



Uniformity ansatz for inverse dielectric function of spatially restricted nonlocal polar medium as a novel approach for calculation of electric characteristics of ion–solvent system

Mikhail A. Vorotyntsev^{a,b,c,d,*}, Andrey A. Rubashkin^{e,*}

^a D. I. Mendeleev University of Chemical Technology of Russia, Moscow, Russia

^b M. V. Lomonosov Moscow State University, Moscow, Russia

^c Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia

^d ICMUB, UMR 6302 CNRS-Université de Bourgogne, Dijon, France

^e Institute of Cytology, Russian Academy of Sciences, Saint-Petersburg, Russia

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ABSTRACT

Till now, calculation of the electrostatic potential distribution and other electric properties of a nonlocal polar medium occupying a restricted spatial region has been carried out within the framework of two different approaches. One of them (which may be called “unrestricted medium approximation”, UMA) disregards the existence of “external region” (where dielectric properties are different from those of the medium), i.e. it assumes that the medium occupies the whole space so that its nonlocal dielectric properties are everywhere identical to those of the bulk medium while the charges (sources of the electric field) are considered as immersed inside the medium, without creating cavities or modifying its dielectric properties. Another approach (usually called “dielectric approximation”, DA) takes into account the difference of dielectric properties between the region occupied by the medium, V , and an “external” region; as for the nonlocal dielectric function inside region V it is assumed to be identical to that of the bulk medium, even for its spatial points near the boundary of the region. The actual study has proposed a novel general procedure (called IDA) for solving the same problem. Similar to the DA one, it also takes into account the difference of dielectric properties in region V and external region(s). However, a different background relation (“uniformity ansatz”) is assumed for dielectric properties of the spatially restricted polar medium: its correlation function of polarization fluctuations has the same form (identical to that for the unrestricted medium) in all points inside spatial region V , even in the vicinity of its boundary. The same property is automatically fulfilled for the inverse dielectric function of the medium inside region V . For several important geometries of the system (e.g. half-space, spherical or cylindrical cavity, etc.) thus defined “the inverse dielectric approach” (IDA) results in simple analytical expressions for the potential and electric field distributions for any nonlocal dielectric function of the bulk polar medium as well as for any distribution of “external charges” (satisfying to the corresponding symmetry conditions). As the first application, the IDA approach has been used for analysis of the electric field and potential distributions for the spherically symmetrical system where a cavity (imitating a “solute ion”) is surrounded by a nonlocal dielectric medium (“polar solvent”). Analytical expressions for these characteristics as well as for the electrostatic contribution to the solvation energy have been derived for any spherically symmetrical distribution of the ionic charge (which may be located in the general case both inside the cavity and outside this region) and for any dielectric responses both inside the cavity and of the polar medium outside the cavity. These results are in perfect agreement with the general principles that both the potential distribution outside the cavity and the ion solvation energy are determined only by the total ionic charge inside the cavity while they are independent of the particular charge distribution in this region. Effects due to the ionic charge penetration into the polar medium are also analyzed. Results for the potential distribution and solvation energy are compared for the novel IDA approach with those for the UMA and for the DA procedures. Conclusion on substantial advantages of the IDA method has been made.

* Corresponding authors.

E-mail addresses: mivo2010@yandex.com (M.A. Vorotyntsev), andrey.rubashkin@gmail.com (A.A. Rubashkin).

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1. Introduction

Electric interactions between charged and dipole components of the system play an important role in many physicochemical and electrochemical phenomena because of their high intensity. These forces are frequently modified essentially owing to the presence of a polar medium (e.g. solvent). Within the framework of a detailed (“microscopic”) description of such systems this medium has to be considered on the same level as dissolved species, e.g. with the use of molecular dynamic methods applied to all these components. Difficulties on the way to achieve an adequate description of a polar liquid, especially in the case of such highly complicated object as water (even in the absence of solute species) originate both from the long-range character of electric interactions and the lack of a reliable information on interactions between molecules of the liquid since in the condensed state one cannot reduce these interactions to purely **binary** forces, i.e. one has to take into account their **many-body** components. These features result in enormous complication for the use of statistical-mechanical theories for description of electric phenomena in pure polar liquids, speaking nothing for ionic solutions in such media.

These mathematical difficulties resulted in intermediate-level phenomenological approaches where electric properties of solute species are modified due to the presence of the polar medium owing to its dielectric properties. In particular, in the case of ions the solvent polarization affects strongly such ionic characteristics as solvation energies of individual ions, binary interactions between ions and collective properties of ionic ensembles. If the relaxation time of the polar medium is shorter than the characteristic time of displacements of ions one may consider the problem as an **electrostatic** one where both sources of electric fields (ions) and the solvent response to these fields may be considered as time-independent.

The simplest and widely used variant of this description is based on consideration of the solvent as a **local** and uniform dielectric medium which occupies the whole space outside the solute species and which is characterized by its (static) **dielectric constant**, ϵ_s . It means that the electric field, $\mathbf{E}(\mathbf{r})$, in a spatial point, $\mathbf{r}$, is proportional to its displacement, $\mathbf{D}(\mathbf{r})$, in the same point:

$$\mathbf{D}(\mathbf{r}) = \epsilon_s \mathbf{E}(\mathbf{r}) \quad (1)$$

Such description is quite justified for fields which change weakly at the molecular scale. However, this condition is often violated in ionic solutions, e.g. for fields around a small-size ion [1–3], extended molecular objects [4] or in the vicinity of a charged surface of the solvent (including electrochemical interfaces, metal/electrolyte solution [5–14]). This problem originates from a complicated nature of the dielectric response of the medium where its local polarization, $\mathbf{P}(\mathbf{r})$, is determined by both the electronic polarizability of solvent molecules and field-driven rotation of their dipole molecules while in structured liquids (first of all in water) orientations of neighboring molecules are strongly correlated due to short-range interactions, e.g. hydrogen or/and donor–acceptor bonds. It is the reason why the medium polarization, $\mathbf{P}$, in a point, $\mathbf{r}_1$, is determined by the electric field, $\mathbf{E}$, not only in the same point, $\mathbf{r}_1$, but also in its surrounding, which means that the relation between the spatial distributions of $\mathbf{P}$ and $\mathbf{E}$ is **nonlocal**:

$$P_\alpha(\mathbf{r}_1) = \int \chi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) E_\beta(\mathbf{r}_2) d\mathbf{r}_2 \quad (2)$$

where $\chi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ is nonlocal tensor (dielectric) susceptibility of the medium which is nonzero only if the distance between its arguments, $\mathbf{r}_1$ and $\mathbf{r}_2$, does not exceed its (maximal) correlation length, Λ [1–3,18]. Summation over repeating indices, e.g. over β in Eq. (2), from 1 to 3 is assumed in Eq. (2) and other relations below. Use of the identity, $\mathbf{D}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi \mathbf{P}(\mathbf{r})$, leads to a nonlocal expression for the displacement via the electric field distribution:

$$D_\alpha(\mathbf{r}_1) = \int \epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) E_\beta(\mathbf{r}_2) d\mathbf{r}_2 \quad (3)$$

where **nonlocal** (tensor) **dielectric function** of the medium, $\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, is given by Eq. (4):

$$\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \delta_{\alpha\beta} \delta(\mathbf{r}_1 - \mathbf{r}_2) + 4\pi \chi_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \quad (4)$$

Eq. (3) is supplemented by conventional electrostatic equations:

$$\text{div} \mathbf{D}(\mathbf{r}) = 4\pi \rho(\mathbf{r}), \quad \mathbf{E}(\mathbf{r}) = -\text{grad } \varphi(\mathbf{r}) \quad (5)$$

where $\rho(\mathbf{r})$ is density of external (with respect to the medium) charges, $\varphi(\mathbf{r})$ is electric potential.

All these distributions are unambiguously determined if both the charge density distribution, $\rho(\mathbf{r})$, and the dielectric function of the system, $\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, are given within the whole space.

If an uniform and isotropic dielectric medium occupies **the whole space** while the external charges are distributed inside the medium without disturbing its properties, in particular without forming interfacial boundaries, then the solution for the electric potential and other electric variables can be written down in an analytical form for any dielectric function of the medium [1–3,15–21]. Such calculation of the potential becomes a much more mathematically complicated problem if the nonlocal polar medium only occupies a certain restricted spatial region, V , while the dielectric properties outside V , i.e. inside the external region, V_{ext} , are essentially different from those inside V .

Two quite different approximate procedures have been proposed so far for determination of electric characteristics of such heterogeneous systems.

The first approach [1–3,15–21] (which may be called “unrestricted medium approximation”, UMA) disregards the existence of this “external” spatial region, V_{ext} , by assuming that the **whole space** ($V + V_{\text{ext}}$) is occupied by the same polar medium while the electric field is induced by “external charges” which are distributed inside the medium, without affecting its nonlocal dielectric properties.

