, $\sigma_v = 12.3$ ml/mol, $\sigma_s = 53.2$ J/Kmol	
(f) Ion transfer energies from nitrobenzene to water						
f	L_c^O (Å)	L_a^O (Å)	L_Q^O (Å)	g_V^O		$\sigma_{\Delta\mu}$ (kJ/mol)
4	0.71	0.08	3.8	1.54		8.8

^{a}Fixed value (not used as an adjustable parameter in the optimization procedure).

illustrated in Fig. 4. The accuracy of Eq. (54) ranges from ±15% for monovalent ions to ±3% for tri- and tetravalent. Data for ions of large charge follow the theoretical predictions better, most probably because the neglected non-electrostatic
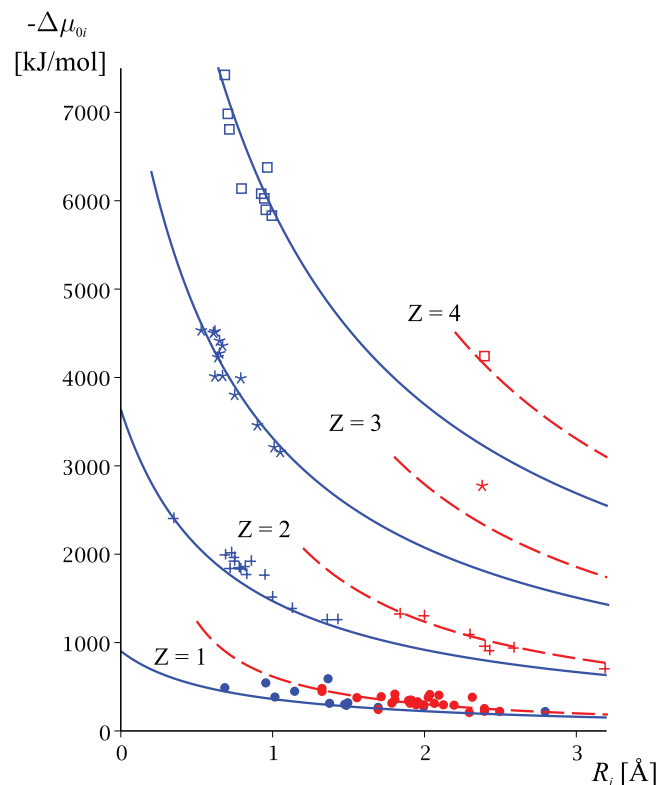

FIG. 4. Molar hydration energy $-\Delta\mu_{0i}$ vs. bare ion radii R_i. Data for cations (blue) and anions (red) of various valence (circles – monovalent, crosses – divalent, stars – trivalent, squares – tetravalent). The lines are drawn according to the theoretical prediction from Eqs. (54) and (57), with $L_c = 0.69$ Å and $L_a = 0$ Å, as obtained from the minimization of $\sigma_{\Delta\mu}$, Eq. (58), at fixed values of g_V and L_Q ($g_V = 1.35$, $L_Q = 1$ Å).

contributions to $\Delta\mu_{0i}$ become less important compared to $u_{el} \propto Z_i^2$. The good coincidence observed in Fig. 4 confirms the assumption of Latimer *et al.* that the lengths L_c and L_a are independent of the ion size, and also proves their independence of the ion valence as well.

Although Eq. (54) is in satisfactory agreement with the experimental data, one must keep in mind it is an oversimplified model of an ion in a medium. The strongest assumption used in its derivation is that the continual model neglects the discrete nature of the solvent-ion interactions. The expression for the Born energy was corrected by many authors in order to take an explicit account for the discrete structure of matter (cf. Chapter 5.7 of Ref. 17 for a summary). The homogeneity condition $\nabla\varepsilon = 0$ has been criticized, e.g., by Abe;[28] the effect of dielectric saturation has been analyzed by Laidler and Pegis.[26] Nonlocal electrostatic theory was applied to the self-energy problem by Basilevsky and Parsons[31,32] (note that the presence of $\boldsymbol{Q} \propto \nabla\boldsymbol{E}$ in definition (6) of the displacement field $\boldsymbol{D}$ makes the electrostatic problems in quadrupolar media nonlocal[13]). Duignan, Parsons, and Ninham[51,52] demonstrated the significance of the specific van der Waals ion-solvent interactions. All these effects contribute to the value of μ_{0i}, but are neglected in our calculations. In addition, the validity of Eq. (16) for liquids is a hypothesis only. Therefore, the comparison of Eq. (53) and its derivatives (Eqs. (64) and (68) below) with the experimental data should be considered with caution.

D. Ion partial molecular volume

The models for the partial molecular volume v_i of ions are reviewed in Ref. 60. We will consider only the values of v_i at infinite dilutions. The partial molecular volume of the ion in aqueous solution is calculated by taking the derivative of the chemical potential $\mu_i = \mu_{0i} + k_B T\ln(C_i/C_0)$, cf.

