An advanced continuum medium model for treating solvation effects: Nonlocal electrostatics with a cavity

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The Born–Kirkwood–Onsager (BKO) model of solvation, where a solute molecule is positioned inside a cavity cut into a solvent, which is considered as a dielectric continuum, is studied within the bounds of nonlocal electrostatics. The nonlocal cavity model is explicitly formulated and the corresponding nonlocal Poisson equation is reduced to an integral equation describing the behavior of the charge density induced in the medium. It is found that the presence of a cavity does not create singularities in the total electrostatic potential and its normal derivatives. Such singularities appear only in the local limit and are completely dissipated by nonlocal effects. The Born case of a spherical cavity with a point charge at its centre is investigated in detail. The corresponding one-dimensional integral Poisson equation is solved numerically and values for the solvation energy are determined. Several tests of this approach are presented: (a) We show that our integral equation reduces in the local limit to the chief equation of the local BKO theory. (b) We provide certain approximations which enable us to obtain the solution corresponding to the preceding nonlocal treatment of Dogonadze and Kornyshev (DK). (c) We make a comparison with the results of molecular solvation theory (mean spherical approximation), as applied to the calculation of solvation energies of spherical ions. © 1996 American Institute of Physics.

I. INTRODUCTION

Continuum models of polar solvents are widely applied in the theory of solvation. They may be considered as a far superior generalization of the simple Born model, which describes a point charge located at the center of a spherical cavity. The cavity imitates the body of a solute particle immersed in a uniform dielectric medium with a constant static permittivity. Recent improvements to the Born model cover cavities of arbitrary shape and consider polarization fields created by arbitrary charge distributions contained in the cavity, which are calculated by quantum-chemical methods. This approach, known as the Born–Kirkwood–Onsager (BKO) solvent model, has a great number of applications. It seems to describe quite satisfactorily a large number of equilibrium solvation phenomena at the expense of introducing a single adjustable parameter which regulates the size of the cavity. In the Born equation, this is the radius \( a \) of the sphere. According to a recent version of the conventional BKO theory, the cavity is constructed as a collection of interlocking spheres surrounding the solute atoms; then the corresponding size parameter is the ratio

\[
\eta = \frac{a_i}{R_i} \text{vdW},
\]

(1.1)

for the radius \( a_i \) of the sphere with the van der Waals radius \( R_i \text{vdW} \) of the respective solute atom. Parameter \( \eta \) is usually treated as a quantity independent of the atom type \( i \) and defined only by the properties of the solvent.

A popular example of an application of the dielectric continuum approach at a dynamical level is the theory of electron transfer reactions, and its subsequent development in terms of a complex-valued dielectric permittivity function. The general case of spatial dispersion of the permittivity \( \varepsilon(\mathbf{k}, \omega) \) (where \( \mathbf{k} \) and \( \omega \) denote wave vector and frequency, respectively) can be formally covered within the framework of a nonadiabatic perturbation treatment without explicitly addressing the size and shape of the solute cavity. The \( \mathbf{k} \) dependence, however, has never been used in practice. Recent adiabatic electron transfer theory is restricted to the case of a spatially unresolved permittivity, \( \varepsilon(\omega) = \varepsilon(\mathbf{k} = 0, \omega) \). Such a treatment is incomplete and various means for its refinement have been discussed by many authors. (We give below key references only, which may serve as a source for a more comprehensive bibliography.) The most obvious physical deficiency of the BKO treatment is that it is fully independent of the size and shape of the solvent molecules. At the very least a single parameter

\[
\zeta = \frac{d(\text{solvent})}{d(\text{solute})},
\]

(1.2)

namely the ratio of the characteristic sizes \( d \) of the solvent and solute particles, introducing some compact information about the internal structure of the solvent, must be present in a physically consistent theoretical treatment.

A detailed microscopic description of a polar solvent is available by means of computer simulation techniques. The microscopic statistical theory of the structure and dynamics of polar liquids is a field of current research and has served as the basis for several molecular theories of solvation. Deficiencies in the simple continuum approach were revealed beyond doubt in studies of nonequilibrium time-dependent phenomena, including dielectric relaxation spectroscopy, and electron transfer.

The present paper is aimed at a formulation of an improved continuum solvent model, allowing for its molecular...
structure in terms of nonlocal electrostatic theory.\textsuperscript{60–63} Being addressed to chemically interesting applications it poses no limitation on the shape and size of solute particles. We concentrate on a static treatment which displays all the essential features of the nonlocal approach introduced into solvation theory by Dogonadze and Kornyshev (DK).\textsuperscript{9,63,60} This treatment is formulated on the basis of a generalized susceptibility integral operator $\hat{\chi}$, defined by its action on an arbitrary spatial function $F(r)$,

$$
\langle \hat{\chi}F \rangle(r) = \int d^3r' \, \chi(r,r')F(r'),
$$

(1.3)

In fact the basic relation (1.3), with a proper allowance made for symmetry, causality and other properties of the susceptibility operator $\hat{\chi}$,\textsuperscript{60–63} serves as the foundation on which a formal phenomenological theory may be developed and investigated. Molecular theories are only invoked at a stage when an explicit form of the susceptibility kernel $\chi(r,r')$, specifying the internal structure of the solvent, is provided. Note, that the characteristic solvent size parameter $d$(solvent) of formula (1.2) in the present theory has no straightforward geometrical interpretation like the diameter of solvent particles in the simplest molecular theories. Similar to other continuum nonlocal treatments,\textsuperscript{60–63} it is subject to a statistical interpretation in terms of correlation lengths, which enter as basic parameters in the susceptibility kernel $\chi(r,r')$ of Eq. (1.3) and represent averaged properties of the potentials governing solvent–solvent interparticle interactions. Amongst applications of nonlocal electrostatics, the simplest uniform case and the case of a plane surface dividing two phases with different permittivities\textsuperscript{60,62} have been described in detail. A spherically symmetric solute ion, the test case of solvation theory, has been considered\textsuperscript{60,62,63} by intuitively extending the equations of the uniform theory to a heterogeneous situation. The result provided a modification of the Born solvation formula which included parameters of the solvent structure of the type (1.2). Below we develop this DK approach by elaborating a general cavity model for nonlocal continuum electrostatics. The nonlocal Poisson equation without symmetry restrictions is converted into an integral equation for the charge distribution induced in the medium. Its solution is studied in detail for a spherically symmetric solute which provides a transparent example appropriate for comparison with earlier nonlocal theories.\textsuperscript{50,62,63}

It is shown that the DK treatment of solvation energy corresponds to the limiting case of a small cavity, i.e., $\xi \to \infty$ in Eq. (1.2), as opposed to the BKO approach corresponding to $\xi \to 0$. Special attention is paid to the limiting transition to the local susceptibility kernel. Consideration of this extreme case clarifies the relation between the basic integral equation of the present advanced continuum theory and that of the conventional BKO model\textsuperscript{1} underlying current chemical applications.

### II. THE KEY RELATIONS OF NONLOCAL ELECTROSTATICS AND PROPERTIES OF BASIC POTENTIAL FUNCTIONS

The following set of equations introduces the relations underlying nonlocal continuum electrostatics:

$$\mathbf{E} = -\nabla \psi,$$

$$\mathbf{P} = \hat{\chi} \mathbf{E},$$

(2.1)

For any space point $\mathbf{r}$, we consider the scalar potential field $\psi(\mathbf{r})$ and the vector fields $\mathbf{E}=\mathbf{E}(\mathbf{r})$, the electric field strength, and $\mathbf{P}=\mathbf{P}(\mathbf{r})$, the polarization field. Henceforth, we shall suppress writing vector quantities in vector notation. This will not lead to confusion because such quantities are regularly combined in scalar products ($\ldots$); the latter notation automatically implies that the quantities inside the brackets are vectors.