The second approach [18,22–34] (which originates from the electrodynamics of plasma where it was called “dielectric approximation”, DA) takes into account the essential difference of the dielectric properties inside these spatial region, V and V_{ext} . Namely, the external region is described by the **local** electrostatic relation, Eq. (1) with its own dielectric constant. It implies automatically the absence of correlations between polarization fluctuations in regions V and V_{ext} which means that the nonlocal dielectric function, $\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (3), is **zero** if spatial points, $\mathbf{r}_1$ and $\mathbf{r}_2$, belong to **different** regions. As a result, integral relation (3) between $\mathbf{D}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ only takes place inside the region, V , occupied by the nonlocal medium, i.e. both $\mathbf{r}_1$ and $\mathbf{r}_2$ belong to region V while the nonlocal dielectric function, $\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, in this relation characterizes dielectric properties of the polar medium **inside this restricted region**, i.e. it is generally **different from those of this medium in the unrestricted space**.

Principal basis of the DA approach is the assumption that the dielectric function of the medium occupied region V , $\epsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, is equal to its **bulk medium form** for all points, $\mathbf{r}_1$ and $\mathbf{r}_2$, inside region V , even in the vicinity of its boundary with the external region, V_{ext} , see Eq. (12DA) below. Then, the electric potential distribution may be expressed via the **inverse dielectric function of the medium in region V** , $\epsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$. However, the latter can only be found via complicated solution of an integral equation, see below.

Our actual study is aimed to propose the third approach (which may be called “inverse dielectric approximation”, IDA) based on a **different** phenomenological assumption, namely that the **inverse dielectric function of the medium in region V** , $\epsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, is equal to its form for **this medium in the unrestricted space**, see Eq. (12) and discussion below for more detail. As a result, the potential distribution for systems of several important types can be expressed immediately via the dielectric function of the **bulk medium**, with no need of solving integral or differential-integral equations. Therefore, the IDA procedure allows one to carry out easily such calculations for **any** form of the bulk-medium dielectric function, contrary to the case of the DA procedure.

One should emphasize that the DA and IDA approaches are based on

different assumptions. Thus, their solutions for the same system are **different**. At the same time we demonstrate below they may be **close** to one another numerically. These features of the novel IDA procedure represent its obvious important merit, compared to the UMA and DA ones.

All the results based on the nonlocal dielectric function of the medium around ion require the validity of the theory of the linear response to the field of the ion. One should expect that this restriction excludes its application for description of ion solvation of small-size multi-charge ions. As for the single-charge ions, the available conclusions on this point (see e.g. [35]) are based on molecular-level modeling of the ion–solvent system, which is sensitive to the particular choice of system's parameters.

Alternative method for calculation of the solvation energies with taking into account the existence of the solvent-free cavity has been proposed in recent publications [36,37]. Contributions due to the electrostatic energy described by the Born theory and the dispersion interactions related to dynamic polarizabilities have been combined in order to calculate the energies of the ion solvation as well as of the ion–solvent boundary and ion-ion interactions. In particular, theoretical predictions for ion solvation energies turned out to be in agreement with experimental data. The dielectric response of the medium around the ion was described with the use of the local model. Since the direct molecular-model calculations for water demonstrate pronounced non-local effects in its dielectric response it will be of interest to combine the model of Refs [36,37] with this factor in the future.

It has been shown in Ref. [38] that nonlinear response effects may be integrated into the continuum model of the ion hydration, but these effects for monovalent ions being less than 2% of their hydration energies. This result justifies the use of nonlocal-electrostatics theory to calculate the solvation energy of such single-charge ions.

One should keep in mind that the nonlocal dielectric-response theory only deals with the electrostatic contribution to the ion solvation energy while there are also other contributions, e.g. due to the energy of the cavity creation inside the solvent [3] as well as due to a preferential orientation of the first coordination sphere solvent molecules around ions resulting in the charge hydration asymmetry [39,40].

Nonlocal electrostatics approach requires significantly less computation time, compared to methods of molecular dynamics, so it is useful for primary estimations of e.g. electrostatic potentials for proteins in water [28–30,41]. In particular, it was shown that the use of the non-local electrostatics for calculation of the solvation energy for an ion located inside a water-filled ion channel allowed one to explain observations of the ion penetration into such channels [31,33].

The principal goal of this paper is to propose a **novel approximate (IDA) approach** towards calculation of electric fields in systems containing a spatially restricted nonlocal polar medium (which is assumed to be uniform inside its region, V). This procedure may be applied for **any functional form of the nonlocal dielectric function of the bulk medium**, $\epsilon(k)$, as well as for various distributions of the ionic charge, $\rho(r)$ (including its penetration into the adjacent layer of the polar medium in contact with the “external region”). In particular, such calculations may be performed in a numerical form.

Application of the IDA approach for determination of the potential and electric field distributions is illustrated below for the spherically symmetrical system where an ion occupying a cavity is surrounded by a nonlocal polar medium. It is demonstrated that simple analytical expressions for them as well as for the ion solvation energy can be derived via $\epsilon(k)$ and $\rho(r)$ for **any functional form** of these characteristics.

Comparison of these results with those provided by two alternative approaches (UMA and DA) is given on the basis of the analytical and graphical analyses with the use of two simple model approximations for the dielectric function of the bulk polar medium (single- and three-mode functions). Since in real systems the ionic charge is generally distributed both inside the ion cavity and (partially) outside of it while the induced potential represents a superposition of contributions of all

these charges, we have considered in detail the generalization of the Born model (uniform charge distribution over a sphere) for three positions of these sphere: inside or outside the cavity or at its surface, in order to compare predictions of all approaches (UMA, DA and IDA) for the induced potential as well as for the solvation energy. As it is shown there this comparison has demonstrated advantageous features of the newly IDA procedure compared to both competitive approaches. These results open the prospect of its application for calculations electric properties of real systems with the use of more substantiated expressions for $\epsilon(k)$ and $\rho(r)$.

2. General relations

Relation (3) may be considered as an integral equation for the electric field distribution, $E(r)$. Its solution is given by the formula:

$$E_\alpha(r_1) = \int \epsilon_{\alpha\beta}^{-1}(r_1, r_2) D_\beta(r_2) d r_2 \quad (6)$$

where the tensor inverse dielectric function, $\epsilon_{\alpha\beta}^{-1}(r_1, r_2)$, satisfies to the relation:

$$\int \epsilon_{\alpha\beta}^{-1}(r_1, r_2) \epsilon_{\beta\gamma}(r_2, r_3) d r_2 = \delta_{\alpha\gamma} \delta(r_1 - r_3) \quad (7)$$

Since $P(r) = [D(r) - E(r)]/4\pi$ Eq. (6) provides an expression for the polarization via the displacement distribution:

$$P_\alpha(r_1) = \int \chi_{\alpha\beta}^{(D)}(r_1, r_2) D_\beta(r_2) d r_2 \quad (8)$$

where

$$\chi_{\alpha\beta}^{(D)}(r_1, r_2) = (4\pi)^{-1} [\delta_{\alpha\beta} \delta(r_1, r_2) - \epsilon_{\alpha\beta}^{-1}(r_1, r_2)] \quad (9)$$

3. Novel approximate (IDA) procedure for calculation of potential distribution

Under certain conditions established in Ref. [42] (see also Appendix 2 in book [18]) the displacement distribution, $D(r)$, is identical to that of the field, $G(r)$, induced by the same system of external charges, $\rho(r)$, **in vacuum**: $D(r) \equiv G(r)$, in particular:

1. If the medium represents a **uniform local** dielectric phase the surfaces of all non-conducting cavities must be equipotential surfaces of the vacuum field, G ;

2. If the system consists of one or several **non-uniform local** dielectric phases, $i = 1, 2, \dots, n$ (each of them occupies its own spatial region, V_i) and $\epsilon(r)$ changes stepwise at each border of two neighboring phases, then the condition in point 1 is to be satisfied (surfaces of all non-conducting boundaries are to be equipotential surface of the vacuum field, G) and $G(r) \parallel \text{grad } \epsilon(r)$ inside each region, V_i .

3. If the system includes a **nonlocal** dielectric phase, then both $\epsilon_{\alpha\beta}(r, r')$ and the interfaces must possess the same symmetry as the vacuum field, G , i.e. the external charge distribution, $\rho(r)$.

In particular, the latter variant takes place in the systems: 1) uniform and isotropic nonlocal medium occupying the whole space; 2) plane interface, $z = 0$, separating two media possessing either local response(s), Eq. (1), or nonlocal dielectric function(s) which are uniform and isotropic along the interface; 3) spherically symmetrical boundary (or several spherically symmetrical boundaries having the same center), $r = a$, separating two media possessing either local response(s), Eq. (1), or nonlocal dielectric function(s) possessing the same spherical symmetry, where the external charge density is also spherically symmetrical, i.e. it only depends on r ; 4) analogous system possessing a cylindrical symmetry.

For the systems described in points 2, 3 and 4 it is usually assumed that there is **no correlation** between the polarization fluctuations in any pair of spatial points belonging to **different spatial regions**. It means that for such values of the coordinates, r_1 and r_2 , the dielectric function in Eq. (3) is equal to zero, and the same property is valid for Eqs. (2), (6)

and (8).