Eq. (53), with respect to p:

$$v_i = \frac{\partial \mu_i}{\partial p} = v_0 \left(1 + \frac{p}{g_V}\frac{\partial g_V}{\partial p}\right) + k_B T \beta_T + \frac{Z_i^2 e^2}{8\pi \varepsilon_0 R_{cav}^2}\frac{\partial R_{cav}}{\partial p}$$

$$- \frac{Z_i^2 e^2}{8\pi \varepsilon^2 R_{cav}}\frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2}\frac{\partial \varepsilon}{\partial p}$$

$$- \frac{Z_i^2 e^2}{8\pi \varepsilon}\frac{3L_Q}{R_{cav}^3}\frac{2 + 3L_Q/R_{cav}}{\left(1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2\right)^2}\frac{\partial L_Q}{\partial p}. \quad (59)$$

Here, the first term accounts for the volume of the ion and the packing factor g_V (the grey hexagon in Fig. 3):

$$v_0 = 4/3 g_V \pi R_i^3. \quad (60)$$

Note that v_0 is smaller than the "dielectric" volume v_{cav}, which involves the distances L_c and L_a, cf. Eq. (56). The contribution of $v_0 p/g_V \times \partial g_V/\partial p$ is negligible and will be omitted below. In the second term of Eq. (59), $\beta_T = -1/v_w \times \partial v_w/\partial p$ is the compressibility of water; v_w is water's molar volume. The term $k_B T \beta_T$ has a relatively small but measurable contribution to v_i, 1.1 ml/mol. In the third term in Eq. (59) proportional to $\partial R_{cav}/\partial p$, we neglected $1/\varepsilon$ in comparison with $1/\varepsilon_0$. To calculate $\partial R_{cav}/\partial p$, we assume that L_c, L_a, and R_i are independent of pressure, therefore, from Eq. (57) it follows that

$$\frac{\partial R_{cav}}{\partial p} = \frac{R_{cav}}{3 g_V}\frac{\partial g_V}{\partial p}. \quad (61)$$

The fourth term in Eq. (59) (proportional to $\partial \varepsilon/\partial p$) reflects the main electrostriction effect on v_i due to the electric field, while the fifth term (proportional to $\partial L_Q/\partial p$) corresponds to electrostriction due to the electric field gradient. The dependence $\varepsilon(p)$ was determined by direct measurements[61] and allows for the calculation of $\partial \varepsilon/\partial p$; we use the following value:[60]

$$\frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial p} = 4.76 \times 10^{-10}\,\text{Pa}^{-1}. \quad (62)$$

The values of $1/\varepsilon \times \partial \varepsilon/\partial p$ and the compressibility[60] $\beta_T = 4.57 \times 10^{-10}$ Pa^{-1} are very close to each other since ε is almost linear function of the water concentration – compare to Eq. (22) for α_Q. Using Eqs. (22) and (62) we can estimate $\partial L_Q/\partial p$:

$$\frac{1}{L_Q}\frac{\partial L_Q}{\partial p} = \frac{1}{2\alpha_Q}\frac{\partial \alpha_Q}{\partial p} - \frac{1}{2\varepsilon}\frac{\partial \varepsilon}{\partial p} \approx -0.095 \times 10^{-10}\,\text{Pa}^{-1}. \quad (63)$$

It turns out that this value is quite small for aqueous solution and, therefore, we can neglect the $\partial L_Q/\partial p$ term in the expression for v_i.

Leaving only the significant terms in Eq. (59), we obtain

$$v_i = \frac{4}{3}\pi R_i^3 g_V + k_B T \beta_T + \frac{Z_i^2 e^2}{24\pi \varepsilon_0 R_{cav}}\frac{1}{g_V}\frac{\partial g_V}{\partial p}$$

$$- \frac{Z_i^2 e^2}{8\pi \varepsilon^2 R_{cav}}\frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2}\frac{\partial \varepsilon}{\partial p}. \quad (64)$$

If $L_Q = 0$, our expression (64) simplifies to the familiar formula[60] for the partial molar volume v_i following from the

Born energy equation (52):

$$v_i = \frac{4}{3}\pi R_i^3 g_V + k_B T \beta_T + \frac{Z_i^2 e^2}{8\pi \varepsilon_0 R_{cav}^2}\frac{\partial R_{cav}}{\partial p} - \frac{Z_i^2 e^2}{8\pi \varepsilon^2 R_{cav}}\frac{\partial \varepsilon}{\partial p}. \quad (65)$$

The expression (64) predicts the limiting partial molecular volume of an ion at infinite dilutions as a function of its crystallographic radius R_i. While the hydration energy $\Delta \mu_{0i}$ is virtually independent of L_Q, the partial molar volume is sensitive (although relatively weakly) to the value of L_Q, which allows us to use Eq. (64) to determine L_Q from the experimental data. We use the data for cations and anions of various valence assembled by Marcus,[55] neglecting ions of complex structure and large R_i, cf. supplementary material D.[66] The merit function of the optimization procedure is defined as

$$\sigma_v^2 \left(\frac{\partial g_V}{\partial p}, L_Q\right)$$

$$= \frac{\sum_{Z=1}^{4} \sum_i \left[v_{i,th}\left(Z, R_i; \frac{\partial g_V}{\partial p}, L_Q\right) - v_{i,\exp}(Z, R_i)\right]^2}{N - f}, \quad (66)$$

the total number of data-points used in the optimization is N = 97. We used the values $L_c = 0.69$ Å, $L_a = 0$ Å, and $g_V = 1.35$ obtained in Sec. IV C from $\Delta \mu_{0i}$ data, cf. Table I, when calculating $R_{cav,c} = g_V^{1/3}(R_i + L_c)$ and $R_{cav,a} = g_V^{1/3}(R_i + L_a)$.