The nonlocal permittivity integral operators $\hat{\epsilon}$ (dielectric permittivity) and $\hat{\chi}$ (susceptibility) are defined in terms of their kernels $\epsilon(r,r')$ and $\chi(r,r')$ as

$$\langle \hat{\epsilon}F \rangle(r) = \int d^3r' \, \epsilon(r,r')F(r'),$$

(2.2)

$$\langle \hat{\chi}F \rangle(r) = \int d^3r' \, \chi(r,r')F(r'),$$

(2.3)

where $F(r)$ is an arbitrary function. The susceptibility kernel $\chi(r,r')$ is the key quantity of the theory and, as a rule, we avoid working with the singular kernel $\epsilon(r,r')$, expressing it rather by means of Eq. (2.3). Finally, we confine our treatment to the isotropic case, so $\epsilon(r,r')$ and $\chi(r,r')$ are always considered as scalar (rather than tensorial) quantities.

The nonlocal Poisson equation reads

$$\nabla(\hat{\epsilon} \nabla) \psi = -4 \pi \rho,$$

(2.4)

where $\rho(r)$ is a solute charge distribution. It will be shown in Sec. III that even in the case where there is a discontinuity in the kernel $\chi(r,r')$ on the cavity surface $S$ (see Fig. 1), both potential $\psi$ and its normal derivative $\partial \psi / \partial n$ remain continuous at the surface. Only in the local limit $\chi(r,r') = \chi_0 \delta(r-r')$, where $\delta(r-r')$ is a three-dimensional Dirac-delta function, does the usual discontinuity of $\partial \psi / \partial n$ arise, and the Poisson equation is supplemented by the boundary conditions

$$\psi_i = \psi_e,$$

(2.5)

$$\frac{\partial \psi}{\partial n} \bigg|_i = \epsilon_0 \frac{\partial \psi}{\partial n} \bigg|_e.$$

In this case $\epsilon_0 = 1+4 \pi \epsilon_0$ is the static dielectric constant. The indices $i$ and $e$ label the internal and external sides of the boundary surface.
At a formal level, the main problem in the treatment of Eq. (2.4) arises due to the fact that operators $\hat{V}$ and $\hat{\chi}$ (or $\hat{e}$) generally do not commute:

$$\left[ \hat{V}, \hat{\chi} \right] = \frac{1}{4\pi} \left[ \hat{V}, \hat{e} \right] \neq 0.$$  
(2.6)

Commutation holds only in the special uniform case with no cavity where $\chi(r, r') = \chi(0)$, for all $r, r' \in R^3$.

Here the function in Eq. (2.7) is continuous over the whole space. Then operators $\hat{V}$, $\hat{\chi}$, and $\hat{e}$ generate a common set of eigenfunctions (the plane waves):

$$\hat{V} e^{i(k,r)} = -ik \hat{e} e^{-i(k,r)},$$  
$$\hat{\chi} e^{i(k,r)} = \chi(r) \hat{e} e^{-i(k,r)},$$  
$$\hat{e} e^{i(k,r)} = e(r) \hat{e} e^{-i(k,r)},$$

where eigenvalues defined in terms of Fourier transforms:

$$\chi(k) = \int d^3r \chi(|r|) e^{i(k,r)},$$

$$e(k) = 1 + 4\pi \chi(k),$$

(2.9)

In the following, we extensively use Green’s formulas:

$$\int_V d^3r u \nabla^2 v + \int_V d^3r \nabla u \nabla v = \int_S d^2r u \frac{\partial v}{\partial n},$$

$$\int_V d^3r (u \nabla^2 v - v \nabla^2 u) = \int_S d^2r \left( u \frac{\partial v}{\partial n} - v \frac{\partial u}{\partial n} \right),$$

(2.10a)

(2.10b)

where the surface $S$ bounds volume $V$, and $u$ and $v$ are nonsingular spatial functions. Formulas (2.10) hold for $V = V_i$ (the internal volume inside $S$). For $V = V_e$ (the external volume outside $S$) a special condition is needed certifying that at least one of the functions $u(r)$, $v(r)$ vanishes sufficiently rapidly as $|r| \to \infty$ (we assume that the cavity includes the point $r = 0$). A special case of Eq. (2.10b), corresponding to $u(r) = 1/(R-r)$, reads

$$- \int_V d^3r \nabla^2 u \frac{1}{|R-r|} = pu(R) + \int_S d^2r u \frac{\partial}{\partial n} \left( \frac{1}{|R-r|} \right)$$

$$- \frac{1}{|R-r|} \frac{\partial u}{\partial n},$$

(2.11)

where the subscript $r$ refers to the space variable involved in the computation of the derivative.

For the case $V = V_i$,

$$p = \begin{cases} 
4\pi, & R \in V_i, \\
2\pi, & R \in S, \\
0, & R \in V_e.
\end{cases}$$

(2.12)

Finally, we consider the potential $\psi(r)$ as a combination of three basic components:

$$\psi(r) = \varphi(r) + \xi(r) + \Phi(r),$$

(2.13)

where

$$\varphi(r) = \int_{V_i} d^3r' \rho(r') \frac{1}{|r-r'|},$$

$$\xi(r) = - \int_{V_e} d^3r' (\mu(r'), \nabla r') \frac{1}{|r-r'|},$$

$$\Phi(r) = \int_S d^2r' \sigma(r') \frac{1}{|r-r'|},$$

(2.14)

(2.15)

(2.16)

Here $(\ldots \cdot \ldots)$ means the scalar product of two vectors.

Hence $\varphi$ is the solute vacuum field potential for the solute charge density $\rho(r)$. $\xi$ is a dipole field potential with a dipole vector density $\mu(r)$ for the medium, and $\Phi$ is a single layer potential with surface charge density $\sigma(r)$. Potential $\varphi$ behaves smoothly on $S$, whereas $\xi$ and $\Phi$ are singular. Potential $\Phi$ is continuous $(\Phi_i = \Phi_e)$, but its normal derivative, for $r \in S$, is expressed as

$$\left( \frac{\partial \Phi}{\partial n} \right)_i = 2\pi \sigma + \int d^2r a(r,r') \sigma(r'),$$

$$\left( \frac{\partial \Phi}{\partial n} \right)_e = -2\pi \sigma + \int d^2r a(r,r') \sigma(r'),$$

(2.17)

where

$$a(r,r') = \left( \frac{\partial}{\partial n} \right)_r \frac{1}{|r-r'|} = - \frac{(n_r, r-r')}{|r-r'|^3}.$$  
(2.18)

The discontinuity in the normal derivatives as seen in Eq. (2.17) can be deduced by using Green’s theorem (2.11). Another important identity:

\[ \text{J. Chem. Phys., Vol. 105, No. 9, 1 September 1996} \]
The second identity allows for a change in the sign of the second part of Eq. (2.11).