Ultimate solution for the electric field distribution inside the region, V , occupied by the medium possessing the inverse dielectric function, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, is given by Eq. (10):

$$\mathbf{E}_\alpha(\mathbf{r}_1) = \int_V \varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2) \mathbf{G}_\beta(\mathbf{r}_2) d\mathbf{r}_2 \quad (10)$$

where the vacuum field, $\mathbf{G}(\mathbf{r})$, for such systems can be written down in the analytical form as integral of the external charge one, $\rho(\mathbf{r})$, and it does not depend on either the parameters of the interface or the dielectric properties of the media in contact. Then, the electric potential, $\varphi(\mathbf{r})$, is related to the field via Eq. (5), i.e. it can be found by its integration.

Analogous Eq. (8) may be used to derive an expression for the polarization distribution inside the same spatial region, V :

$$\mathbf{P}_\alpha(\mathbf{r}_1) = \int_V \chi_{\alpha\beta}^{(D)}(\mathbf{r}_1, \mathbf{r}_2) \mathbf{G}_\beta(\mathbf{r}_2) d\mathbf{r}_2 \quad (11)$$

One may note that for any functional form of the $\mathbf{G}(\mathbf{r})$ distribution (for the system satisfying to the symmetry conditions) there exists a corresponding distribution of the external charge: $\rho(\mathbf{r}) = -(4\pi)^{-1} \Delta \mathbf{G}(\mathbf{r})$. Therefore, Eq. (11) may be considered as the linear response of the dielectric medium to the **arbitrary** external field. Then, the fluctuation–dissipation theorem expresses the kernel in Eq. (11), $\chi_{\alpha\beta}^{(D)}(\mathbf{r}_1, \mathbf{r}_2)$, via the correlator of polarization fluctuations in the absence of external fields, $\langle P_\alpha(\mathbf{r}_1, t_1) P_\beta(\mathbf{r}_2, t_2) \rangle$, which reflects the spatial–temporal structure of the polar medium [18,43].

If the structure of the bulk medium and its fluctuation properties remain unmodified up to its boundary, then its susceptibility, $\chi_{\alpha\beta}^{(D)}(\mathbf{r}_1, \mathbf{r}_2)$, which is uniform and isotropic far from the boundary retains its form inside the whole spatial region, V , occupied by the medium, i.e. it only depends of the distance between the spatial arguments of this function: $\chi_{\alpha\beta}^{(D)}(|\mathbf{r}_1 - \mathbf{r}_2|)$. According to Eq. (9) the inverse dielectric function, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, possesses the same property inside region V while this function for the **bulk medium**, i.e. for the medium occupying the whole space, $\delta_{\alpha\beta} \varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|)$, is directly related to the Fourier transform of its dielectric function, $\varepsilon(k)$ [2,18]. As a result, the inverse dielectric function, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, in Eq. (10) is expressed immediately via the bulk-medium dielectric function, i.e. for all points, $\mathbf{r}_1$ and $\mathbf{r}_2$, inside region V :

$$\begin{aligned} \varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2) &\approx [\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)]_{\text{IDA}} \equiv \delta_{\alpha\beta} \varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|) = \\ &= \delta_{\alpha\beta} (2\pi)^{-3} \int [\varepsilon(k)]^{-1} \exp[ik(\mathbf{r}_1 - \mathbf{r}_2)] dk = \\ &= \delta_{\alpha\beta} (2\pi^2 |\mathbf{r}_1 - \mathbf{r}_2|)^{-1} \int_0^\infty [\varepsilon(k)]^{-1} k \sin(k |\mathbf{r}_1 - \mathbf{r}_2|) dk \end{aligned} \quad (12)$$

Thus, the distribution of the electric field in the presence of a dielectric medium, $\mathbf{E}(\mathbf{r})$, may be found with the use of Eqs. (10) and (12) on the basis of known properties of the system: its geometry (in particular, spatial region, V , occupied by the polar medium); dielectric function of the **unrestricted** medium in the k -space, $\varepsilon(k)$; electric field induced by external charges in vacuum, $\mathbf{G}(\mathbf{r})$.

This calculation procedure is applicable to systems composed of two or more spatial regions possessing different dielectric properties. Any of these regions, or all regions, may possess nonlocal dielectric properties. Calculations of the field inside regions where the medium may be described by the local relation, Eq. (1), are routine. Distributions of the electric potential in neighboring regions should be matched to ensure the **continuity condition**. Potential value at the infinite distance is usually taken as zero.

One should keep in mind that the so-called “dielectric approximation” (DA) [18,22–34] is based on a similar approximation for the **nonlocal dielectric function** of the same spatially restricted medium, $\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, in Eq. (3), i.e. for all points, $\mathbf{r}_1$ and $\mathbf{r}_2$, inside region V :

$$\begin{aligned} \varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) &\approx [\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)]_{\text{DA}} \equiv \delta_{\alpha\beta} \varepsilon(|\mathbf{r}_1 - \mathbf{r}_2|) = \\ &= \delta_{\alpha\beta} (2\pi)^{-3} \int \varepsilon(k) \exp[ik(\mathbf{r}_1 - \mathbf{r}_2)] dk = \\ &= \delta_{\alpha\beta} (2\pi^2 |\mathbf{r}_1 - \mathbf{r}_2|)^{-1} \int_0^\infty \varepsilon(k) k \sin[k |\mathbf{r}_1 - \mathbf{r}_2|] dk \end{aligned} \quad (12\text{DA})$$

The DA and IDA approaches are **not equivalent mathematically**. Namely, if the dielectric function of the **restricted** polar medium, $\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, within the DA approach is given by Eq. (12DA), i.e. it only depends on the difference of its arguments, $\mathbf{r}_1 - \mathbf{r}_2$, then the corresponding inverse dielectric function of the medium, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, does depend on **both spatial arguments**, $\mathbf{r}_1$ and $\mathbf{r}_2$, **separately**. On the contrary, within the framework of the novel IDA procedure, i.e. on the basis of Eq. (12) for the inverse dielectric function of the medium, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, dependent on $\mathbf{r}_1 - \mathbf{r}_2$, its dielectric function within region V , $\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, must be determined from integral Eq. (7) and it depends on **both spatial arguments**, $\mathbf{r}_1$ and $\mathbf{r}_2$, **separately**. In other words, the dielectric function, $[\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)]_{\text{DA}}$, and the inverse dielectric function, $[\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)]_{\text{IDA}}$, of the same restricted polar medium defined by Eq. (12DA) and Eq. (12), respectively, do **not satisfy relation (7)** since the integration in Eq. (7) is carried out over a **spatially restricted region**, V . Because of this non-equivalence of the DA and IDA procedures the results for any electric characteristic provided by them for the same system must be **different**. This point is specially discussed in section “Effect of various ionic charge localization” below.

In practical terms, for the above listed systems where the displacement, $\mathbf{D}(\mathbf{r})$, is identical to the field in vacuum, $\mathbf{G}(\mathbf{r})$, in the **whole space**, the solution within the framework of the IDA procedure is reduced to **single integration** over the corresponding variable. Therefore, this calculation can easily be performed numerically for **any functional form of the nonlocal dielectric function**, i.e. for any $\varepsilon(k)$. This peculiar feature of the IDA approach provides it with enormous advantages, compared to the widely used alternative DA method [18,22–34] since the latter leads to necessity of solving **integral equation (7)** for determination of the inverse dielectric function, $\varepsilon_{\alpha\beta}^{-1}(\mathbf{r}_1, \mathbf{r}_2)$, **inside a spatially restricted region**, V , with the use of the dielectric function, $\varepsilon_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$, defined by Eq. (12DA), while its expression (12) is **inapplicable** within the framework of the DA approach.

The proposed IDA approach also possesses obvious advantages with respect to the UMA theory which assumes that the polar medium occupies **the whole space** while the “external charges”, $\rho(\mathbf{r})$, are distributed inside the medium **without forming cavities** [1–3,15–21]. Within the framework of the IDA procedure based on Eqs. (10) and (12) the presence of the polar medium only within a **spatially restricted** region, V , is taken into account **automatically**, owing to integration in Eq. (10) over the V region only. Thus, one can take into account the presence of the medium inside a semi-space (if it forms a plane boundary with another phase, e.g. with metal or local dielectric), or the existence of a **cavity** (or cavities) inside the V region, e.g. a spherical (occupied by ion) or cylindrical (occupied by a solute molecule) one, etc.

One should pay attention to an importance consequence of this difference between the models. Within the framework of both the DA and novel IDA approaches, the electric field distribution, $\mathbf{E}(\mathbf{r})$, inside the region, V , occupied by the medium, depends of the form of the $\mathbf{G}(\mathbf{r})$ function **only inside this region** whereas for the UMA model of “the spatially unrestricted polar medium” [1–3,15–21] the field, $\mathbf{E}(\mathbf{r})$, in all spatial points, $\mathbf{r}$, depends on the form of $\mathbf{G}(\mathbf{r})$ within the **whole space**. Therefore, within the DA and IDA approaches the same property is also valid for the work of the test charge transfer between any points located with the V region if it is calculated with the use of the Guntelberg charging procedure, i.e. this work does **not** depend on the particular distribution of the external charge density **outside the V region** if it does not affect the form of the $\mathbf{G}(\mathbf{r})$ field **inside** the V region. This distinction between the models results in an essential difference in their predictions, see below.