The comparison between Eq. (64) and the experimental data is illustrated in Fig. 5 (parameters from row c in Table I). The results from the optimization are:
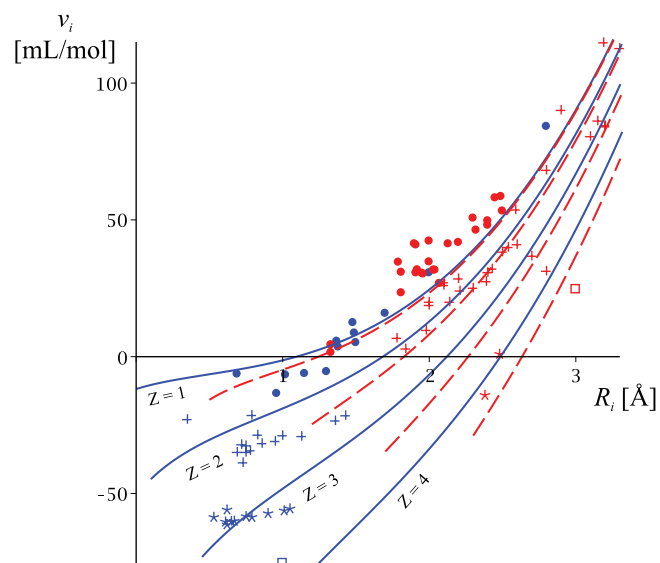

FIG. 5. Partial molar volumes v_i of ions of various valencies in infinitely diluted aqueous solutions as functions of the ionic crystallographic radii R_i. Solid circles: monovalent ions; crosses: divalent; stars: trivalent; boxes: tetravalent; blue and red – cations and anions. Data assembled by Marcus.[55] Lines: Eq. (64) with Z = 1, 2, 3, 4 and $R_{cav} = g_V^{1/3}(R_i + L_c)$ or $g_V^{1/3}(R_i + L_a)$. The values for the parameters were obtained from the optimization of σ_v, Eq. (66). Two fitting parameters were used, $L_Q = 1.8$ Å and $1/g_V \times \partial g_V/\partial p = -0.37$, for all 8 curves.

(i) σ_v has a shallow minimum and the uncertainty of the values of the fitting parameters is high. This is illustrated in Fig. S1 in the supplementary material C.[66]

(ii)   The derivative $1/g_V \times \partial g_V/\partial p$ is found to be negative and has the value of -0.37×10^{-10} Pa^{-1}. This value can be compared to the compressibility of water; since $v_w \propto g_{V,w}$,

$$-\beta_T = \frac{1}{v_w}\frac{\partial v_w}{\partial p} = \frac{1}{g_{V,w}}\frac{\partial g_{V,w}}{\partial p} = -4.57 \times 10^{-10}\text{Pa}^{-1}. \tag{67}$$

Thus, $1/g_{V,w} \times \partial g_{V,w}/\partial p$ for water is one order of magnitude larger than $1/g_V \times \partial g_V/\partial p$ for the ion's hydration shell, which suggests that the structure of the hydration shell is far more incompressible than the structure of water itself. This effect is long known and the assumption for negligible compressibility of the hydration shell was used to calculate hydration numbers from compressibility data long ago.[62,63] The value of the hydration shell compressibility obtained by us can be used to correct the so-obtained hydration numbers, but this falls outside the scope of our paper (an increase of about 10% in the final values of the hydration numbers will arise due to $1/g_V \times \partial g_V/\partial p \neq 0$).

(iii)   The value obtained for L_Q is 1.8 Å. The quadrupolar length L_Q affects the data for the smallest ions only (Li$^+$, Be^{2+}, Al^{3+}) and it explains why their partial molar volumes are more positive than the ones predicted from the classical model with $L_Q = 0$. For example, the partial molar volume calculated for Al^{3+} ($R_i = 0.53$ Å) with the parameters from row c in Table I is -69 ml/mol, and if one sets $L_Q = 0$, the result will be -84 ml/mol. The experimental value is[55] -59 ml/mol. From the theoretical estimation of α_Q in Sec. II, we can predict that L_Q is several times larger than 0.2 Å. Still, a difference of one order of magnitude between the value of L_Q estimated from Eqs. (17) and (27) and the experimental one is puzzling. We will obtain a similar value of L_Q from independent data for the partial molar entropy of various ions in Sec. IV E and from activity coefficient data in a following paper, which suggest that the ideal gas formula (17) underrates α_Q significantly (10–100 times).

E. Standard entropy of hydration

The partial molar entropy s_i of the ion in water can be calculated by taking minus the derivative of $\mu_{0i} + k_BT\ln C_i/C_0$, cf. Eq. (53), with respect to T. The molar entropy *for hydration*, Δs_i, is calculated analogously as $-\partial(\Delta\mu_{0i} + k_BT\ln C_i/C_0 - k_BT\ln p/p_0)/\partial T$, cf. Eq. (54) for $\Delta\mu_{0i}$. The *standard* molar entropy for hydration Δs_{0i} is obtained[2,55] by setting $p = p_0$ and $C_i = C_0$ in Δs_i. Using Eq. (53), one finds the following expression for Δs_{0i} (in units J/K):

$$\Delta s_{0i} = -k_B \ln\frac{k_BTC_0}{p_0} + k_B(T\alpha_p^v - 1)$$

$$-\frac{pv_0}{g_V}\frac{\partial g_V}{\partial T} - \frac{e_i^2}{8\pi R_{cav}^2}\frac{1}{\varepsilon_0}\frac{\partial R_{cav}}{\partial T}$$

$$+\frac{e_i^2}{8\pi\varepsilon^2 R_{cav}}\frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2}\frac{\partial\varepsilon}{\partial T}$$

$$+\frac{e_i^2}{8\pi\varepsilon R_{cav}^2}\frac{3(2L_Q/R_{cav} + 3L_Q^2/R_{cav}^2)}{(1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2)^2}\frac{\partial L_Q}{\partial T}. \tag{68}$$