In order to demonstrate some particular properties of the function \( \xi(r) \), we perform integration by parts on the right-hand part of Eq. (2.15) with the aid of the following identities:

\[
(\nabla, aF) = a(\nabla, F) + (F, \nabla a),
\]

\[
\int_{V_e} d^3r \hat{N}(\nabla, F) = - \int d^2r(F(r), \nabla r),
\]

where \( a(r) \) and \( F(r) \) are scalar and vector functions, respectively. The second identity allows for a change in the sign of the normal unit vector \( \hat{r} \) when \( r \) approaches \( S \).

We observe now that by accepting the following boundary condition:

\[
(n(r), \mu(r)) = -\sigma(r) \quad (r \in S),
\]

(22.22)

We note now that by accepting the following boundary condition:

\[
\frac{\partial}{\partial n} \left( \xi + \Phi \right)(r) = \left[ n(r), \nabla r \right] \times \left( \int_{V_e} d^3r' \frac{1}{|r-r'|} (\nabla r', \mu(r')) \right)
\]

\[
= \int_{V_e} d^3r' (\nabla r', \mu(r')) a(r,r').
\]

(22.23)

This important special case underlies our subsequent derivations.

We shall also need second derivatives in the form

\[
\nabla^2 \varphi = -4\pi \rho,
\]

\[
\nabla^2 \xi = -4\pi \left( \nabla \mu, \right)_{r \in V_e},
\]

\[
\nabla^2 \Phi = 0 \quad (r \in V_i \text{ or } r \in V_e).
\]

The relation for \( \xi \) can be obtained by using the identity

\[
\nabla^2 \left( \frac{1}{|r-r'|} \right) = -4\pi \delta(r-r'),
\]

(22.25)

together with the properties of the gradient of the three-dimensional Dirac delta function.\(^{65}\)

\[
\int_{V_e} d^3r' F(r') [\nabla', \delta(r-r')] = -\nabla F(r), \quad r \in V_e,
\]

(2.26)

where \( F(r) \) is a spatial function. The behavior of Eqs. (2.24) and (2.26) on the surface is a delicate question that will be discussed further.

### III. The Nonlocal Poisson Equation

We first consider Eq. (2.4) for the simplest uniform case (2.7)–(2.9). Due to the commutation relation

\[
[\nabla, \xi] = 0,
\]

(3.1)

one immediately finds

\[
\nabla^2 \psi = -4\pi \rho_e,
\]

(3.2)

In terms of the Fourier transforms \( \chi(\kappa) \) and \( \rho(\kappa) \), namely

\[
\chi(r-r') = \left( \frac{1}{2\pi} \right)^3 \int d^3\kappa \chi(\kappa) e^{-i\kappa \cdot (r-r')},
\]

\[
\rho(r) = \left( \frac{1}{2\pi} \right)^3 \int d^3\kappa \rho(\kappa) e^{-i\kappa \cdot r},
\]

(3.3)

we arrive at the explicit expressions

\[
\rho_e(r) = \left( \frac{1}{2\pi} \right)^3 \int d^3\kappa \frac{\rho(\kappa)}{1+4\pi \chi(\kappa)} e^{-i\kappa \cdot r},
\]

(3.4)

Evaluation of integrals with \( \chi(r-r') = \chi(|r-r'|) \) and \( \chi(\kappa) = \chi(k) \), where \( k = |k| \), is performed using standard techniques for expanding plane waves in terms of spherical harmonics.\(^{66}\)

For a point charge,

\[
\rho(r) = \delta(\nabla)(r-r),
\]

(3.5)

one obtains the familiar expression \(^{60,62}\)

\[
\psi(r) = \frac{2Q}{\pi} \int_0^\infty \frac{dk}{1 + 4\pi \chi(k)} \frac{\sin(k|r-r|)}{|k| |r-r|}.
\]

(3.6)

Proceeding now to the case with a cavity (Fig. 1), we specify the charge density \( \rho(r) \) and susceptibility kernel \( \chi(r-r') \) as double-valued quantities:

\[
\rho = \left\{ \begin{array}{ll}
\rho(r), & r \in V_i, \\
0, & r \in V_e,
\end{array} \right.
\]

(3.7)

\[
\chi(r-r') = \left\{ \begin{array}{ll}
\chi(|r-r'|), & \text{both } r \text{ and } r' \in V_i, \\
0, & \text{one or both of } r, r' \in V_e.
\end{array} \right.
\]

(3.8)

The basic relations (3.7) and (3.8) explicitly introduce the concept of the cavity into nonlocal electrostatics. Note, that in accepting the kernel in the form \( \chi(|r-r'|) \) for the external volume, we invoke the uniform model as an auxiliary tool.
The uniform relation (2.7) does not hold in the whole of space, and as a consequence the nonlocal Poisson Eq. (2.4) is recast in the form
\[ \nabla^2 \psi = -4 \pi \rho, \quad r \in V_i, \]
\[ \nabla (\varepsilon \nabla \psi) = 0, \quad r \in V_e. \tag{3.9} \]

We now need an explicit transcription of the second formal operator equation in terms of the definition of the susceptibility as given by Eq. (3.8). Expressing \( \varepsilon \) in terms of \( \chi \), one obtains for \( r \in V_e \),
\[ \nabla (\varepsilon \nabla \psi) = \nabla^2 \psi + 4 \pi \nabla \int_{V_e} d^3 r' \chi(|r-r'|) \nabla \psi(r') \]
\[ = \nabla^2 \psi - 4 \pi \int_{V_e} d^3 r' \nabla \cdot \chi(|r-r'|) \nabla \psi(r'). \]

One can now apply Green’s formula (2.10a) to the integral over the external volume \( V_e \). The inversion of sign for the normal derivative relative to the definition given by Fig. 1, addressed to \( V_i \), must be kept in mind. Hence, specifying the normal derivative as \( \partial \psi/\partial n \) according to Fig. 1, the following equation holds for the external region:
\[ \frac{1}{4 \pi} \nabla^2 \psi = - \int_{V_e} d^3 r' \chi(|r-r'|) \nabla^2 \psi(r') \]
\[ - \int d^2 r' \chi(|r-r'|) \frac{\partial \psi}{\partial n} (r'), \quad r \in V_e. \tag{3.10} \]

One can observe from Eq. (3.10) that deviation from the simple local equation \( \nabla^2 \psi = 0 \) (\( r \in V_e \)) essentially arises due to the surface term, so that the surface perturbation, as represented by \( \partial \psi/\partial n \), is extended over the whole external region by the nonlocal effect.

As a final step, we substitute \( \psi \) in the form of Eqs. (2.13)–(2.16) into the Poisson Eq. (3.9) and make use of formulas (2.24). The first equation reduces to \( \nabla^2 \psi = -4 \pi \rho \) which is satisfied by Eq. (2.14). Hence, we need only to solve the equation for the external region, which reads
\[ (\nabla, \mu) = -4 \pi \int_{V_e} d^3 r' \chi(|r-r'|) (\nabla, \mu(r')) \]
\[ + \int d^2 r' \chi(|r-r'|) \left[ \frac{\partial \psi}{\partial n} + \frac{\partial \xi}{\partial n} + \frac{\partial \Phi}{\partial n} (r') \right], \quad r \in V_e. \tag{3.11} \]

We recall now that, according to Eqs. (2.17) and (2.21), \( \partial \Phi/\partial n \) and \( \partial \xi/\partial n \) have discontinuities on the boundary surface \( S \). An unambiguous application of Green’s theorem, leading to Eqs. (3.10) and (3.11), implies that \( \partial \psi(r)/\partial n \) has no discontinuities and is single valued on \( S \) as the point \( r \in V_e \) approaches \( S \). This can only be attained by imposing the boundary condition of Eq. (2.22),
\[ (n_r, \mu(r)) = -\alpha(r), \quad (r \in S). \tag{3.12} \]