4. Charged spherical cavity inside nonlocal dielectric medium. Electric field and potential distributions

Applicability of the newly proposed procedure is illustrated for the model of the system: **ion inside polar solvent** where a spherical cavity

of a radius, r_i , is surrounded by a nonlocal uniform and isotropic dielectric medium occupying the V region, $r > r_i$, its dielectric properties satisfying to conditions of Eq. (12). The charge density distribution of the ion, ρ (which is “external” for the medium), depends on the radial coordinate, r , but not on the angular ones: $\rho(r)$.

Then, in view of the spherical symmetry of the system all vector variables, $\mathbf{G}$, $\mathbf{D}$ and $\mathbf{E}$, in any spatial point, $\mathbf{r}$, are oriented along the radius-vector, $\mathbf{r}$, their absolute values (G , d and E) and the scalar variables (in particular, electric potential, φ) are functions of r .

According to Eq. (5) the identical G and D distributions are given by the expression:

$$D(r) = G(r) = q(r)/r^2, \quad q(r) = \int_0^r 4\pi(r')^2 \rho(r') dr' \quad (13a)$$

where $q(r)$ is the ionic charge which is located inside the sphere of the radius, r . Outside the region where this charge density, $\rho(r)$, is nonzero the charge, $q(r)$, tends to the total charge of the ion, e . This expression for $G(r)$ may be inserted into Eq. (10) for the distribution of the electric field, $\mathbf{E}(\mathbf{r})$, inside the polar medium (for $r > r_i$) where the integration is carried out outside the cavity.

This result for the electric field may be further simplified depending on the form of the ionic charge density distribution, $\rho(r)$.

Its simplest form is given by the **Born model** [1–3,18–19,44] where the total ionic charge, e , is uniformly distributed over the surface of the cavity:

$$\rho(r) = (e/4\pi r_i^2) \delta(r - r_i), \quad \text{so that } q(r) = e, \quad G(r) = e/r^2 \text{ for } r > r_i \quad (13b)$$

i.e. within the whole region occupied by the polar medium while q and $G(r)$ are equal to 0 at $r < r_i$.

More recently [19–21] “Smeared Born model” has been proposed where the ionic charge is distributed along the radius, r . One may distinguish two different cases.

First, the whole charge is located inside the cavity or at its surface [20,21] (in this context the Born model represents a particular example of such a distribution):

$$\rho(r) = 0 \text{ for all values of the radius outside the cavity, } r > r_i \quad (13c)$$

Then, expressions (13b) for $q(r)$ and $G(r)$ are valid again for the whole region occupied by the polar medium. On the contrary, their form inside the cavity depends on the particular distribution of the ionic charge density, $\rho(r)$, inside the cavity, in conformity with Eq. (13a).

In a more complicated situation the ionic charge density, $\rho(r)$, can **penetrate** into the region occupied by the solvent, $r > r_i$, so that a spherical layer is formed around the cavity where $\rho(r)$ is still nonzero while the dielectric properties are already determined by the nonlocal medium [19–21].

Then, inside the whole region, $r > r_i$, occupied by the medium Eq. (13a) gives expressions for the $q(r)$ and $G(r)$ distributions:

$$q(r) = q_{\text{cav}} + q_{\text{ext}}(r), \quad G(r) = [q_{\text{cav}} + q_{\text{ext}}(r)]/r^2 \text{ for } r > r_i \quad (13d)$$

where q_{cav} is the total ionic charge **inside the cavity** (including its external boundary) while $q_{\text{ext}}(r)$ is only related to ionic charge density outside the cavity:

$$q_{\text{cav}} = \int_0^{r_i} 4\pi r^2 \rho(r) dr, \quad q_{\text{ext}}(r) = \int_{r_i}^r 4\pi (r')^2 \rho(r') dr' \quad \text{for } r > r_i \quad (14)$$

Total charge if the ion, e , is generally composed of these two contributions: $e = q_{\text{cav}} + q_{\text{ext}}(\infty)$.

In the particular case where the ionic charge density **vanishes** outside the cavity, $r > r_i$, $q_{\text{ext}}(r)$ is equal to zero, $q_{\text{cav}} = e$, Eq. (13d) is reduced to Eq. (13b).

Amplitude of the electric field, $E(r)$, inside the spatial region occupied by the nonlocal dielectric medium, $r > r_i$, is given by Eq. (10) (where the integration is performed over the external region, $r > r_i$)

after insertion of expression (13b) or (13d) for the vacuum field, $G(r)$, for any form of the inverse dielectric function of the medium, $\varepsilon_{\alpha\beta}^{-1}(r_1, r_2)$. Then, the distribution of the electric potential, $\varphi(r)$, in the outer region, $r > r_i$, may be found immediately by single integration of the electric field profile.

In conformity with the general result for spherically symmetrical systems without correlations of fluctuations between the cavity and the external region [23,26,27,34] both functions, $E(r)$ and $\varphi(r)$, at $r > r_i$ do **not depend on the particular form of the ionic charge density distribution inside the cavity** (including its boundary with the solvent), i.e. only the **total charge in this region**, q_{cav} , Eq. (14), affects $E(r)$ and $\varphi(r)$ at $r > r_i$ according to Eq. (13d).

This important general property is **not** fulfilled for the UMA model where the nonlocal dielectric medium occupies **the whole space including the region where the ionic charge is distributed** [1–3,15–21]. As a result the $E(r)$ and $\varphi(r)$ distributions at $r > r_i$ are modified depending on the form of $\rho(r)$ in the internal region, $r \leq r_i$.

As for the $E(r)$ distribution **inside the cavity**, $r < r_i$, within the framework of the newly proposed procedure it is only dependent on the ionic charge density, $\rho(r)$, at $r < r_i$ and the dielectric properties inside the cavity while it is **independent of the dielectric properties of the polar medium** located outside the cavity. It means that both $E(r)$ and its potential (with respect to the potential of the boundary), $\varphi(r) - \varphi(r_i)$, **remain unchanged** if the medium is replaced e.g. by vacuum (assuming that the ionic charge density, $\rho(r)$, is not modified).

Owing to the spherical symmetry of the system Eq. (10) can be simplified with the use of transformations proposed in Ref [23]. In view of the uniform and isotropic properties of the inverse dielectric function of the medium outside the cavity it can be represented in the form of an expansion over products of spherical harmonics:

$$\varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|) = (r_1 r_2)^{-1} \sum_{l=0}^{\infty} \sum_{m=-l}^l \varepsilon_l^{-1}(r_1, r_2) Y_{lm}^*(\Omega_{r_1}) Y_{lm}(\Omega_{r_2}) \quad (15)$$

where the expansion coefficients may be found via integration of the dielectric function, $\varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|)$:

$$\varepsilon_l^{-1}(r_1, r_2) = r_1 r_2 \iint Y_{l0}^*(\Omega_{r_1}) Y_{l0}(\Omega_{r_2}) \varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|) d\Omega_{r_1} d\Omega_{r_2} \quad (16)$$

Since $E_{\alpha}(\mathbf{r}) = E(r) r_{\alpha}/r$ and $G_{\beta}(\mathbf{r}) = G(r) r_{\beta}/r$, substitution of expansion (15) into Eq. (10) results in expression (17) for the electric field and its potential inside the polar medium, i.e. outside the cavity:

$$E(r_i) = r_i^{-1} \int_{r_i}^{\infty} \varepsilon_{l=1}^{-1}(r_1, r_2) G(r_2) r_2 dr_2, \quad \varphi(r) = \int_r^{\infty} E(r_1) dr_1 \quad \text{for } r > r_i. \quad (17)$$

Thus, for calculation of the electric field and then of its potential outside the cavity it is sufficient to find the component of expansion (15) for $l = 1$ with the use of Eq. (16) for the inverse dielectric function of the medium, $\varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|)$.

If the dielectric function of the medium is known in the form of its Fourier transform, $\varepsilon(k)$, one can use it first for determination of the inverse dielectric function via Eq. (12), to insert it then into Eq. (16), with the further use of Eq. (17). However, it is possible to derive much simpler expressions for both expansion coefficients (15) and the electric field via the dielectric function, $\varepsilon(k)$. For its derivation one should apply Eq. (34.3) of monograph [45]:

$$\exp(i\mathbf{k}\mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(kr) Y_{lm}^*(\Omega_k) Y_{lm}(\Omega_r), \quad j_l(x) = \sqrt{\pi/2x} J_{l+1/2}(x) \quad (18)$$

After substitution of this expression for $\exp(i\mathbf{k}\mathbf{r}_1)$ and $\exp(-i\mathbf{k}\mathbf{r}_2) = [\exp(i\mathbf{k}\mathbf{r}_2)]^*$ into Eq. (12) and integration over Ω_k , with taking into account the orthogonality property of spherical functions: $\int Y_{lm}^*(\Omega_k) Y_{lm}(\Omega_k) d\Omega_k = \delta_{ll'} \delta_{mm'}$, one arrives at an expression for the

inverse dielectric function, $\varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|)$, over spherical functions expressed via $\varepsilon(k)$:

$$\varepsilon^{-1}(|\mathbf{r}_1 - \mathbf{r}_2|) = (2/\pi) \int_0^\infty [\varepsilon(k)]^{-1} k^2 \left\{ \sum_{l=0}^\infty \sum_{m=-l}^l j_l(kr_1) Y_{lm}^*(\Omega_{r_1}) j_l(kr_2) Y_{lm}(\Omega_{r_2}) \right\} dk \quad (19)$$