The first two terms in this equation arise from the choice of standard state. Their contribution to Δs_{0i} is significant, -34.3 J/Kmol (for the coefficient of thermal expansion, we take[46] $T\alpha_p^v = 0.0763$). The mechanistic term $pv_0/g_V \times \partial g_V/\partial T$ is very small and will be neglected below. In the fourth term in Eq. (68) proportional to $\partial R_{cav}/\partial T$, we neglected $1/\varepsilon$ in comparison with $1/\varepsilon_0$. The derivative $\partial R_{cav}/\partial T$ is calculated by assuming that L_c, L_a, and R_i are independent of temperature – in that case, from Eq. (57) it follows the relation

$$\frac{\partial R_{cav}}{\partial T} = \frac{R_{cav}}{3g_V}\frac{\partial g_V}{\partial T}, \tag{69}$$

compared to Eq. (61). According to Eq. (69), the thermal expansion of the hydration shell is proportional to R_{cav} (compare, e.g., to Eqs. 13 and 14 in Ref. 58, which predict that dR_{cav}/dT is the same for all ions). For the temperature dependence of ε, we use the experimental data for $\varepsilon(T)$ from Refs. 2 and 46, from which it follows that

$$\frac{T}{\varepsilon}\frac{\partial\varepsilon}{\partial T} = -1.35. \tag{70}$$

We can also estimate $\partial L_Q/\partial T$ from Eqs. (27), (24), and (70),

$$\frac{T}{L_Q}\frac{\partial L_Q}{\partial T} = \frac{T}{2\alpha_Q}\frac{\partial\alpha_Q}{\partial T} - \frac{T}{2\varepsilon}\frac{\partial\varepsilon}{\partial T} \approx 0.18. \tag{71}$$

Since this value is quite small, the term proportional to $\partial L_Q/\partial T$ has insignificant contribution to the value of Δs_{0i}. Leaving only the significant terms in Eq. (68), we obtain

$$\Delta s_{0i} = -k_B \ln\frac{k_BTC_0}{p_0} + k_B(T\alpha_p^v - 1) - \frac{e_i^2}{24\pi\varepsilon_0 R_{cav}}\frac{1}{g_V}\frac{\partial g_V}{\partial T}$$

$$+\frac{e_i^2}{8\pi\varepsilon^2 R_{cav}}\frac{1 + 3L_Q/R_{cav}}{1 + 3L_Q/R_{cav} + 3L_Q^2/R_{cav}^2}\frac{\partial\varepsilon}{\partial T}. \tag{72}$$

The hydration entropy Δs_{0i} is known with reasonable accuracy for a large number of ions.[55] The experimental data assembled by Marcus[55] can be used to obtain a second estimation of L_Q from an independent set of data (besides the partial volumes), by comparing Eq. (72) to them. To do so, we define the merit function:

$$\sigma_s^2(\partial g_V/\partial T, L_Q)$$

$$= \frac{\sum_{Z=1}^{4}\sum_i [\Delta s_{0i,th}(Z, R_i; \partial g_V/\partial T, L_Q) - \Delta s_{0i,exp}(Z, R_i)]^2}{N - f},$$

$$\tag{73}$$

where $\Delta s_{0i,th}$ is given by Eq. (72) and $\Delta s_{0i,exp}$ is the experimental value. Data for N = 68 ions of valence Z = 1÷4 are analyzed (cf. supplementary material D).[66]
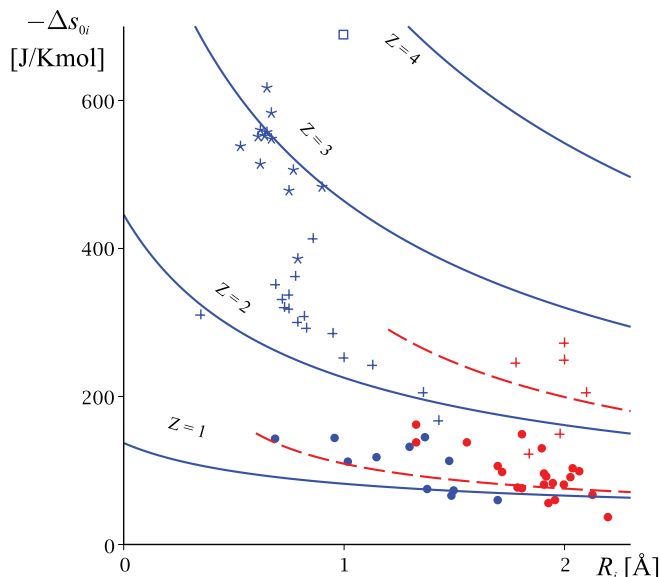
FIG. 6.   Negative entropies of hydration Δs_{0i} for mono-, di-, tri-, and tetravalent ions as functions of the crystallographic ionic radii R_i. Data assembled by Marcus.[55] Lines: Eq. (68) with two fitting parameters: $L_Q = 1.3$ Å and $T/g_V \times \partial g_V/\partial T = 0.082$, obtained from the minimization of σ_s, Eq. (73). Solid circles: monovalent ions; crosses: divalent; stars: trivalent; boxes: tetravalent; blue and red – cations and anions.

The comparison between Eq. (72) and the experimental data is shown in Fig. 6. The results from the optimization are:

(i) σ_s has a shallow minimum and does not allow for a very precise determination of the parameters involved. The dependence of σ_s on L_Q and $T/g_V \times \partial g_V/\partial T$ (cf. row d of Table I) is illustrated in Fig. S2 in supplementary material C.[66]

(ii)   The derivative $T/g_V \times \partial g_V/\partial T$ has a positive value of 0.082. This value can be compared to the coefficient of thermal expansion of water through the relation

$$T\alpha_p^v = \frac{T}{v_{\mathrm{w}}}\frac{\partial v_{\mathrm{w}}}{\partial T} = \frac{T}{g_{V,\mathrm{w}}}\frac{\partial g_{V,\mathrm{w}}}{\partial T} = 0.0763. \qquad (74)$$

It turns out that, within the experimental error, the water in the hydration shell of the ion has the same thermal expansion coefficient as water in the bulk.