Then, we apply Eq. (2.23) and reduce the nonlocal Poisson Eq. (3.11) to the final form
\[ (\nabla, \mu) + 4 \pi \int_{V_e} d^3 r' \chi(|r-r'|) (\nabla, \mu(r')) \]
\[ = \int d^2 r' \chi(|r-r'|) \left[ \frac{\partial \psi}{\partial n} (r') + \int_{V_e} d^3 r'' a(r', r'') \right] \times (\nabla, \mu(r'')), \quad r \in V_e. \tag{3.13} \]

It is now expedient to introduce the notation
\[ (\nabla, \mu(r)) = g(r), \tag{3.14} \]
and rewrite the total potential field as a sum of two nonsingular terms
\[ \psi(r) = \int_{V_i} d^3 r' \frac{\rho(r')}{|r-r'|} + \int_{V_e} d^3 r' \frac{g(r')}{|r-r'|}, \tag{3.15} \]
which is suggested by Eqs. (2.13)–(2.16), (2.21), (2.22), and (3.14). The quantity \( g(r) \) refers to the charge density induced in the medium. We suppose it to be a smooth function, so that the potential (3.15) has no singularities on the boundary.

By introducing the integral kernel
\[ l(r, r'') = \int d^2 r' \chi(|r-r'|) a(r', r''), \tag{3.16} \]
we rewrite the external Poisson Eq. (3.11) in the form
\[ g(r) + 4 \pi \int_{V_e} d^3 r' \chi(|r-r'|) g(r') \]
\[ = \int_{V_i} d^3 r'' \rho(r'') l(r, r'') \]
\[ + \int d^2 r' \chi(|r-r'|) \frac{\partial}{\partial n_{r'}} \int_{V_e} d^3 r'' l(r', r''), \tag{3.17} \]
where \( r \in V_e \). Contrary to Eq. (3.13), this last equation is valid for both singular and nonsingular functions \( g(r) \). The necessity for such a generalization is motivated in Sec. IV. The description in terms of \( g(r) \) requires no reference to the surface charge density \( \sigma \), which has been eliminated with the surface terms. Nonetheless, given \( g(r) \) as a solution to Eq. (3.17), we can regenerate \( \mu(r) \) by inverting Eq. (3.14), and thereby arrive at \( \sigma(r) \) with the aid of Eq. (3.12). However, there is usually no need for this effort. A simple description in terms of Eq. (3.15) with a continuous medium charge distribution \( g(r) \) is sufficient to construct the nonlocal theory, the variables \( \mu \) and \( \sigma \) appearing only as auxiliary quantities. We have included them in our reasoning because the medium field is conventionally treated in terms of a polarization variable, which is nothing other than our quantity \( \mu(r) \).

It is easy to demonstrate that in fact
\[ \mu = \hat{\chi} \nabla \psi = -P, \tag{3.18} \]
where \( P \) is the polarization vector in Eq. (2.1). For then, from the nonlocal Poisson Eq. (3.9) for the external region, we find that

\[
\nabla^2 \psi = -4\pi \nabla (\hat{\nabla} \psi) = -4\pi \nabla (\nabla \mu),
\]

which is satisfied by

\[
\psi(r) = \varphi(r) + \int_{V_e} d^3r' \frac{(\nabla \mu)(r')}{|r-r'|}.
\]

The last expression is identical with the representation (3.15) derived above.

### IV. THE TRANSITION TO THE LIMITING LOCAL CASE

We were able to demonstrate in Sec. III that a continuous expression (3.15) for the potential \( \psi \) is sufficient to represent a solution of the nonlocal Poisson equation with a cavity:

\[
\psi(r) = \varphi(r) + \xi_0(r),
\]

\[
\xi_0(r) = \xi(r) + \Phi(r) = \int_{V_e} d^3r' \frac{g(r')}{|r-r'|}.
\]

This is indeed so until one deals with the local limit

\[
\chi(x, r') = \chi_0 \delta(r-r'),
\]

where \( \chi_0 = \chi(k=0) \). The corresponding limiting transition deserves a special investigation. In particular, it is worth commenting on the transformation of the smooth medium field \( \xi_0(r) \) into the singular layer potential \( \Phi_0(r) \):

\[
\xi_0(r) = \int_{V_e} d^3r' \frac{g(r')}{|r-r'|} - \Phi_0(r) = \int_{V_e} d^3r' \frac{\sigma_0(r')}{|r-r'|}.
\]

The key problem at a technical level becomes the meaning of the integral \( \int_{V_e} d^3r' \delta(r-r')F(r') \) on the boundary \( r \in S \). A related problem concerns the meaning of the normal derivative \( \partial \Phi_0 / \partial n \). We resolve the ambiguity by a special asymmetric convention

\[
\int_{V_e} d^3r' \delta(r-r')F(r') = F(r), \quad r \in S,
\]

\[
\frac{\partial \xi_0}{\partial n} (r) \rightarrow \frac{\partial \Phi_0}{\partial n} (r)
\]

\[
= \left[ \frac{\partial \Phi_0}{\partial n} \right]_i (r)
\]

\[
= \int d^2r' \sigma_0(r')a(r, r') + 2\pi \sigma_0(r), \quad r \in S.
\]

These relations cannot be mathematically derived, rather they reflect some intrinsic properties of the present cavity model. The guideline to our confidence in their internal consistency is the integral equation defining \( \sigma_0 \) in the limit (4.2), namely

\[
(1 + 4\pi \chi_0) \sigma_0(r) = \chi_0 \left[ \int_{V_e} d^3r' \rho(r')a(r, r') + \int d^2r' \sigma_0(r')a(r, r') + 2\pi \sigma_0(r) \right].
\]

This is the well-known matching equation of the local theory.\(^{1,2,67}\)

We shall now show that only after specifying the singularities, which arise when the local case is considered, in terms of conventions (4.4) and (4.5), will the nonlocal Poisson Eq. (3.17) transform into the local matching expression (4.6). According to the convention (4.5) we express the medium-induced part of Eq. (3.17) as

\[
\int d^2r' \chi(|r-r'|) \frac{\partial \xi_0}{\partial n} (r')
\]

\[
\chi_0 \int d^2r' \delta(r-r')
\]

\[
\times \left[ \int d^2r'' \sigma_0(r'')a(r, r'') + 2\pi \sigma_0(r') \right] (4.7)
\]

It can now be seen that the resulting limit of Eq. (3.17) is satisfied by accepting

\[
g(r) = \int d^2r' \sigma_0(r') \delta(r-r'),
\]

which agrees fully with the result we anticipated in Eq. (4.3) only if convention (4.4) is accepted.

By using expressions (4.7) and (4.8), we indeed transform the Poisson Eq. (3.17) to the desired form (4.6). This transition does not seem to be smooth because the singular term \( 2\pi \sigma_0 \) appears stepwisely. It is missing if we perform the local limit in the essentially nonlocal approximation (3.13). However, since the relation (4.4) is always true for \( r \in V_e \), the transition (4.2) is expected to be performed before a consideration of surface quantities \( r \in S \) is addressed. A natural consequence of this convention is the prescription (4.5) for evaluating surface derivatives. In this formulation a smooth transition to the limiting local case is gained.