Comparison of Eqs. (19) and (15) gives an expression for expansion coefficients (15) for any integer value of l :

$$\begin{aligned} \varepsilon_l^{-1}(\mathbf{r}_1, \mathbf{r}_2) &= (2/\pi) r_1 r_2 \int_0^\infty [\varepsilon(k)]^{-1} j_l(kr_1) j_l(kr_2) k^2 dk \\ &= (r_1 r_2)^{1/2} \int_0^\infty [\varepsilon(k)]^{-1} J_{l+1/2}(kr_1) J_{l+1/2}(kr_2) dk \end{aligned} \quad (20)$$

All spherical Bessel functions, $j_l(x)$, in this formula can be written down via elementary functions, in particular $j_1(x) = x^{-1}(\cos x - x^{-1} \sin x)$ for $l = 1$ so that

$$\begin{aligned} \varepsilon_{l=1}^{-1}(\mathbf{r}_1, \mathbf{r}_2) &= (2/\pi) \int_0^\infty [\varepsilon(k)]^{-1} [\cos(kr_1)][\cos(kr_2) - \sin(kr_2)/kr_2] dk \end{aligned} \quad (21)$$

Expression under the integral sign in Eqs. (20) and (21) does not have singularities at $k = 0$ and it is an even function of k . Therefore, it is equal to a half of the integral over the whole real axis, e.g.:

$$\begin{aligned} \varepsilon_l^{-1}(\mathbf{r}_1, \mathbf{r}_2) &= (1/\pi) r_1 r_2 \int_0^\infty [\varepsilon(k)]^{-1} j_l(kr_1) j_l(kr_2) k^2 dk \\ &= (1/2)(r_1 r_2)^{1/2} \int_{-\infty}^\infty [\varepsilon(k)]^{-1} J_{l+1/2}(kr_1) J_{l+1/2}(kr_2) dk \end{aligned} \quad (22)$$

Such a presentation enables one to calculate this integral **analytically** if $\varepsilon(k)$ is a **rational** function, i.e. a ratio of two polynomials, see examples below.

The further analysis is different depending on whether the ionic charge density, $\rho(r)$, is localized only inside the cavity, Eq. (13c), or it is extended outside the cavity, Eq. (14).

If $\rho(r)$ is **nonzero only inside the cavity** including its boundary (Born model is a particular case), $r \leq r_i$, Eq. (13c), then the vacuum field, $G(r)$, inside the external region is given by Eq. (13b).

Combining Eqs. (17) and (21) with the relation:

$$\int_{r_i}^\infty j_1(kr) dr = -(k^2 r_i)^{-1} \sin(k r_i)$$

one can derive expressions for the electric field and potential distributions inside the polar medium [46]:

$$E(r) = -(2e/\pi r_i) \int_0^\infty [\varepsilon(k)]^{-1} \sin(kr_i) j_1(kr) dk \quad \text{for } r > r_i \quad (23a)$$

$$\varphi(r) = (2e/\pi r_i r) \int_0^\infty [\varepsilon(k)]^{-1} k^{-2} \sin(kr_i) \sin(kr) dk \quad \text{for } r > r_i \quad (24a)$$

The derived distribution of the electric potential **inside the region occupied by the polar medium**, $r > r_i$, coincides for **any dielectric function**, $\varepsilon(k)$, with the solution for the “unrestricted medium approximation” (UMA) [1–3,18] where **the medium occupies the whole space without a cavity** while **the ionic charges are distributed uniformly over the Born sphere surface**, $r = r_i$.

At the same time the electric potential and field distributions are quite different in these approaches **inside the ion region**, $r < r_i$. Novel IDA calculation procedure takes into account **specific** dielectric properties inside this cavity, e.g. if the local dielectric response is assumed there, then $E(r) = G(r)/\varepsilon_{\text{cav}}$ where ε_{cav} is the dielectric constant of the space inside the cavity. On the contrary the “unrestricted medium approximation” (UMA) [1–3,18] assumes the dielectric response inside the ion as being identical to that of the polar medium so that the field and potential distributions cannot reflect dielectric properties inside the ionic cavity.

This difference leads to important consequences.

As for the external region occupied by the solvent, $r > r_i$, in conformity with the general result [23,26,34] the electric field and

potential profiles given by Eqs. (23a) and (24a) do **not depend on the particular form of the ionic charge distribution inside the cavity**, $\rho(r)$ at $r \leq r_i$ (they are only dependent on the total charge in this region, e).

In the UMA model which does not take into account the existence of the cavity [1–3,18,19] the $E(r)$ and $\varphi(r)$ distributions are given by a **universal** expression for **any** ionic charge distribution, $\rho(r)$ [19]:

$$\varphi(r) = (2/\pi) \int_0^\infty [\rho(k)/\varepsilon(k)] [\sin kr/kr] dk \quad (24UMA)$$

where $\rho(k)$ is the Fourier-transform of $\rho(r)$:

$$\rho(k) = \int \rho(r) \exp(i \mathbf{k} \cdot \mathbf{r}) d\mathbf{r}$$

Let us assume again (similar to Eqs. (23a) and (24a)) that the ionic distribution, $\rho(r)$, is nonzero only inside the internal region, i.e. at $r \leq r_i$, Eq. (13c). Then, both $\rho(k)$ and $\varphi(r)$ in Eq. (24UMA) **depend on the particular form of the ionic charge distribution** inside this region, in particular $\varphi(r)$ inside the polar medium, i.e. at $r > r_i$. This result is at variance with the general conclusion [34] that this form **cannot affect** this potential distribution. The above conclusion on the identity of predictions by Eqs. (24a) and (24UMA) is only valid for **the Born model** for the ionic charge distribution, Eq. (13b), where $\rho(k) = e \sin kr_i/kr_i$.

The predictions are also quite different for the **internal region**, $r \leq r_i$. Both the electric field, $E(r)$, and the difference, $\varphi(r) - \varphi(r_i)$, are **independent of the external dielectric properties** (owing to the spherical symmetry of the system and the absence of correlations between fluctuations across the boundary). In particular, they are unaffected by the ion transfer between vacuum and polar solvent surroundings. On the contrary, according to the UMA model [1–3,18] such a change of the surrounding medium results in a radical modification of the electric field and potential distributions **inside the cavity** which is again in disagreement with general principles.

It is shown below that these distinct features of the models manifest themselves seriously also in their predictions for the ionic solvation energy.

Let us analyze now the electric field and potential profiles in the more general case where the ionic charge distribution, $\rho(r)$, is extended partially outside the cavity, Eq. (14). The difference compared to the previous case is in a more complicated expression for the vacuum field, $G(r)$, given by Eq. (13d). As a result, one has to transform the integral over r :

$$\int_{r_i}^\infty q(r) j_1(kr) dr = -k^{-2} \left[q_{\text{cav}} r_i^{-1} \sin kr_i + 4\pi \int_{r_i}^\infty r \rho(r) \sin kr dr \right]$$

Here, q_{cav} is the total ionic charge in the cavity and its boundary, $r \leq a$, Eq. (14) while the integral contains the ionic charge density, $\rho(r)$, outside the cavity, $r > a$. As a result, Eqs. (23a) and (24a) are modified to Eqs. (23b) and (24b):

$$\begin{aligned} E(r) &= -(2/\pi) \int_0^\infty [\varepsilon(k)]^{-1} j_1(kr) dk [q_{\text{cav}} r_i^{-1} \sin kr_i \\ &\quad + 4\pi \int_{r_i}^\infty r' \rho(r') \sin kr' dr'] \quad \text{for } r > r_i' \end{aligned} \quad (23b)$$

$$\begin{aligned} \varphi(r) &= (2/\pi r) \int_0^\infty [\varepsilon(k)]^{-1} k^{-2} \sin kr dk [q_{\text{cav}} r_i^{-1} \sin kr_i \\ &\quad + 4\pi \int_{r_i}^\infty r' \rho(r') \sin kr' dr'] \quad \text{for } r > r_i \end{aligned} \quad (24b)$$

The first term in the brackets reflects the contribution of the ionic charges in the internal region (cavity and its boundary) while the second one is related to ionic charges penetrating into the polar medium. In conformity with the general principle (see e.g. Eqs. (3–13) in [23] and Eq. (14) in [34]) the former one only depends on the **total internal charge**, q_{cav} , while the latter is influenced by a particular form of the $\rho(r)$ distribution outside the cavity. If the ionic charge density, $\rho(r)$, is zero in the external region, $r > r_i$, the integral terms in Eqs. (23b) and (24b) vanishes, $q_{\text{cav}} = e$, and these expressions are reduced to Eqs. (23a) and (24a).

Potential distribution, $\varphi(r)$, within the framework of the UMA model (where no cavity is excluded from the region occupied by the

polar solvent) [1–3,18], Eq. (24UMA), gives **different** predictions, compared to Eq. (24b), if the ionic charge density is nonzero (at least somewhere) **inside the cavity region**, $\rho(r) \neq 0$ at $r < r_i$.