(iii)   The value of L_Q obtained from the fit is 1.3 Å, of the same order as the one obtained from the partial molecular volume data. The effect of L_Q on Δs_{0i}, and respectively, on the dispersion σ_s, is not very large. It mainly affects Δs_{0i} of very small ions, by decreasing the absolute value of their entropies by 10%-20%. For example, the entropy of Al^{3+} calculated from Eq. (68) with the parameters given in row d in Table I is -603 J/Kmol, while with $L_Q = 0$ it is -726 J/Kmol (the experimental value of Δs_{0i} of Al^{3+} is[55] -538 J/Kmol). The value of α_Q corresponding to $L_Q = 1.3$ Å is $\alpha_Q = 3\varepsilon L_Q^2 = 36 \times 10^{-30}$ Fm, an order of magnitude higher than the estimate following from the ideal gas formula (17).

F.   Improved optimization procedure for the determination of g_V, L_c, L_a, and L_Q for aqueous solution

The partial molar volumes are very sensitive to the packing factor g_V, due to the $4/3\,\pi R_i^3 g_V$ term in Eq. (64). Both v_i and Δs_{0i} are sensitive to the dielectric cavity parameters L_c and L_a. Therefore, to achieve higher accuracy it is better to minimize with respect to all unknown parameters the dispersions σ_μ^2, σ_v^2, and σ_s^2 simultaneously instead of consecutively. Towards this, we define the merit function:

$$\sigma^2\left(g_V, \frac{\partial g_V}{\partial T}, \frac{\partial g_V}{\partial p}, L_c, L_a, L_Q\right) = \frac{\sigma_\mu^2}{\sigma_{\mu 0}^2} + \frac{\sigma_v^2}{\sigma_{v 0}^2} + \frac{\sigma_s^2}{\sigma_{s 0}^2}, \qquad (75)$$

here, σ_μ^2, σ_v^2, and σ_s^2 are given by Eqs. (58), (66) and (73), and for the weight factors we use the values $\sigma_{\mu 0} = 149.6$, $\sigma_{v 0} = 12.5$, $\sigma_{s 0} = 53.1$, obtained in Secs. IV C–IV E (cf. rows b-d in Table I). The merit function minimizes the deviation of the three theoretical equations (54), (64) and (72) following from the generalized Born model from all 251 experimental data points for hydration energy, partial molecular volume, or hydration entropy. The result from the optimization of σ^2 is given in row e of Table I. The value of g_V obtained from the fit is 1.39, in good agreement with the one assumed above (1.35, as for hexagonal lattice). The values obtained in Sec. IV C above for L_c and L_a are confirmed. The values of the compressibility of the hydration shell ($1/g_V \times \partial g_V/\partial p = -0.40$) and its coefficient of thermal expansion ($T/g_V \times \partial g_V/\partial T = 0.092$) are slightly higher in absolute value than those obtained in Secs. IV D and IV E. The procedure is the least sensitive to the quadrupolar length: the value obtained for L_Q from the minimization of the merit function (75) is $L_Q = 2.5$ Å but only with high uncertainty (± 1.5 Å). Therefore, we can conclude that the comparison of our model (51) for the Born energy with the available thermodynamic parameters of ions in water allow at best to set some limits to the value of the quadrupolar length L_Q (1-4 Å).

G.   Transfer energies of an ion from water to polar oil

The transfer energy $\Delta\mu_{0i}^{\mathrm{OW}} = \Delta\mu_{0i}^{\mathrm{W}} - \Delta\mu_{0i}^{\mathrm{O}}$ of an ion from polar oil solution (index "O" superscript) to aqueous solution (index "W" superscript) is obtained as the difference of the solvation energies in both phases. According to Eq. (54),

$$\Delta\mu_{0i}^{\mathrm{OW}}$$
$$= -\frac{Z_i^2 e^2}{8\pi R_{\mathrm{cav}}^{\mathrm{W}}}\left[\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon^{\mathrm{W}}}\frac{1 + 3L_Q^{\mathrm{W}}/R_{\mathrm{cav}}^{\mathrm{W}}}{1 + 3L_Q^{\mathrm{W}}/R_{\mathrm{cav}}^{\mathrm{W}} + 3\left(L_Q^{\mathrm{W}}/R_{\mathrm{cav}}^{\mathrm{W}}\right)^2}\right]$$
$$+ \frac{Z_i^2 e^2}{8\pi R_{\mathrm{cav}}^{\mathrm{O}}}\left[\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon^{\mathrm{O}}}\frac{1 + 3L_Q^{\mathrm{O}}/R_{\mathrm{cav}}^{\mathrm{O}}}{1 + 3L_Q^{\mathrm{O}}/R_{\mathrm{cav}}^{\mathrm{O}} + 3\left(L_Q^{\mathrm{O}}/R_{\mathrm{cav}}^{\mathrm{O}}\right)^2}\right]. \qquad (76)$$