More generally, one can state that the operations of taking the limit (4.2) and differentiation in \( \partial \xi_0 / \partial n \) do not commute. The differentiation may be specified as an asymmetric limit transition:

\[
\left( \frac{\partial \xi_0}{\partial n} (r) \right)_i = \lim_{\epsilon \rightarrow 0} \frac{\xi_0(n_0) - \xi_0(n_0 - \epsilon)}{\epsilon}
\]

where \( n \) changes in the direction of the normal vector \( n(r) \) in the vicinity of the surface point \( r \) and \( n = n_0 \) on the surface. Accordingly in Eq. (3.17) the limit (4.9) must be performed first, in accordance with the prescription of Eq. (4.5), before the limit (4.2) is applied.
V. SYSTEMS WITH SPHERICAL SYMMETRY

We consider now a spherical cavity of radius \( a \) with a point solute charge \( Q \) at its center:

\[
\rho(r) = Q \delta(r).
\]  

(5.1)

Space points are represented in terms of spherical coordinates

\[
r = (R, \theta, \varphi), \quad r' = (R', \theta', \varphi').
\]  

(5.2)

Surface integration can then be specified as

\[
\int_{S(R')} d^2 r' \frac{1}{|r-r'|} = \text{constant} \quad (R \approx R').
\]  

(5.3)

The second relation refers to an arbitrary spherically symmetric single layer potential \( \Phi \) with a constant charge density \( \sigma \) on the sphere \( S(R') \) and will be required presently.

As an immediate consequence we obtain the following property of the polarization field potential \( \xi_0(r) \):

\[
\xi_0(r) = \int_{V_e} d^3 r' \frac{g(r')}{|r-r'|} = \text{constant}
\]

\[
= 4 \pi \int_a R' dR' g(R'), \quad R \approx a \text{(i.e., } r \in V_i). \tag{5.5}
\]

The first line is an \( r \)-independent constant for \( r \in V_i \), which follows from Eq. (5.4) when we consider \( g(R') \) as a combination of spherically symmetric single layer charge distributions \( \sigma \) arranged along \( R \); the second line is then obtained by calculating this constant at the point \( r=0 \).

The equilibrium solvation energy, generally defined as

\[
U_{\text{solv}} = \frac{1}{2} \int d^3 r \rho(r) \xi_0(r),
\]  

(5.6)

simplifies in the present case to

\[
U_{\text{solv}} = \frac{Q}{2} \xi_0(0) = 2 \pi Q \int_a^\infty dR \ R \ g(R). \tag{5.7}
\]

It is expedient to define the quantity

\[
\gamma(R, R') = \int_{S(R')} d^2 r' \ \chi(|r-r'|)
\]

\[
= R'^2 \int \sin \theta' d\theta' \ d\varphi' \ \chi(|r-r'|). \tag{5.8}
\]

Relations (5.4) then allow us to reduce the integral Eq. (3.17) to the form (see Appendix A)

\[
g(R) + 4 \pi \int_a^\infty dR' \ g(R') \gamma(R, R') = - \frac{Q}{a^2} \gamma(R, a). \tag{5.9}
\]

For further investigation a specification of the susceptibility kernel \( \chi(|r-r'|) \) is required. We make use of a multimode description in terms of the Fourier transform \( \chi(k) \) [see Eq. (3.3)]:

\[
\chi(k) = \sum_i \frac{X_i}{1 + \kappa_i^2} e^{-|r-r'| \kappa_i}
\]

\[
= \sum_i \frac{X_i}{4 \pi \kappa_i^2} \frac{\sinh(\kappa_i R)}{|r-r'|}, \tag{5.10}
\]

with the normalization condition

\[
\sum_i X_i = x_0, \quad \epsilon_0 = 1 + 4 \pi x_0, \tag{5.11}
\]

where \( x_0 \) and \( \epsilon_0 \) are the limiting values of the respective dielectric functions when \( k = 0 \). The relationship between the present parametrization given by formulas (5.10) and (5.11), and a conventional form of the nonlocal theory is discussed in Appendix B. A discussion of the deficiencies in this Lorentzian representation of the nonlocal integral kernels is given in Sec. VIII.

We can now provide an explicit expression for the integral kernel \( \gamma(R, R') \):

\[
\gamma(R, R') = \sum_i \frac{X_i}{\kappa_i^2} \frac{\sinh(R/\kappa_i)}{R}, \quad R \approx R',
\]

\[
= \sum_i \frac{X_i}{\kappa_i} \frac{e^{-R/\kappa_i}}{R}, \quad R > R'. \tag{5.12}
\]

An exact treatment henceforward is only available numerically. Some asymptotic results are derived in Appendix C. In the local limit the solution to Eq. (5.9) becomes a one-dimensional Dirac delta function \( g(R) \sim \delta(R-a) \) and the classical Born solvation energy expression comes out from the general formula (5.6):

\[
U_{\text{solv}} = - \frac{Q^2}{2a} \left( \frac{1}{\epsilon_0} - 1 \right). \tag{5.13}
\]

This derivation reveals explicitly the singularities discussed in general terms in Sec. IV.

VI. COMPARISON WITH THE EARLIER APPROXIMATE NONLOCAL THEORY

Expressions (5.6) and (5.9) provide a solid background for studying the range of validity of the Dogonadze–Kornyshev (DK) model describing equilibrium solvation of spherical ions. In order to get a deeper insight into the simplifications inherent to their treatment, we return to the general Eq. (3.13) for the external charge distribution \( g(r) \). Let us introduce two approximations:

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(a) Change integrals over the external volume \( V_e \) into integrals over all of space:

\[
\int_{V_e} d^3r' \chi(|r-r'|)(\cdots) = \int_{\mathbb{R}^3} d^3r' \chi(|r-r'|)(\cdots). \tag{6.1}
\]

(b) Neglect the \( g \) dependent second term on the right-hand side of Eq. (3.13).

The first assumption allows one to employ the operator relations (2.8) and (2.9) of the uniform theory. The second is satisfied identically for a spherically symmetric solute (see Appendix A) but is essential in the general case.

Under these approximations one obtains from Eq. (3.13) the following simple result:

\[
g(r) = \frac{1}{4\pi} \left( \hat{f} \int d^3r' \delta(r-r') \frac{\partial \phi}{\partial n}(r') \right) (r)
= \frac{1}{4\pi} \int d^3r' f(|r-r'|) \frac{\partial \phi}{\partial n}(r'), \tag{6.2}
\]

where we introduced the operator

\[
\hat{f} = \left( 1 - \frac{1}{\epsilon} \right) = \frac{4\pi \chi}{1 + 4\pi \chi}, \tag{6.3}
\]

with the integral kernel given in terms of its Fourier transform:

\[
f(k) = \left( 1 - \frac{1}{\epsilon(k)} \right) = \frac{4\pi \chi(k)}{1 + 4\pi \chi(k)}. \tag{6.4}
\]

In calculating solvation energy the approximation (6.1) must be invoked once more, transforming the function \( \xi_0(r) \) [see Eq. (4.1)] to an integral over total space:

\[
\xi_0(r) = \int d^3r' \frac{g(r')}{|r-r'|}. \tag{6.5}
\]

The main DK result is then obtained by defining the solute charge density as a surface charge:

\[
\rho(r) = Q \delta(r-a)/4\pi a^2. \tag{6.6}
\]

This charge distribution generates a simple layer potential \( \varphi(r) \) for which we must accept \( \frac{\partial \phi}{\partial n} = (\varphi/\partial n)_0 \). Using this \( \rho(r) \) and \( \xi_0 \) defined in terms of Eqs. (6.2) and (6.5), formula (5.6) yields the DK expression for the solvation free energy:

\[
U_{\text{solv}} = -\frac{Q^2}{\pi} \int_0^\infty dk f(k) \frac{\sin^2 ka}{k^2 a^2}. \tag{6.7}
\]

This complicated route is necessary for reproducing the DK result. A seemingly more natural derivation, based on the same approximation (6.1) and the consequent Eq. (6.2), turns back to the exact reaction field expression (5.5) instead of using the approximate expression Eq. (6.5). The resulting free energy expression as extracted from Eq. (5.6) is then

\[
U_{\text{solv}} = -\frac{Q^2}{\pi} \int_0^\infty dk f(k) \frac{\sin 2ka}{2ka}. \tag{6.8}
\]

It is obtained with both charge densities (5.1) and (6.6) because, according to Eq. (5.5), the polarization potential is constant inside the cavity and any spherically symmetric charge distribution within the cavity gives the same solvation free energy.