On the contrary, if $\rho(r) \equiv 0$ at $r < r_i$ while the ionic charge density is distributed generally at the cavity surface (total charge, q_{cav} , at $r = r_i$) and outside the cavity (at $r > r_i$), then the UMA potential profile, $\varphi(r)$, Eq. (24UMA), **inside the polar medium coincides with predictions of the novel IDA approach**, Eq. (24b). At the same time, even for this ionic charge distribution the UMA result for $\varphi(r)$, Eq. (24UMA), **inside the cavity** (at $r < r_i$) is **different** from the one given by the IDA approach where it is determined by the dielectric properties **inside the cavity**.

The above general expression for the potential distribution within the framework of the IDA approach, Eq. (24b), may be simplified for two particular forms of the ionic charge distribution outside the cavity.

First, the whole ionic charge is located at the sphere, $r = r_e$, **outside the cavity**: $r_e > r_i$:

$$\begin{aligned}\rho(r) &= (e/4\pi r_e^2)\delta(r - r_e), \\ q(r) &= 0, \quad G(r) = 0 \quad \text{for } r < r_e, \\ q(r) &= e, \quad G(r) = e/r^2 \quad \text{for } r > r_e\end{aligned}\quad (25a)$$

then

$$\varphi(r) = (2e/\pi r_e) \int_0^\infty [\varepsilon(k)]^{-1} k^{-2} \sin kr \sin kr_e dk \quad \text{for } r > r_i \quad (24c)$$

This expression has got the same functional form as Eq. (24a) for the Born model of the ionic charge distribution, with substitution of the cavity radius, r_i , by the radius of the charge localization, r_e .

If the ionic charge density outside the cavity may be approximated by an exponential function (see e.g. [19]):

$$\begin{aligned}\rho(r) &= \rho_0 (4\pi\eta)^{-1} \exp[-(r - r_i)/\eta] \quad \text{for } r > r_i \\ \rho_0 &= q_{\text{ext}}(r_i^2 + 2r_i\eta + 2\eta^2)^{-1}\end{aligned}\quad (25b)$$

then

$$\varphi(r) = (2/\pi r) \int_0^\infty [\varepsilon(k)]^{-1} k^{-2} \sin k r dk [q_{\text{cav}} r_i^{-1} \sin k r_i + F(k)] \quad (24d)$$

$$\begin{aligned}F(k) &= \rho_0 (1 + k^2\eta^2)^{-2} [k\eta(r_i + 2\eta + r_i k^2\eta^2) \cos k r_i \\ &\quad + (r_i + \eta + r_i k^2\eta^2 - k^2\eta^3) \sin k r_i].\end{aligned}$$

5. Electrostatic contribution to the ion solvation energy

According to the Born procedure for calculation of the electrostatic contribution to the ionic solvation energy, W , one should calculate the difference in the energies of transfer of the total ionic charge, e , from the infinity into the ion either in vacuum or via the dielectric surrounding of the ion. It is assumed that both the ionic charge distribution, $\rho(r)$, and the dielectric properties inside the cavity are the same for both configurations of the system. Then, the electric field, $E(r)$, and the difference, $\varphi(r) - \varphi(r_i)$, are not affected by the change of the dielectric properties outside the cavity. It means that the work to transfer a charge between the boundary of the cavity and any point inside the cavity is identical for the vacuum and dielectric surroundings. As a result, this contribution to the solvation energy is **cancelled**, and it is sufficient to calculate the work of transfer of ionic charges **between the infinity and the cavity surface**, $r = r_i$, **or r_i point outside the cavity** (if the ionic charge is extended beyond this boundary).

Thus, the electrostatic contribution, W , is given by the formula based on the Guntelberg charging procedure:

$$\begin{aligned}W(r_i; \{\rho(r)\}) &= \int_0^1 [q_{\text{cav}} \delta\varphi(r_i; q_{\text{cav}}x, \{\rho(r)x\}) + \\ &\quad + 4\pi \int_{r_i}^\infty r'^2 \rho(r') \delta\varphi(r'; q_{\text{cav}}x, \{\rho(r)x\}) dr'] dx\end{aligned}\quad (26)$$

$$\delta\varphi(r; q_{\text{cav}}x, \{\rho(r')x\}) \equiv \varphi_{\text{vac}}(r) - \varphi(r)$$

for the specified values of ionic charges where x is the fraction of the already transferred total ionic charge, $e dx$ is the small charge under transfer which is to be distributed proportionally between the total charge in the internal region, $q_{\text{cav}} dx$, and the fractions of the ionic charge outside this region located near the r point, $4\pi r^2 \rho(r) dr dx$. The difference between the potential distributions for the vacuum and dielectric surroundings, $\delta\varphi(r; q_{\text{cav}}x, \{\rho(r)x\})$, may be obtained immediately from Eq. (24b) since $\varepsilon(k) \equiv 1$ for vacuum in the outside region:

$$\begin{aligned}\delta\varphi(r'; q_{\text{cav}}x, \{\rho(r)x\}) &= \\ &= (2x/\pi r') \int_0^\infty \{1 - [\varepsilon(k)]^{-1}\} k^{-2} \sin kr' [q_{\text{cav}} r_i^{-1} \sin kr_i + \\ &\quad + 4\pi \int_{r_i}^\infty r'' \rho(r'') \sin kr'' dr''] dk\end{aligned}\quad (24e)$$

Since the potential values in both points, r_i and r , are proportional to x , Eq. (24e), the whole function under the integral sign is proportional to x and its integration gives the expression for W :

$$\begin{aligned}W(r_i; \{\rho(r)\}) &= (1/2) q_{\text{cav}} \delta\varphi(r_i; q_{\text{cav}}, \{\rho(r)\}) + \\ &\quad + 2\pi \int_{r_i}^\infty r'^2 \rho(r') \delta\varphi(r'; q_{\text{cav}}, \{\rho(r)\}) dr'\end{aligned}\quad (27a)$$

where expression (24f) for the potential difference, $\delta\varphi(r; q_{\text{cav}}, \{\rho(r)\})$, should be inserted:

$$\begin{aligned}\delta\varphi(r'; q_{\text{cav}}, \{\rho(r)\}) &= \\ &= (2/\pi r') \int_0^\infty \{1 - [\varepsilon(k)]^{-1}\} k^{-2} \sin kr' [q_{\text{cav}} r_i^{-1} \sin kr_i + \\ &\quad + 4\pi \int_{r_i}^\infty r'' \rho(r'') \sin kr'' dr''] dk\end{aligned}\quad (24f)$$

If the ionic charge is located entirely inside the internal region, $r \leq r_i$, Eq. (13c), then the integral terms in Eqs. (24b), (24f) and (27a) are absent. Then, one may use Eq. (24a) for the potential distribution inside the outer region, $r \geq r_i$, and Eq. (27b) for W :

$$\begin{aligned}W(r_i; \{\rho(r)\}) &= (e/2) [e/r_i - \varphi(r_i)] = \\ &= (e^2/\pi r_i^2) \int_0^\infty \{1 - [\varepsilon(k)]^{-1}\} k^{-2} \sin^2 k r_i dk\end{aligned}\quad (27b)$$

In conformity with the general principle (see e.g. Eq. (25) in [34]) the value of W does not depend on the particular distribution of the ionic charge density inside the cavity and its dielectric properties, it is only determined by the cavity radius, a , and the total charge inside the cavity (including its surface), Eqs. (27a) and (27b).

Therefore, for any distribution of the total ionic charge, e , inside or on the surface (but without penetration into the polar medium, Eq. (13c)) the electrostatic contribution to the solvation energy, $W(r_i; \rho(r))$ is identical to that for the **Born model of the ion** where the whole ionic charge is located at the external surface of the cavity, $W^B(r_i)$ [34]:

$$W(r_i; \{\rho(r)\}) = W^B(r_i) \quad (28)$$

As it has already been indicated above, within the framework of the **Born model for the ionic charge distribution** the electric potential profile outside the cavity, Eq. (24a), **coincides** with the result of the UMA model where the **polar medium occupies the whole space**, with embedded ionic charges [1–3,18] for any form of its dielectric function, $\varepsilon(k)$. In view of Eq. (27b) these two procedures also result in **identical** predictions for the contribution to the solvation energy, $W^B(r_i)$.

At the same time their results are **different** for other ionic charge distributions, e.g. if $\rho(r)$ is **spread inside the ion**. There are two different origins of this difference. First, as it has been discussed above the distributions of the electric field and its potential inside the cavity in the novel procedure are determined not only by the form of $\rho(r)$ but also by particular dielectric properties inside the cavity. The existence of such region is completely disregarded in the UMA model [1–3,18] so that the potential distribution changes automatically compared to that for the Born model automatically while such a change is at variance with the result of the most general theory. Second, the novel IDA approach assumes that the work for the charge transfer from its outer boundary, $r = r_i$, to a point inside the ion is **not affected by dielectric properties of**

the external medium, on whether it is vacuum or polar solvent. As a result, these terms are *cancelled* in the course of the solvation energy calculation. On the contrary, the “continuous model” has to change the dielectric properties of vacuum to those of the medium *everywhere*, i.e. not only *outside the ion* but also *inside its internal region*.