In this expression, the large $1/\varepsilon_0$ term is to a large extent canceled provided that the cavity radii $R_{\mathrm{cav}}^{\mathrm{O}}$ and $R_{\mathrm{cav}}^{\mathrm{W}}$ in the two phases are close to each other. If this is the case, the contribution of the quadrupolar term can be significant and the determination of L_Q is possible.
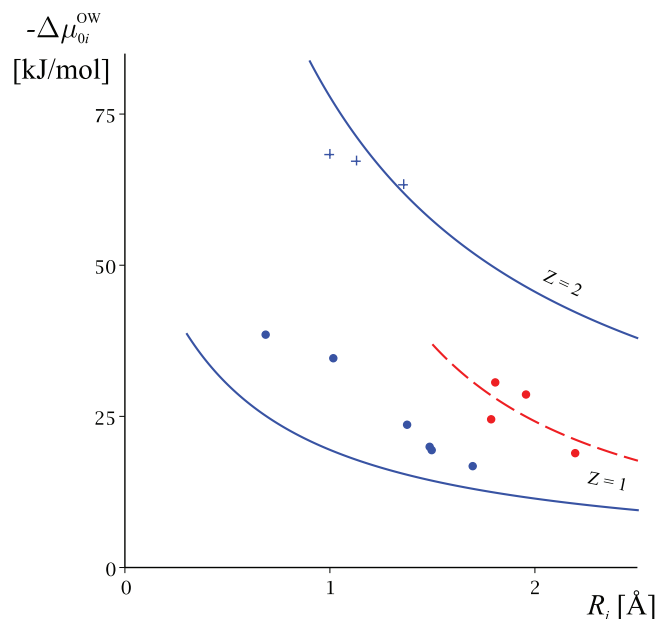
FIG. 7. Negative standard free energies for transfer of an ion from nitrobenzene to water $\Delta\mu_{0i}^{OW}$ [J/Kmol] for mono- and divalent ions as functions of the crystallographic ionic radii R_i [Å]. Experimental data from Refs. 64 and 65. Lines: Eq. (76) with four fitting parameters: $L_c^O = 0.71$ Å, $L_a^O = 0.08$ Å, $L_Q^O = 3.8$ Å, and $g_V^O = 1.54$. Solid circles: monovalent ions; crosses: divalent; blue and red – cations and anions.

Transfer energy data for nitrobenzene are available.[64,65] We compared Eq. (76) to the data for $\Delta\mu_{0i}^{OW}$ of 13 ions, cf. supplementary material D[66] for the list. We minimized a merit function similar to Eq. (58) with respect to four parameters: g_V^O, L_c^O, L_a^O, and L_Q^O. The respective parameters for water are taken as obtained from the optimization of Eq. (75) (cf. row e of Table I). For the dielectric permittivity of nitrobenzene we used the value $\varepsilon^O = 34.8 \times \varepsilon_0$ F/m.

The comparison between Eq. (76) and the measured transfer energies is shown in Fig. 7, and the obtained values of the fitting parameters are given in row f of Table I. In summary:

(i)   The standard deviation for the transfer energies $\Delta\mu_{0i}^{OW}$ is $\sigma_\mu = 8.8$ kJ/mol; the deviation is highest for monovalent cations.

(ii) The value obtained for g_V, 1.54, suggests that the solvation shell of the ions in nitrobenzene is less densely packed than in water, due to the large size of the nitrobenzene molecules.

(iii) According to Latimer-Pitzer-Slansky hypothesis, the value of L_c^O for a cation in nitrobenzene must correspond to the distance between the electron pair of an oxygen atom in the nitrogroup and the cation (compare to Fig. 3). Not surprisingly, within the error, the value obtained for this distance ($L_c^O = 0.71$ Å) is the same as for a cation in water. The positive charge of the nitrobenzene molecule is delocalized towards benzene ring (-NO$_2$ has negative mesomeric effect), and L_a^O is not easy to interpret. We obtained the value $L_a^O = 0.1$ Å.

(iv) For the quadrupolar length of liquid nitrobenzene we obtained the value $L_Q^O = 3.8$ Å. The respective quadrupolarizability follows from Eq. (27): $\alpha_Q^O = 3\varepsilon^O(L_Q^O)^2$

$= 130 \times 10^{-30}$ Fm. This can be compared to the quadrupolarizability of water: for $L_Q^W = 2.5$ Å, $\alpha_Q^W = 3\varepsilon^W(L_Q^W)^2 = 130 \times 10^{-30}$ Fm, i.e., both solvents have similar quadrupolarizabilities. In nitrobenzene, however, the effect from the quadrupoles will be more pronounced compared to water due to the higher dielectric permittivity of the latter. The effect of the quadrupolar lengths is to decrease the absolute values of the transfer energies of the small ions. For example, the transfer energy of Ca^{2+}, according to Eq. (76) is -78 kJ/mol, while if L_Q^W and L_Q^O are set to 0, one obtains -93 kJ/mol (compare to the experimental value: -68.3 kJ/mol).

V. CONCLUSIONS

Our work investigates the effects of the quadrupole moment of the molecules in a medium on the properties of charged particles dissolved in this medium, using a macroscopic approach based on the quadrupolar Coulomb-Ampere law (26), generalizing the classical Poisson equation of electrostatics.

(i)   We derived a new equation of state, Eq. (16), relating the macroscopic density of quadrupole moment $\boldsymbol{Q}$ and the field gradient $\nabla\boldsymbol{E}$ in gas of quadrupoles. The tensor $\boldsymbol{Q}$ has zero trace, unlike the one used in Refs. 12 and 13. Our constitutive relation involves a single scalar coefficient, the quadrupolarizability α_Q, which was estimated to be $\alpha_Q = 1 \times 10^{-30}$ Fm or several times larger for water.

(ii) We derived the boundary conditions needed for the fourth-order quadrupolar Coulomb-Ampere law (26) at a spherical surface between two media of different dielectric permittivity ε and quadrupolarizability α_Q, Eqs. (38) and (39).

(iii) The potential of a point charge in quadrupolar medium is finite even at $r = 0$, cf. Eq. (43). This unexpected result was obtained previously by Chitanvis[12] with another constitutive relation for $\boldsymbol{Q}$.