On the other hand, only the charge density defined according to Eq. (6.6) reproduces the DK expression (6.7). Note, that both distributions (5.1) and (6.6), as well as any other spherically symmetric distribution inside the cavity, give the same potential \( \varphi(r) \) in \( V_e \) but they differ inside the cavity, when \( R < a \). Integration over the volume \( V_i \) \( (R < a) \), which is introduced by Eq. (6.5) but is not needed in the exact treatment, gives rise to the discrepancy between formulae (6.7) and (6.8). In fact the basic approximation (6.1) is used only once in deriving Eq. (6.8) but twice in deriving Eq. (6.7); both these analytic expressions are obtained at the expense of neglecting the presence of the cavity.

The two free energy expressions, however, coincide in the local limit, both giving the Born result (5.12), and in the limit of a vanishing cavity giving

\[
\lim_{a \to 0} U_{\text{solv}} = -\frac{Q^2}{\pi} \int_0^\infty dk f(k). \tag{6.9}
\]

The asymptotic result (6.9) is exact since the substitution (6.1) becomes exact in this case. Only in the local case does it show divergence, which can be explicitly seen if one sets \( a \to 0 \) in the Born formula.

VII. NUMERICAL TESTS

In constructing a numerical solution to the integral Eq. (5.9) we introduce a set of piecewise basis functions:

\[
\nu_n(R) = \nu(R-R_n) = \frac{1}{\sqrt{\Delta}} \theta(R_n + \Delta - R) \theta(R - R_n), \tag{7.1}
\]

\[
R_n = a + (n-1)\Delta, \quad n = 1,2,\ldots,N. \]

Here \( \theta(z) \) equals 0 for \( z < 0 \) and 1 for \( z > 0 \), the Heaviside step function. Functions \( \nu_n \) obey the orthonormality condition

\[
\int_a^R \nu_m \nu_n \, dR = \delta_{mn}. \tag{7.2}
\]

We expand the radial charge distribution \( g(R) \) over this basis set:

\[
g(R) = \sum_{n=1}^N C_n \nu_n(R), \tag{7.3}
\]

and insert the expansion into Eq. (5.9). After standard manipulation the following set of linear equations appears:

\[
C_m + 4\pi \Delta \sum_{n=1}^N C_n \gamma(R_m, R_n) = -\frac{Q \Delta}{a^2} \gamma(R_m, a). \tag{7.4}
\]

Its solution reduces to the inversion of matrix \( T \) with elements

\[
T_{mn} = \delta_{mn} + 4\pi \Delta \gamma(R_m, R_n). \tag{7.5}
\]
The corresponding calculations were performed and their results are shown in Figs. 2–5. A perfect convergence was attained for $N = 200–500$ where $\Delta = 10a/N$ and $a = 1.5$ Å, $Q = 1$ a.u. (a unit proton charge). Figures 2 and 3 show the function $g(R)$ and the solvation energy $U_{solv}$, as a function of the cavity radius $a$. We used one- and three-mode representations for the susceptibility $\chi(k)$ [see Eq. (5.10)]. Values for the parameters $\chi_i$ and $\lambda_i$ were extracted from the similar DK parametrization $^{60}$ of the function $f(k)$, represented by Eq. (6.4). Their values, calculated as described in Appendix B, for $\epsilon_0 = 78.8$, $\chi_0 = 6.191$, are

One mode $\chi(k)$: $\chi_1 = \chi_0 = 6.191$,

$\lambda_1 = \sqrt{\epsilon_0} \text{Å} = 8.877$ Å

Three-mode $\chi(k)$: $\chi_1 = 0.06366$, $\lambda_1 = 0.05$ Å

(or $\lambda_1 = 0.1$ Å for $a \geq 3.3$ Å in Fig. 3)

$\chi_2 = 0.2223$, $\lambda_2 = 1.623$ Å

Simplified analytical expressions (6.2) [for the induced charge distribution $g(r)$] and Eqs. (6.7) and (6.8) (for the solvation free energy) are compared with the exact calculations in Figs. 4 and 5. Three-mode expressions for functions $\chi(k)$ and $f(k)$ are applied here. The value $\Lambda_1 = 0.05$ Å—see Appendix B—has been used instead of $\Lambda_1 = 0$ Å in Eq. (6.2), the DK calculation of $g(r)$, in order to avoid numerical divergence in the result, as was similarly done for our exact calculation [see Eq. (7.6)]. Note that formula (6.2) provides an extrapolation of the DK approach for asymmetrical solutes. An intrinsic deficiency of this approach is also seen in that $g(r)$, according to Eq. (6.2), represents a surface integral. Hence spatial correlations described by operator $\hat{f}$ operate only on the boundary of the cavity, whereas correlations extending deep into the external volume are missing.
TABLE I. Values of parameter λ for a single-mode Lorentzian model of χ(k), fitted to the experimental data (Refs. 70 and 71) of solvation energy of monovalent cations and anions in eight different solvents. The accepted dielectric constant (Ref. 76) ε₀ each solvent is also listed.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant ε₀</th>
<th>λ, Å (Cations)</th>
<th>λ, Å (Anions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water</td>
<td>78.30</td>
<td>7.46</td>
<td>1.74</td>
</tr>
<tr>
<td>2. Methanol</td>
<td>32.66</td>
<td>4.75</td>
<td>0.91</td>
</tr>
<tr>
<td>3. Ethanol</td>
<td>24.55</td>
<td>4.19</td>
<td>0.75</td>
</tr>
<tr>
<td>4. 1-Propanol</td>
<td>20.45</td>
<td>3.78</td>
<td>0.67</td>
</tr>
<tr>
<td>5. 2-Butanol</td>
<td>17.51</td>
<td>3.37</td>
<td>0.54</td>
</tr>
<tr>
<td>6. Propylene carbonate (PC)</td>
<td>64.92</td>
<td>7.19</td>
<td>3.45</td>
</tr>
<tr>
<td>7. Dimethyl formamide (DMF)</td>
<td>36.71</td>
<td>4.67</td>
<td>2.63</td>
</tr>
<tr>
<td>8. Dimethyl sulfoxide (DMSO)</td>
<td>46.45</td>
<td>5.23</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Another set of calculations was performed in order to investigate the solvation energy of spherical ions in a series of solvents in terms of the exact Eqs. (5.6)–(5.9). The results were compared with similar calculations based on the mean spherical approximation (MSA).