6. Effect of various ionic charge localization

As the illustrative example of applications of the novel IDA procedure it is used below to show the effect of various positions of the ionic charge on the solvation energy, W , both inside and outside the cavity. To retain the spherical symmetry of the system the total ionic charge, e , is uniformly distributed over a sphere of the radius, r_e , Eq. (25a), where it may be equal to the cavity radius (Born model), $r_e = r_i$, or less than it (charge inside the cavity), $r_e < r_i$, or larger than it (ion charge outside the cavity), $r_e > r_i$.

In the former two cases the potential outside the cavity is given by Eq. (24a) while the energy contribution, W , corresponds to Eqs (27b), (28) for the Born model for the ion charge, Eq. (13b), since the redistribution of the ionic charge inside the cavity (including its external surface) does not change these characteristics, in conformity with the most general theory (see e.g. Eqs. (14) and (25) in [34]).

If the charged sphere, $r = r_e$, Eq. (25a), is located *outside* the cavity, $r_e > r_i$, then Eqs. (27a) and (24f) should be used:

$$W(r_i, r_e) = (e^2/\pi r_e^2) \int_0^\infty \{1 - [\varepsilon(k)]^{-1}\} k^{-2} \sin^2 k r_e dk \quad (27c)$$

The derived expression has got the same functional form as that in Eq. (27b), in particular the one for the Born model of the ionic charge distribution.

If the predictions of the IDA calculation procedure, Eqs. (27b) and (27c), are compared with the corresponding results of the unrestricted medium approximation (UMA) [1–3,18] for the same charge distributions one can see that they are *identical* if the charged sphere, $r = r_e$, coincides with the surface of the cavity (Born model), $r_e = r_i$, or located *outside* the cavity, $r_e > r_i$. At the same time predictions of these approaches are *different* from one another for the ionic charges located *inside* the cavity.

For graphical illustration of these results let us employ two approximations for the nonlocal dielectric response of the polar medium. One of them proposed for the first time by Dogonadze and Kornyshev [1,3,18,19,25] may be called “three mode dielectric function”:

$$[\varepsilon_{3M}(k)]^{-1} = 1 - \sum_{i=1}^3 c_i [1 + (k\lambda_i)^2]^{-1} \quad (29a)$$

where the three terms reflect contributions of the electronic, vibrational and (orientational) long-range structure components of the polar solvent, λ_i are the corresponding correlation lengths: $\lambda_1 \cong 0.5 \text{ \AA}$ for the electronic mode, $\lambda_2 \cong 1 \text{ \AA}$ for the vibrational mode, $\lambda_3 \equiv \Lambda \cong 3 \text{ \AA}$ for the orientational mode. Coefficients, C_i , can be expressed via effective dielectric constants of this medium: $C_1 = 1 - 1/\varepsilon_1 = 0.444$, $C_2 = 1/\varepsilon_1 - 1/\varepsilon_2 = 0.352$, $C_3 = 1/\varepsilon_2 - 1/\varepsilon_3 = 0.191$; $\varepsilon_1 = 1.8$, $\varepsilon_2 = 4.9$, $\varepsilon_3 \equiv \varepsilon_s = 78.5$ (ε_s is the static dielectric constant of water) [1,3,18,19,25].

Integration over k in Eqs. (27b) and (27c) of the IDA approach may be carried out in the analytical form for this dielectric function, Eq. (29a) (similar to UMA formulas in [1,3]). It results in explicit expressions for W :

$$W_{3M}(r_i, r_e) = (e^2/2r_i)[C_1 f(2r_i/\lambda_1) + C_2 f(2r_i/\lambda_2) + C_3 f(2r_i/\Lambda)] \text{ for } r_e \leq r_i, \quad (30a)$$

$$W_{3M}(r_i, r_e) = (e^2/2r_e)[C_1 f(2r_e/\lambda_1) + C_2 f(2r_e/\lambda_2) + C_3 f(2r_e/\Lambda)] \text{ for } r_e > r_i, \quad (30b)$$

where $f(y) = 1 - y^{-1} [1 - \exp(-y)]$, and the lower index, 3 M, shows that Eqs. (30a) and (30b) are based on the “three mode dielectric

function”, Eq. (29a).

These results may be compared with those given by the UMA approach [1–3,18] which assumes that the dielectric properties of the polar medium are valid *for the whole space*, i.e. it disregards the existence of a cavity occupied by the ion and having different dielectric properties. Then, the expression for W within this model (denoted below as W_{3M}^{UMA} for the “three mode dielectric function”, Eq. (29a)) for the ionic charge distribution over the sphere, $r = r_e$, Eq. (25a) is only dependent on its radius, r_e , independent of whether this charged sphere is located *inside* or *outside* the ionic cavity:

$$W_{3M}^{DK}(r_e) = (e^2/2r_e)[C_1 f(2r_e/\lambda_1) + C_2 f(2r_e/\lambda_2) + C_3 f(2r_e/\Lambda)] \text{ for any } r_e \quad (30UMA)$$

For a particular case of the Born model for the ionic charge distribution, Eq. (13b), this formula, Eq. (30UMA), was derived in [1,3] with the use of the UMA procedure.

Comparison of Eqs. (30a,30b) with Eq. (30UMA) shows the *identity* of these predictions by two approaches *if the ionic charge is located at the boundary of the cavity (Born model) or outside the cavity*, $r_e \geq r_i$. At the same time, if the ionic charge is located *inside the cavity*, $r_e < r_i$, Eq. (30a) predicts that W is *independent* of the particular position of the ionic charge, i.e. of r_e , in conformity with the general principle [23,26,34]. On the contrary, Eq. (30UMA) demonstrates an explicit dependence of W_{3M}^{UMA} on r_e , see Fig. 1, at variance with the general principle.

The situation is illustrated in Fig. 1 where the graphs for these approaches are overlapping for $r_e \geq r_i$ while “the continuous model” (squares 2) deviates strongly from the behavior proven by the most general theory: independence of W from the position of the charged sphere *inside* the cavity, while the latter is correctly reproduced by the novel IDA approach (line 1).

Another useful illustration is provided by the “single-mode” dielectric function which has been used in numerous publications [2,4–18,22–28,31–34] based on either UMA or DA approximations:

$$[\varepsilon(k)]^{-1} = 1/\varepsilon_{\min} - (1/\varepsilon_{\min} - 1/\varepsilon_s)[1 + (k\Lambda)^2]^{-1} \quad (29b)$$

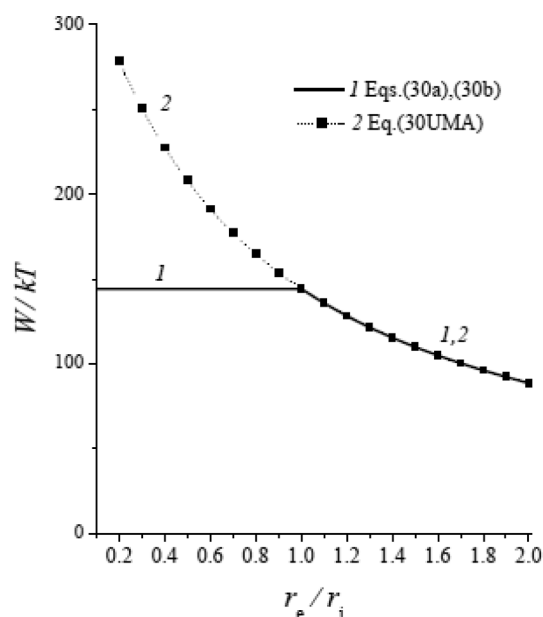


Fig. 1. Dependence of the ion solvation energy $W(r_i, r_e)$ (divided by $kT = 0.025 \text{ eV}$) on the radius of the charged sphere, $r = r_e$, for the three mode dielectric function of the polar medium, Eq. (29a) (values of its parameters are given in the text). Comparison of results of the novel IDA approach, Eqs. (30a,30b) (line 1), with those for the unrestricted medium approximation (UMA), W_{3M}^{DK} in Eq. (30UMA) (squares 2); $r_i = 1.17 \text{ \AA}$.

It represents particular cases of the more general “three mode approximation”, Eq. (29a), if $\lambda_1 = \lambda_2 = 0$, $\varepsilon_{\min} = \varepsilon_2$, or if $\lambda_1 = 0$, $\lambda_2 = \Lambda$, $\varepsilon_{\min} = \varepsilon_1$, etc. Special notation, $\varepsilon_{\min}$, is used in this expression to cover all these variants.

Expressions for W for various radii, r_e , for the novel approach may be deduced from Eqs. (30a) and (30b), or directly from Eqs. (27b) and (27c):

$$W_{IM}(r_i, r_e) = (e^2/2r_i)\{1 - \varepsilon_s^{-1} - (\varepsilon_{\min}^{-1} - \varepsilon_s^{-1})[1 - \exp(-2r_i/\Lambda)]\Lambda/(2r_i)\} \text{ for } r_e \leq r_i \quad (31a)$$

$$W_{IM}(r_i, r_e) = (e^2/2r_e)\{1 - \varepsilon_s^{-1} - (\varepsilon_{\min}^{-1} - \varepsilon_s^{-1})[1 - \exp(-2r_e/\Lambda)]\Lambda/(2r_e)\} \text{ for } r_e \geq r_i \quad (31b)$$

As previously, the unrestricted medium approximation (UMA) [1–3,18] results in a **universal** functional form of W for any position of the charged sphere, **inside or outside the cavity** (since the existence of the cavity is neglected by this model)

$$W_{IM}^{DK}(r_e) = (e^2/2r_e)\{1 - \varepsilon_s^{-1} - (\varepsilon_{\min}^{-1} - \varepsilon_s^{-1})[1 - \exp(-2r_e/\Lambda)]\Lambda/2r_e\} \text{ for any } r_e \quad (31UMA)$$

This formula was derived in [2] for the case where the ionic charge is located over the surface of the ion, $r_e = r_i$ (Born model). Similar to the above observation for the 3 M dielectric function of the medium, Eq. (29a), Eq. (31UMA) coincides with the result of the novel IDA approach for $r_e \geq r_i$, Eq. (31b), while it gives incorrect predictions if the ionic charge is located inside the cavity, see Eq. (31a), as one can see from Fig. 2a,b (square points 2).