As an illustration of the approach, we further investigated the effect of quadrupolarizability on the Born energy of an ion in solution. The classical model for a dissolved ion as a charge in a cavity was generalized for the case of quadrupolar medium. We had no intentions to provide a complete theory of ion solvation, but rather we wanted to analyze the limits of the standard Poisson equation (4) and to search for cases where observable deviations from the observations will occur due to the neglected multipole terms. This resulted in the following conclusions:

(iv) It was shown that the hydration energies $\Delta\mu_{0i}$ of all ions are insensitive to the quadrupolar correction of Poisson equation. In contrast, the quadrupolarizability of water affects measurably (up to 10%-20%) the derivatives of $\Delta\mu_{0i}$ – partial molar volume v_i and entropy for hydration Δs_{0i} – of small ions in aqueous solution. From this effect and the experimental thermodynamic data for v_i and Δs_{0i} from Ref. 55, the value of the quadrupolar length, $L_Q = (\alpha_Q/3\varepsilon)^{1/2} = 2.5 \pm 1.5$ Å, could be estimated.

(v)   The transfer energies $\Delta\mu_{0i}^{\mathrm{OW}}$ of an ion from polar oil to water have also been shown to depend on the quadrupolar lengths in both phases. Data for $\Delta\mu_{0i}^{\mathrm{OW}}$ in nitrobenzene were analyzed and they yield for L_Q of this solvent the value 3.8 Å.

(vi)   The order of magnitude of α_Q and L_Q obtained from these 3 sets of experimental data (v_i, Δs_{0i}, and $\Delta\mu_{0i}^{\mathrm{OW}}$) compares well with the order predicted by other authors[12,13] for other liquids.

(vii)   The pressure and temperature derivatives of α_Q were estimated theoretically, cf. Eqs. (22) and (23). The estimated values of $\partial\alpha_Q/\partial p$ and $\partial\alpha_Q/\partial T$ show that the effect from these derivatives on the partial molar volume and entropy, Eqs. (64) and (68), of the dissolved ion is negligible.

(viii)   The pressure and temperature derivatives of the radius of the dielectric cavity R_{cav} around an ion were determined from experimental data (Table I). From their values it can be concluded that the structure of the hydration shell of an ion is about 10 times less compressible than the structure of water. The thermal expansion coefficient is about the same for the hydration shell and for pure water.

Although the results obtained here are encouraging, one must not forget that our approach uses some strong approximations. First, the constitutive relation (16) is strictly valid for ideal gas only. The assumption that the equation of state keeps the same form in dense liquid needs additional justification. Also, our model for the dissolved ion (point charge in a cavity) is clearly an oversimplification, as discussed in Sec. IV B. Nevertheless, we obtain self-consistent results and we have enough proof to assert that quadrupolarizability has measurable effect on many thermodynamic characteristics of the dissolved ions (v_i, Δs_{0i}, and $\Delta\mu_{0i}^{\mathrm{WO}}$).

The results obtained here for the equation of state for **Q**, the boundary condition for the generalized Maxwell equations of electrostatics, and the value of the quadrupolarizability α_Q of water will be used in the following study of this series for the extension of the Debye-Hückel model for the activity coefficient to quadrupolar media. It is also an interesting problem to analyze both the interaction of the multipole moments (dipole, quadrupole, etc.) of the dissolved particle with the quadrupolar moment of the solvent,[12,13] on the one hand, and the octupole moment of the solvent with the charge distribution of the dissolved particle.[36]