For the sake of comparison, we borrowed the values of ion radii a from the MSA treatment and, within the framework of a single-mode model of Eq. (5.10), we adjusted the correlation lengths λ for each solvent so as to obtain the best fit for the experimental data of different ions.

The λ values thus obtained are collected in Table I. The seemingly exaggerated λ values for several of the solvents (water, propylene carbonate) can be interpreted by the relation λ₁ = √ε₀Λ₁ where Λ₁ is a parameter for the single-mode model of function f(k) (see Appendix B). Figures 6 and 7 show the solvation energy as a function of ion radius a by our calculation compared with MSA and experimental results. Figure 6 shows the solvation energies of monovalent ions in water as a typical example; Fig. 7 shows U_solv for ions in propanol, wherein the highest disparity between our energies and MSA energies was seen.

Two different dependencies for cations and anions in the same solvent occur in both nonlocal and MSA treatments.

This apparent inconsistency could be removed by empirically rescaling the radii of the ions, so that a single curve would represent the solvation energy function, but we preferred to follow the treatment of Ref. 70. With the given ion radii both MSA and the one-mode nonlocal schemes involve a single parameter chosen to give the best fit with experiment. One can see from Figs. 6 and 7 that, after such a fitting, the calculations of both theories show a close resemblance. The comparison was also made for other of the solvents investigated in Ref. 70 (see Table I); the results are similar and we do not show them here for the sake of brevity.

FIG. 7. Solvation energy U_solv of monovalent ions in 1-propanol. Shown are our results for a single-mode Lorentzian model with parameter λ adjusted separately for cations and anions to give a best fit; MSA results (Ref. 70) and experimental results (Refs. 70 and 71).

FIG. 6. Solvation energy U_solv of monovalent ions in water. Shown are our results for a single-mode Lorentzian model with parameter λ adjusted separately for cations and anions to give a best fit; MSA results (Ref. 70) and experimental results (Refs. 70 and 71).

VIII. DISCUSSION

Our final comments are concerned with the significance of the present results with respect to recent achievements in the microscopic theory of polar fluids. A nonlocal study of medium effects is a general phenomenological approach which, within the bounds of the linear response approximation, contains any effect occurring at a microscopic level. In this work, we assumed another important approximation: that nonlocal susceptibility integral kernels are isotropic nontensorial quantities. Therefore, these two limitations, the linear and isotropic nature of the polarization response, are inherent in the present treatment.

In actual fact two sources of nonlocality can be recognized: one determined by the presence of the solute and another being an intrinsic property of the pure solvent. The first one, namely, the cavity effect, is explicitly treated by the equations elaborated above. The second kind of nonlocality is introduced into these equations via the empirical function χ(k). This function can be taken either from phenomenological studies in terms of general principles such as causality, the fluctuation–dissipation theorem, etc., or from microscopic molecular theories together with computer simulations. Corresponding studies and derivation of specific forms of the susceptibility functions in pure liquids are beyond the scope of the present work. Nevertheless, some comments are needed about the simple expansion over a set of...
Lorentzian terms, used in Secs. V and VII. This form of integral kernel, suggested in earlier nonlocal theories, has been brought to doubt in recent studies based on molecular theory and simulations. It was shown that the kernel $f(k)$ becomes negative over a certain range of $k$, a case which cannot be covered by the Lorentzian expression (B1). The zeros of the function $f(k)$ appear along with the poles of $\chi(k)$ and $\varepsilon(k)$, but are absent in the smooth representation (5.10). A complicated empirical function has been presented, which describes this kind of behaviour. In the domain of physical space, the complication of these poles generates oscillations in the nonlocal kernel $\chi(r,r')$. A typical example is provided by representing the susceptibility by a pure polar form:

$$\chi(k) = \sum_i P \frac{\chi_i}{1 - \lambda_i^2 k^2},$$  \hspace{1cm} (8.1)

where $P$ indicates the principle value operator. The inverse Fourier transform then gives

$$\chi(|r-r'|) = -\sum_i \frac{\chi_i}{4\pi\lambda_i} \cos |r-r'|/\lambda_i.$$  \hspace{1cm} (8.2)

In basic nonlocal expressions like Eq. (1.3), this kernel plays essentially the same role as the exponentially damping kernel of the Lorentzian model, with the one modification that the damping mechanism emerges from oscillations. The correlation lengths $\lambda_i$ thus qualitatively retain their significance as a measure of damping.

However, there exist problems in a direct application of kernels like Eq. (8.1). For this case our calculations revealed an irregular (oscillatory) behavior in the dependence of the solvation energy $U(a)$ on the ion radius $a$. The same problem occurred in recent work with oscillating kernels. This is why we based our calculations in Sec. VII on a smooth Lorentzian parametrization and leave the problem of an oscillating kernel for future studies.

The use of representation (5.10) is not an essential element of our approach. The general analyses of Secs. V and VI are independent of the form of function $\chi(k)$ accepted. The numerical examples of Sec. VII merely provide a transparent illustration of manipulations with nonlocal equations. These results, however, demonstrate that a Lorentzian representation of the nonlocality is sufficient to give a satisfactory description of solvation energies. On the other hand, an improved parametrization of functions $\chi(k)$ and $f(k)$, if one were to be elaborated, can be equally well included in the theory. With this improved theory, a numerical implementation of the full version solving the integral Eq. (3.17) for the general asymmetric case seems to be a promising development of the recent BKO calculations of solvation effects.

ACKNOWLEDGMENTS

The authors would like to dedicate this paper to the memory of G. E. Chudinov (23.6.1956–31.12.1994). The work was funded by the Russian Foundation of Fundamental Research and the International Science Foundation.

APPENDIX A: COMMENTS ON THE DERIVATION OF THE BASIC EQUATION (5.9) FOR SPHERICALLY SYMMETRIC SYSTEMS

An important simplification of the general nonlocal Poisson Eq. (3.17), which leads to the integral Eq. (5.9), is made when the second (surface) term on the right-hand side of Eq. (3.17) vanishes as a result of spherical symmetry:

$$\int_{S(a)} d^2 r' \chi(|r-r'|) \frac{\partial \xi_0}{\partial n}(r') = 0.$$  \hspace{1cm} (A1)

To prove this last identity let us consider separately the cases of smooth and singular distributions $g(R)$. When $g(R)$ is smooth, the operators of the normal derivative $(\partial/\partial n)$ and of integration $\int f_v d^3 r' (\cdots)$ commute. Therefore,

$$\frac{\partial \xi_0}{\partial n}(r') = \int_{V_e} d^3 r'' g(r'') a(r',r'')$$

$$= 2\pi \int_a^\infty dR'' g(R'') R'^2$$

$$\times \int_0^{2\pi} \sin \theta'' d\theta'' a(r',r'').$$

The $\theta''$ integral equals

$$\int_0^{2\pi} \sin \theta'' d\theta'' a(r',r'') = \begin{cases} \frac{-2}{R'^2}, & R'>R'', \\ \frac{1}{R'^2}, & R'=R'', \\ 0, & R'<R''. \end{cases}$$

Equation (A1) follows from this result if $g(R)$ is nonsingular. Otherwise, we obtain according to Eqs. (4.1), (4.8), and (4.9),

$$g(R) = \bar{\sigma} \delta(R-a), \quad \xi_0(r) = \bar{\sigma} \int_{S(a)} d^2 r' \frac{1}{|r-r'|}.$$  \hspace{1cm} (A2)

and $\partial \xi_0/\partial n$ is interpreted as $(\partial \xi_0/\partial n)_l$. Hence, we again arrive at the result (A1) by making use of the second line of Eq. (5.4).