Besides the approaches discussed above, expression for W for the “single-mode dielectric function” was also derived [26,34] within the framework of the “dielectric approximation” (DA) [18,23] based on an assumption concerning the form of the nonlocal dielectric function in Eq. (3). This third approach gives for any distribution of the ionic charge density **inside the cavity** (including its external boundary):

$$W(r_i, r_e) = [e^2/(2r_i)]\{1 - \varepsilon_s^{-1} - (\varepsilon_{\min}^{-1} - \varepsilon_s^{-1})B(r_i)\} \text{ for } r_e \leq r_i \quad (31c)$$

$$B(r_i) = \{[\beta r_i \coth(\beta r_i) - 1] \varepsilon_s/\varepsilon_{\min} + r_i/\Lambda + 1\}^{-1}, \quad \beta = \Lambda^{-1}\sqrt{\varepsilon_{\min}/\varepsilon_s}$$

Result for the same DA approach for the charged sphere located **outside** the cavity may be derived from the combination of Eqs. (22) and (20) in Ref [34]:

$$W(r_i, r_e) = (e^2/2r_e)\{1 - \varepsilon_s^{-1} - (\varepsilon_{\min}^{-1} - \varepsilon_s^{-1})B(r_e)\exp[-(r_e - r_i)/\Lambda]\} \text{ for } r_e > r_i \quad (31d)$$

Results of calculations with the use of the expressions for all three approaches are compared in Fig. 2a,b for two different values of the smaller dielectric constant: $\varepsilon_{\min} = \varepsilon_1 = 1.8$ and $\varepsilon_{\min} = \varepsilon_2 = 4.9$.

Even though the functional forms of the dependence, W vs. r_e , are different for the novel IDA procedure and the one based on “the dielectric approximation” (DA), Eqs. (31a) vs. Eq. (31c) or Eqs. (31b) vs. (31d), quantitatively they are very close to one another (Fig. 2a and b). Moreover, for the case where the charged sphere is located on the surface of the cavity (Born model) or outside the cavity, all three approaches provide practically identical predictions. Therefore, one may expect that they all might be considered as trustful under these conditions.

At the same time one can observe again a drastic deviation of the result for the unrestricted medium approximation (UMA) (a strong increase of W for lower values of r_e , squares 2 in Fig. 2a and b) from predictions of two approaches (IDA and DA) which take into account the absence of the polar medium inside the cavity (lines 1 and empty triangles 3, respectively). Since the latter are in a perfect conformity with the most general principle (no dependence of W on the particular ionic charge distribution inside the cavity) the result of the UMA approach has to be considered as non-justified for systems where the ionic charge is present inside the cavity, at $r < r_i$.

7. Conclusions

This paper proposes a novel IDA method for calculation of electrostatic field and its potential distributions in systems where the polar medium possessing a nonlocal dielectric response occupies a part of the whole space while the dielectric properties inside the rest of the space are quite different (they may be local or even nonlocal). For certain geometries of the system (in particular, having a plane, or a spherical, or a cylindrical symmetry) the result for these characteristics may be written down in the form of integrals, with no need to solve integral or integral-differential equations, as one has to do with the use of the procedure based on the “dielectric approximation” (DA) [22,23]. Unlike the well-known unrestricted medium approximation (UMA) [1–3,15–21] where the dielectric response of the polar medium is formally extended for the whole space, i.e. without taking into account the

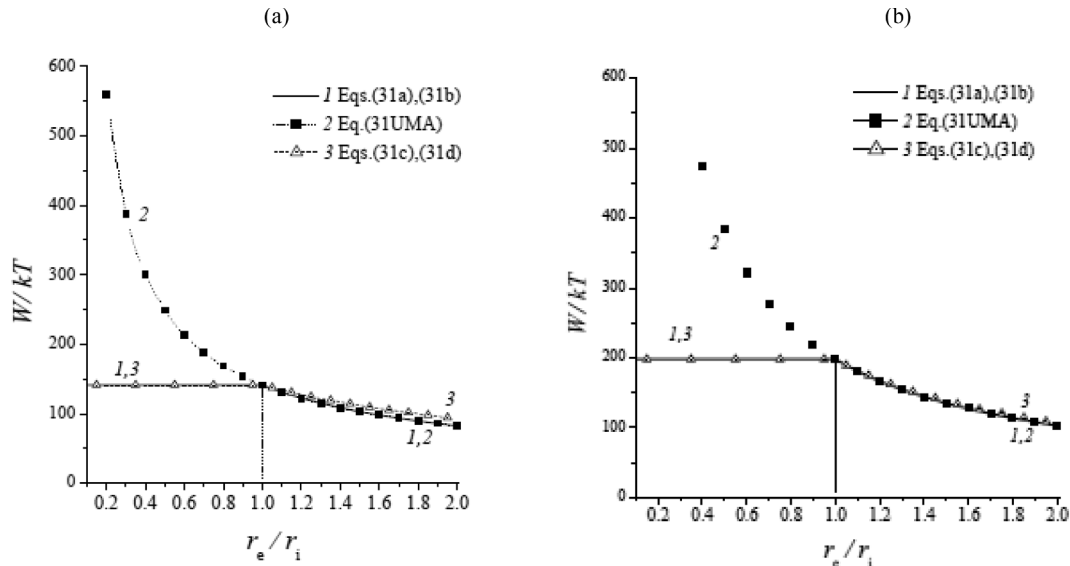


Fig. 2. See Fig. 1. Single-mode dielectric function of the polar medium, Eq. (29b). Comparison of results of the IDA approach, Eqs. (31a,31b) (line 1), with those for the UMA one, W_{IM}^{DK} in Eq. (31UMA) (squares 2) and with those for the “dielectric approximation” (DA) [23,34], Eqs. (31c,31d) (empty triangles 3). $\varepsilon_{\min} = 1.8$ (a) or 4.9 (b), other parameters are given for the 3 M dielectric function, Eq. (29a); $r_i = 1.17 \text{ \AA}$.

existence of spatial regions having quite different dielectric properties, the proposed IDA approach describes these properties of both spatial regions in a substantiated manner.

Important advantages of the IDA calculation procedure have been illustrated for the system simulating a spherical ion inside a polar solvent possessing nonlocal dielectric properties. It has been demonstrated that for any distribution of the ionic charge density, $\rho(r)$, the expressions for the electric field and its potential inside the polar solvent, i.e. outside the spherical cavity, are given by single integrals over k variable containing the inverse dielectric function of the medium, $\epsilon(k)$. If the ionic charge density, $\rho(r)$, is nonzero only inside the cavity (including its external surface), then both the electric potential distribution outside the cavity, $\phi(r)$, and the electrostatic contribution to the ion solvation energy, W , are **independent of the particular form of $\rho(r)$** , i.e. they are determined by **the total ionic charge** and may be found with the use of the Born model for the ionic charge distribution (the whole charge is located on the spherical boundary of the cavity).

It turns out that for the Born model of the ionic charge distribution these characteristics, $\phi(r)$ outside the cavity and W , coincides with predictions of the unrestricted medium approximation (UMA).

At the same time the latter gives obviously incorrect expressions for the potential distribution, $\phi(r)$, inside the cavity region while the IDA approach relates it to local dielectric properties inside the cavity. This difference in predictions results in a drastic deviation of results for W within the framework of the UMA approach from that for the most general treatment (with no use of any model assumptions) where the value of W must be independent of the form of $\rho(r)$, the latter being in conformity with predictions of the IDA approach.

If comparing expressions for the potential, $\phi(r)$, and solvation energy, W , provided by two approaches which take into account particular dielectric properties inside the ionic cavity, i.e. the IDA and DA procedures, **their functional forms are quite different**, in formity with the general prediction in section “Novel approximate (IDA) procedure...”: However, numerical estimations for the single-mode dielectric function of the polar medium (Fig. 2a,b) show their close proximity within the whole range of parameters of the system.

This result (in combination with the identity of the electric characteristics outside the cavity for the IDA method and for the unrestricted medium approximation, UMA) may be considered as a strong evidence in favor of at least semi-quantitative validity of the newly proposed IDA calculation procedure. Besides, the IDA method may be applied easily for calculations of various electric properties for **any** form of the nonlocal dielectric function of the medium (given either analytically or numerically), with no need to perform a complicated task of solving an integral equation, as it is necessary in most case for the approach based on the “dielectric approximation” (DA).

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