ACKNOWLEDGMENTS

[1]P. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
[2]R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworth Scientific Publications, London, 1959).
[3]L. G. Gouy, J. Phys. (Paris) **9**, 457 (1910).
[4]H. Ohshima, *Theory of Colloid And Interfacial Electric Phenomena* (Elsevier, 2006).
[5]J. T. Davies, Proc. R. Soc. London, Ser. A **245**, 417 (1958).
[6]J. T. Davies and E. Rideal, *Interfacial Phenomena* (Academic, New York, 1963).
[7]I. Langmuir, J. Chem. Phys. **6**, 873 (1938).
[8]B. V. Derjaguin and L. D. Landau, Acta Physicochim. URSS **14**, 633 (1941).
[9]E. J. W. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).
[10]M. von Smoluchowski, Bull. Int. Acad. Sci. Cracovie **1903**, 184.
[11]J. D. Jackson, *Classical Electrodynamics*, 1st ed. (John Wiley & Sons, Inc., New York, 1962); 3rd ed. (John Wiley & Sons, Inc., New York, 1962).
[12]S. M. Chitanvis, J. Chem. Phys. **104**, 9065 (1996).
[13]J. Jeon and H. J. Kim, J. Chem. Phys. **119**, 8606 (2003).
[14]H. Fröhlich, *Theory of Dielectrics* (Clarendon, Oxford, 1958).
[15]J. J. Bikerman, Philos. Magn. **33**, 384 (1942).
[16]D. Ben-Yaakov, D. Andelman, D. Harries, and R. Podgornik, J. Phys.: Condens. Matter **21**, 424106 (2009).
[17]J. M. G. Barthel, H. Krienke, and W. Kunz, *Physical Chemistry of Electrolyte Solutions – Modern Aspects*, edited by Deutsche Bunsen-Gesellschaft für Physicalische Chemie e.V. (Steinkopff, Darmstadt, 1998).
[18]B. W. Ninham and V. Yaminsky, Langmuir **13**, 2097 (1997).
[19]I. B. Ivanov, R. I. Slavchov, E. S. Basheva, D. Sidzhakova, and S. I. Karakashev, Adv. Colloid Interface Sci. **168**, 93 (2011).
[20]D. Frydel, J. Chem. Phys. **134**, 234704 (2011).
[21]D. D. Eley and M. G. Evans, Trans. Faraday Soc. **34**, 1093 (1938).
[22]J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd ed. (Elsevier, 2011).
[23]S. Levine, K. Robinson, G. M. Bell, and J. Mingins, J. Electroanal. Chem. **38**, 253 (1972).
[24]A. Levy, D. Andelman, and H. Orland, Phys. Rev. Lett. **108**, 227801 (2012).
[25]V. N. Paunov, R. I. Dimova, P. A. Kralchevsky, G. Broze, and A. Mehreteab, J. Colloid Interface Sci. **182**, 239 (1996).
[26]K. J. Laidler and C. Pegis, Proc. R. Soc. London, Ser. A **241**, 80 (1957).
[27]P. J. Stiles, Aust. J. Chem. **33**, 1389 (1980).
[28]T. Abe, J. Phys. Chem. **90**, 713 (1986).
[29]R. R. Dogonadze and A. A. Kornyshev, J. Chem. Soc., Faraday Trans. 2 **70**, 1121 (1974).
[30]S. Buyukdagli and T. Ala-Nissila, Phys. Rev. E **87**, 063201 (2013).
[31]M. V. Basilevsky and D. F. Parsons, J. Chem. Phys. **108**, 9107 (1998).
[32]M. V. Basilevsky and D. F. Parsons, J. Chem. Phys. **108**, 9114 (1998).
[33]R. A. Satten, J. Chem. Phys. **26**, 766 (1957).
[34]D. Adu-Gyamfi and B. U. Felderhof, Physica A **81**, 295 (1975).
[35]E. B. Graham and R. E. Raab, Proc. R. Soc. London, Ser. A **390**, 73 (1983).
[36]R. E. Raab and O. L. de Lange, *Multipole Theory in Electromagnetism* (Clarendon, Oxford, 2005).
[37]E. R. Batista, S. S. Xantheas, and H. Jonsson, J. Chem. Phys. **109**, 4546 (1998).
[38]A. D. Buckingham, Q. Rev. Chem. Soc. **13**, 183 (1959).
[39]E. B. Graham and R. E. Raab, Proc. R. Soc. London, Ser. A **456**, 1193 (2000).
[40]V. V. Batygin and I. N. Toptygin, *Sbornik Zadach po Elektrodinamike i Spetzialnoy Teorii Otnositelnosti*, 4th ed. (Lan, 2010), p. 283 (in Russian).
[41]D. Adu-Gyamfi, Physica A **108**, 205 (1981).
[42]D. E. Logan, Mol. Phys. **46**, 271 (1982).
[43]A. D. McLean and M. Yoshimine, J. Chem. Phys. **47**, 1927 (1967).
[44]L. D. Landau and E. M. Lifshitz, *The Classical Theory of Fields*, 7th ed. (Nauka, Moscow, 1988) (in Russian); Chap. 5 (Butterworth-Heinemann, 1980) (in English).
[45]O. L. de Lange and R. E. Raab, Phys. Rev. E **71**, 036620 (2005).
[46]*C R C Handbook of Chemistry and Physics*, edited by W. M. Haynes (CRC, New York, 2011).
[47]D. Bedeaux and J. Vlieger, *Optical Properties of Surfaces* (Imperial College, London, 2002), 2nd ed.
[48]A. M. Albano, D. Bedeaux, and J. Vlieger, Physica A **102**, 105 (1980).
[49]M. Born, Z. Phys. **1**, 45 (1920).
[50]W. M. Latimer, K. S. Pitzer, and C. M. Slansky, J. Chem. Phys. **7**, 108 (1939).
[51]T. T. Duignan, D. F. Parsons, and B. W. Ninham, J. Phys. Chem. B **117**, 9412 (2013).
[52]T. T. Duignan, D. F. Parsons, and B. W. Ninham, J. Phys. Chem. B **117**, 9421 (2013).

[53] M. H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. I **74**, 1604 (1978).

[54] M. H. Abraham and J. Liszi, J. Chem. Soc., Faraday Trans. I **74**, 2858 (1978).

[55] Y. Marcus, *Ion Properties* (Marcel Dekker, New York, 1997).

[56] A. A. Rashin and B. Honig, J. Phys. Chem. **89**, 5588 (1985).

[57] L. Blum and W. R. Fawcett, J. Phys. Chem. **96**, 408 (1992).

[58] W. R. Fawcett, J. Phys. Chem. B **103**, 11181 (1999).

[59] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).

[60] Y. Marcus, Chem. Rev. **111**, 2761 (2011).

[61] D. G. Archer and P. Wang, J. Phys. Chem. Ref. Data **19**, 371 (1990).

[62] A. Passinsky, Acta Physicochim. URSS **8**, 385 (1938).

[63] J. Padova, J. Chem. Phys. **40**, 691 (1964).

[64] J. Koryta, J. Dvorak, and L. Kavan, *Principles Of Electrochemistry*, 2nd ed. (John Wiley & Sons, Chichester, 1993).

[65] F. Scholz, R. Gulaboski, and K. Caban, Electrochem. Commun. **5**, 929 (2003).

[66] See supplementary material at http://dx.doi.org/10.1063/1.4865878 for (A) derivation of the macroscopic Maxwell equations of electrostatics with account for the quadrupole moment. (B) Born energy of an ion modeled as a conducting sphere placed into a cavity. (C) Analysis of the merit function of the optimization problems for the partial molecular volumes and entropies of ions in aqueous solution. (D) Data-table of the crystallographic radii, the hydration free energies, the partial molar volumes, the hydration entropies used for the determination of L_Q in water (from Refs. 55 and 53), and the transfer energies of an ion from nitrobenzene to water (from Refs. 64 and 65).