APPENDIX B: THE RELATIONSHIP BETWEEN THE PARAMETERS OF THE DIELECTRIC FUNCTIONS $\chi(k)$ AND $f(k)$

The basic quantity of the DK nonlocal theory is the permittivity function (6.4). Its standard parametrization is given by a Lorentzian pole expansion

$$f(k) = \sum_{i=1} \frac{c_i}{1 + k^2 \lambda_i^2}.$$  \hspace{1cm} (B1)

In the present work, we borrow the same scheme (5.10) for the permittivity $\chi(k)$:
\[
\chi(k) = \sum_{i=1}^{\infty} \frac{\chi_i}{1 + k^2 \Lambda_i^2}, \quad \sum_{i=1}^{\infty} \chi_i = \chi_0.
\]

The representation (B1) has no implementation in our scheme. It seems most obvious to straightforwardly consider the parameters of expression (B2) given the permittivity function (B1).

Underlying the calculation is the main relation
\[
\chi(k) = \frac{f(k)}{4\pi[1 - f(k)]}.
\]

Expression (B1) is inserted into this formula, then a comparison with the needed set of equations. Some results are listed below.

**Single-mode case**

\[
f(k) = \frac{c_1}{1 + k^2 \Lambda_1^2}, \quad c_1 = 1 - \frac{1}{\varepsilon_0},
\]

\[
\chi(k) = \frac{\chi_1}{1 + k^2 \Lambda_1^2}, \quad \chi_1 = \chi_0 = \frac{\varepsilon_0 - 1}{4\pi},
\]

\[
\lambda_1 = \sqrt{\varepsilon_0 \Lambda_1^2}.
\]

**Two-mode case**

\[
f(k) = \frac{c_1}{1 + k^2 \Lambda_1^2} + \frac{c_2}{1 + k^2 \Lambda_2^2},
\]

\[
\chi(k) = \frac{\chi_1}{1 + k^2 \Lambda_1^2} + \frac{\chi_2}{1 + k^2 \Lambda_2^2},
\]

The results are

\[
\lambda_1^2 = \frac{\Lambda_1^2(1 - c_2) + \Lambda_2^2(1 - c_1) - \sqrt{\Delta}}{2(1 - c_1 - c_2)},
\]

\[
\lambda_2^2 = \frac{\Lambda_1^2(1 - c_2) + \Lambda_2^2(1 - c_1) + \sqrt{\Delta}}{2(1 - c_1 - c_2)},
\]

\[
\chi_1 = \frac{c_1 + c_2}{4\pi(1 - c_1 - c_2)} \chi_2,
\]

\[
\chi_2 = -\frac{c_1 \Lambda_2^2 + c_2 \Lambda_1^2 - (c_1 + c_2) \Lambda_2^2}{4\pi \sqrt{\Delta}},
\]

where

\[
\Delta = \Lambda_1^4(1 - c_2)^2 + \Lambda_2^4(1 - c_1)^2
\]

\[-2\Lambda_1^2 \Lambda_2^2(1 - c_1 - c_2 - c_1 c_2).
\]

The following case is important:

\[
f(k) = \frac{A}{1 + k^2 \Lambda^2} + B,
\]

where \(\Lambda_1 = 0, \Lambda_2 = \Lambda, c_1 = B, c_2 = A\). In this case

\[
\lambda_1 = 0, \quad \lambda_2 = \Lambda \sqrt{\frac{1 - B}{1 - A - B}},
\]

\[
\chi_1 = \frac{B}{4\pi(1 - B)}, \quad \chi_2 = \frac{A}{4\pi(1 - B)(1 - A - B)}.
\]

**Three-mode case**

A treatment of the general three-mode case needs a solution in six equations for six unknown quantities \(\lambda_i, \chi_i\) \((i = 1, 2, 3)\). We performed this computation based on the three-mode parametrization (A1) for water. The results were used in the numerical tests in the first part of Sec. VII. Note that according to Ref. 59, \(\lambda_1 = 0\), correspondingly \(\lambda_1 = 0\). This value causes the calculations of Sec. VII to exceed the numerical bounds of the computer; for this reason the value \(\lambda_1 = 0.05\) has been used for \(\alpha > 3.3\) Å, as shown in Eq. (7.6); and \(\lambda_1 = 0.1\) Å for \(\alpha > 3.3\) Å.

**APPENDIX C: ASYMPTOTIC ANALYSIS OF SPHERICALLY SYMMETRIC EQUATIONS IN THE LOCAL LIMIT**

To proceed analytically, starting from the basic Eqs. (5.5), (5.6), and (5.9) of the spherical model, one needs a simple approximate function for \(g(R)\). We may accept an exponential function:

\[
g(R) \approx \bar{g}(R) = g_0 \exp(-\frac{R - a}{\beta}).
\]

We make use of the integral Eq. (5.9) for determining the parameters \(g_0\) and \(\beta\). Let us write the equation in a compact form:

\[
\hat{F}g - F_0 = 0,
\]

\[
(\hat{F}g)(R) = g(R) + 4\pi \int_a^R dR' g(R') \gamma(R, R'),
\]

\[
F_0 = -\frac{Q}{a^2} \gamma(R, a).
\]

Here \(\hat{F}\) represents a linear integral operator. This equation is not exactly satisfied when we use the approximate model (C1). The error given by function \(\bar{g}(R)\) is defined as

\[
\eta[\bar{g}(R)] = \eta(g_0, \beta) = \int_a^R R^2 dR (\hat{F}g - F_0)^2.
\]

By minimizing it, two equations for \(g_0\) and \(\beta\) appear:

\[
\frac{\partial \eta}{\partial g_0} = \int_a^R R^2 dR 2(\hat{F}g - F_0) \hat{F} \left( \frac{\partial \bar{g}}{\partial g_0} \right) = 0,
\]

\[
\frac{\partial \eta}{\partial \beta} = \int_a^R R^2 dR 2(\hat{F}g - F_0) \hat{F} \left( \frac{\partial \bar{g}}{\partial \beta} \right) = 0.
\]

A numerical solution, which is only available for the general expression (5.10), has no advantages over the general numerical procedure considered in the Sec. VII. The present scheme is useful to give an illustration of the local limiting transition which, within the parametrization of Eq. (5.10), corresponds to \(\lambda_i \to 0\). As the results of Sec. IV suggest, in
we note that Eq. (3746) and keep only the leading contributions to the expansion of Eq. (C4) in terms of \( \lambda_i, g_0, \) and \( \beta. \) The most delicate point in such an analysis is concerned with the evaluation of \( F_0: \)

\[
\lim_{\lambda_i \to 0} \gamma(R, a) = \sum_i \frac{\chi_i}{2\lambda_i R} e^{-(R-a)/\lambda_i} \frac{g_0}{\beta a^2 (1 + 4 \pi \chi_0)}.
\]

(C6)

In accord with our previous expectations in Eq. (C5). We substitute this result into the expression for the solvation energy obtained from formula (5.7) with \( g(R) = g(R): \)

\[
U_{\text{solv}} = 2\pi g_0 \beta (a + \beta).
\]

(C7)

In this way we arrive at the classical Born expression

\[
\lim_{\lambda_i \to 0} U_{\text{solv}} = -\frac{Q^2}{2a} \left( 1 - \frac{1}{\epsilon_0} \right),
\]

(C8)

which completes the asymptotic analysis of the local case.